

Computational and Spectroscopic Structural Determination of Lithiated Benzylic Nitriles in THF/HMPA Solution

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ABSTRACT

The synthetic utility of nitrile-stabilized carbanions as reactive intermediates for selective carbon-carbon bond formation has prompted numerous studies toward characterization of the solution structure of these nucleophiles. In hopes of eventually gaining a better understanding of the structural properties which may mediate reactivity and selectivity, researchers have designed elegant structure elucidation strategies. These studies have offered key advancements toward the characterization of these intermediates; however, contradictory evidence has hindered unambiguous structural determination—particularly for lithiated benzylic nitriles in low dielectric, ethereal media.

Chapter 1 of this dissertation presents a review of the synthetic utility of metalated nitriles and the spectroscopic and computational techniques employed to characterize their solution structure. Also reviewed herein are the controversial determinations drawn from these efforts. The research and data which follow in Chapters 2 and 3 focus on resolution of the conflicting structural determinations drawn from multinuclear magnetic resonance (NMR) and vibrational (IR and Raman) spectroscopy. Employing a strategy to slow the lithium-nitrogen exchange rate in low dielectric media, new ^7Li , ^{31}P , and ^{15}N NMR spectroscopic evidence (with support from computational modeling) lead us to amend our previous assessments and propose that lithiated

arylacetonitriles adopt an aggregated triple-ion structure in THF/hexane with sub-stoichiometric HMPA.

Due to the limitations of computer resources and the effect of non-linear scaling, theoretical modeling of aggregated and solvated lithiated benzylic nitriles became impractical at the 6-31+G(d) basis set. These limitations led to the use and comparative analysis of two alternative basis sets for the DFT analysis of lithiated benzylic nitrile derivatives—6-31(+LiX)G(d) and 6-31'+G(d). Defined upon the principal of resonance stabilization, these basis sets were constructed by application of varying levels of computational theory on a per-atom basis. By applying higher levels of theory only to the atoms most intimately involved in the electronic distribution, “accurate” replacement models for 6-31+G(d) structures were obtained with considerable savings in computational resources. This study in basis set economy is detailed fully within Chapters 4 and 5.

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List of Abbreviations

.chk	Gaussian '03 checkpoint file extension
.gjf	Gaussian '03 file extension for job input
.out	Gaussian '03 file extension for job output
.pdb	device independent file extension for molecular visualization
.xyz	Gaussian '03 Cartesian coordinate file extension
δ	chemical shift (ppm)
Å	angstrom, 10^{-10} m
AcOH	acetic acid
Ar	aryl
Bn	benzyl
Bu	butyl
BSSE	basis set superposition error
<i>c</i> -C ₆ H ₁₁	cyclohexyl
CDCl ₃	deuterated chloroform
CIP	contact ion pair
cm ⁻¹	wavenumber
CP	counterpoise
D _n	dimer (n = # solvating ligands)
DMEA	dimethylethylamine
DMSO	dimethylsulfoxide
E	energy (kcal/mol, unless otherwise noted)
Et	ethyl
Et ₂ O	diethyl ether
EtOAc	ethyl acetate
EX	electrophile
FAB	fast atom bombardment
FT-IR	Fourier Transform-Infrared
G	Gibbs free energy (kcal/mol, unless otherwise noted)
GB	gigabytes

h_n	HMPA solvate ($n = \#$ solvating ligands)
H	enthalpy (kcal/mol, unless otherwise noted)
HMDS	hexamethyldisilazane
HMPA	hexamethylphosphoramide
HMQC	heteronuclear Multiple-Quantum Coherence
HBr	hydrobromic acid
HCl	hydrochloric acid
HSAB	hard- and soft-acid and base
Hz	hertz
I	spin number
<i>i</i> -Pr	isopropyl
IR	infrared
J	coupling constant (Hz, unless otherwise noted)
LiTMP	lithium 2,2,6,6-tetramethylpiperidide
M_n	monomer ($n = \#$ solvating ligands)
M	molar
Me	methyl
Mes	mesityl (2,4,6-trimethylphenyl)
mp	melting point ($^{\circ}\text{C}$, unless otherwise noted)
MS	mass spectroscopy
mult.	multiplicity
NaHCO_3	sodium bicarbonate
Na_2SO_4	sodium sulfate
NBA	3-nitrobenzylalcohol
NMR	nuclear magnetic resonance
NOE	Nuclear Overhauser Effect
Ph	phenyl
ppm	parts per million
R	alkyl
rt	room temperature (25°C , unless otherwise noted)
S_n	separated ion pair ($n = \#$ solvating ligands)

S	entropy (cal/mol, unless otherwise noted)
SIP	separated ion pair
T	temperature
TB	terabytes
THF	tetrahydrofuran
TLC	thin layer chromatography
TMEDA	<i>N,N,N,N</i> -tetramethylethylenediamine
TMS	trimethylsilyl
TI _n	triple ion (n = # solvating ligands)
TRIP	triisopropyl
ν	frequency (Hz, unless otherwise noted)
$\nu_{1/2}$	half-width (Hz, unless otherwise noted)

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Jason Harmon

Chapter 1 Metalated nitrile reactivity, structure, and controversy

1.1 Introduction to nitrile-stabilized carbanions

The use of stabilized carbanions as reactive frameworks from which symmetric and asymmetric carbon-carbon bond construction can occur is a cornerstone of synthetic organic chemistry.¹ Although conceptually related to enolates of ketones, esters, and amides in both formation and function, carbanions stabilized by a proximate nitrile functional group uniquely benefit from potent nucleophilicity with comparatively reduced steric requirements.^{2, 3} Cooperative to this size advantage, the highly inductive nature of the nitrile^{1, 2, 4} directly influences its nucleophilicity, and thereby the wide synthetic applicability of nitrile-stabilized carbanions. Consequent of these structural and electronic properties, metalated nitriles often exhibit unique stereo- and regioselectivity relative to the analogous enolate intermediates.^{2, 5}

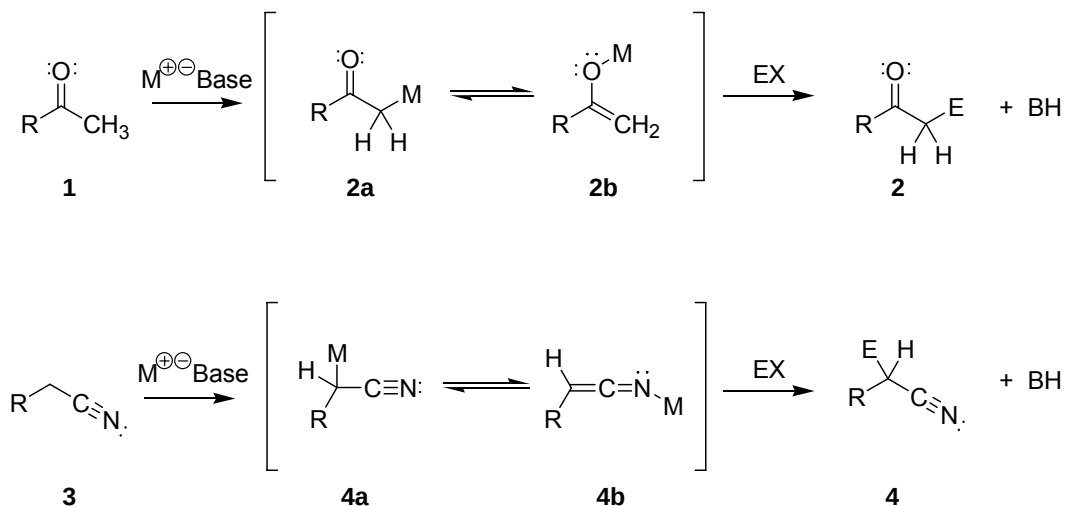
Despite the prominence of synthetic schemes featuring metalated nitriles as key reactive intermediates, surprisingly little is definitively known with regard to the structure adopted by their stabilized carbanions in solution. Herein we will review the pertinent literature with a focus on the synthetic utility of metalated nitriles as intermediates for stereoselective and regioselective carbon-carbon bond formation, the experimental and theoretical techniques employed to ascertain their structural properties, and the determinations drawn from these efforts to date.

1.2 Nitrile-stabilized carbanions in organic synthesis

The synthetic utility of nitrile-stabilized carbanions is vast.⁵⁻⁷ Below we report a representative sampling of the recent literature which showcases the broad utility of metalated nitriles—specifically as it pertains to selective carbon-carbon bond formation.

1.2.1 Alkylation reactions

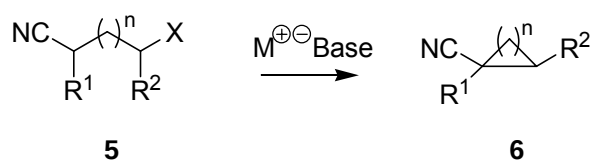
Analogous to the formation of enolates **2a** and **2b**, nitrile-stabilized carbanions are typically generated through the deprotonation of weakly acidic organonitriles (characteristic DMSO pK_a values: 21-31)⁸ by strong base, as depicted in Scheme 1.1. Continuation of this analogy suggests that nitrile-stabilized carbanion intermediates would adopt tautomeric structural representations **4a** and **4b** upon deprotonation of the parent nitrile **3**. Much like carbonyl-stabilized enolates, metalated nitrile intermediates are potent nucleophiles which readily react with a host of electrophiles (designated EX) to affect asymmetric or symmetric bond formation.



Scheme 1.1 Formation and alkylation of enolates and metalated nitriles

1.2.1.1 Intramolecular cyclization reactions

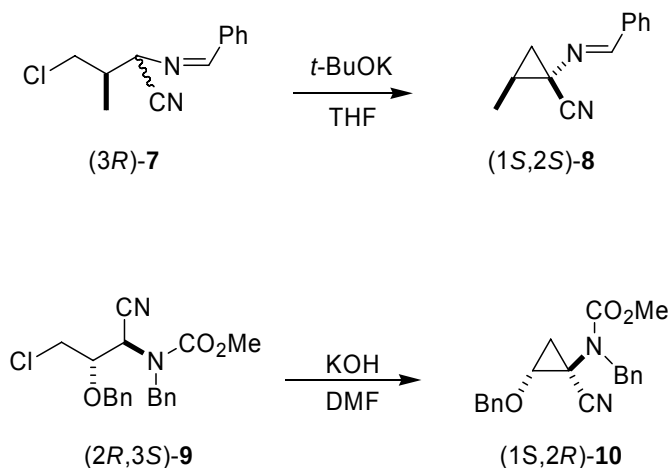
By virtue of the minimal steric demand of the nitrile functional group and the potent nucleophilicity of their respective stabilized carbanions, metalated nitriles are well suited to the formation of strained small-membered ring systems including cyclopropanes,^{5-7, 9-14} cyclobutanes,¹⁵⁻¹⁷ and cyclopentanes,¹⁸⁻²⁰ as illustrated in Scheme 1.2 ($n = 1 - 3$, respectively). Halonitriles (e.g. **5**) have been proposed to cyclize through an invertive S_Ni (intramolecular substitution) pathway allowing for some degree of stereochemical predictability in the construction of substituted small-membered ring systems (e.g. **6**).⁷



Scheme 1.2 Intramolecular cyclization of nitrile-stabilized carbanions

Cyclization reactions of nitrile-stabilized carbanions possessing both an adjacent stereocenter and a secondary leaving group (X) have been employed to direct distinct diastereoselectivity towards the assembly of substituted cyclopropyl nitrile derivatives (**6**, $n = 1$).^{6, 7, 9-11} In the general reaction scheme depicted above, the small relative steric demand of the $C\equiv N$ group allows the nitrile to preferentially eclipse R², thus avoiding potentially problematic steric interactions between the larger R¹ and R² substituents. Representative examples of this selectivity are illustrated in the diastereoselective

preparation of cyclopropyl nitrile derivatives (1*S*,2*S*)-**8** and (1*S*,2*R*)-**10**, as detailed in Scheme 1.3.



Scheme 1.3 Diastereoselective intramolecular cyclization of halonitriles

Deprotonation of (3*R*)-2-(*N*-benzylideneamino)-4-chloro-3-methylbutyryl nitrile **7** by potassium *tert*-butoxide (*t*-BuOK) promotes invertive S_Ni displacement of the halogen to affect the formation of (1*S*,2*S*)-1-(phenylmethyleneamino)-2-methylcyclopropyl nitrile **8** in a diastereomeric ratio of 84:16.^{9, 10} Similarly, hydroxide-induced intramolecular cyclization of (2*R*,3*S*)-3-benzyloxy-2-(*N*-methoxycarbonyl-*N*-benzyl-amino)-4-chlorobutyryl nitrile **9** proceeds with the nearly exclusive diastereoselective production of (1*S*,2*R*)-2-benzyloxy-1-(*N*-methoxycarbonyl-*N*-benzylamino)cyclopropyl nitrile **10** (98:2 ratio of diastereomers).¹¹ In each of these cases, the less sterically demanding nitrile substituent is preferentially aligned *cis*- to the substituent at the 2-position.

1.2.1.2 Applications to total synthesis

Enhancing the wide synthetic applicability of nitrile-stabilized carbanions is the ease with which $\text{C}\equiv\text{N}$ functional group transformations can occur. Representative examples of facile nitrile functional group interconversion are presented in Figure 1.1.²¹ As shown below, nitriles are readily hydrolyzed under either acidic or basic conditions to yield amides or carboxylic acids. Hydride reduction of the nitrile to the imine anion can be followed by hydrolysis to the aldehyde or by further reduction to the corresponding amine. Grignard reagents also readily add to organonitriles, generating an intermediate imine anion which can then be hydrolyzed by addition of water to yield the corresponding ketone. The mild conditions required to affect such functional group conversions allow metalated nitriles to be of significant use as masked functionalities in total synthesis.

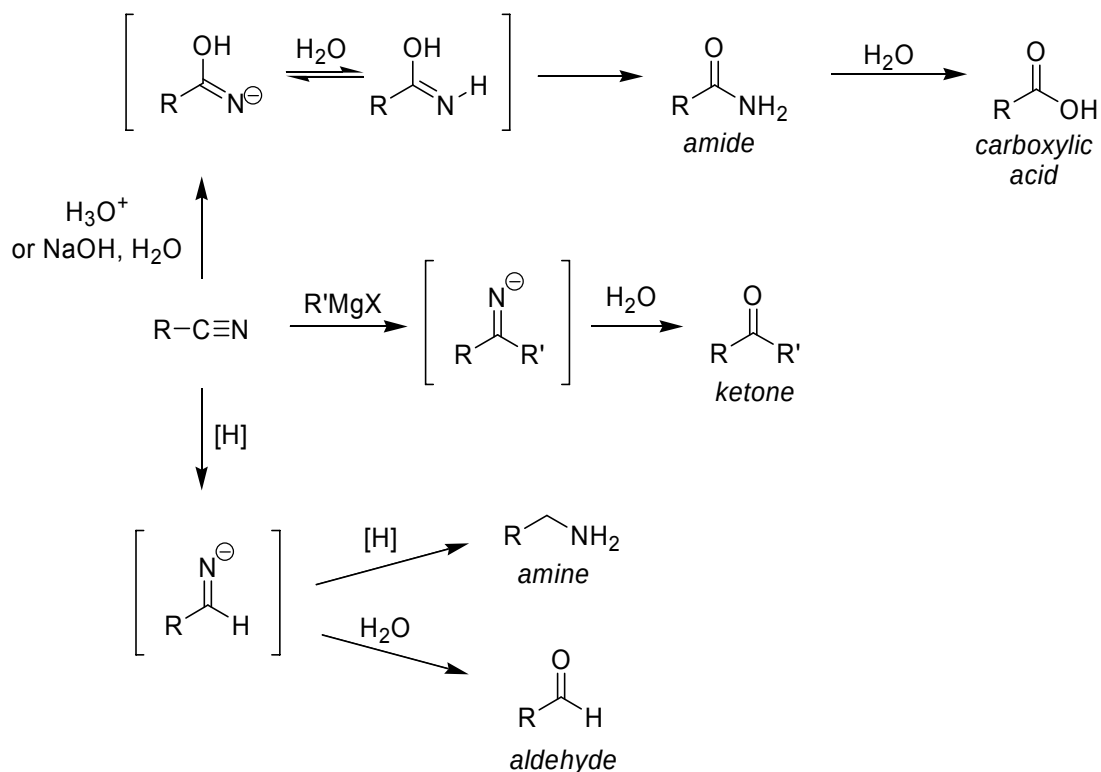
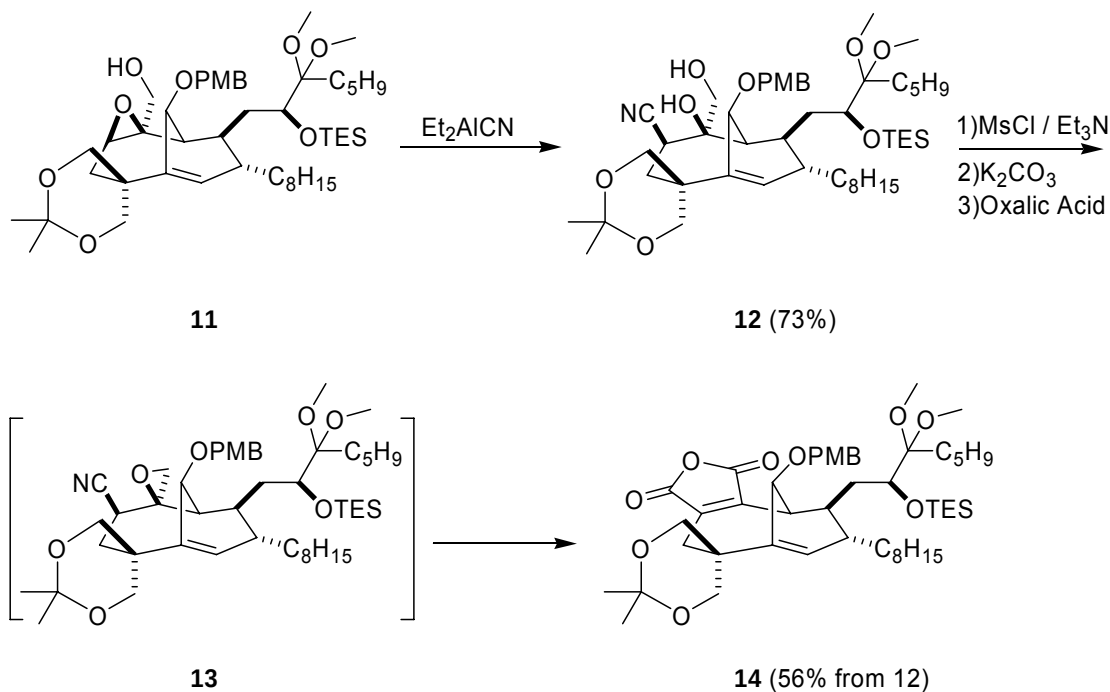


Figure 1.1 Representative functional group transformations of the nitrile group

The small size of the $\text{C}\equiv\text{N}$ functional group enables nitrile-stabilized carbanions to be ideally suited for substitution reactions into sterically congested architectures, which, in concert with the ease of nitrile functional group transformation, presents vast opportunities within total synthesis designs of complex natural products. Illustrated in Scheme 1.4 is a relevant portion of Nicolaou's approach^{22, 23} toward the total synthesis of CP-263,114^{24, 25} employing Nagata's reagent (Et_2AlCN)²⁶ to stereoselectively install a nitrile functionality into epoxide **11**, thus affecting the formation of cyano diol **12** in 73% yield. Nicolaou attributed the anomalous stereochemistry of **12** (confirmed by NOE experiments) to effects stemming from the nitrile substitution into the hindered environment of the epoxide moiety within the bicyclic skeleton of the CP-263,114

precursor.²² As shown, the cyano diol is then readily converted to cyano epoxide **13**, ultimately allowing for formation of maleic anhydride **14** (56% yield from **12**) en route to CP-263,114.

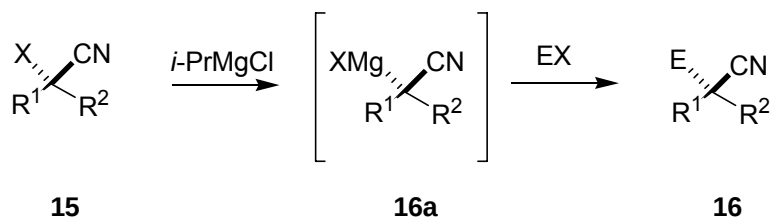


Scheme 1.4 Stereoselective nitrile insertion toward the total synthesis of CP-263,114

1.2.1.3 Halogen-metal exchange

An emerging strategy for the stereocontrolled alkylation of nitrile-stabilized carbanions relies upon the effective use of halogen-metal exchange. Deprotonative formation of nitrile-stabilized carbanions by strong base, typically chosen from lithium amides such as lithium diisopropylamide (LDA) and lithium hexamethyldisilazide (LiHMDS), generally proceeds through preferential formation of the N-metalated reactive intermediate (evidenced by X-ray crystal structures and limited spectroscopic

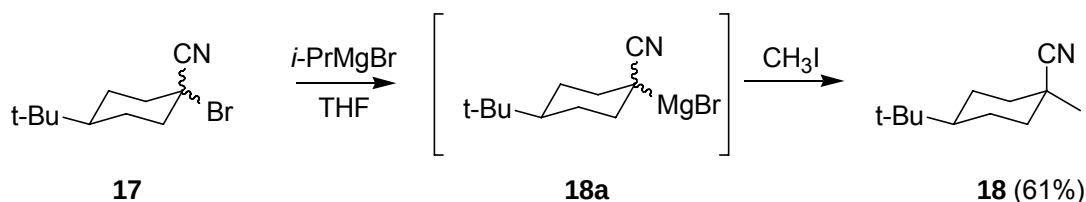
data which will be expanded upon in Section 1.4). However, distinct stereoselectivity differences could potentially be achieved through the exclusive formation of the corresponding C-metalated constitutional isomer in solution. The successful non-deprotonative route to chiral intermediate **16a** from α -halonitrile **15** in the presence of reactive electrophile EX is predicated upon the rapid rate of halogen-metal exchange with alkyllithium or Grignard reagents. As shown in Scheme 1.5, halogen-metal exchange immediately followed by an in situ electrophilic trapping step of the reactive intermediate potentially allows for an efficient, stereoselective pathway to the retentive formation of **16** via alkylation of chiral C-metalated nitrile carbanion **16a**.



Scheme 1.5 Halogen-metal exchange scheme for the selective generation of C-metalated intermediates. Retentive substitution is depicted, but reaction stereochemistry is at present unknown

The halogen-metal exchange approach to stereocontrolled alkylation of C-metalated nitrile anions has garnered considerable interest in the recent literature.²⁷⁻³¹ The utility of this approach can most readily be observed in the non-deprotonative formation of C-magnesiated intermediate **18a** via Grignard insertion by isopropylmagnesium bromide (*i*-PrMgBr) from the *cis*- and *trans*- isomers of 1-bromo-4-*tert*-butyl-cyclohexylnitrile **17** in THF (Scheme 1.6). The immediate electrophilic

trapping of **18a** by methyl iodide (CH_3I) results in the exclusive production of the single diastereomer **18** in 61% yield.²⁷

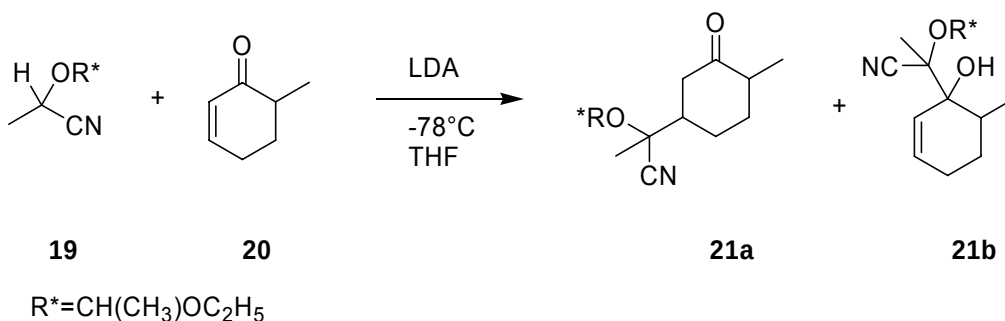


Scheme 1.6 Diastereoselective halogen-metal exchange reaction

1.2.2 Nucleophilic additions of nitrile-stabilized carbanions

1.2.2.1 Addition to α,β -unsaturated systems

The addition of nitrile-stabilized carbanions to α,β -unsaturated ketones is well documented.^{26, 32-36} In 1974, Stork and Maldonado first reported regioselectivity in the unexpected observation of a high 1,4-/1,2-addition product ratio resulting from the addition of protected cyanohydrins to select enones.³⁵ Previously reported additions of other acyl anion equivalents (including lithiated di- and trithianes³⁷ and also metalated vinyl ethers³⁸) to conjugated α,β -unsaturated systems had typically resulted in the predominant formation of the 1,2-adduct. However, for the conjugate addition of protected acetaldehyde-derived cyanohydrin **19** to 6-methylcyclohexenone **20** at $-78\text{ }^\circ\text{C}$ in THF, a 6:1 regioisomeric ratio of the 1,4-addition product **21a** to the corresponding 1,2-adduct **21b** was observed (Scheme 1.7).³⁵



Scheme 1.7 1,4- and 1,2-addition products of cyanohydrin **19** and 6-methylcyclohexenone **20**

The unexpected preference for 1,4-addition led the authors to propose a transition state model for the regioselective conjugate addition constructed upon an *N*-lithiated nitrile carbanion (similar to keteniminate structure **4b**, Scheme 1.1) which could rationalize their observed selectivity (Figure 1.2, **21a-TS**). This transition state exhibits and benefits from an extended, planar arrangement of $\text{R}_2\text{C}_\alpha\text{-CN}$, which localizes the nucleophilic C_α in close proximity to the β -position of the substituted cyclohexenone derivative. Similarly, Stork and Maldonado inferred that the lesser 1,2-addition product **21b** was likely the consequence of addition through the analogous four-membered cyclic transition state, **21b-TS** (based upon the formal nitrile carbanion structure **4a**). In this proposed transition state model, the close contact of the nucleophilic carbanion to the chelating metal cation would preclude the possibility for 1,4-conjugate addition. By their reasoning, the resulting product distribution is a direct consequence of the relative populations (or energies) of transition states **21a-TS** and **21b-TS**.

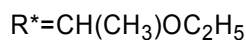
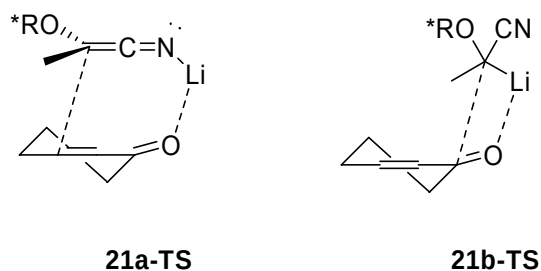
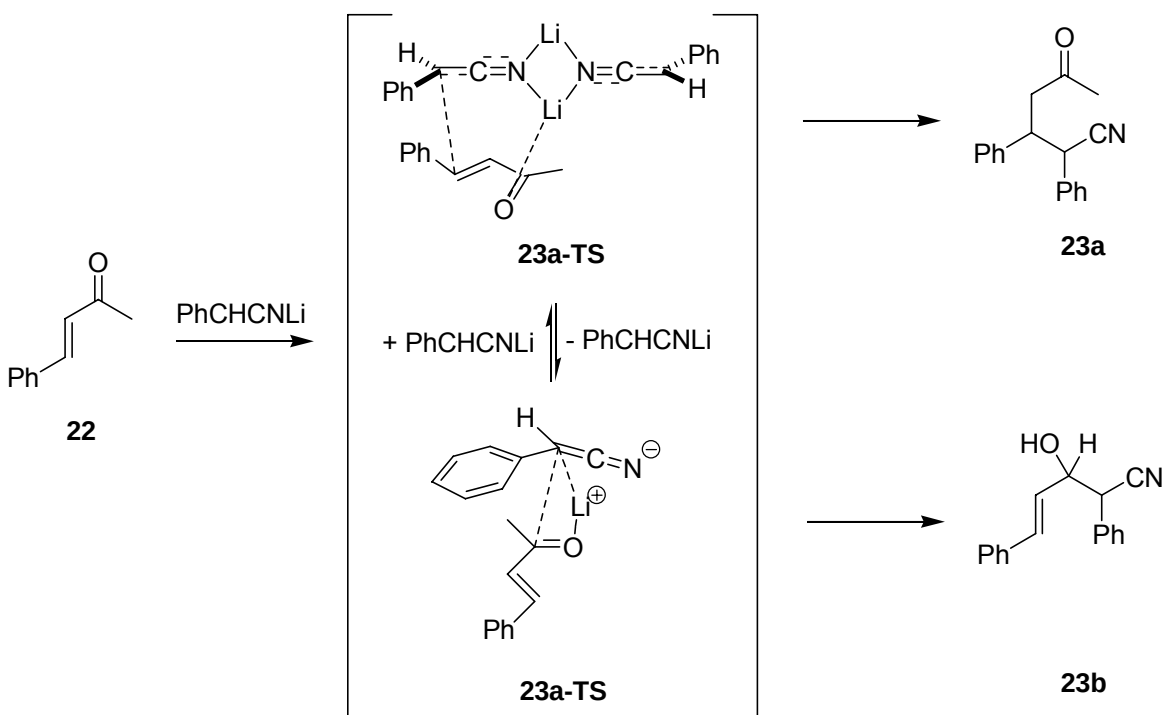


Figure 1.2 Stork and Maldonado's proposed transition states leading to 1,4- and 1,2-addition product formation

It is very important to note that the factors mediating the observed 1,4-regioselectivity of nitrile-stabilized carbanion addition to α,β -unsaturated ketones are still actively debated in the literature,³⁹⁻⁴⁴ specifically with regard to differentiation between kinetic and thermodynamic mechanisms of regiocontrol. Like Stork, two other recent studies have also attributed the observed 1,4-/1,2-regioselectivity to kinetic control. For example, the 1,4-regioselectivity of addition reactions of lithiophenylacetonitrile to benzylideneacetone **22** has been correlated to aggregative equilibrium of nitrile-stabilized carbanions in solution rather than Stork's constitutional isomerization model. Reporting a linear relationship between relative solution-phase dimer and monomer proportions (as determined from integrated $\nu(\text{C}\equiv\text{N})$ bands) in ethereal media and the 1,4-/1,2-addition product ratio, Wartschi and Corset inferred that aggregation state was the primary factor mediating the observed 1,4-adduct regioselectivity observed in these addition reactions (Scheme 1.8).^{39, 40, 45, 46} With newly available solid-state X-ray crystallographic evidence revealing the existence lithiophenylacetonitrile as an *N,N*-cyclic dimer (vide infra), the authors amended Stork and Maldonado's previously proposed 1,4-addition product

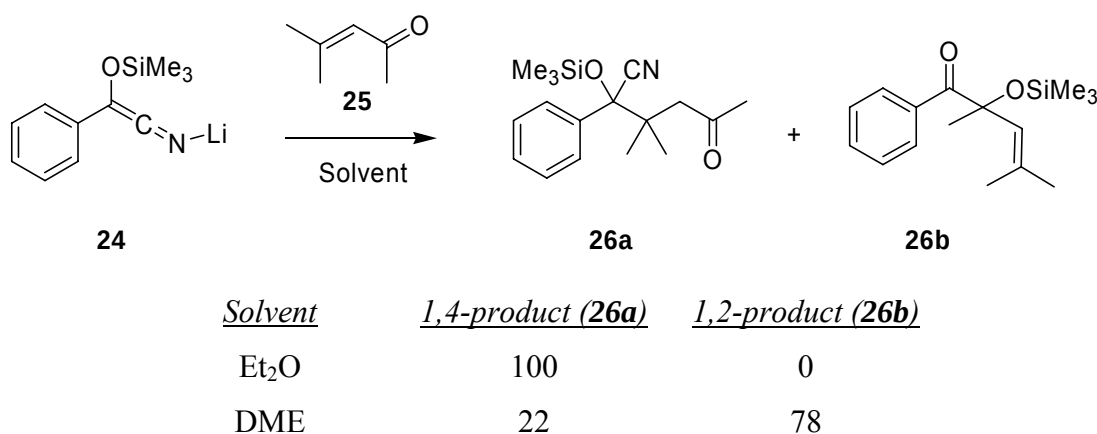
transition state model (**21a-TS**) to feature the N,N-cyclic dimeric structure showcased prominently in the solid state, as illustrated by **23a-TS**. Using parallel reasoning to that initially proposed by Stork and Maldonado, Wartski and Corset suggested that 1,4-adduct **23a** arises as a consequence of the proximity of the nucleophilic C_α, to the β-position of **22**. Furthermore, conjugate addition proceeding through the less populated monomeric C-lithiated transition state **23b-TS** would result in the minor 1,2-addition product **23b**.



Scheme 1.8 Proposed aggregative regiocontrol of metalated nitrile additions to α,β -unsaturated ketones

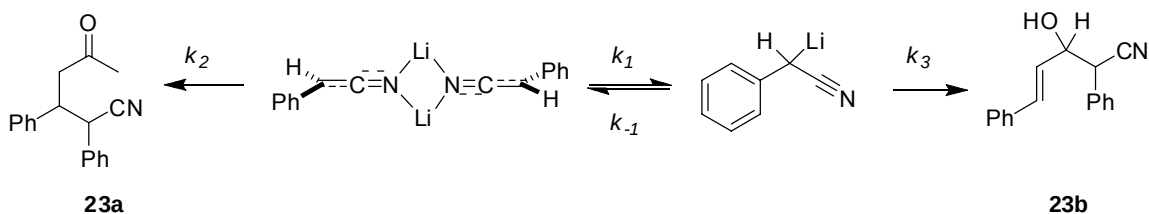
An alternate explanation for the observed regioselectivity of nitrile anion addition reactions relates product composition to the ion pair status of the metalated nitrile reactive intermediate based upon a hard and soft acid-base (HSAB) theory argument.^{41, 47}

In studies of phosphonate anion addition to α,β -unsaturated ketones, Deschamps proposed that 1,2-addition should be charge controlled (harder), whereas 1,4-addition should be orbital controlled (softer).⁴¹ Because ionization state is to some degree governed by solvent polarity/donicity (which will be discussed in further detail in Section 1.5), it was reasoned that weakly polar media complement softer contact ion pair formations, thus favoring 1,4-addition products. Likewise, more polar solvents would induce the formation of harder separated ion pairs and ultimately lead to 1,2-addition product formation.⁴¹ Hünig's earlier solvent dependency study of metalated nitrile addition to α,β -unsaturated ketones lends support to this hypothesis, as detailed in Scheme 1.9. The addition of lithiated cyanohydrin **24** to 4-methyl-pent-3-en-2-one **25** in diethyl ether (Et₂O) yields 100% conversion to the 1,4-adduct **26a**.⁴² However, the use of more polar solvents such as dimethoxyethane (DME) reverses the observed regioselectivity, as evidenced by the 78:22 ratio of the silyl-shifted 1,2-addition product **26b**.⁴²



Scheme 1.9 Hünig's proposed ionization state dependence of conjugate addition regioselectivity

In the first two proposed transition state models (based on constitutional isomerism and aggregation equilibrium), product distribution is directly correlated to the relative population (or energies) of the two reactive intermediates. These hypotheses, if true, necessarily imply reaction irreversibility and therefore kinetic control over the 1,4-regioselectivity observed from the addition of nitrile-stabilized carbanions to α,β -unsaturated ketones. This manner of kinetic control requires that the rate of reaction (k_2 , k_3) is much faster than the rate of equilibration (k_1/k_{-1}) between the reactive intermediates, or more specifically, that $k_2, k_3 \gg k_1$, as illustrated in Scheme 1.10. For example, in the addition reaction of lithiophenylacetonitrile to benzylideneacetone **22**, nucleophilic addition must necessarily be faster than the equilibration rate of the monomeric and dimeric intermediates. This view of the regiocontrol pathway strongly suggests that the Curtin-Hammett principle⁴⁸ does not apply to these systems.

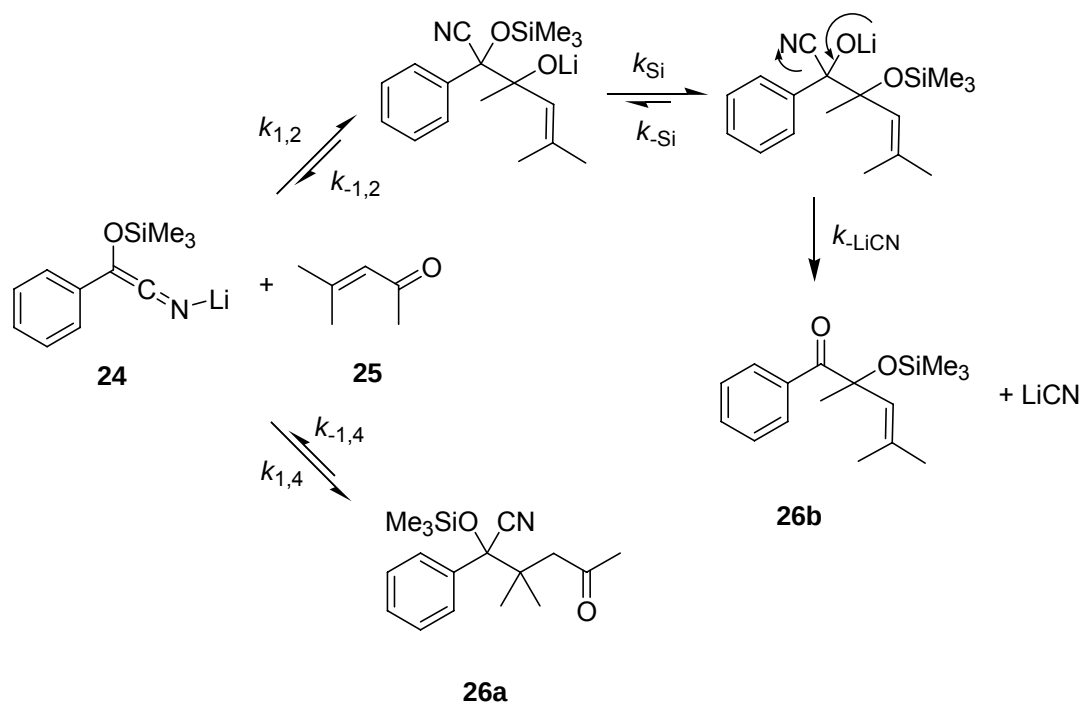


Scheme 1.10 Curtin-Hammett considerations for the addition of metalated nitriles to α,β -unsaturated ketones

In an important study published in 2005, Reich reexamined the conjugate addition of lithiophenylacetonitrile to benzylideneacetone **22** and reported that the 1,4-/1,2-addition product ratio is time-dependent. For reaction times less than 30 seconds, a predominance of the 1,2-addition product is observed. Longer reaction times, however,

result in a much higher yield of the corresponding 1,4-addition product.⁴⁴ This observed reaction reversibility strongly suggests that the proposed kinetically controlled selectivity explanations are incorrect, and that the reported 1,4-regioselectivity results from thermodynamically preferred isomerization of the kinetic 1,2-product.

This argument, in itself, does not rationalize Hünig's observed preference for the 1,2-addition of lithiated cyanohydrin **24** to 4-methyl-pent-3-en-2-one **25** in DME. Recall that Hünig's rationale was based in HSAB theory. In his proposed reaction pathway, the more polar DME promotes ionization of the metalated nitrile in solution, thus prompting the more charge controlled 1,2-addition. Reich, however, provided evidence for an alternative interpretation of their results. The loss of LiCN associated with the silyl shift leading to the formation of 1,2-adduct **26b** is effectively irreversible. Therefore, the rate of isomerization of the kinetic 1,2-addition product to the thermodynamically favored 1,4-adduct is the result of competition between the rate of silyl shift (k_{Si}) and the retro-1,2-addition ($k_{-1,2}$), and *not* of the inherent HSAB properties of the lithiated nitrile stabilized carbanion intermediates, as shown in Scheme 1.11.⁴⁴



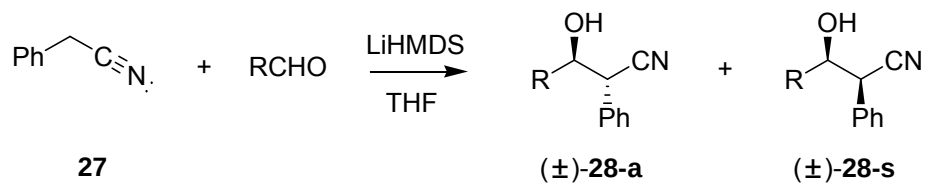
Scheme 1.11 Reich's isomerization pathway of kinetic 1,2-addition products⁴⁴

1.2.2.2 Addition to carbonyls

Despite the attention given to addition reactions of nitrile-stabilized carbanions to α,β -unsaturated systems, relatively little focus has been directed towards the addition of metalated nitriles to non-conjugated carbonyl compounds. In 1987, Trost reported the axially-selective addition of lithioacetonitrile (CH_2CNLi) to conformationally biased cyclohexenones,⁴⁹ however analogous attempts toward the addition of metalated nitriles to substituted aldehydes achieved little to no complementary diastereoselectivity.⁵⁰

The first reported successful stereoselective addition of metalated nitriles to aldehydes appeared in 1994. Carlier and co-workers observed that the addition of lithiophenylacetonitrile **27-Li** to substituted aldehydes (RCHO) in THF exhibits anti-

selectivity toward the formation of β -hydroxynitriles (e.g. **28**), as shown in Scheme 1.12. Dependent upon the size of the aldehyde substituent (R), the *anti/syn* diastereomeric product ratios (**28-a**/**28-s**) range from 4:1 to 63:1.⁵¹ An increase in the steric bulk of the R substituent promotes increased *anti*-selectivity, thus favoring product **28-a**. Where R is n-propyl, an *anti/syn* ratio of only 4:1 is observed. However, increased size (e.g., where R is t-butyl) results in a much larger observed *anti/syn* product ratio for **28** (63:1).⁵¹ Although omitted from Scheme 1.12 for brevity, it is worthwhile to note that there is no appreciable deviation in the reported *anti/syn* product ratios of **28** when Et₂O and LDA are substituted as solvent and base, respectively.⁵¹



Anti:Syn ratio

<u>R</u>	<u>28-a:28-s</u>
<i>n</i> -Pr	4.1:1
Ph	5.5:1
4-MeC ₆ H ₄	6.4:1
4-MeOC ₆ H ₄	4.1:1
<i>c</i> -C ₆ H ₁₁	6.8:1
<i>t</i> -Bu	63:1

Scheme 1.12 Anti-selectivity from the nitrile-aldol reaction

1.3 Structural and electronic properties of the nitrile functional group

1.3.1 Physical properties

The synthetic utility of nitrile-stabilized carbanions is attributed, at least in part, to the compact size of the nitrile group. Structurally, the $\text{C}\equiv\text{N}$ functional group is most appropriately described as a linear rod (encapsulated within a cylindrical cloud of two orthogonal π -orbitals)³ measuring approximately 2.60 Å in length (Figure 1.3, **29**).⁵² In contrast, the carbonyl functional group (e.g., **30**) is geometrically best characterized as triangular with hemispherical, stacked π -orbitals.⁵³ The size of carbonyl-based functional groups varies largely by the identity of the R group itself (ketone, ester, etc.). Where R is methyl (**30-CH₃**), L is approximately 2.34 Å.⁵² In the case of methyl ester **30-OCH₃**, the O-R interspatial distance measures 2.07 Å.⁵² Regardless of the identity of substituent R, the trigonal nature of the carbonyl functional group creates a substantially larger surface area than does the analogous nitrile, thereby imposing greater access restrictions into sterically hindered architectures. Furthermore, the cylindrical nature of the nitrile π -electron cloud allows for multi-directional interaction with adjacent π -systems independent of rotatory orientation.³ Carbonyl groups, by contrast, necessarily rely upon proper orientation for effective interaction with neighboring π -systems as a consequence of their stacked hemispherical π -orbitals.⁵³ This directionality constraint further limits approach into congested frameworks.

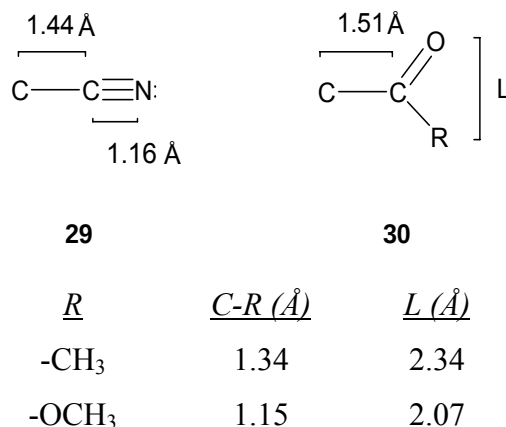


Figure 1.3 Size comparisons of the nitrile and carbonyl functional groups

Conformational inversion of monosubstituted cyclohexane derivatives has been utilized to quantify the absolute and relative steric demand of select functional groups.⁵⁴ Measurement of the equilibrium populations of the axial and equatorial conformers of the cyclohexanone derivatives (Scheme 1.13) provides a direct means for comparison of effective functional group size. Winstein and Holness define ‘A values’ as the difference in axial and equatorial free-energy ($-\Delta G^0$) of monosubstituted cyclohexanes, as shown in Equation 1.1.⁵⁵ By definition, positive A values indicate an equatorial preference whereas negative A values correspond to an axial preference.

$$A = -\Delta G^0 = -(G_{eq}^0 - G_{ax}^0) = (RT \ln K) / 1000$$

Equation 1.1 Calculation of A values for monosubstituted cyclohexane derivatives

As shown in Scheme 1.13, cyclohexylnitrile **31-CN** exhibits an A value ranging from only 0.12-0.25 kcal/mol,⁵⁴ with an expected dependence upon experimental

considerations including solvent choice and temperature. Carbonyl functionalities, by comparison, uniformly show larger A values (between 0.84-1.96 kcal/mol), signifying greater equatorial preference indicative of the larger size of the carbonyl moiety. Furthering this relationship between size and equatorial preference, the A value for cyclohexanal **31-CHO** is expectedly much smaller than that of the potassium salt of cyclohexanecarboxylic acid **31-CO₂⁻K⁺** (0.84 and 1.96 kcal/mol, respectively).⁵⁴ For comparative purposes, the A value for *tert*-butylcyclohexane **31-*t*-C₄H₉** (commonly known to exist exclusively in the equatorial conformation) is reported to be no less than 5.4 kcal/mol.⁵⁵

31_{ax}

K

31_{eq}

<u>R</u>	<u>Solvent</u>	<u>Temperature (K)</u>	<u>A Value (kcal/mol)</u>
-C≡N	t-BuOH	339	0.25
	CCl ₄	303	0.12
-CHO	CD ₂ Cl ₂ /CS ₂	173	0.84
	CD ₂ Cl ₂	180	0.82
-COCH ₃	CD ₂ Cl ₂ /CS ₂	173	1.02
	CH ₃ OH	298	1.52
-CO ₂ H	dodecane	298	1.38
	diglyme	298	1.36
	HOCH ₂ CH ₂ OH	298	1.96
-CO ₂ ⁻ K ⁺	HOCH ₂ CH ₂ OH	453	1.89
-CO ₂ CH ₃	CS ₂	195	1.31
	CH ₃ OH	198	1.27
-CO ₂ C ₂ H ₅	CH ₃ CH ₂ OH	353	1.10

Scheme 1.13 Conformational inversion of monosubstituted cyclohexanes⁵⁵

1.3.2 Electronic effects

In addition to the minimal native steric requirement of the nitrile functional group, key electronic properties contribute to the observed nucleophilicity of nitrile-stabilized carbanions. Both the nitrile and carbonyl functional groups are powerful electron withdrawing substituents.^{2, 3} The attachment of strong electron-withdrawing groups to an anionic center serve to stabilize adjacent electron density through various electronic mechanisms including induction and resonance delocalization.

Whereas carbonyl-stabilized carbanions typically delocalize electron density by resonance stabilization (as commonly depicted in tautomeric representations **2a** and **2b**, Scheme 1.1),⁵⁶ it has been reported that the nitrile functional group stabilizes adjacent charge density principally by induction.⁵⁶⁻⁵⁸ Pagani and Bradamante conducted extensive ¹³C NMR spectroscopic measurements encompassing a wide range of sodiated nitriles in dimethylsulfoxide (DMSO) correlating chemical shift to electron density.⁵⁸ Their results suggest that, unlike carbonyl compounds, the nitrile functional group imposes comparatively little through-bond charge demand upon adjacent carbanions, thus revealing almost negligible resonance stabilization into the nitrile functional group itself.⁵⁸ Stabilization through electron induction, however, allows for significant charge density to be retained on C_α, thereby directly influencing the nucleophilicity of the carbanion. The significant impact upon nucleophilicity by inductive stabilization is underlined by the virtual non-existence of *N*-alkylated products stemming from reactions of nitrile-stabilized carbanions.⁶

1.4 Structural evidence of nitrile stabilized carbanions

The synthetic value of nitrile stabilized carbanions to organic chemistry as reactive intermediates promoting asymmetric carbon-carbon bond formation has motivated considerable effort into the characterization of these structures both in solution and in the solid state. Although ground state structural determinations of these reactive intermediates cannot be directly correlated to reaction outcomes in the absence of experimentally determined rate laws (as per the Curtin-Hammett principle⁴⁸), insight may eventually be useful in the design of new experimental methodologies.

1.4.1 X-ray crystal structures

As X-ray crystal structures of metalated nitriles in the solid state first began to appear in the literature (structures **32-37**, Figure 1.4),⁵⁹⁻⁶⁴ key structural motifs emerged. Most noticeably, metalated nitriles in the solid state predominately appeared as aggregates, with only two monomeric species currently known (**36** and **37**).^{60, 61} With the exception of sodiated tetramer **35**, the remaining nitriles exist as solvated dimers. That the sodiated analogue exhibits higher order aggregation relative to the lithiated nitriles is not surprising given the larger size of the Na⁺ cation relative to the Li⁺ cation. Additionally, all published X-ray structures to date, with the exception of the infinite ladder structure observed from lithiated 2,2-dimethylcyclopropyl nitrile **34**,⁶² feature exclusive N-metalation. The preferential formation of the C-metalated cyclopropyl nitrile derivative (in this case) is a likely consequence of the energetic penalty imposed by the placement of a trigonal carbon within a cyclopropyl ring in the hypothetical *N*-metalated alternative.

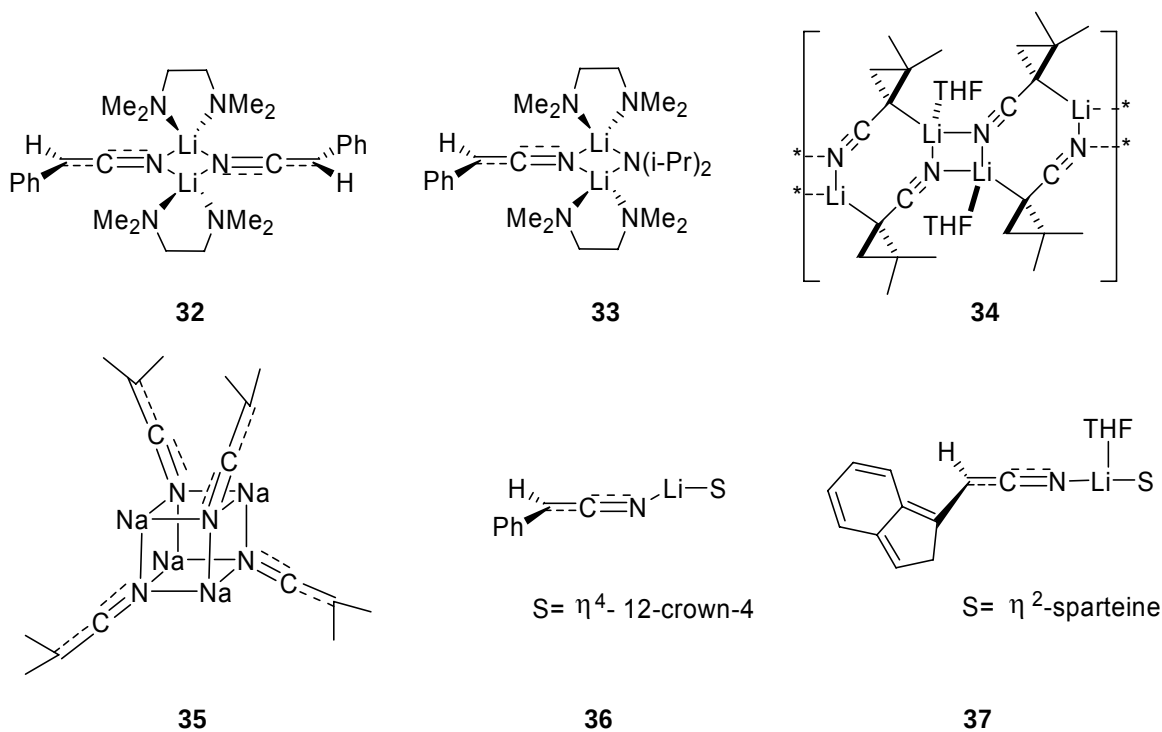


Figure 1.4 Solid-state X-ray structures of metalated nitriles

As originally depicted in Scheme 1.1, analogy to enolate formation suggests that nitrile-stabilized carbanions would adopt the simple valence bond isomers **4a** and **4b** upon deprotonation of the parent nitrile **3**. Bond length analysis of these solid-state structures by X-ray crystallography, however, reveals that although the experimental data shows nitrile-stabilized carbanions to exist in both *C*- and *N*-lithiated constitutional isomeric forms, neither are adequately described by these simple tautomeric representations. Comparisons of X-ray crystal structures **32-37** reveal a substantial deviation from the expected bonding characteristics of these structures based on valence bond isomerism. As shown in Table 1.1, neutral nitriles typically exhibit average C≡N bond lengths of approximately 1.14 Å.^{52, 65, 66} *N*-metalated nitrile analogues such as **4b** would be expected to exhibit significantly lengthened nitrile bonds as the triple bond

character of C≡N is lost upon formation of the cumulated bond structure. The preceding experimentally observed bond lengths, however, do not support this view. Only minimal increases in C≡N bond length are actually observed (0.01-0.05 Å relative to the neutral nitrile), which suggests that despite N-metalation, the nitrile retains significant triple bond character. Given the minimal lengthening observed within the C≡N bond, a proportionate decrease in C_α-CN bond length (representative of a slight increase in bond order) might be expected. This is also not observed experimentally. X-ray data for N-metalated structures **32**, **33**, and **35-37** reveal C_α-CN bond lengths between 1.36 and 1.40 Å, intermediate between that of a C-N single bond (1.54 Å)⁵² and a C=N double bond (1.34 Å).⁵² Moreover, based on formal nitrile carbanion structure **4a**, C-metalated structures such as cyclopropynitrile anion **34** would be expected to feature substantial C≡N triple bond character and a C_α-CN bond length closely resembling that of the neutral nitrile consequent of the absence of resonance stabilization. (C,N)-bridged dimer structure **34**, however, exhibits bond lengths which are nearly indistinguishable from those observed from N-lithiated monomers and dimers (C≡N: 1.17 Å; C_α-CN: 1.41 Å).⁶²

<u>Nitrile</u>	<u>C≡N (Å)</u>	<u>C_α-CN (Å)</u>
Neutral ⁵²	1.14	1.54
32 ⁶³	1.15	1.38
33 ⁵⁹	1.17	1.38
34 ⁶²	1.17	1.41
35 ⁶⁴	1.18	1.36
36 ⁶¹	1.17	1.38
37 ⁶⁰	1.16	1.40

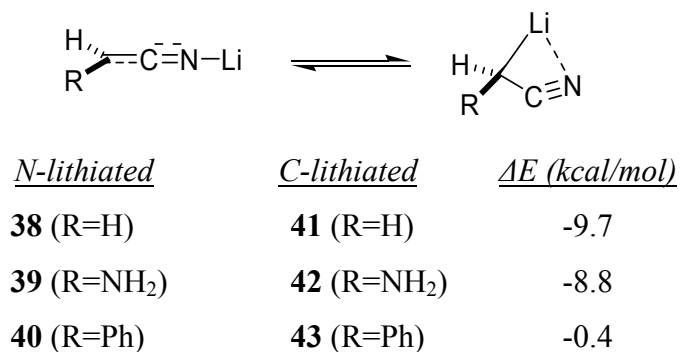
Table 1.1 Metalated nitrile X-ray structure C≡N and C_α-CN bond lengths

That the X-ray structures for both N- and C-metalated structures **32-37** show only minimal lengthening of the nitrile bond, while simultaneously exhibiting a substantial decrease in C $_{\alpha}$ -CN bond length suggests significantly disproportionate bond sharing. This peculiarity in bond distribution is primarily owed to the powerful inductive nature of the nitrile functional group, and led Boche to develop a bond formalism for metalated nitriles which more accurately describes the solid-state structures observed from X-ray crystallography. This formalism, featured in the structures shown in Figure 1.4, portrays an effective “two-and-a-half” nitrile bond and an approximate “one-and-a-half” C $_{\alpha}$ -CN bond.

1.4.2 Computational investigations

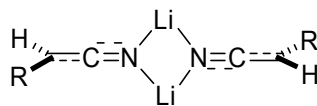
Several theoretical studies have been employed to gain insight into the structural characteristics of nitrile-stabilized carbanions, particularly with focus on identification of aggregation state and position of metalation. Schleyer and co-workers were among the first to attempt to computationally locate the position of metalation in lithiated acetonitrile derivatives. As shown in Scheme 1.14, a 9.7 kcal/mol preference for C-metalated lithioacetonitrile **41** over the corresponding N-lithiated constitutional isomer **38** was predicted by MP2/6-31G(d)//HF/6-31G(d) (this nomenclature signifies MP2/6-31G(d) energies at Hartree-Fock/6-31G(d) geometries).⁶⁷ A similar 8.8 kcal/mol preference for C-lithiation was subsequently calculated by Enders for lithiated aminonitrile isomers **39** and **42** using the same computational protocol.⁶⁸ Finally, Wartski and Corset reported a modest preference for C-lithiated phenylacetonitrile **43** ($\Delta E = -0.4$ kcal/mol relative to **40**)^{40, 69} with HF/3-21+G(d) calculations. With the

experimental X-ray evidence previously reported, it is clear that these gas-phase theoretical assessments do not adequately describe the position of metalation observed in most reported solid-state structures.

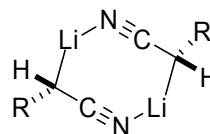


Scheme 1.14 Theoretical preference for unsolvated C-lithiated constitutional isomer

Schleyer also attempted to address the issue of lithioacetonitrile aggregation state by MNDO semi-empirical methods.⁶⁷ His study revealed a 41.8 kcal/mol preference for (C,N)-bridged dimer **45-H** over the corresponding *N,N*-cyclic dimer, **44-H**, see Figure 1.5. Schleyer conceded that the relative energy differences between these dimeric species may not be as high as reported due to the inaccurate MNDO parameterization of Li⁺ cations, which could potentially lead to an overestimation of the C-Li bond strength. Consequently, **44-H** and **45-H** may be much closer in energy than initially predicted at this level of theory. Nevertheless, the experimental predominance of the *N,N*-cyclic dimer suggests a structural trend not duplicated by the theoretical modeling of these nitrile intermediates.



44



45

Figure 1.5 Computational assessment of aggregate structures

It is important to note that these reported gas-phase determinations do not directly account for the effect of solvation—a factor which could greatly influence experimental structure, and indeed the X-ray data shown in Figure 1.4 do feature solvated cations. To address the effect of solvation upon metalated nitrile structure, Schleyer expanded the MNDO analysis of lithiated acetonitrile to include H₂O solvates of *N*- and *C*-metalated constitutional isomers **38** and **41** (mono, bis, and tris solvates), and also their respective solvated dimeric analogues **44-H** and **45-H** (bis and tetrakis solvates).⁶⁷ As detailed in Table 1.2, Schleyer reported that “complete solvation” by the explicit inclusion of three water solvent molecules (presuming maximum tetrahedral coordination to the Li⁺ cation) stabilizes unsolvated *C*-lithiated constitutional isomer **41** by 39.1 kcal/mol (total solvation energy) and the analogous unsolvated *N*-lithiated isomer **38** by 40.0 kcal/mol. The increased (albeit small) relative solvation stabilization of **38•3H₂O**, however, does not offset the native 18.6 kcal/mol preference for the *C*-lithiation predicted for the unsolvated constitutional isomers.⁶⁷ Consequently, the modeling of water solvation upon monomeric lithioacetonitrile isomers by MNDO semi-empirical methods does not reverse the calculated preference for the *C*-metalated monomeric isomer. Much like the case for the monomeric H₂O solvates of lithioacetonitrile, the explicit inclusion of coordinated H₂O solvent molecules to the respective aggregate structures (tetrakis total solvation)

preferentially stabilizes the *N,N*-cyclic dimer **44-H** relative to the (C,N)-bridged dimeric species **45-H** (-46.0 and -36.1 kcal/mol total solvation energy, respectively), but again fails to overcome the calculated relative energetic preference for the unsolvated (C,N)-bridged dimer ($\Delta E = -45.0$ kcal/mol).⁶⁷ In this manner, MNDO-predicted H₂O solvates of monomeric and dimeric lithioacetonitrile do not account for the structural characteristics of most observed solid state metalated nitriles.

<i>N</i> -Lithiated <u>Monomer</u>	<i>Relative Energy (kcal/mol)</i>	<i>Incremental Energy (kcal/mol)</i>	<i>C</i> -Lithiated <u>Monomer</u>	<i>Relative Energy (kcal/mol)</i>	<i>Incremental Energy (kcal/mol)</i>
38	18.6	--	41	0	--
38•H₂O	0.1	-18.5	41•H₂O	-18.5	-18.5
38•2H₂O	-12.2	-12.3	41•2H₂O	-31.4	-12.9
38•3H₂O	-21.4	-9.2	41•3H₂O	-39.1	-7.7
		-40.0 (total)			-39.1 (total)
<i>N,N</i> -Cyclic <u>Dimer</u>	<i>Relative Energy (kcal/mol)</i>	<i>Incremental Energy (kcal/mol)</i>	(C,N)-Bridged <u>Dimer</u>	<i>Relative Energy (kcal/mol)</i>	<i>Incremental Energy (kcal/mol)</i>
44	45.0	--	45	0	--
44•2H₂O	20.4	-24.6	45•2H₂O	-24.6	-24.6
44•4H₂O	-1.0	-21.4	45•4H₂O	-36.1	-11.5
		-46.0 (total)			-36.1 (total)

Table 1.2 Computational assessment of nitrile-stabilized carbanion monomer and dimer solvation by H₂O

Despite the inability of Schleyer's theoretical water solvation studies to accurately model the experimentally observed structural parameters of metalated nitriles, interesting energetic behavior for the explicit solvates was observed. Incremental (stepwise)

solvation of unsolvated, monomeric *N*- and *C*-metalated constitutional isomers **38** and **41** reveals diminishing energetic stabilization from the successive coordination of explicit H₂O molecules to the Li⁺ cation.⁶⁷ As detailed in Table 1.2, mono(H₂O)-solvation of both **38** and **41** (forming **38•H₂O** and **41•H₂O**) provides approximately 18.5 kcal/mol stabilization energy. Addition of a second solvent molecule to give **38•2H₂O** and **41•2H₂O** yields only a 12.3 and 12.9 kcal/mol benefit, respectively. Completion of the presumed tetrahedral Li⁺ cation coordination sphere by addition of a third equivalent of solvent yields only 7.7 and 9.2 kcal/mol additional stabilization.

Sequential pair-wise solvation of dimeric species **44-H** and **45-H** reveals similar results with respect to the diminishing energetic stabilization achieved from stepwise coordination to the Li⁺ cation.⁶⁷ Bis(H₂O)-solvation of each dimer (**44-H•2H₂O** and **45-H•2H₂O**) provides approximately 24.6 kcal/mol solvation stabilization energy to each of the unsolvated aggregates. Tetrakis(H₂O)-solvation of **44-H** and **45-H** again shows a decreased solvation benefit (21.4 and 11.5 kcal/mol, respectively), however the tetrakis(H₂O)-solvated *N,N*-cyclic dimer **44-H•4H₂O** is apparently stabilized to a much more significant degree than the (*C,N*)-bridged dimeric analogue, **45-H•4H₂O**.⁶⁷

In order to rationalize the difference between theoretically predicted and experimentally observed metalated nitrile structures, Carlier and Madura proposed that despite Schleyer's previous determinations, solvation *is* a key determinant in the accurate theoretical modeling of the position of metalation and the aggregation state for lithiophenylacetonitrile derivatives **40** and **43**.⁷⁰ Attempting to determine the lowest level of computational theory necessary to adequately model the structural properties of metalated nitrile derivatives observed experimentally by X-ray crystallography, Carlier

and Madura modeled both unsolvated and solvated *C*- and *N*-metalated constitutional isomers (monomers and dimers) of lithiophenylacetonitrile by semi-empirical, ab initio, and density functional methods. As shown in Table 1.3, semi-empirical, Hartree-Fock, and B3LYP energetic determinations of unsolvated monomeric PM3 geometries show a uniform preference for *N*-lithiated phenylacetonitrile **40** over the corresponding *C*-lithiated constitutional isomer **43** ($\Delta E = 7\text{--}11$ kcal/mol).⁷⁰ This view is in general agreement with solid-state monomeric structures **36** and **37**. Upon consideration of Hartree-Fock geometries, however, the predicted energetic preference for *N*-lithiation diminishes substantially. At HF/3-21G, structure **40** is only predicted to be 5.6 kcal/mol more stable than **43**.⁷⁰ Expansion to HF/3-21+G(d) reverses this preference in favor of *C*-lithiation ($\Delta E = 0.40$ kcal/mol). B3LYP/6-31+G(d) energies at HF/6-31G(d) geometries yield yet another reversal by once again favoring **40** by 0.87 kcal/mol.⁷⁰ This small energetic difference between constitutional isomers **40** and **43** at higher levels of theory suggests that the experimentally observed position of metalation is likely not a consequence of any native preference for nitrile *N*-lithiation, but rather a product of external factors such as crystal-packing effects or solvation stabilization.

<u>Method/Basis set</u>	<u>Relative Energy (kcal/mol)</u>	
	<u>N-lithiated monomer (40)</u>	<u>C-lithiated monomer (43)</u>
PM3	0.00	9.36
HF/3-21G//PM3	0.00	11.15
HF/6-31+G(d)//PM3	0.00	7.00
B3LYP/6-31+G(d)//PM3	0.00	9.90
HF/3-21G	0.00	5.63
HF/3-21+G(d)	0.40	0.00
HF/6-31G(d)	1.19	0.00
B3LYP/6-31+G(d)//HF/6-31G(d)	0.00	0.87

Table 1.3 Relative energies of N- and C-lithiated constitutional isomers for lithiophenylacetonitrile

Following a similar approach to Schleyer's solvation study, Carlier and Madura modeled the effect of explicit solvation upon monomeric and dimeric lithiophenylacetonitrile analogues at HF/3-21G//PM3. Table 1.4 reveals that explicit 12-crown-4 ether solvation of monomers **40** and **43** results in a 6.8 kcal/mol preference for N-lithiated **40•(η⁴-12-crown-4)**⁷⁰ over the hypothetical C-lithiated **43•(η⁴-12-crown-4)** structure, which is in good agreement with the position of metalation of the experimentally observed solid-state structure **36**.⁶¹

Similar to previous studies, energetic determinations at HF/3-21G//PM3 reveal that unsolvated N,N-cyclic dimer **44-Ph** is 4.9 kcal/mol higher in energy than the corresponding (C,N)-bridged dimeric structure **45-Ph** (Table 1.4).⁷⁰ For aggregates **44-Ph** and **45-Ph**, bis(η²-TMEDA)-solvation stabilizes the N,N-cyclic dimer by 90.2 kcal/mol solvation energy compared to only 75.4 kcal/mol for the analogous (C,N)-

bridged dimer.⁷⁰ The increased relative solvation stabilization of the *N,N*-cyclic dimer translates into a 9.8 kcal/mol energetic preference for **44-Ph**, suggesting that HF/3-21G//PM3 is a reliable model for the prediction of the experimentally observed bis(η^2 -TMEDA)-solvated dimer **32**. In this manner, bis(η^2 -TMEDA)-solvated heterodimer **33** identified by X-ray crystallography⁵⁹ was also predicted to be 6.5 kcal/mol lower in energy than the corresponding hypothetical (*C,N*)-bridged dimeric structure.⁷⁰ This study confirms that the inclusion of solvation is necessary for the accurate prediction of the experimentally observed *N*-lithiated monomeric and *N,N*-cyclic dimeric structures despite the relatively low level of computational theory.

<u>Nitrile</u>	<u>Solvent</u>	<u>Relative Energy (kcal/mol)</u>
40	--	0.0
43	--	11.2
40	η^4 -12-crown-4	0.0
43	η^4 -12-crown-4	6.8
44-Ph	--	4.9
45-Ph	--	0.0
44-Ph	bis(η^2 -TMEDA)	0.0
45-Ph	bis(η^2 -TMEDA)	9.8

Table 1.4 Relative HF/3-21G//PM3 energies of monomeric and dimeric solvates of lithiophenylacetonitrile in the modeling of known X-ray structures

In hopes of modeling the solution structure(s) of lithiophenylacetonitrile in THF (conditions for which no confirming solid-state X-ray crystal structures are available),

PM3 geometries of explicit THF-solvates were examined with HF/3-21G energies. Tris(THF)-solvation of monomers **40** and **43** (Table 1.5, **40•3THF** and **43•3THF**) results in larger relative solvation stabilization of unsolvated *N*-lithiated **40** compared to the corresponding *C*-lithiated monomer ($\Delta E = 10.9$ kcal/mol).⁷⁰ Expansion to larger basis sets for this analysis does not alter the predicted energetic favoring of the tris(THF)-solvated *N*-lithiated isomer. Calculations at HF/3-21G, B3LYP/6-31+G(d)//PM3, and B3LYP/6-31+G(d) support the higher relative stability of tris(THF)-solvated **40•3THF** over corresponding **43•3THF** by 6.8-10.2 kcal/mol.⁷⁰ Similar to the modeling of the experimentally observed *N,N*-lithiated cyclic dimers **32** and **33**, tetrakis(THF)-solvation models of dimers **44-Ph** and **45-Ph** at HF/3-21G//PM3 reaffirm the preferential stabilization of the *N,N*-cyclic dimer over the (*C,N*)-bridged dimer ($\Delta E = 6.4$ kcal/mol).⁷⁰ Carlier and Madura concluded that in THF solution, lithiated phenylacetonitrile would likely feature *N*-lithiation independent of aggregation state, in good agreement with most of the solvated structures observed via X-ray crystallography.

	<u><i>N-Lithiated Monomer</i></u>			<u><i>C-Lithiated Monomer</i></u>		
	40•THF	40•2THF	40•3THF	43•THF	43•2THF	43•3THF
HF/3-21G//PM3	0.00	0.00	0.00	11.48	6.31	10.88
Solvation Energy	-36.52	-23.38	-20.12	-36.19	-28.54	-15.56
B3LYP/6-31+G(d)//PM3	0.00	0.00	0.00	9.85	6.88	10.19
Solvation Energy	-24.37	-13.98	-11.81	-24.43	-16.95	-8.5
HF/3-21G			0.00			6.83
B3LYP/6-31+G(d)			0.00			6.75
	<u><i>N,N-cyclic dimer</i></u>		<u><i>(C,N)-bridged dimer</i></u>			
	44-Ph•2THF	44-Ph•4THF	45-Ph•2THF	45-Ph•4THF		
HF/3-21G//PM3	0.00	0.00	1.46	6.37		
Solvation Energy	-67.38	-37.37	-61.02	-31.45		

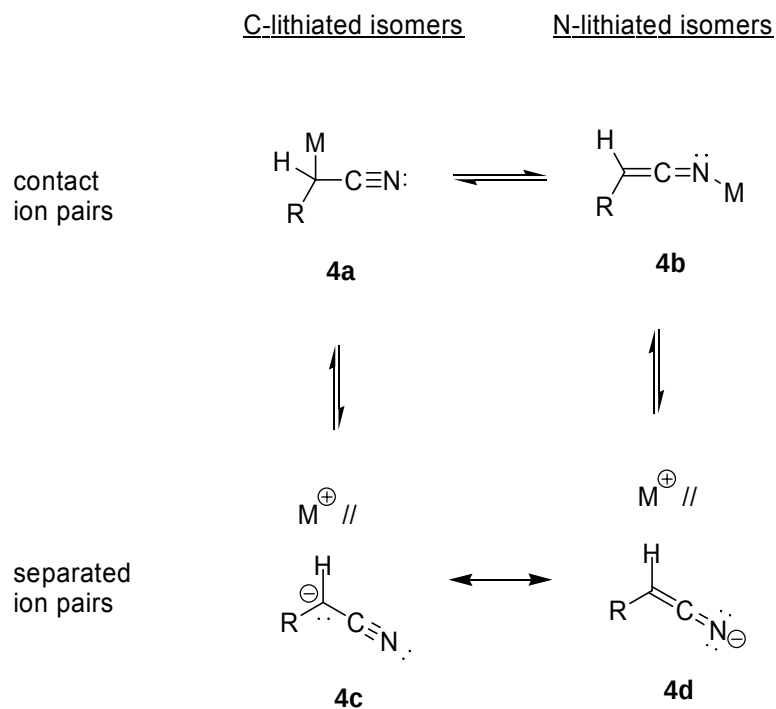
Table 1.5 Incremental and total solvation energies for monomeric and dimeric analogues; All energies reported in kcal/mol.

Like Schleyer's incremental water solvation analysis of lithioacetonitrile, Carlier and Madura showed that successive coordination of THF to the Li^+ cation provides incrementally less stabilization as the cation approaches presumed maximal tetrahedral coordination. Mono(THF)-solvation of *N*- and *C*-lithiated phenylacetonitrile monomers (**40•THF** and **43•THF**, respectively) provides 36.5 and 36.2 kcal/mol respective stabilization energy, whereas bis and tris(THF)-solvation yields stepwise decreases in calculated solvation stabilization energy.⁷⁰ This trend is repeated with higher level energetic determinations performed at B3LYP/6-31+G(d)//PM3. In similar fashion, bis(THF)-coordination of dimers **44-Ph** and **45-Ph** provides greater than 60 kcal/mol solvation energy, however tetrakis(THF)-solvation predicts substantially less stabilization (37.4 and 31.5 kcal/mol, respectively).⁷⁰

It is important to note that the solvation stabilization energies reported in these studies do not include corrections to compensate for the basis set superposition error incurred in calculation of molecular complexes, and thus are artificially inflated. This basis set superposition error (BSSE) and its effect on the respective solvation energies of these THF-solvates will be fully addressed in Chapter 2.

1.5 Solution structure determination of nitrile-stabilized carbanions

X-ray crystal structures conclusively address the physical parameters of metalation site and aggregation state in the solid. Unambiguous description of metalated nitrile structure in solution, however, has proven significantly more difficult. Solvent polarity/donicity plays a key role in the physical nature of the nitrile-stabilized carbanion. As previously mentioned, Pagani and Bradamente's ^{13}C NMR chemical shift measurements in DMSO reveal that the nitrile functional group stabilizes adjacent anionic charge principally by induction rather than through resonance. Consequently, the large charge density on C_α lends itself to ionization by highly polar solvents such as DMSO, and as a result separated ion pairs **4c** and **4d** are plausible structures for metalated nitriles in polar media (Scheme 1.15). Less polar solvents, however, do not possess the electrostatic properties necessary to fully solvate this charge density and the Li^+ cation. As such, weakly polar media encourage the retention of covalent metal coordination to the carbanion (as shown by tautomers **4a** and **4b**).⁷¹ These studies underline the key role of solvent on the ionization state of metalated nitriles in solution and provide insight into the difficulties encountered in the elucidation of the nitrile-stabilized carbanion solution structure.



Scheme 1.15 Plausible structures of metalated nitriles in solution

The propensity for aggregation of stabilized carbanions further complicates solution structure determination. Seebach conducted freezing point depression studies of dilute lithioacetonitrile solutions in THF and concluded that these metalated nitriles predominantly exist as aggregates in low dielectric media.⁷² Studies of lithiophenylacetonitrile under the same conditions, however, showed contrasting behavior in the predominance of a monomeric ion pair.⁷² While the susceptibility of colligative studies to impurities has been noted,⁷³ supporting equilibrium pK_a measurements have shown that the acidity of lithiophenylacetonitrile in THF is roughly constant over a 20-fold concentration range,⁷⁴ suggesting that these nitrile-stabilized do not aggregate into dimers and other higher order solution structures in this concentration range. Freezing point depression studies by Das and co-workers, however, provided evidence for the

aggregation of lithioacetonitrile to a principally tetrameric species in DMSO.⁷⁵ Similar results were observed in an apparent dimeric formation of lithiophenyl-acetonitrile.⁷⁵

The association of lithioacetonitrile carbanions in non-polar media is a likely consequence of electrostatic stabilization. As discussed, metalated nitrile contact ion pairs predominate in solvents of low polarity/donicity. As a result, these carbanions can achieve stabilization through self-association (i.e., the energetic benefit of electrostatic stabilization is greater than the entropic cost of association). Benzylic nitrile carbanions, however, exhibit sufficient delocalization into the phenyl ring that the electrostatic stabilization provided by aggregation is insufficient to overcome this entropic penalty.⁷⁴ Highly polar media, which promote ion-pair separation, encourages the free ions to aggregate as a means of electrostatic stabilization.⁷⁴

1.5.1 Direct measurements of solution structure

Multinuclear NMR has emerged as a powerful tool for the structural determination of metalated nitriles in solution. Collum's ^6Li - ^{15}N NMR double labeling technique offered the first direct descriptions of lithium-nitrogen connectivity in aggregate formations of lithium amides LDA⁷³ and LiHMDS⁷⁶ in ethereal solvent. Based on the multiplicity of the coupled ^6Li ($I=1$) and ^{15}N ($I=1/2$) nuclei,⁷⁷ structural determinations regarding the chemical environment surrounding each atom could be directly determined. As detailed in Table 1.6, monomeric *N*-metalated lithium amides ($\mathbf{M}_0$) would appear as a doublet and triplet by ^6Li and ^{15}N NMR, respectively. An *N,N*-cyclic dimer, by contrast, would be characterized by a ^6Li triplet and a ^{15}N quintet. If

experimental conditions favored the formation of a solvent separated ion pair, however, the loss of connectivity would result in singlets observable in both NMR spectra.

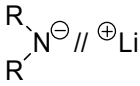
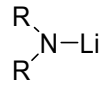
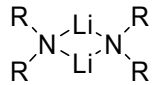
<u>Structural form</u>	<u>${}^6\text{Li}$ NMR</u>	<u>${}^{15}\text{N}$ NMR</u>
 S_0	Singlet	Singlet
 M_0	Doublet	Triplet
 D_0	Triplet	Quintet

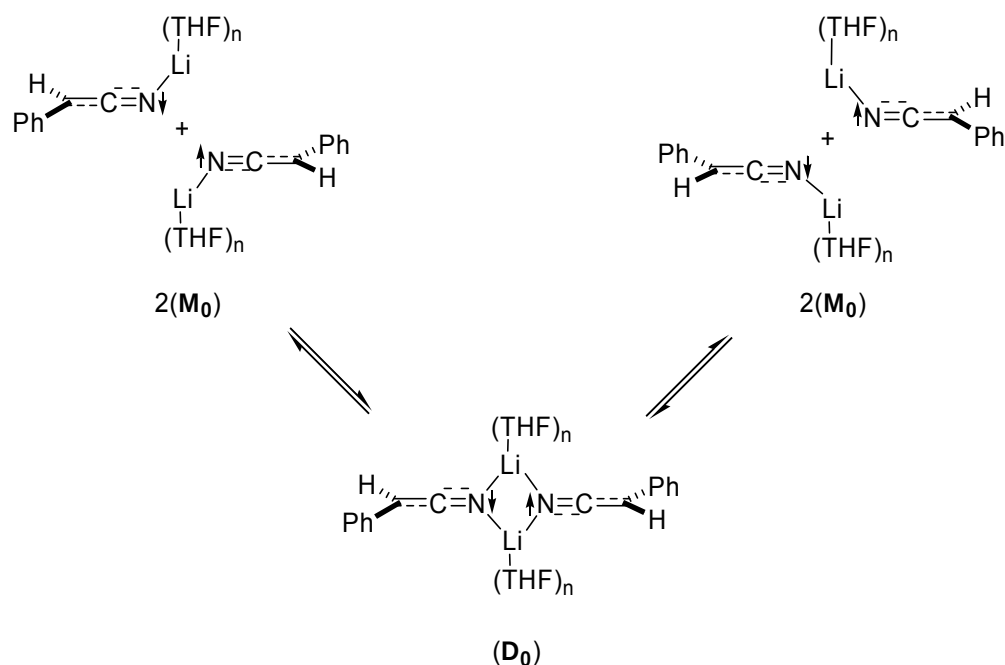
Table 1.6 Predicted NMR resonance multiplicities for ${}^6\text{Li}$, ${}^{15}\text{N}$ double labeled lithium amides

1.5.1.1 Identification of an N-lithiated dimer

In collaboration with Collum, Carlier applied this double-labeling technique to determine the solution structure of lithiophenylacetonitrile [${}^6\text{Li}$, ${}^{15}\text{N}$]**27-Li** in Et_2O and TMEDA solution.⁷⁸ Observing a triplet by ${}^6\text{Li}$ NMR and a quintet by ${}^{15}\text{N}$ NMR, it was concluded that **27-Li** exists as an aggregate in these weakly polar solvent systems. While Table 1.6 presents a very specific view of cyclic dimers, it is important to note that any aggregate formation featuring dual lithium coordination to nitrogen (and vice versa) will exhibit this same NMR splitting pattern. To concretely identify the observed aggregate as *N,N*-cyclic dimer **D₀** (as depicted above) rather than other higher aggregate oligomers, two-dimensional ${}^6\text{Li}$ - ${}^{15}\text{N}$ HMQC experiments⁷⁹ were conducted, providing unambiguous

identification of the of **27-Li** as *N,N*-cyclic dimer **D₀**.⁷⁸ Thus, *N,N*-lithiated dimers have been characterized both in solution (NMR) and in the solid (X-ray).

When attempting the double labeling experiment in THF and hydrocarbon mixtures thereof, however, no scalar ⁶Li-¹⁵N coupling for [**⁶Li,¹⁵N**]**27-Li** could be observed down the freezing point of THF. One possible explanation for the loss of connectivity information is the loss of scalar coupling due to rapid chemical exchange. If **27-Li** exists as a contact ion pair (e.g. **M₀** or **D₀**) and the rates of the Li-N bond-breaking/bond-forming processes are faster than the ⁶Li-¹⁵N coupling constant, then no scalar coupling would be observed. Connectivity information would be lost as one Li nucleus exchanges formal connections with an α- (↓) and β-spin (↑) ¹⁵N nuclei, as illustrated in Scheme 1.16. This type of exchange-facilitated scalar decoupling has been previously observed by Fraenkel in the studies of benzyllithium compounds.⁸⁰ Alternatively, THF could promote the formation of separated ion pairs **S₀**, thus removing formal connectivity between the two atoms.



Scheme 1.16 Deconstruction of scalar coupling by rapid chemical exchange. Note that from the perspective of a Li nucleus, conversion of $2(\mathbf{M}_0)$ on the left into $2(\mathbf{M}_0)$ on the right swaps nuclear spins of the attached N atoms.

1.5.1.2 Ion-pair determinations

In 1993, Reich et al. reported an NMR technique to characterize lithium ion pairs in THF/HMPA solutions based on the observation that ligand-exchange rates of HMPA-coordinated Li^+ were sufficiently slow at temperatures less than $-125\text{ }^\circ\text{C}$ to allow for distinction between coordinated and free HMPA.⁸¹ In this slow-exchange domain, 2-bond Li-P scalar coupling ($^2J_{\text{Li-P}}$) could be resolved, thus allowing for differentiation between the HMPA solvated contact ion pairs ($\mathbf{M}_n$, $\mathbf{D}_n$) and separated ion pairs ($\mathbf{S}_n$) illustrated in Figure 1.6. By observing the changes in multiplicity and chemical shift (δ , ppm) in both $^6,7\text{Li}$ and ^{31}P NMR as a function of incrementally increasing concentrations of HMPA, general classifications regarding ion pair status could be made, but moreover

individual solvates could be readily identified, as described in Table 1.7. Note that the HMPA-solvate nomenclature shown in Figure 1.6 and Table 1.7 (**M**₀, **D**₀, **S**₀, etc.) is adopted from Jackman's ¹³C NMR study of lithium phenolate solution structure.⁸²

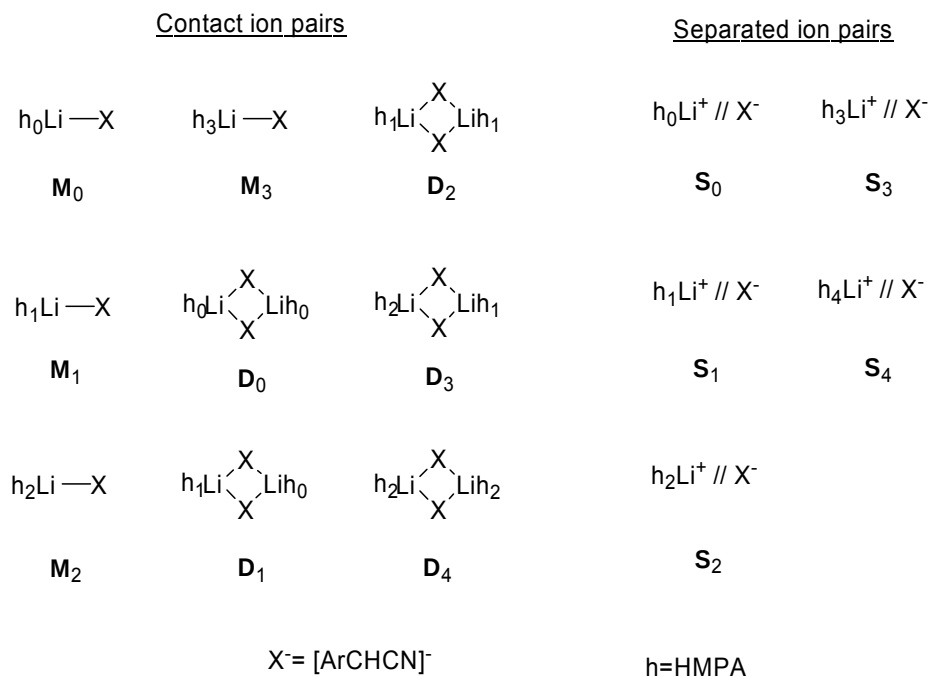


Figure 1.6 Potential HMPA solvate structures of lithiophenylacetonitrile

In order to first establish a general boundary profile for the NMR behavior of salient separated ion pairs and contact ion pairs, Reich studied structures expected to exist as separated ion pairs by virtue of the stability of their respective conjugate bases (specifically fluorenyllithium and trityllithium). Upon sequential addition of HMPA, he was able to characterize (primarily through ⁷Li splitting patterns) solvates corresponding to separated ion pairs **S**₀-**S**₄ (⁷Li: singlet-quintet, respectively). At one equivalent added HMPA (relative to the Li⁺ concentration), a 1:3:1 ratio of **S**₀:**S**₁:**S**₂ was observed. Further

addition to three equivalents added HMPA gave complete conversion into **S**₃. Titration to four equivalents HMPA showed approximately a 1:1 ratio of **S**₃ to **S**₄ suggesting that the last HMPA molecule is weakly coordinated to the Li⁺ cation. These molecules were termed “THF-separable ion pairs.”

<u><i>Solution species</i></u>	<u><i>⁷Li (multiplicity)</i></u>	<u><i>³¹P (multiplicity)</i></u>
M ₀	Singlet	--
M ₁	Doublet	Quartet
M ₂	Triplet	Quartet
M ₃	Quartet	Quartet
D ₀	Singlet	--
D ₁	Doublet/singlet	Quartet
D ₂	Doublet	Quartet
D ₃	Triplet/doublet	Quartet
D ₄	Triplet	Quartet
S ₀	Singlet	--
S ₁	Doublet	Quartet
S ₂	Triplet	Quartet
S ₃	Quartet	Quartet
S ₄	Quintet	Quartet

Table 1.7 Theoretical prediction of ⁷Li and ³¹P NMR splitting patterns of representative HMPA solvates

Note from above that theoretical ⁷Li NMR multiplicities alone cannot readily distinguish contact ion pairs **M**₀-**M**₄ from separated ion pairs **S**₀-**S**₄. These characterizations are made possible due to the nuclear properties of the ⁷Li isotope. In

the slow exchange domain, ^6Li nuclei give characteristically sharp NMR signals. ^7Li nuclei, however, typically give very broad resonances due to rapid T_1 relaxation caused by a 58-fold larger quadrupole moment relative to the ^6Li isotope.⁸³ Thus, ^7Li linewidth ($\nu_{1/2}$) can effectively be used to differentiate between contact ion pairs (e.g., $\mathbf{M}_n$) and separated ion pairs in solution by virtue of the symmetric geometry of the Li^+ cation coordination sphere featured in solvates such as $\mathbf{S}_4$. Tetrahedral solvation of ^7Li nuclei fosters a highly symmetric coordination environment with little to no imposed electric field gradient.⁸³ Consequently, $\mathbf{S}_4$ produces sharp ^7Li NMR resonances due to the lower electric field gradient at the Li nucleus. Solvation of contact ion pairs by HMPA necessarily leads to unsymmetrical coordination geometries. As a result, contact ion pairs typically exhibit large ^7Li linewidths ($\nu_{1/2} > 3 \text{ Hz}$), whereas separated ion pairs typically give rise to narrow ^7Li linewidths ($\nu_{1/2} < 1.5 \text{ Hz}$).⁸¹

Reich et al. also examined lithium compounds expected to exist as contact ion pairs in ethereal solvent (including lithium halides, lithium methanethiolate, and lithium methaneselenoate). In each case, HMPA was observed to solvate the contact ion pair, and then promote the formation of separated ion pairs, giving $\mathbf{S}_4$ at six equivalents added HMPA.⁸¹ Incremental addition of HMPA induced formation of separated ion pairs, leading Reich to classify them as “HMPA-separable ion pairs”. The defining characteristic for HMPA-separable ion pairs is the appearance of free HMPA by ^{31}P NMR at concentrations less than four equivalents relative to $[\text{Li}^+]$.⁸¹ Presuming optimal tetrahedral coordination of HMPA to the Li^+ cation, separated ion pairs have four available coordination sites. Conversely, each covalent bond to the Li^+ cation occupies a coordination site. Thus, the appearance of unbound HMPA at low concentrations relative

to the Li^+ cation suggests that one (or more) of the sites are occupied by a formal bond. Finally, Reich classified phenyllithium and methyllithium as “HMPA-inseparable ion pairs”. For these compounds, addition of HMPA results only in the formation of $\mathbf{M}_1$ with no observable aggregation or ionization as the relative HMPA concentration was increased. Addition of HMPA in excess of ten equivalents relative to the Li^+ cation resulted in no visible formation of solvent separated species.⁸¹

1.5.1.3 Application of Reich’s HMPA titration protocol

In order to identify the mechanism of scalar decoupling observed for lithiophenylacetonitrile **27-Li** (and also lithionaphthylacetonitrile) in THF, Carlier and Lo examined ^7Li linewidths to confirm (or refute) the existence of **27-Li** as a contact ion pair. Reich’s salient examples of separated ion pairs in THF displayed sharp ^7Li linewidths for fluorenyllithium and trityllithium ($\nu_{1/2}$ =1.1 Hz, and 3Hz, respectively).⁸¹ In 2:1 THF/pentane and 2:1 THF/toluene, however, **27-Li** exhibits line widths of 8.9 and 5.6 Hz, respectively. Under large excesses of THF, **27-Li** and lithionaphthylacetonitrile show linewidths of 7.9 and 5.8 Hz, respectively.⁸⁴ These linewidth data suggest that these lithiated benzylic nitriles exist as contact ion pairs.

For more conclusive ionization state determination, Carlier and Lo applied Reich’s HMPA titration protocol to confirm the identity of arylacetonitriles as a contact ion pair. In 20:1 THF/hexane, addition of one equivalent HMPA shows three distinct signals by ^{31}P NMR (δ 27.5 ppm, δ 27.0 ppm, and δ 26.7 ppm), all characterized as 1:1:1:1 quartets (Chart 1.1, B).⁸⁴ Addition of two equivalents of HMPA shows the disappearance

of the quartet at $\delta 27.5$ ppm, and the emergence of a singlet at $\delta 26.1$ ppm (Chart 1.1, C), corresponding to the appearance of uncoordinated HMPA in solution. That unbound HMPA appears at two added equivalents relative to the Li^+ cation strongly supports the existence of metalated benzylic nitriles as contact ion pairs,⁸⁴ thereby prompting the conclusion that the loss of scalar coupling in the previous study was attributable to rapid solvent-facilitated Li-N nuclear exchange.

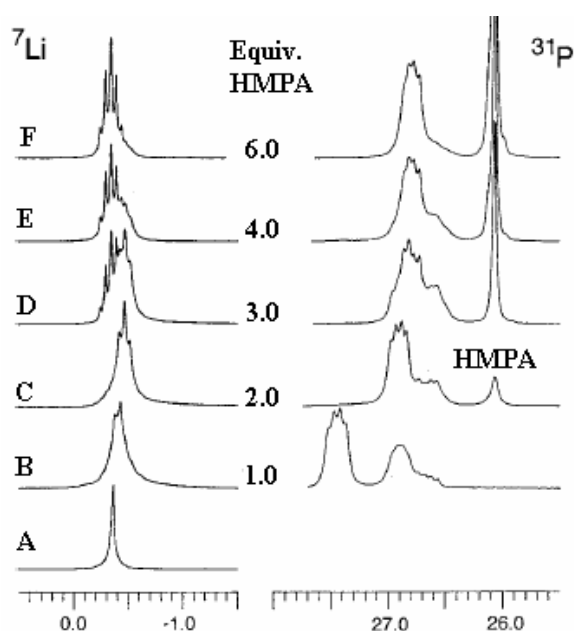


Chart 1.1 ^7Li and ^{31}P NMR of **27-Li** in 20:1 THF/Hexane at $-125\text{ }^\circ\text{C}$ as a function of added HMPA

Characterization of the individual solvates present in solution was achieved through dilution measurements at fixed HMPA concentration (one equivalent relative to $[\text{Li}^+]$) and also titration of the arylacetonitrile derivatives by sub-stoichiometric $[\text{HMPA}]$, as depicted in Chart 1.2. The concentration dependence of the relative peak intensities at $\delta 27.5$ and $\delta 27.0$ ppm (A-E) and the presence of a single peak with a 2:1 stoichiometry of

[Li⁺] to [HMPA] observed at 0.5 equivalents added HMPA (G) suggests that the compound in solution responsible for the peak at $\delta 27.5$ ppm is dimeric analogue **D**₁.⁸⁴ By this reasoning, the peak appearing at $\delta 27.0$ should be monomer **M**₁.

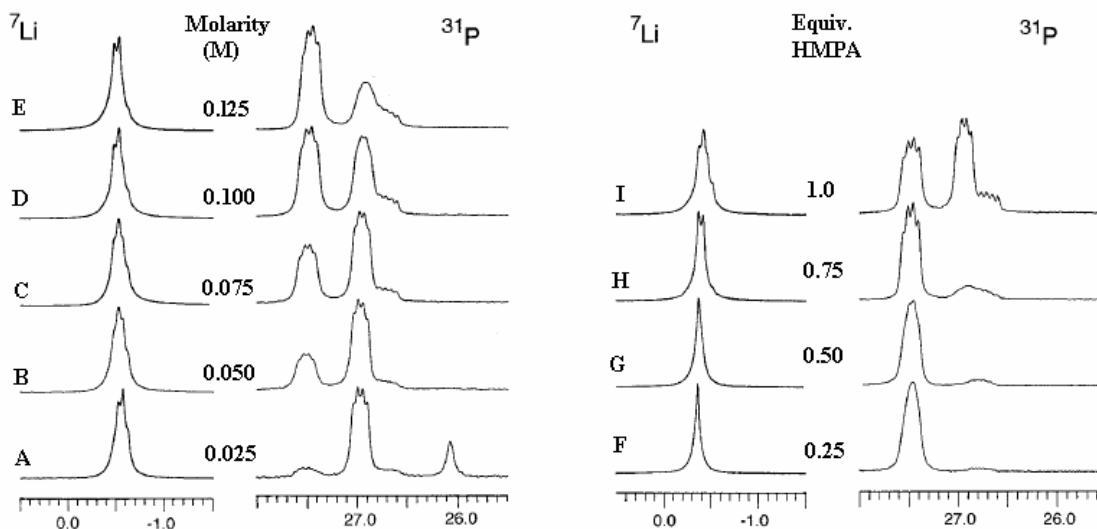


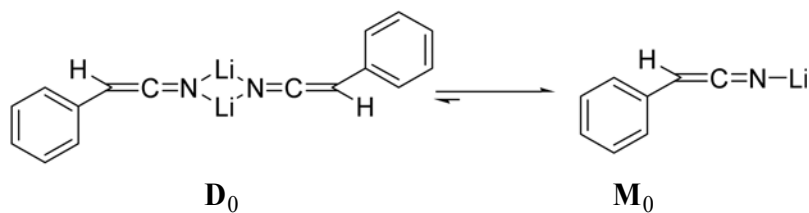
Chart 1.2 Concentration dependence of ⁷Li and ³¹P NMR of **27-Li** in 20:1 THF/Hexane (A-E); and titration of sub-stoichiometric [HMPA] (F-I)

The conclusion that addition of sub-stoichiometric concentration of HMPA serves to induce aggregation of organolithium compounds in solution is controversial given that the conventional wisdom which pervades the literature suggests that HMPA increases reaction rates through deaggregation of the reactive species. This conclusion, however, is not without precedent. Jackman had previously reported that solvation of lithium phenolates by HMPA can induce both aggregation *and* deaggregation on the basis of ²J_{Li-P}, ¹³C NMR and analysis of ⁷Li quadrupolar splitting constants.⁸² Jackman reported that for dimeric and trimeric phenolates, addition of sub-stoichiometric concentrations of

added HMPA (<1 equivalent) induces aggregation to the corresponding tetrameric species. At higher concentrations of added HMPA, deaggregation of the tetrameric species to corresponding monomers and separated ion pairs is then observed.⁸²

1.5.2 IR determinations

Integral to their studies of regiocontrol mechanisms for metalated nitrile addition to α,β -unsaturated systems, Wartski and Corset reported the measurement of integrated $\nu(\text{C}\equiv\text{N})$ bands from vibrational spectroscopy to characterize lithiophenylacetonitrile **27-Li** structure in solution. In pure THF, they noted two distinct vibrational stretches in the nitrile frequency region in an approximate 9:1 ratio by IR spectroscopy (2091 and 2059 cm^{-1}). Dilution studies revealed a direct concentration interdependence on the relative intensities of these integrated IR bands, thus leading to the putative characterization of these two species as a M_0/D_0 equilibrium pair in pure THF, as illustrated in Scheme 1.17.^{46, 69}



Scheme 1.17 Aggregate equilibrium of **27-Li** in THF

Similar spectral behavior was reported by Raman vibrational spectroscopy, however an IR-invisible $\nu(\text{C}\equiv\text{N})$ stretch at 2071 cm^{-1} was also observed. This stretch was attributed to the symmetric $\nu(\text{C}\equiv\text{N})$ vibrational stretching mode of the dimeric species, **D**₀ ($\nu(\text{C}\equiv\text{N})_s$ Figure 1.7).⁶⁹ Providing support for this determination, Wartski and Corset calculated theoretical $\nu(\text{C}\equiv\text{N})_{as}$ vibrational frequencies for the monomer and dimer to be 2087 and 2052 cm^{-1} by B3LYP/6-31+G(d), respectively.⁶⁹ In light of the observed concentration dependence of the IR $\nu(\text{C}\equiv\text{N})_{as}$ bands, and also the appearance of a Raman visible asymmetric $\nu(\text{C}\equiv\text{N})_s$ band, the authors assigned the nitrile stretch at 2057 cm^{-1} to dimeric species **D**₀, and the corresponding $\nu(\text{C}\equiv\text{N})$ band at 2089 cm^{-1} to monomer **M**₀.⁴⁰ Their conclusion was further supported by computational vibrational frequency calculations which successfully replicated the experimentally observed ordering of **M**₀ and **D**₀ $\nu(\text{C}\equiv\text{N})_{as}$ stretches.

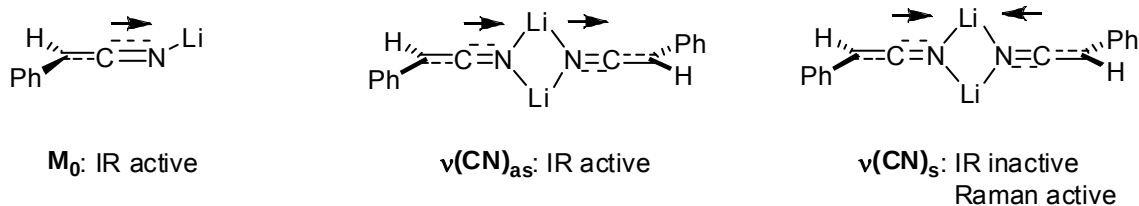


Figure 1.7 Symmetric and asymmetric vibrational modes for **M**₀ and **D**₀ $\nu(\text{C}\equiv\text{N})$; Anti diastereomers of **D**₀ are shown arbitrarily

Following Carrier's determination that HMPA induces aggregation of **27-Li** under disclosed experimental conditions (0.1M **27-Li** in 20:1 THF/Hexane, $-125\text{ }^{\circ}\text{C}$), Wartski and Corset used IR spectroscopy to monitor the effect of sequential HMPA titration upon the integrated $\nu(\text{C}\equiv\text{N})$ stretches for 0.12M **27-Li** in 20:1 THF/Hexane (at room

temperature). At 0 equivalents added HMPA, they observed a two species ratio nearly identical to their previously reported **M**₀/**D**₀ equilibrium in pure THF. Upon incremental addition of sub-stoichiometric HMPA concentrations (0.25 to 0.75 equivalents per Li⁺ cation),⁶⁹ they observed an increase in the intensity of the $\nu(\text{C}\equiv\text{N})$ band at 2089 cm⁻¹ at the expense the stretch at 2057 cm⁻¹. At these HMPA concentrations, the minor $\nu(\text{C}\equiv\text{N})$ stretch at 2057 cm⁻¹ was reduced to a mere shoulder on the major band at 2089 cm⁻¹. Further addition of HMPA to an equimolar concentration (relative to **27-Li**), prompted the complete disappearance of the previously designated **D**₁ $\nu(\text{C}\equiv\text{N})$ stretch. Large excesses of HMPA (>2.0 equivalents) prompted little further change in the recorded IR $\nu(\text{C}\equiv\text{N})$ bands aside from a small, progressive shift in the purported **M**₁ $\nu(\text{C}\equiv\text{N})$ frequency from 2089 cm⁻¹ to 2091 cm⁻¹.⁶⁹

Wartski and Corset concluded that the addition of sub-stoichiometric concentrations HMPA to **27-Li** in THF displaces one solvent molecule in the first solvation shell of the Li⁺ cation in **D**₀. Further replacement of THF in the lithium coordination sphere subsequently deaggregates the HMPA-solvated dimer **D**₁ to mono-HMPA solvated monomer **M**₁.⁶⁹ Their conclusion that sub-stoichiometric concentration of added HMPA solely deaggregates **27-Li** in 20:1 THF/Hexane directly contradicts the conclusions drawn by Carlier's multinuclear NMR study.⁸⁴ Whether their study refutes Carlier's published conclusions, or whether these two studies can be harmonized, is addressed in Chapter 2.

1.6 Conclusions

Nitrile-stabilized carbanions are very important intermediates for asymmetric and symmetric carbon-carbon bond forming reactions. They have proven to be useful toward the formation of small-membered ring systems, for regioselective addition to aldehydes, ketones, and α,β -unsaturated systems, and also as masked functionalities in total synthesis designs. Despite definitive structural evidence offered by solid-state X-ray crystallography, the structural properties defining their solution structure remain elusive. Contrasting structural assessments from multinuclear NMR and vibrational spectroscopy have thus far hindered the definitive structural characterization of metalated nitriles in low dielectric media. As mentioned above, we will address these contradictory conclusions in attempt to resolve these apparent discrepancies within Chapter 2.

Chapter 2 Theoretical and experimental determination of the solution structure of lithiated benzylic nitriles

2.1 Summary and reinvestigation of prior experimental structural determination

As detailed within Chapter 1, direct solution-phase structure determination by multinuclear NMR spectroscopy has emerged as one of the most powerful and descriptive analytical techniques available for nitrile-stabilized carbanion structure elucidation. In summary, Carlier and Lo demonstrated the utility of $^6\text{Li}/^{15}\text{N}$ NMR spectroscopy in the unambiguous identification of both the position of metalation and aggregation state for Et_2O - and TMEDA-solvated lithiophenylacetonitrile [$^6\text{Li},^{15}\text{N}$]**27-Li**⁷⁸ through application of Collum's [$^6\text{Li},^{15}\text{N}$] double isotopic labeling technique for the characterization of lithium amide aggregates in low dielectric media.⁷³ These spectral data revealed structural characteristics in excellent agreement with the solid-state evidence offered by X-ray crystallography, but complementary spectroscopic analysis of benzylic nitriles in THF solution offered no discernable structural information. In response, Carlier and Lo employed Reich's HMPA titration method⁸¹ to characterize both monomeric (**M**₁) and dimeric (**D**₁) contact ion pair analogues of HMPA-solvated **27-Li** in 20:1 THF/Hexane solution on the basis of the concentration interdependence and multiplicity of the observed $^7\text{Li}/^{31}\text{P}$ NMR signals.

The spectral evidence from Carlier and Lo's multinuclear NMR analysis further prompted the key determination that sub-stoichiometric addition of HMPA to the low dielectric solution induced dimerization of monomeric **27-Li**⁸⁴—a controversial assessment which has since been challenged in the recent literature. As part of their continued experimental efforts to identify the mechanisms of regiocontrol for the addition

of metalated nitriles to α,β -unsaturated systems, Wartski and Corset had reported that in weakly polar solvent systems, **27-Li** exists as an $\mathbf{M}_0\cdot\mathbf{D}_0$ contact ion pair equilibrium, the position of which is directly related to the dielectric constant of the chosen solvent system.⁴⁵ In pure THF, their IR spectroscopic studies had revealed two distinct vibrational stretches in the nitrile frequency region in an approximate 9:1 ratio.^{39, 40} They suggested, through the observed concentration interdependence of the $\nu(\text{C}\equiv\text{N})$ bands, that the individual solution structures comprising the **27-Li** monomer-dimer equilibrium could be identified on the basis of these unique nitrile vibrational frequencies. With support from a theoretical vibrational frequency analysis of hypothetical monomeric and dimeric structures by ab initio and density functional computational methods, Wartski and Corset assigned the $\nu(\text{C}\equiv\text{N})$ stretches at around 2057 and 2089 cm^{-1} to dimeric and monomeric **27-Li**, respectively.^{39, 40} Providing additional support for their structural assignments was the emergence of an IR-invisible $\nu(\text{C}\equiv\text{N})$ stretch near 2071 cm^{-1} by Raman spectroscopy, which they subsequently attributed to the symmetric vibrational mode of dimer $\mathbf{D}_0$, $\nu(\text{C}\equiv\text{N})_s$.⁶⁹

Following Carlier and Lo's published report of the HMPA-induced aggregation of **27-Li** in 20:1 THF/Hexane upon sub-stoichiometric titration by HMPA, Wartski and Corset applied their IR spectroscopic techniques to monitor the titration of **27-Li** by HMPA under similar experimental conditions.⁶⁹ They observed that the 2057 cm^{-1} $\nu(\text{C}\equiv\text{N})$ stretch assigned to the **27-Li** dimer incrementally minimized relative to the designated monomeric band at 2089 cm^{-1} with no evidence for the HMPA-induced aggregation suggested by Carlier and Lo at low concentrations added HMPA (0.25-0.75 equivalents relative to **27-Li**).⁸⁴ These observations led Wartski and Corset to conclude

that the addition of HMPA serves only to break up the dimeric lithiated benzylic nitrile preexisting as a part of the observed $\mathbf{M}_0\mathbf{:D}_0$ contact ion pair equilibrium in low dielectric media.

Herein we detail our focused efforts toward the resolution of these contrasting structural evaluations in attempt to definitively identify the solution-phase structure of lithiated benzylic nitriles in low dielectric media. To objectively assess the validity of the conclusions drawn from each of these experimental studies, we revisit both the multinuclear NMR investigation which prompted the characterization of **27-Li** as HMPA-induced aggregate $\mathbf{D}_1$ in 20:1 THF/hexane and the determinations deriving from vibrational spectroscopy which dismiss this assessment in favor of a strictly dissociative model.

2.1.1 Reexamination of the HMPA titration of lithiophenylacetonitrile in THF/Hexane by IR spectroscopy

Resolution of the contrasting structural assessments offered by vibrational and NMR spectroscopy begins with a reinvestigation of Wartski and Corset's vibrational spectroscopic analysis of **27-Li** in THF and the sub-stoichiometric HMPA titration thereof. IR spectroscopic data reported herein are recorded under anhydrous conditions on a MIDAC FT-IR spectrometer equipped with an ICL Model SL-2 FT-IR CaF_2 flow cell (path length 0.05 mm). For a more detailed description of the IR spectroscopic experimental methodologies and the apparatus used to gather these data, refer to Section 3.1.2.

As shown in Chart 2.1, our own examination of 0.1M **27-Li** in pure THF by IR spectroscopy reveals two principle stretches in the nitrile frequency region existing in an approximate 9:1 ratio. The major $\nu(\text{C}\equiv\text{N})$ band appears at 2090.5 cm^{-1} while the minor $\nu(\text{C}\equiv\text{N})$ stretch is observable at 2057.7 cm^{-1} . Both the frequency and proportionate intensity of these vibrational stretches are in very close agreement with the spectral data first reported by Wartski and Corset.

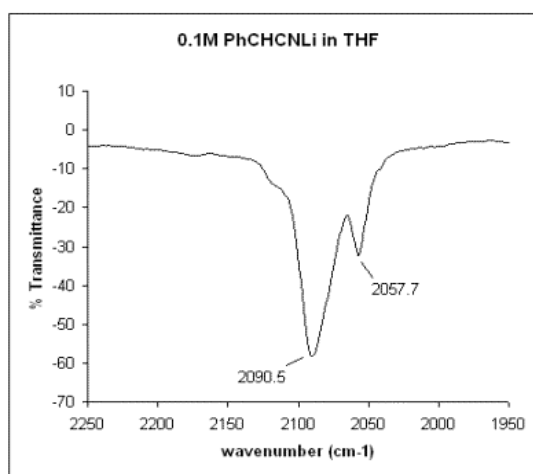


Chart 2.1 IR signature $\nu(\text{C}\equiv\text{N})$ of 0.1M **27-Li** in THF

Recall from Section 1.5.2 that Wartski and Corset had further observed an IR-invisible nitrile vibrational band by Raman spectroscopy (employing a stabilized Nd:YAG laser emitting at 1064 nm), which they had attributed to the symmetric nitrile vibrational mode of dimeric **27-Li**. Our own attempted investigations by Raman spectroscopy, however, were unsuccessful. Collaborating with Professor Robert Bodnar in the Department of Geosciences at Virginia Tech, we attempted Raman data collection on neat acetonitrile CH_3CN , bulk benzyl cyanide **27**, and 0.1M **27-Li** in THF in quartz

sample vials on an Instruments S.A. Laser Raman Microprobe equipped with both a green laser (emitting at 514.5 nm) and near-UV laser (emitting at 488.0 nm). In each attempted experiment, we were unable to observe Raman vibrations due to the high laser-induced fluorescence of the nitriles by these particular wavelengths of light.

Wartski and Corset's proposal for the complete deaggregation of dimeric species **D**₁ to **M**₁ upon serial titration of **27-Li** with sub-stoichiometric concentrations of HMPA was based largely on the observed minimization in the intensity of the purported dimeric $\nu(\text{C}\equiv\text{N})_{\text{as}}$ band relative to the assigned monomeric stretch.⁶⁹ Our reinvestigation of this HMPA titration experiment by IR spectroscopy reveals similar behavior in the incremental disappearance of the minor $\nu(\text{C}\equiv\text{N})$ stretch at 2057.7 cm⁻¹ upon serial addition of sub-stoichiometric HMPA, as shown below in Chart 2.2. The addition of 0.5 equivalents HMPA to 0.1M **27-Li** in 20:1 THF/hexane solution reduces the relative intensity of this vibrational stretch to a shoulder against the major $\nu(\text{C}\equiv\text{N})$ band at 2090.5 cm⁻¹. Further addition of large excesses of HMPA (e.g., 6.0 equivalents relative to the Li⁺ cation) results in the complete disappearance of the vibrational stretch at 2057.7 cm⁻¹ and a small (but observable) progression of the 2090.5 cm⁻¹ band to 2096.2 cm⁻¹, which had also been noted by Wartski and Corset.

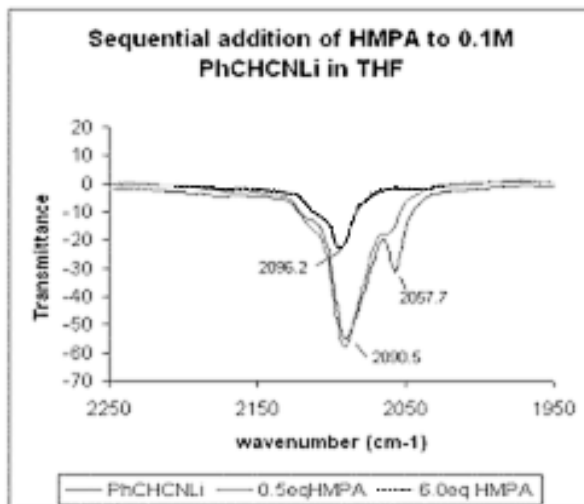


Chart 2.2 HMPA titration experiment by IR spectroscopy

2.1.2 Reexamination of lithiophenylacetonitrile in THF/ Hexane by ⁷Li/³¹P NMR spectroscopy

Having replicated the spectral evidence ultimately used to challenge Carlier and Lo's characterization of **27-Li** as an HMPA-induced aggregate in 20:1 THF/Hexane solution under select experimental conditions, we direct our attention to a full reinvestigation of the multinuclear NMR spectroscopic experiments upon which that original assessment had been based.

The ⁷Li NMR (155.455 MHz) and ³¹P NMR (161.923 MHz) NMR spectral data reported herein are acquired unlocked at -125 °C in 20:1 THF/Hexane. Chemical shifts (δ, ppm) are measured relative to the external references 0.3 M LiCl in MeOH (δ 0.0 ppm) and 0.1 M HMPA in 20:1 THF/hexane (δ 26.10 ppm), respectively. For a more detailed description of NMR methodologies, refer to Section 3.1.1.

2.1.2.1 Reinvestigation of ion pair status by ^7Li linewidth

As previously described, ^7Li linewidth ($\nu_{1/2}$) can often be effectively used to qualitatively differentiate between contact ion pairs (e.g., $\mathbf{M_n}$ or $\mathbf{D_n}$) and separated ion pairs (e.g., $\mathbf{S_n}$) in solution as a consequence of the variance in Li^+ cation coordination sphere geometry inherent in these solution structures (see Section 1.5.1.2). Recall that contact ion pairs typically exhibit larger ^7Li linewidths ($\nu_{1/2} \geq 3 \text{ Hz}$), whereas the highly symmetric solvated separated ion pairs give rise to narrow ^7Li linewidths ($\nu_{1/2} \leq 1.5 \text{ Hz}$).⁸¹ Carlier had previously provided indirect evidence for the existence of **27-Li** as a contact ion pair in 2:1 THF/pentane ($\nu_{1/2} = 8.9 \text{ Hz}$),⁷⁸ 2:1 THF/toluene ($\nu_{1/2} = 5.6 \text{ Hz}$),⁷⁸ and 20:1 THF/hexane ($\nu_{1/2} = 7.9 \text{ Hz}$).⁸⁴

Our reexamination of the ^7Li linewidth of **27-Li** in 20:1 THF/Hexane at -125°C reveals a linewidth of 3.52 Hz (Chart 2.3), providing support for the description of **27-Li** as a contact ion pair rather than a separated ion pair under these experimental conditions. Note that in Carlier's previous studies the ^7Li linewidths were measured to be somewhat larger than are currently observed. We attribute this difference to subtle improvements in shimming, but maintain that the measured linewidth is still indicative of contact ion pair formations.

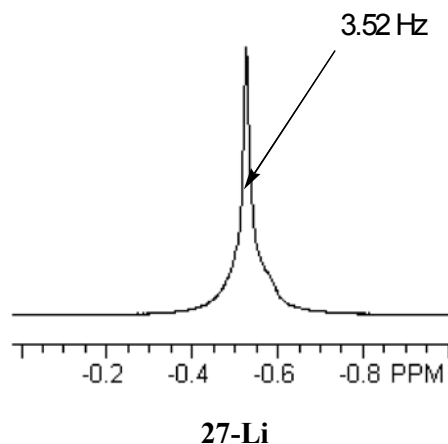


Chart 2.3 ^7Li linewidth ($\nu_{1/2}$) of **27-Li** in 20:1 THF/Hexane

For comparative purposes, salient examples of both separated and contact ion pairs from this study can be further observed in the measured ^7Li linewidths of 0.3 M LiCl in methanol ($\nu_{1/2} = 0.90$ Hz, obtained at -90 °C) and 0.1 M LiHMDS in 20:1 THF/Hexane ($\nu_{1/2} = 24.36$ Hz, acquired at -125 °C), as shown in Chart 2.4.

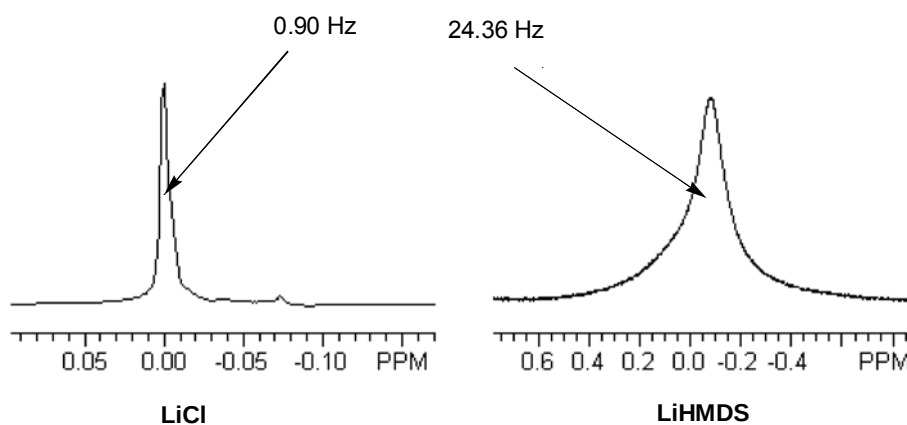


Chart 2.4 ^7Li linewidths ($\nu_{1/2}$) for LiCl (separated ion pair) and LiHMDS (contact ion pair)

2.1.2.2 Reinvestigation of the HMPA titration of lithiophenylacetonitrile

More direct evidence for the existence of **27-Li** as a contact ion pair in 20:1 THF/hexane derives from the application of Reich's HMPA titration experiment.⁸¹ Recall from Section 1.5.1.2 that the relative concentration at which unbound HMPA is first observable by ³¹P NMR spectroscopy provides more conclusive information regarding the ion pair status of lithiated anions in solution as a consequence of the occupancy (or lack thereof) of the ⁷Li cation coordination sphere.

Reinvestigation of the HMPA titration of 0.1 M **27-Li** in 20:1 THF/Hexane by ⁷Li and ³¹P NMR spectroscopy is in excellent agreement with Carlier and Lo's reported observations (Section 1.5.1.3, Chart 1.1).⁸⁴ As illustrated by the ³¹P NMR spectra in Chart 2.5 C, unbound HMPA (δ 26.1 ppm, s) can be observed at concentrations as low as 2.0 equivalents relative to **27-Li**. In concert with the observed ⁷Li linewidth data, the presence of free HMPA at less than four equivalents HMPA supports the assessment of **27-Li** as a contact ion pair under experimental conditions.

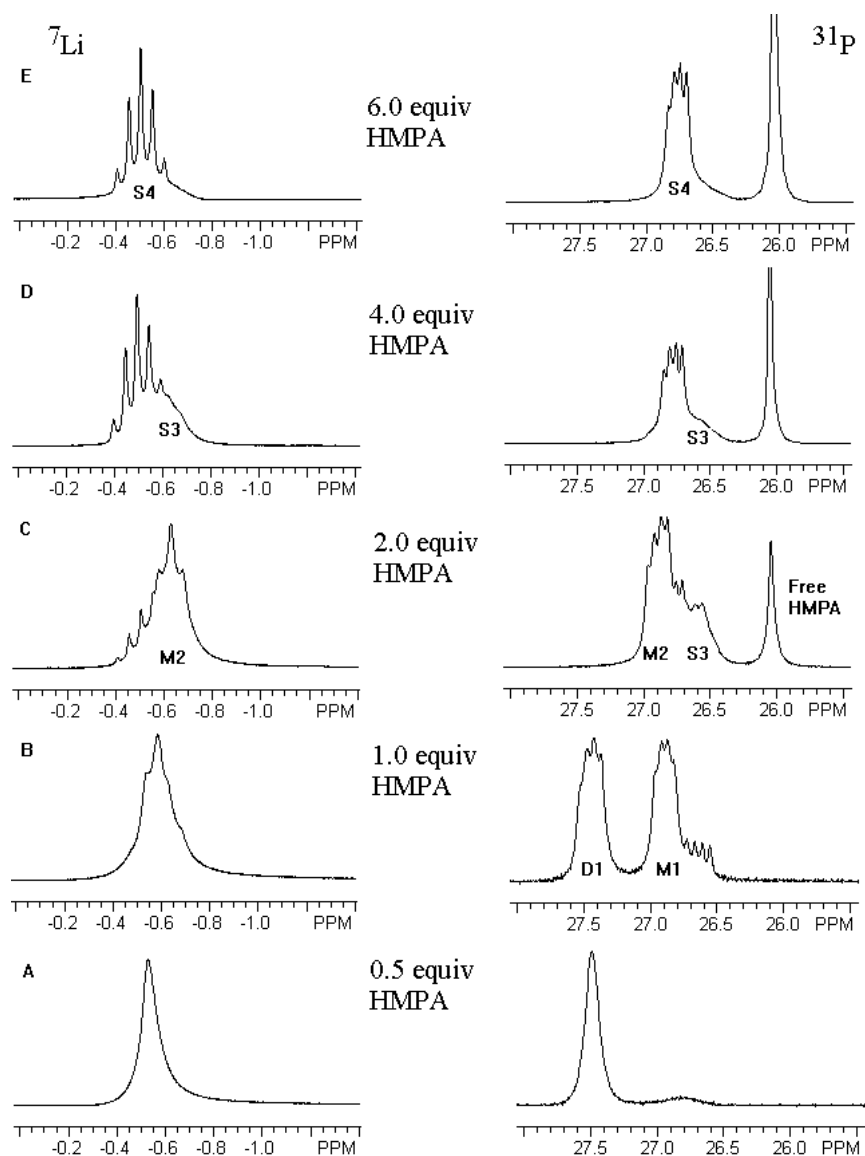


Chart 2.5 HMPA titration of **27-Li** in 20:1 THF/Hexane

Nearly identical to the data originally reported by Carlier and Lo, our reinvestigation of the ^{31}P NMR spectra of 0.1 M **27-Li** with one equivalent added HMPA (Chart 2.5, B) reveals the presence of three distinct HMPA-coordinated species in solution, each characterized as a 1:1:1:1 quartet: δ 27.5 ppm (q, 7.9 Hz), δ 26.9 ppm (q,

8.3 Hz), and δ 26.6 ppm (q, 8.7 Hz). At this concentration of added HMPA, the ^7Li NMR spectrum exhibits only a broad, unresolved resonance (δ -0.59 ppm, br) providing no discernable structural information. Note that at this concentration of added HMPA (one equivalent relative to **27-Li**), Wartski and Corset's vibrational spectroscopy study had indicated only one principle species in solution.⁶⁹ This discrepancy suggests that ^{31}P NMR spectroscopy may be a much higher resolution structural probe of nitrile stabilized carbanion solution structure than IR spectroscopy.

At higher concentrations added HMPA (Chart 2.5 C-E), ^7Li NMR spectroscopy provides more descriptive structural information. As initially reported by Carlier and Lo, the undefined ^7Li resonance observed at low concentrations added HMPA resolves as a triplet at 2.0 equivalents HMPA (Chart 2.5 C, δ - 0.63 ppm, t, 7.5 Hz), and ultimately as a quintet at 6.0 added equivalents (Chart 2.5 E, δ - 0.50 ppm, qn, 7.6 Hz). By ^{31}P NMR spectroscopy, the addition of excess HMPA results in the disappearance of the 1:1:1:1 quartet at δ 27.5 ppm (q, 7.9 Hz) upon addition of two equivalents HMPA, and ultimately only one phosphorus coordinated species remains in solution 26.75 (q, 7.5) at the highest concentrations of added HMPA.

2.2 Interpretation of $^7\text{Li}/^{31}\text{P}$ NMR spectroscopic data

Having provided substantiating spectral evidence for both Carlier and Lo's $^7\text{Li}/^{31}\text{P}$ NMR analysis of the titration of 0.1 M **27-Li** by HMPA in 20:1 THF/hexane and Wartski and Corset's analogous IR spectroscopic study thereof, it must be concluded, therefore, that the contradicting structural assessments drawn from these data (specifically at sub-

stoichiometric HMPA concentration) derives not from the collection of that data, but rather its interpretation.

2.2.1 Characterization of individual HMPA solvates by NMR

Following the structural characterization approach utilized by Carlier and Lo, the identification of the species present at one equivalent added HMPA is assisted through a dilution study monitoring the concentration interdependence of the proportionate intensity of the ^{31}P NMR resonances observable in Chart 2.5 B, specifically those appearing at δ 27.5 ppm (q, 7.9 Hz) and δ 26.9 ppm (q, 8.3 Hz). With the relative concentration of HMPA fixed equimolar to **27-Li**, the Li^+ cation concentration is varied from 0.125 M to 0.025 M. As shown in Chart 2.6 A-E, the proportionate magnitude of the quartet at δ 27.5 ppm decreases relative to the quartet at δ 26.9 ppm upon incremental dilution; likewise, an increase in the concentration of **27-Li** results in an increase in the relative intensity of the quartet appearing at δ 27.5 ppm. As initially reported by Carlier and Lo, this observation strongly suggests that the relative population of these solvates is concentration interdependent.

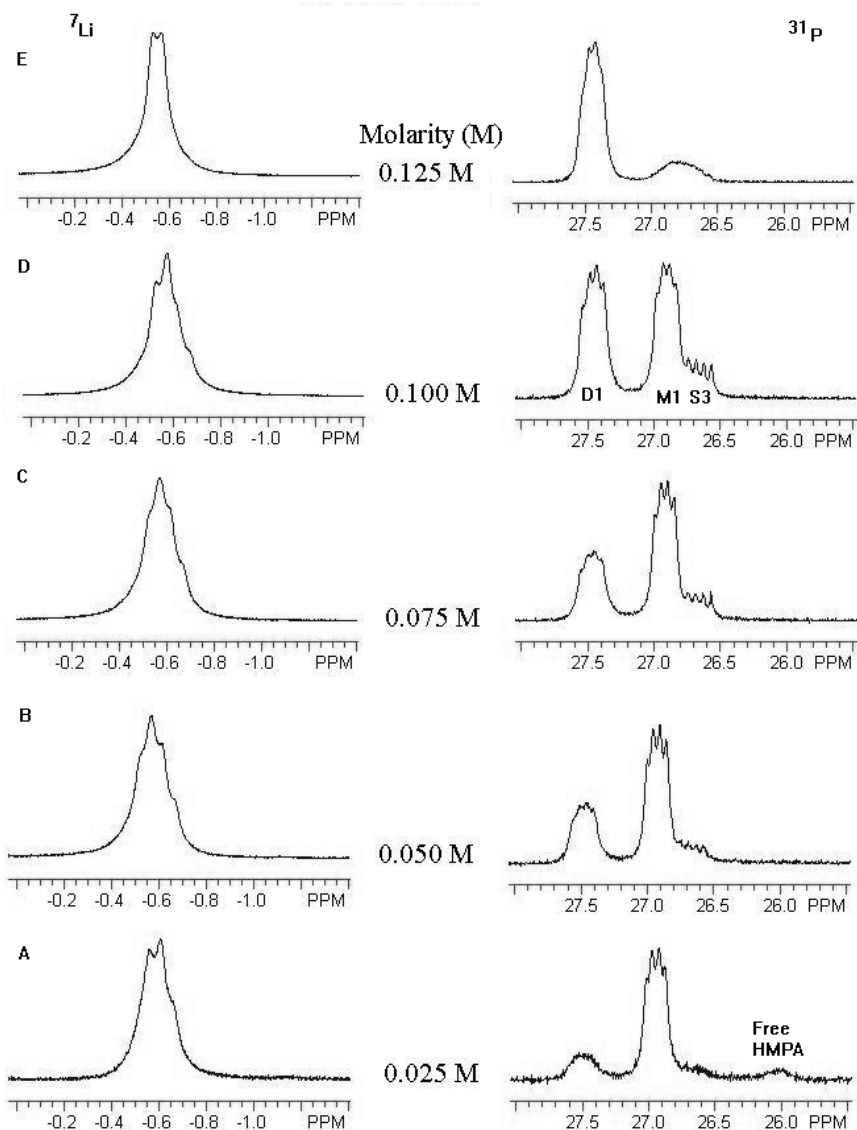


Chart 2.6 Dilution study of **27-Li** at 1 equivalent HMPA

These dilution data, in combination with the presence of only a single species at 0.5 equivalents added HMPA by ^{31}P NMR (recall Chart 2.5 A) strongly suggest a 2:1 stoichiometry ($^{7}\text{Li}:$ ^{31}P) of the solution structure giving rise to the 1:1:1:1 quartet at δ 27.5 ppm. In agreement with the initial conclusions drawn by Carlier and Lo, we attribute this species to mono(HMPA)-solvated dimer, **D₁**. By extension of this assessment, the

solution structure observed at δ 26.9 ppm is designated as mono(HMPA)-solvated monomer, **M₁**.

Referencing Chart 2.5 C, the further addition to two total equivalents HMPA promotes the formation of a solvate characterized by a ^7Li triplet at δ -0.62 ppm ($J_{\text{Li-P}} = 7.5$ Hz). The major corresponding ^{31}P resonance at this concentration is coincident with the **M₁** signal. The ^7Li multiplicity is suggestive of two bound HMPA molecules per lithium nucleus, thus supporting its characterization as **M₂**. In agreement with Carlier and Lo's assessment, the addition of excesses of HMPA appears to induce separated ion pair formation. At six equivalents added HMPA (Chart 2.5, E), only one species appears in solution by both ^7Li and ^{31}P NMR. This species, characterized by a ^7Li quintet (δ -0.50 ppm, $J_{\text{Li-P}} = 7.6$ Hz) and complementary ^{31}P quartet (δ 26.8 ppm, $J_{\text{Li-P}} = 7.5$ Hz), is suggestive of a structure featuring one ^7Li nuclei coordinated to four ^{31}P nuclei. The quartet by ^{31}P signifies that each HMPA is coordinated to one lithium cation. In this manner, the major species in solution at 6 equivalents added HMPA is characterized as separated ion pair **S₄**. At four equivalents added HMPA (Chart 2.5 D), the same dominant signal of **S₄** is observable in both ^7Li and ^{31}P NMR. Minor ^7Li and ^{31}P resonances are also seen at this concentration, which are tentatively assigned **S₃** based on Reich's studies of chemical shifts and solution behavior of separated ion pairs.⁸¹

In conclusion, this reinvestigation of the structural identification of HMPA-solvated **27-Li** in 20:1 THF/Hexane by ^7Li and ^{31}P NMR spectroscopy strongly mirrors Carlier and Lo's original data as summarized in Table 2.1. Note the small variability in the chemical shifts exists between the two studies, which are most likely consequent of small variations in external referencing protocols.

<i>Solvate</i>	<i>Original assessment</i> ⁸⁴		<i>Reinvestigation</i>	
	<i>⁷Li δ (mult., J)</i>	<i>³¹P δ (mult., J)</i>	<i>⁷Li δ (mult., J)</i>	<i>³¹P δ (mult., J)</i>
D₁	-0.45 (br)	27.5 (q, 7.9)	-0.53 (br)	27.43 (q, 8.4)
M₁	-0.45 (br)	27.0 (q, 8.3)	-0.58 (br)	26.88 (q, 7.5)
M₂	-0.47 (t, 7.6)	27.0 (q, 8.0)	-0.63 (t, 7.5)	26.87 (q, 8.4)
S₃	-0.45 (br)	26.7 (q, 8.7)	not resolved	26.75 (q, 9.3)
S₄	-0.34 (qn, 7.6)	26.8 (q, 7.6)	-0.50 (qn, 7.6)	26.75 (q, 7.5)

Table 2.1 ⁷Li and ³¹P NMR spectral data for putative characterizations of HMPA-solvated ion pairs; $J_{\text{Li-P}}$ coupling constants reported in Hz

2.3 Computational modeling of nitrile vibrational frequency

With confidence in the ⁷Li/³¹P NMR-based structural characterization described in Section 2.2 but no clear resolution to the contrasting spectral determinations outlined above, we direct our attention toward a density functional analysis of $\nu(\text{C}\equiv\text{N})$ vibrational frequency. While DFT methods cannot reasonably be expected to provide exact replication of experimentally observed vibrational stretches (due to inherent errors arising from vibrational anharmonicity and the incomplete treatment of electron correlation in the theoretical model),⁸⁵ these computational methods have been shown to reliably reproduce experimental data within 34-48 cm⁻¹.⁸⁶ From a practical standpoint, however, these computational methods may be able to take advantage of key structural differences existing between monomeric and dimeric isomers allowing for qualitative spectroscopic differentiation of these species based on calculated $\nu(\text{C}\equiv\text{N})$ frequencies.

In order to better understand the structural properties influencing experimentally observed nitrile vibrational stretches, monomeric and dimeric isomers of **27-Li** including unsolvated, THF-solvated, and HMPA-coordinated models are considered at B3LYP/6-

31G(d) and B3LYP/6-31+G(d). For the analysis of the monomeric isomers, contact ion pair monomers (*C*- and *N*-lithiated) as well as separated ion pair structure **S**₀ (represented by the anion PhCHCN) of phenylacetonitrile **27** are each considered. While Carlier and others have provided experimental evidence for the existence of **27-Li** as a contact ion pair in ethereal solvent (or with low concentrations of HMPA added thereto), the “separated” anion structure, **S**₀, warrants due consideration here for the potential formation of separated ion pairs under experimentally viable conditions (i.e., large excesses of HMPA). Dimer structure **D**₀ is modeled after the previously reported *N,N*-cyclic dimers observed from X-ray crystallography and predicted by ⁷Li/³¹P NMR spectroscopy. For this study, only the anti-symmetric (IR visible) ν(C≡N) frequency is reported for the *N,N*-cyclic dimer structure. Results of this analysis are detailed below.

It is important to note that all calculated nitrile vibrational frequencies are adjusted by an empirical scaling factor to compensate for the computational errors previously mentioned. B3LYP/6-31+G(d) and B3LYP/6-31G(d) calculated nitrile vibrational frequencies are scaled by 0.9546 and 0.9494, respectively. These scaling factors are determined from the ratio of the experimentally observed IR vibrational stretch of benzyl cyanide **27** relative to its theoretically determined ν(C≡N) stretch frequency at each basis set. Note also that calculation of several of the structures could not be completed at the B3LYP/6-31+G(d) level. For these structures, it became clear that modeling at the commonly accepted “best choice” 6-31+G(d) basis set was impractical or impossible on a reasonable time scale with available computer resources. To overcome these limitations and model the more complex lithiated nitrile structures seen later within this chapter, we developed two user-defined basis sets explicitly for

“accurate” modeling of the energetic and physical parameters of lithiated nitriles which would be predicted by the more expensive 6-31+G(d) basis set. In cases such as these, where calculations at the full 6-31+G(d) basis set are infeasible, we substitute a truncated version of this basis set referred to hereafter as 6-31'+G(d). For a complete review of this rigorous study in basis set economy and a quantitative analysis of the accuracy of these user-defined basis sets against published metalated nitrile structures relative to the target model, refer to Chapters 4 and 5.

2.3.1 Computational modeling of unsolvated monomeric and dimeric structures

As shown previously in Chart 2.2 (Section 2.1.1), our reinvestigation of 0.1 M **27-Li** in THF by IR spectroscopy reveals two principal $\nu(\text{C}\equiv\text{N})$ stretches: a major band at 2091 cm^{-1} and a minor band at 2058 cm^{-1} . In the parent study from which this reinvestigation was based, Wartski and Corset had assigned these vibrational stretches to **M₀** and **D₀**, respectively, based at least in part on the relative ordering of the calculated monomer and dimer nitrile vibrational frequencies by ab initio and density functional methods. Our computational analysis of the nitrile vibrational frequency for unsolvated monomeric and dimeric analogues of **27-Li** at B3LYP/6-31G(d) and B3LYP/6-31+G(d) detailed in Table 2.2 mirrors the relative ordering initially suggested by Wartski and Corset. The *C*- and *N*-lithiated monomers uniformly exhibit higher $\nu(\text{C}\equiv\text{N})$ stretch frequencies than the corresponding *N,N*-cyclic dimer structure. Interestingly, the data suggest a strong correlation between calculated nitrile stretch frequency and bond length, $r(\text{C}\equiv\text{N})$, as shown in Chart 2.7. Broadly, shorter CN bond lengths, which are indicative

of stronger bonds, can be directly related to higher calculated $\nu(\text{C}\equiv\text{N})$ frequencies. At B3LYP/6-31G(d), comparatively shorter bond lengths in the *C*- and *N*-lithiated monomeric structures ($r(\text{C}\equiv\text{N})$: 1.188 and 1.198 Å, respectively) correlate to higher $\nu(\text{C}\equiv\text{N})$ frequencies of 2045 and 2061 cm^{-1} . The N,N-cyclic dimer features an average nitrile bond length of 1.210 Å and a corresponding anti-symmetric stretch frequency of only 2006 cm^{-1} . Presumably due to complexation by two distinct Li^+ cations, each nitrile bond of the N,N-cyclic dimer structure is sufficiently weakened to result in substantially longer CN bonds and thus lower nitrile stretch frequencies relative to the calculated monomeric isomers. In the case of the PhCHCN^- anion, absence of coordination to a Li^+ cation results in a stronger, shorter CN bond relative to the $\mathbf{M}_0$ models ($r(\text{C}\equiv\text{N})$: 1.181). The decreased relative bond length in the $\mathbf{S}_0$ structure is accompanied by an increase in calculated nitrile stretch frequency relative to the two lithiated monomers, $\nu(\text{C}\equiv\text{N})$: 2111 cm^{-1} .

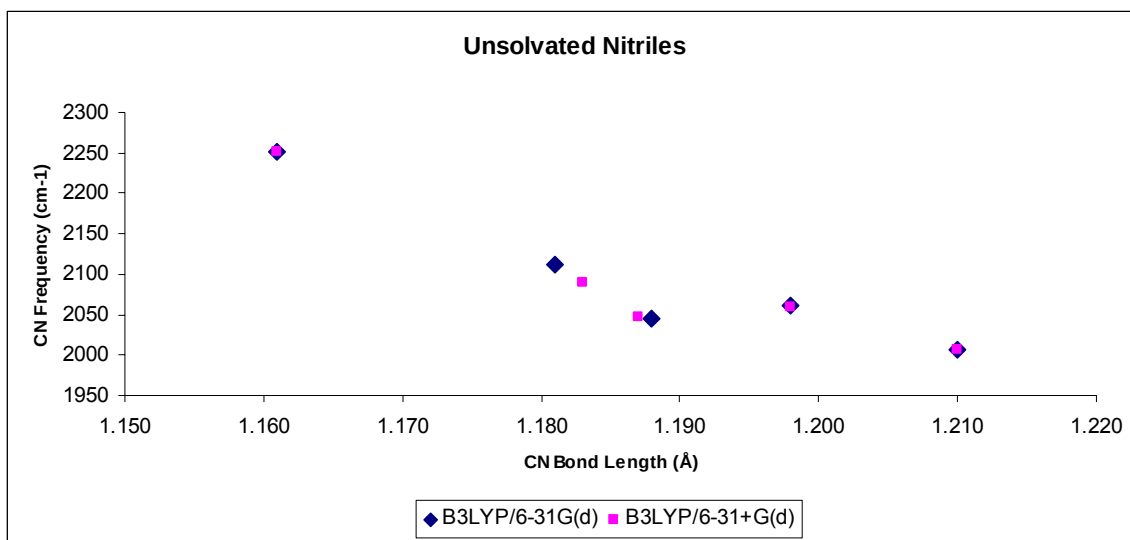


Chart 2.7 Correlation of nitrile bond length to $\nu(\text{C}\equiv\text{N})$ for the unsolvated nitrile series

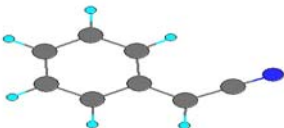
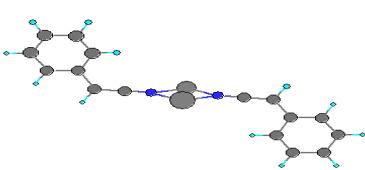
<i>Nitrile</i>	<i>Calculated Structure</i>	Calculated $\nu(\text{C}\equiv\text{N})$ cm^{-1} ; CN bond length ($\text{\AA}$)	
		$^\dagger\text{B3LYP}/$ $6\text{-}31\text{G}(\text{d})$	$^{\dagger\dagger}\text{B3LYP}/$ $6\text{-}31\text{+G}(\text{d})$
PhCH₂CN		2252 cm^{-1} 1.161 $\text{\AA}$	2252 cm^{-1} 1.161 $\text{\AA}$
PhCHCN⁻ S₀		2111 cm^{-1} 1.181 $\text{\AA}$	2090 cm^{-1} 1.183 $\text{\AA}$
PhCHCNLi M₀		2061 cm^{-1} 1.198 $\text{\AA}$	2060 cm^{-1} 1.198 $\text{\AA}$
PhCH(Li)CN M₀		2045 cm^{-1} 1.188 $\text{\AA}$	2047 cm^{-1} 1.187 $\text{\AA}$
[PhCHCNLi]₂ D₀		2006 ‡ cm^{-1} 1.210 $\text{\AA}$ 1.210 $\text{\AA}$	2007 ‡* cm^{-1} 1.210 $\text{\AA}$ 1.209 $\text{\AA}$

Table 2.2 Scaled $\nu(\text{C}\equiv\text{N})$ frequencies and nitrile bond lengths for theoretical PhCHCNLi monomers and dimers; † Calculated vibrational frequencies are scaled by 0.9494; †† Calculated vibrational frequencies are scaled by 0.9546; ‡ Anti-symmetric $\nu(\text{C}\equiv\text{N})$ for dimeric species; * Calculated at B3LYP/6-31'+G(d)

Consistent results are observed for structures calculated at B3LYP/6-31+G(d). The *C*- and *N*-lithiated monomers ($r(\text{C}\equiv\text{N})$: 1.187 and 1.198 Å, respectively) exhibit calculated $\nu(\text{C}\equiv\text{N})$ stretches measuring 2047 cm^{-1} and 2060 cm^{-1} , whereas the *N,N*-cyclic dimer features a smaller nitrile vibrational frequency and longer average nitrile bond lengths ($\nu(\text{C}\equiv\text{N})$: 2007 cm^{-1} , $r(\text{C}\equiv\text{N})$: 1.210 Å). Within the unsolvated monomeric series, both B3LYP/6-31G(d) and B3LYP/6-31+G(d) are closely matched with respect to calculated $\nu(\text{C}\equiv\text{N})$ frequencies and nitrile bond lengths, the most notable exception arising from the phenylacetonitrile anion, PhCHCN^- , with a calculated nitrile stretch frequency measuring 2090 cm^{-1} at B3LYP/6-31+G(d). In this case, the 21 cm^{-1} difference in calculated nitrile stretch frequency is likely a consequence of the improved modeling of anionic charge resulting from the incorporation of diffuse functions by the larger basis set.

The correlation of nitrile bond length and vibrational stretch frequency holds true among the individual unsolvated monomers featured in Table 2.2 with the exception of the *C*-lithiated monomer. This structure, which features added stabilization of the Li^+ cation by η^3 -coordination to the nitrile bond as well as C_1 of the phenyl substituent, exhibits a large decrease in nitrile vibrational frequency relative to the parent nitrile. This change in $\nu(\text{C}\equiv\text{N})$ frequency would suggest a substantial lengthening of the CN bond. This, however, is not observed. The *C*-lithiated monomer retains a nitrile bond length closer to that of the unsolvated anion (1.187 Å). This deviation from the trend is likely attributed to the more complex electronic effects introduced with the η^3 -coordination to the carbanion. Relative bond strength considerations aside, at B3LYP/6-31+G(d), the *C*-

lithiated monomer exhibits a CN bond length approximately 0.01 Å smaller than that of the corresponding N-lithiated monomer, which would be expected.

2.3.2 Computational modeling of solvated monomeric and dimeric structures

As previously discussed in Section 1.4.2, solvation considerations play a key role in the accurate modeling of the experimentally observed preference for N-lithiation by lithiated nitriles.⁷⁰ To evaluate the effect of solvation on the calculated nitrile vibrational frequencies for monomeric and dimeric solvated structures, explicit THF molecules are added in sufficient quantity to complete a presumed tetrahedral Li^+ cation coordination sphere geometry. The determination that the solvation shell of the Li^+ cation is satisfied by tetrahedral coordination is quantitatively substantiated by a comparative study of incremental solvation energies and solution thermodynamics as summarized later in Section 2.3.4.1.

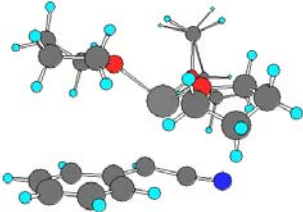
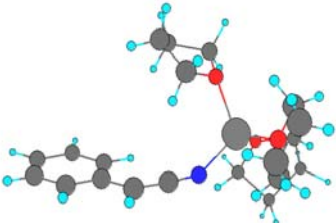
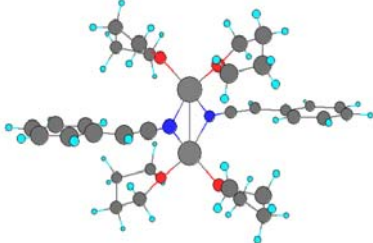
<i>Nitrile</i>	<i>Calculated Structure</i>	Calculated $\nu(\text{C}\equiv\text{N})$ cm^{-1} ; <u>CN bond length ($\text{\AA}$)</u>	
		${}^{\dagger}\text{B3LYP}/$ $6\text{-}31\text{G}(\text{d})$	${}^{\dagger\dagger}\text{B3LYP}/$ $6\text{-}31+\text{G}(\text{d})$
PhCH(Li(THF)₃)CN		2107 cm^{-1} (+62) CN: 1.179 $\text{\AA}$ (-0.009)	2085 cm^{-1} (+38) CN: 1.179 $\text{\AA}$ (-0.009)
PhCHCNLi(THF)₃		2048 cm^{-1} (-13) CN: 1.194 $\text{\AA}$ (-0.004)	2059 cm^{-1} (-1) CN: 1.192 $\text{\AA}$ (-0.006)
[PhCHCNLi(THF)₂]₂		2032 [‡] cm^{-1} (+26) CN: 1.196 $\text{\AA}$ CN: 1.196 $\text{\AA}$ (-0.014)	2037 ^{‡*} cm^{-1} (+30) CN: 1.196 $\text{\AA}$ CN: 1.196 $\text{\AA}$ (-0.014)

Table 2.3 Scaled $\nu(\text{C}\equiv\text{N})$ frequencies and bond lengths for **27-Li** monomeric and dimeric THF-solvates (relative to unsolvated species); [†]Calculated vibrational frequencies (reported as cm^{-1}) are scaled by 0.9494; ^{††}Calculated vibrational frequencies are scaled by 0.9546; [‡]Anti-symmetric $\nu(\text{C}\equiv\text{N})$ for dimeric species; ^{*}Calculated at B3LYP/6-31++G(d)

As shown in Table 2.3, the anti-symmetric $\nu(\text{C}\equiv\text{N})$ frequency calculated for the tetrakis(THF)-solvated dimer, $[\text{PhCHCNLi}(\text{THF})_2]_2$, at both B3LYP/6-31G(d) and

B3LYP/6-31++G(d) features significant vibrational frequency changes relative to the unsolvated structure. At B3LYP/6-31++G(d), the tetrakis (THF)-solvate exhibits a $\nu(\text{C}\equiv\text{N})$ frequency of 2037 cm^{-1} , which is 30 cm^{-1} greater than that of the unsolvated structure. Structurally, this increase in CN bond strength is evidenced by a decrease in the average nitrile bond length of $0.014\text{ \AA}$. At B3LYP/6-31G(d), an identical decrease in bond length corresponds to a 26 cm^{-1} increase in $\nu(\text{C}\equiv\text{N})$ frequency. These data suggest that the inclusion of donor molecules to the Li^+ cation may weaken the coordination of the lithium to the nitrile, thus resulting in a stiffer CN bond.

Tris(THF)-solvation of the C-lithiated monomer produces a dramatic effect on the calculated nitrile vibrational frequency relative to the unsolvated structure at B3LYP/6-31G(d). Upon formation of the tris(THF)-solvate, the Li^+ cation coordination mode shifts from η^3 to η^1 . Consequently, $r(\text{C}\equiv\text{N})$ decreases from $1.188\text{ \AA}$ to $1.179\text{ \AA}$, and the frequency increases from 2045 cm^{-1} to 2107 cm^{-1} . Disruption of the η^3 -coordination featured in the unsolvated model presumptively serves to strengthen the CN bond, thus resulting in the large increase in $\nu(\text{C}\equiv\text{N})$ frequency. At B3LYP/6-31+G(d), the $\nu(\text{C}\equiv\text{N})$ frequency is calculated to be considerably lower than predicted by B3LYP/6-31G(d); however, the rationale holds that disruption of the coordination mode strengthens the nitrile bond. At the larger 6-31+G(d) basis set, the C-lithiated monomer has a calculated nitrile bond length of $1.179\text{ \AA}$ ($0.009\text{ \AA}$ smaller than the corresponding unsolvated structure) and a nitrile vibrational frequency of 2085 cm^{-1} ($+38\text{ cm}^{-1}$ relative to the unsolvated model). The significant differences in calculated $\nu(\text{C}\equiv\text{N})$ frequency across the two basis sets is indicative of a the more complete description of electronic behavior resulting from inclusion of extra diffuse functions.

As observed with solvation of the *C*-lithiated monomer, inclusion of explicit solvation would be expected to decrease the coordination strength of the Li^+ cation to the nitrile, thus resulting in an increased $\nu(\text{C}\equiv\text{N})$ frequency; however, this is not observed in the case of the *N*-lithiated monomer. Upon consideration of explicit solvation, the vibrational frequency of the tris(THF)-solvated *N*-lithiated monomer actually decreases relative to the unsolvated *N*-lithiated isomer. At B3LYP/6-31G(d), a 0.004 Å decrease in bond length is observed, which would suggest expected bond strengthening, however this effect is not realized in the calculated vibrational frequency (2048 cm^{-1} , -13 cm^{-1} relative to the unsolvated monomer). Similar results are observed at B3LYP/6-31+G(d) ($\Delta r(\text{C}\equiv\text{N})$: -0.006 Å; $\Delta \nu(\text{C}\equiv\text{N})$: -1 cm^{-1}).

In summary, we show that with consideration given to the effect of explicit solvation of monomeric and dimeric **27-Li** by THF, the tris(THF)-solvated monomeric isomers are predicted to exhibit uniformly greater $\nu(\text{C}\equiv\text{N})$ frequency than the corresponding tetrakis(THF)-solvated *N,N*-cyclic dimer at both B3LYP/6-31G(d) and B3LYP/6-31++G(d). In this manner, we must reason that incorporation of THF-solvation into the theoretical monomeric and dimeric models does not alter the view of nitrile solution structure vibrational frequencies initially reported by Wartski and Corset. Also noteworthy is the furthered computational support for the relationship between bond length and calculated vibrational frequency despite the notable exception of the tris(THF)-solvated *N*-lithiated monomer, see Chart 2.8.

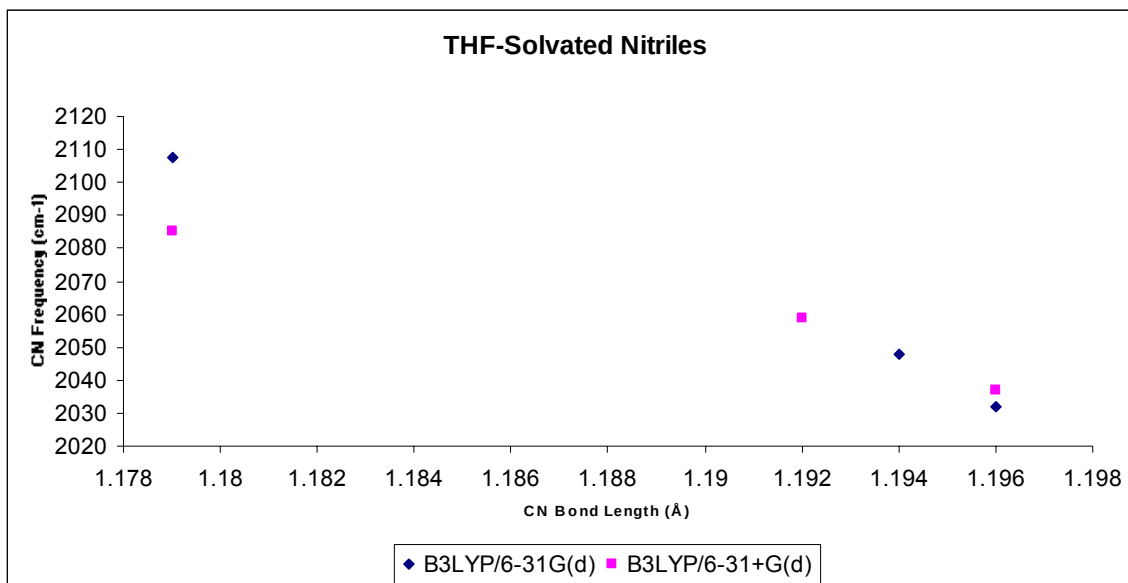


Chart 2.8 Correlation of nitrile bond length to $\nu(\text{C}\equiv\text{N})$ for the THF-solvated nitrile series

2.3.3 Computational modeling of HMPA-solvated monomeric and dimeric structures

^7Li and ^{31}P NMR spectroscopic assessments of **27-Li** structure by HMPA titration have given rise to the proposal of HMPA solvates **M**₁, **D**₁, and **S**₄, as generically represented in Figure 2.1. To address the effect of HMPA coordination of the Li^+ cation on the calculated nitrile vibrational stretch frequencies and bond lengths, we include explicit HMPA to the proposed solvation models of the monomeric and dimeric solvates for comparison of the observed $\nu(\text{C}\equiv\text{N})$ stretches. The excellent coordinative ability of HMPA to complex the Li^+ cation strongly suggests that **M**₀ and **D**₀ would not exist as discrete solvates in the presence of HMPA, but rather as HMPA solvates such as those represented by **M**₁ and **D**₁. Also, ^7Li NMR has suggested that at high concentrations of titrated HMPA, **27-Li** exists as the solvent-separated structure **S**₄, while at that same

concentration IR spectroscopy depicts an observed $\nu(\text{C}\equiv\text{N})$ stretch similar to that of the monomeric species.

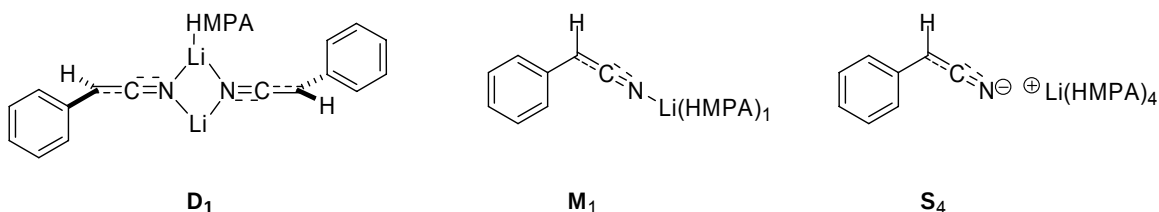


Figure 2.1 Theoretical HMPA-solvates of monomeric and dimeric **27-Li**

As shown in Table 2.4 and Chart 2.9, the theoretical assessment of these HMPA-solvates at B3LYP/6-31G(d) and B3LYP/6-31'+G(d) remains generally consistent with the observations of the unsolvated and THF-solvated models. Mono(HMPA)-coordination of the THF-solvated *N*-lithiated monomer reveals a $\nu(\text{C}\equiv\text{N})$ frequency of 2067 cm^{-1} at B3LYP/6-31G(d) with a CN bond length of $1.189\text{ \AA}$. The minimal 6 cm^{-1} increase in nitrile stretch frequency relative to the unsolvated *N*-lithiated monomer suggests that the inclusion of HMPA does not greatly alter the strength of the nitrile bond, which is structurally evidenced by a small $0.009\text{ \AA}$ decrease in bond length. Note that geometry optimization at a higher level of theory could not be completed for this structure.

The tetrakis(HMPA)-solvated separated ion pair representing structure **S₄** exhibits a nitrile vibrational stretch at 2080 cm^{-1} , approximately 11 cm^{-1} greater than that of the HMPA-coordinated *N*-lithiated monomer at B3LYP/6-31G(d). At B3LYP/6-31'+G(d), the nitrile vibrational stretch appears at 2075 cm^{-1} . Recall from Table 2.2 that the $\nu(\text{C}\equiv\text{N})$

frequency for the phenylacetonitrile anion, S_0 , was approximately 2090 cm^{-1} ($+15\text{ cm}^{-1}$ relative to the coordinated S_4 structure). The similarity in these predicted frequencies suggests that in the solvent separated theoretical model, there is only small influence upon the nitrile stretch consequent of interactions with the solvated cation. This suggestion is supported by nitrile bond lengths. In the unsolvated separated ion, PhCHCN^- , the CN bond length is measured at 1.181 and 1.183 Å (B3LYP/6-31G(d) and B3LYP/6-31+G(d), respectively). Upon solvation by HMPA, these nitrile bond lengths change by less than 0.005 Å.

HMPA solvation of the *N,N*-cyclic dimer is remarkably similar to the tetrakis(THF)-solvated model. Incorporation of one HMPA into the Li^+ coordination sphere results in a decrease in CN bond length and a substantial increase in $\nu(\text{C}\equiv\text{N})$ frequency. At B3LYP/6-31G(d), the average nitrile bond length decreases by 0.015 Å relative to the unsolvated structure, corresponding to 31 cm^{-1} increase in vibrational frequency. At B3LYP/6-31'+G(d), the average nitrile bond length decreases by 0.014 Å, which correlates to a 36 cm^{-1} increase in stretch frequency.

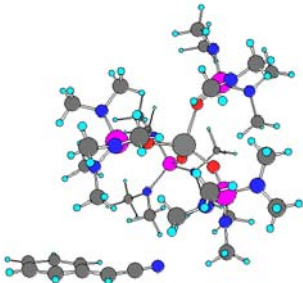
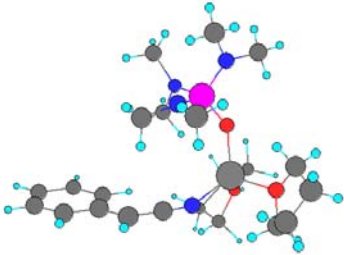
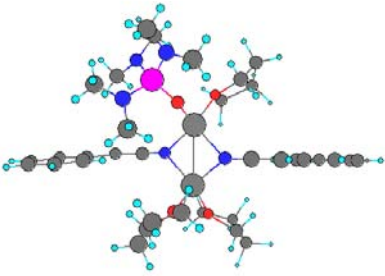
<u>Nitrile</u>	<u>Calculated Structure</u>	Calculated $\nu(\text{C}\equiv\text{N})$ cm^{-1} ; <u>CN bond length ($\text{\AA}$)</u>	
		$^\dagger\text{B3LYP}/$ <u>6-31G(d)</u>	$^{\dagger\dagger}\text{B3LYP}/$ <u>6-31+G(d)</u>
PhCHCN⁻// ⁺Li(HMPA)₄ S₄		2078 cm^{-1} (-33)	2075 [*] cm^{-1} (-15)
		1.186 $\text{\AA}$ (0.005)	1.185 $\text{\AA}$ (-0.002)
PhCHCNLi$\cdot$ (THF)₂HMPA M₁		2067 cm^{-1} (+6)	--
		1.189 $\text{\AA}$ (-0.009)	
[PhCHCNLi]₂$\cdot$ (THF)₃(HMPA) D₁		2037 [‡] cm^{-1} (+31)	2043 ^{‡*} cm^{-1} (+36)
		1.195 $\text{\AA}$ 1.195 $\text{\AA}$ (-0.015)	1.194 $\text{\AA}$ 1.194 $\text{\AA}$ (-0.014)

Table 2.4 Scaled $\nu(\text{C}\equiv\text{N})$ frequencies and bond lengths for **27-Li** monomeric and dimeric HMPA-solvates (relative to unsolvated species); † Calculated vibrational frequencies (reported as cm^{-1}) are scaled by 0.9494; †† Calculated vibrational frequencies are scaled by 0.9546; ‡ Anti-symmetric $\nu(\text{C}\equiv\text{N})$ for dimeric species; * Calculated at B3LYP/6-31'+G(d)

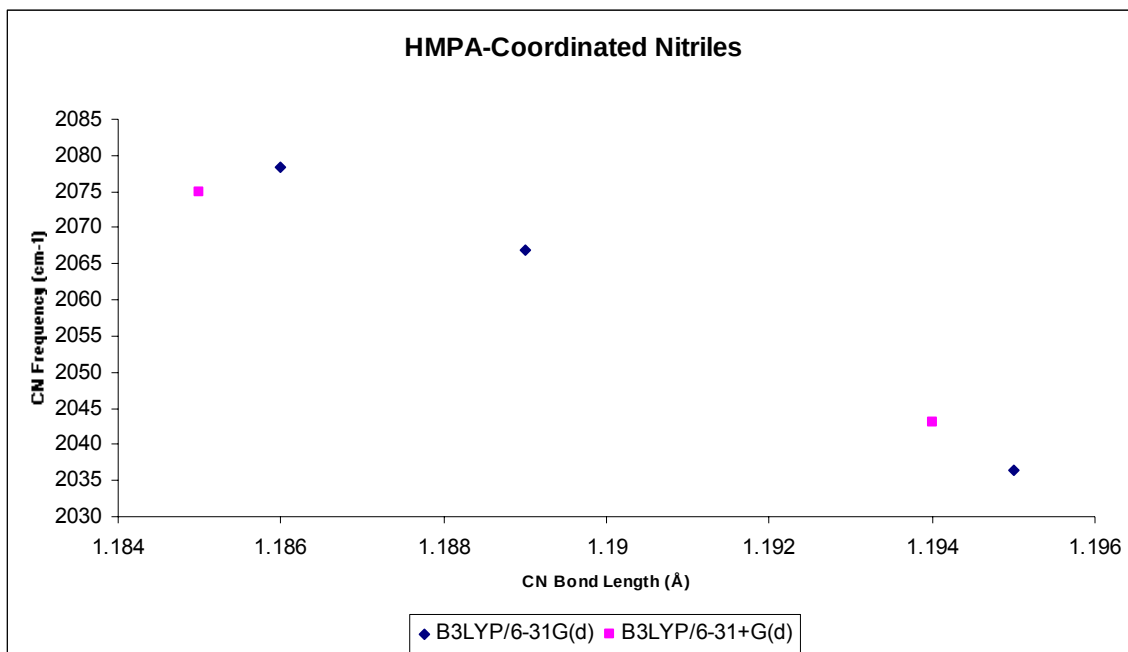


Chart 2.9 Correlation of nitrile bond length to $\nu(\text{C}\equiv\text{N})$ for the HMPA-coordinated nitrile series

2.3.4 Summary of computational data

A motivating premise for the theoretical nitrile vibrational frequency detailed above was resolution of the contradictory structural assessments deriving from $^7\text{Li}/^{31}\text{P}$ NMR and IR spectroscopy. Recall that at 0.5 equivalents added HMPA, a 0.1M **27-Li** solution in 20:1 THF/hexane had revealed a single peak by ^{31}P NMR spectroscopy, which through dilution studies, had been characterized as a mono(HMPA)-solvated *N,N*-cyclic dimer. IR spectroscopy, under identical experimental conditions, also showed one primary species in solution, however this vibrational stretch had been characterized as a mono(HMPA)-solvated lithiophenylacetonitrile monomer. After providing supporting evidence for both sets of data through experimental reinvestigations of the parent studies

upon which these contradictory evaluations had been based, we concluded that the conflicting structural determinations resulted from data misinterpretation rather than data collection. We had hoped that a computational nitrile vibrational frequency analysis would reveal that upon consideration of THF- and/or HMPA-complexation, the calculated nitrile vibrational frequency of the dimeric species would be nearly indistinguishable from that of the corresponding monomer, thus lending support to Carlier and Lo's prior structural characterization. As shown in Table 2.5, this is not the case.

<u>Experimental</u>	<u>Nitrile</u>	<u>PhCHCNLi</u> ^{††}	<u>[PhCHCNLi]₂^{‡,††,*}</u>
2091	Unsolvated	2060	2007
2058	THF-Solvated	2059	2037
	HMPA-Coordinated	2067 [†]	2043

Table 2.5 Summary of vibrational data; [†]Calculated vibrational frequencies (reported as cm⁻¹) are scaled by 0.9494; ^{††}Calculated vibrational frequencies are scaled by 0.9546; [‡]Anti-symmetric $\nu(\text{C}\equiv\text{N})$ for dimeric species; *Calculated at B3LYP/6-31'+G(d)

While the addition of experimental factors including THF- and HMPA-solvation does indeed affect the predicted $\nu(\text{C}\equiv\text{N})$ frequency for the lithiophenylacetonitrile monomeric and dimeric structures, the results do not lead to the conclusion that IR spectroscopy is ineffective in the discrimination between HMPA-solvated monomers and dimers in solution. By IR spectroscopy, 33 cm⁻¹ separates the two species observable in solution. In the absence of solvation effects, B3LYP/6-31+G(d) predicts a separation of

53 cm^{-1} (dimer calculated at B3LYP/6-31++G(d)). For the solvated theoretical monomers and dimers, this separation decreases to 22 cm^{-1} (dimer calculated at B3LYP/6-31+G(d)).

Interestingly, throughout this analysis a strong correlation between nitrile bond length and stretch frequency is observed. Chart 2.10 illustrates the generally linear relationship between calculated nitrile bond length and vibrational frequency. As shown, this relationship holds true at both B3LYP/6-31G(d) and B3LYP/6-31+G(d). There is considerable variability, however, in the relationship between vibrational frequencies calculated at B3LYP/6-31G(d) and those determined at B3LYP/6-31+G(d). This is due in large part to incorporation of additional diffuse functions in the larger basis set which allow for a more complete description of the electronic effects existing within the molecule.

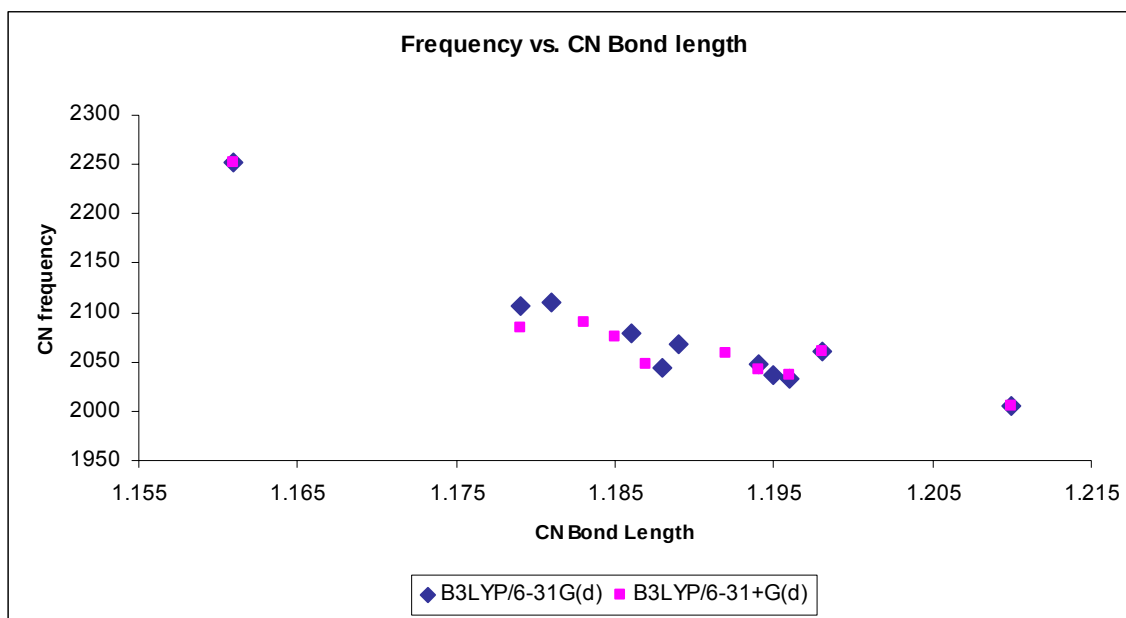


Chart 2.10 Correlation summary of nitrile bond length to $\nu(\text{C}\equiv\text{N})$

2.3.4.1 Energetic and thermodynamic analysis of solvation

The preceding computational analysis of the monomeric and dimeric lithiophenylacetonitrile isomers are predicated to a large extent on the assumption that the Li^+ cation maximally accepts tetrahedral coordination. Herein we attempt to validate this assumption with a computational analysis of the stepwise solvation stabilization energies and resulting thermodynamic parameters arising from each sequential solvation step for both the N-lithiated monomer and *N,N*-cyclic dimer by THF at B3LYP/6-31G(d).

Previously reported solvation studies of **27-Li** by THF at HF/3-21G//PM3 and B3LYP/6-31+G(d)//PM3 firmly established the pattern of the diminishing energetic stabilization returns upon successive coordination of the Li^+ cation by solvent molecules.⁷⁰ Directly stated, the stabilization energy achieved through coordination of a first solvent molecule to the Li^+ cation is greater than the stabilization attained for a second addition, which is greater than that received for a third addition, until it is ultimately no longer energetically or thermodynamically favorable for the Li^+ cation to accept further coordination. This study attempts to locate the point of maximal coordination by directly comparing the change in electronic energy and free energy for each solvation pathway in hopes of validating the assumptions upon which the previous calculations within this analysis have been based.

For each step in the incremental solvation pathway, ΔE and ΔG (kcal/mol) are calculated and reported in terms of the uncorrected raw electronic and thermodynamic energy, the corrected energy with consideration given to basis set superposition error, and also the energies with inclusion of a temperature correction factor to more closely model

the experimental conditions at which the $^7\text{Li}/^{31}\text{P}$ NMR spectroscopic measurements are obtained.

Previously reported theoretical studies of the incremental solvation stabilization of **27-Li** have failed to consider the effect of basis set superposition error (BSSE) in these stepwise solvation pathways. BSSE is a computational error propagated through the energy determination of molecular complexes relative the substructures comprising that complex.⁸⁷ Calculated energetic differences between products and reactants for systems involving molecular assembly (i.e., dimerization and solvation) experience basis set superposition errors, which result in artificially lowered energy for the complex. Errors such as these lead to overestimations of “stabilization energy.” For a conceptual example of the effect of BSSE, consider the simple dimerization reaction, $A_1 + A_2 \rightarrow B$. Typically, the stabilization energy achieved through complexation of A_1 and A_2 to give B (dimerization energy), may be calculated as $\Delta E = E_B - 2(E_A)$. In this example, however, the energy of B cannot be directly compared to that of $(A_1 + A_2)$. During the energy determination B, electrons from A_1 can be dispersed throughout the larger orbital structure of A_2 and vice-versa. For the energy determination of A_1 , these extra orbitals are not available. In short, electrons from A_1 cannot share such interactions with A_2 . This extended orbital delocalization results in an energy for dimer B which is artificially lowered relative to the combined energy of $(A_1 + A_2)$. To accommodate for such errors, a counterpoise correction can be applied to these models to systematically remove this inherent stabilization of molecular complexes relative to their constituents. The result is a positive energetic correction which affects both electronic and thermodynamic

evaluations. For a more detailed explanation of the calculation of counterpoise corrections for molecular complexes, refer to Section 3.2.1.

Temperature effects also have a significant impact on the calculated thermodynamic properties of these solvation pathways. Thermodynamic corrections to electronic energy are generally calculated at standard temperature, however because most of our spectral data are obtained at -125 °C, it is beneficial to evaluate the thermodynamic characteristics of these solvation pathways under experimentally relevant temperatures. Changes in temperature alters the entropic contribution to the total free energy for the given pathway. Consequently, thermodynamic parameters such as ΔG may be stabilized or destabilized. While the correction factors from BSSE and temperature offset to a certain extent, it is desirable to apply both in attempt to achieve more computationally valid results.

The diminishing energetic stabilization achieved through sequential solvation of monomeric PhCHCNLi by THF is illustrated by the decrease in both stabilization energy (ΔE) and free energy (ΔG) as a function of increasing solvation. As shown in Table 2.6 A, the first addition of THF to the monomer offers 26.90 kcal/mol uncorrected energetic solvation stabilization. In the absence of correction factors, the low free energy ($\Delta G = -17.22$ kcal/mol) suggests solvation to be highly exothermic. Inclusion of a counterpoise correction results in an approximate +3.45 kcal/mol change in both ΔE and ΔG . With consideration to reduced temperature, a sizable 4.45 kcal/mol stabilization to ΔG is predicted. Together, these correction factors result in a +3.45 kcal/mol adjustment to the electronic energy and a net -1.00 kcal/mol correction to ΔG .

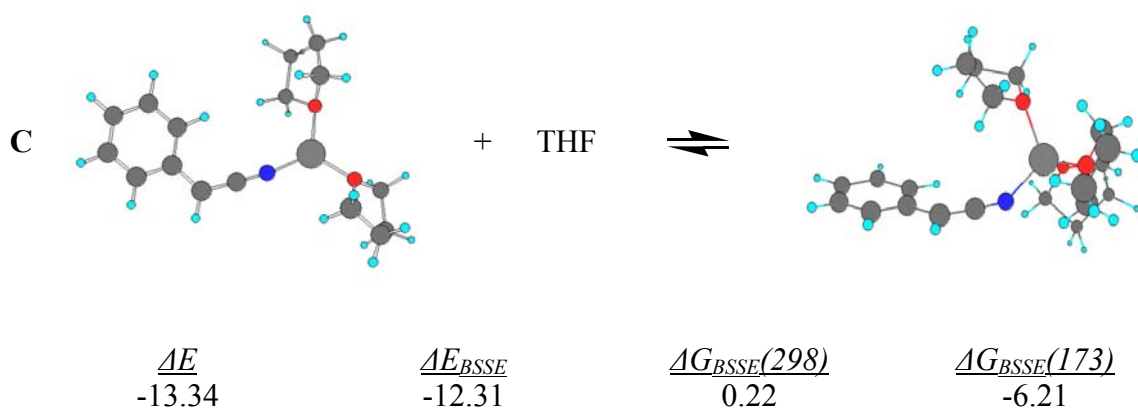
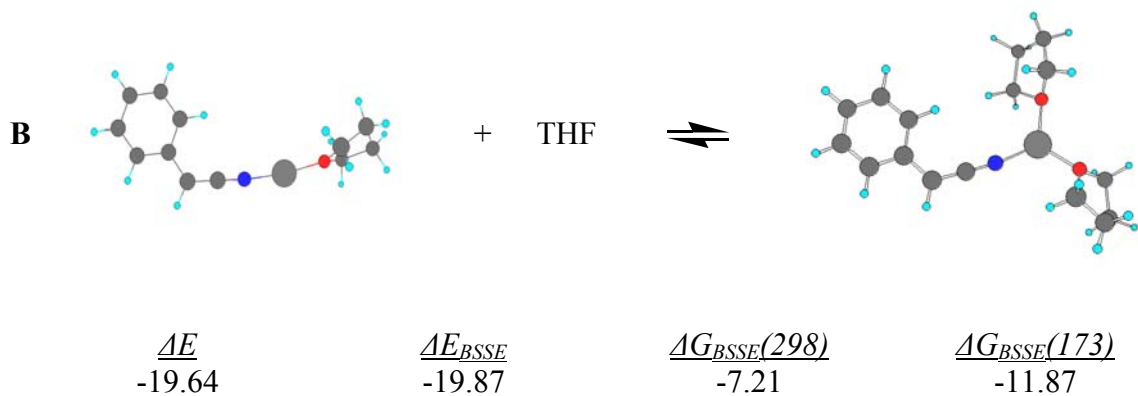
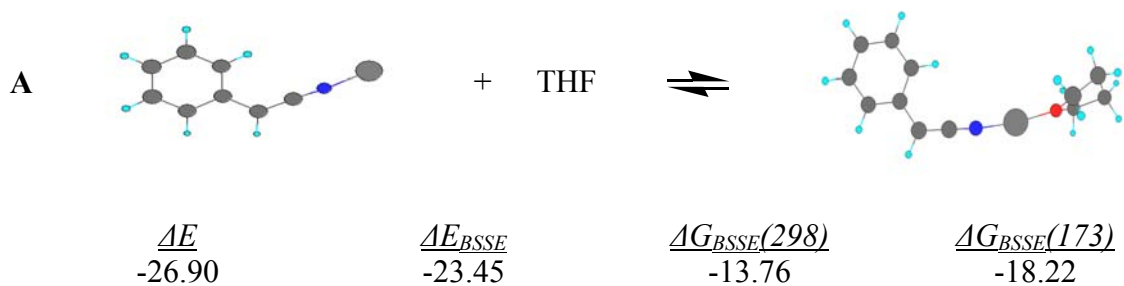
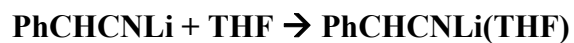


Table 2.6 Incremental solvation of N-lithiophenylacetonitrile by THF; ΔE and ΔG reported in kcal/mol; All structures calculated at B3LYP/6-31G(d)

As shown in Table 2.6 B, addition of a second THF solvent molecule to the mono-solvate is also predicted to be quite exothermic with a corrected ΔG of -11.87 kcal/mol, however this is a substantial decrease from the exothermicity predicted from solvation pathway A. For this step, bis (THF)-solvation of PhCHCNLi benefits from 19.87 kcal/mol corrected stabilization energy. Tris-solvation of PhCHCNLi completes the presumed tetrahedral coordination sphere of the Li^+ cation. In the absence of applied correction factors, pathway C (Table 2.6 C) of PhCHCNLi would appear to be largely thermoneutral ($\Delta G = -0.81$ kcal/mol). Application of both a correction for BSSE and reduced temperature, however, predicts a more stabilized -6.21 kcal/mol ΔG , suggesting that the Li^+ cation could possibly accept further solvation.

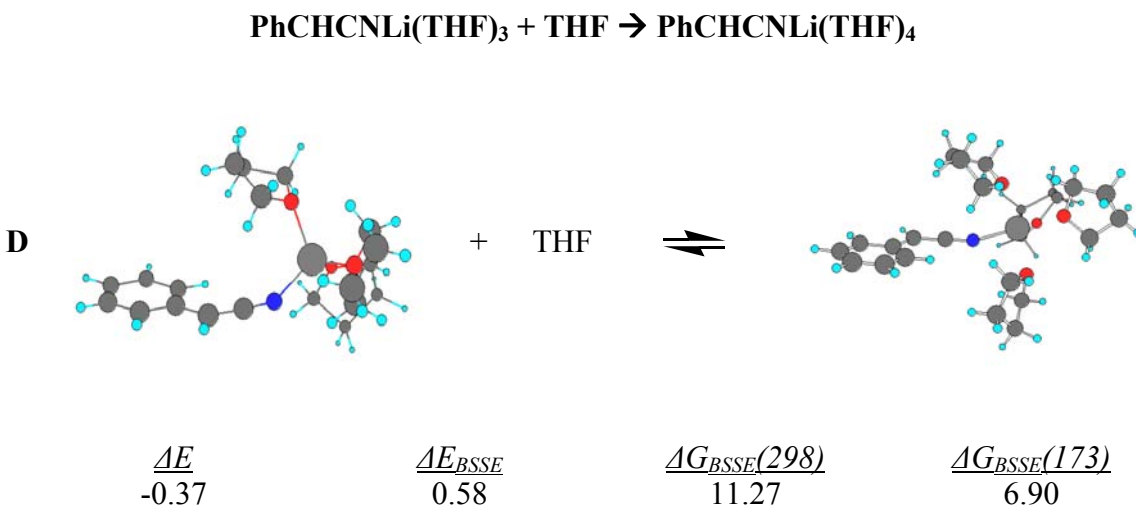


Table 2.7 Incremental solvation of N-lithiophenylacetonitrile by THF; ΔE and ΔG reported in kcal/mol; All structures calculated at B3LYP/6-31G(d)

As shown in Table 2.7 D, the tetrakis(THF)-N-lithiated contact ion pair can be located, although, the association of a fourth THF brings only minimal stabilization (-0.37 kcal/mol). However, application of BSSE and thermodynamic correction factors indicate this coordination event is unfavorable. The summation of these electronic and thermodynamic data can most easily be evaluated graphically in Chart 2.11 below. Note that there is a nearly linear relationship between ΔE and ΔG as a function of the number of coordinated solvent molecules. As the number increases, the solvation approaches thermoneutrality until, at 4 solvent molecules added, both the energy and free energy of the tetrakis solvation are greater than zero.

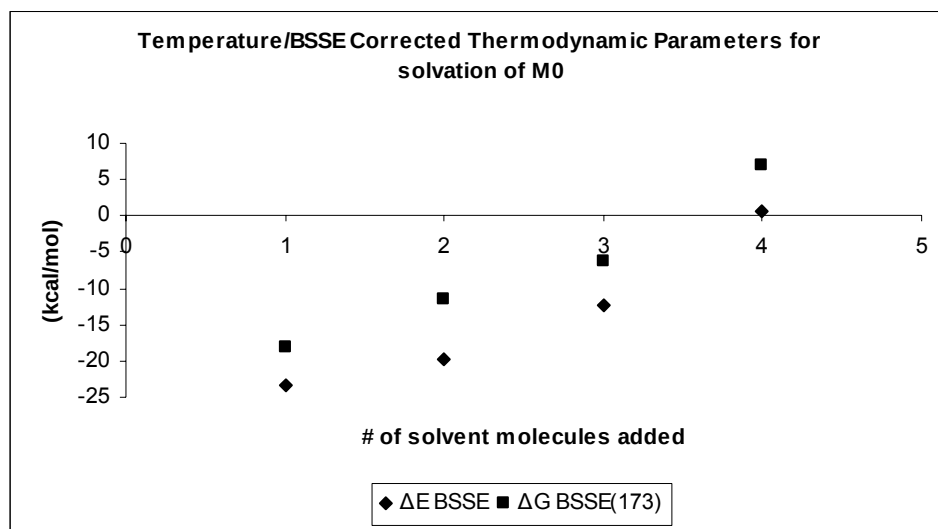
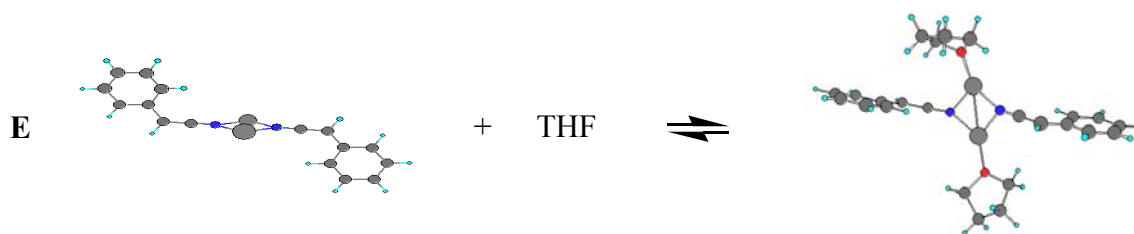
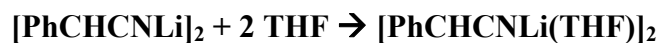


Chart 2.11 Temperature and BSSE-corrected energetic and thermodynamic parameters of solvation of PhCHCNLi by THF

In the same manner, the energetic and thermodynamic parameters governing Li^+ cation complexation by sequential pair wise solvation are calculated at B3LYP/6-31G(d).

As shown in Table 2.8 E, bis-solvation of the N,N-cyclic dimer structure results in an uncorrected solvation stabilization energy of approximately 45.55 kcal/mol. Application of a counterpoise correction for BSSE reveals that this stabilization is overestimated by approximately 7.7 kcal/mol. Correction for the lower experimental temperature stabilizes the free energy by approximately 1.04 kcal/mol, resulting in the prediction of a highly exothermic solvation ($\Delta G = -24.13$ kcal/mol). Similarly, tetrakis-solvation of the cyclic dimer by two additional THF solvent molecules sees a considerable reduction in the energetic and thermodynamic stability of the solvation pathway. As detailed in Table 2.8 F, further solvation is still thermodynamically favorable, but the effect of diminishing returns is exemplified (corrected $\Delta G = -10.10$ kcal/mol).

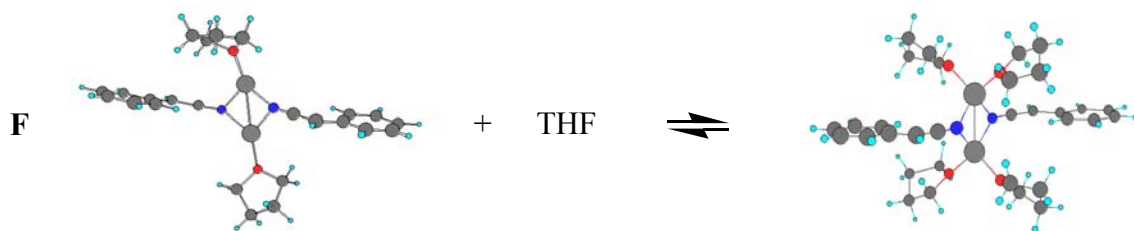


$$\frac{\Delta E}{-45.55}$$

$$\frac{\Delta E_{BSSE}}{-37.86}$$

$$\frac{\Delta G_{BSSE}(298)}{-15.39}$$

$$\frac{\Delta G_{BSSE}(173)}{-24.13}$$



$$\frac{\Delta E}{-26.40}$$

$$\frac{\Delta E_{BSSE}}{-25.21}$$

$$\frac{\Delta G_{BSSE}(298)}{-0.42}$$

$$\frac{\Delta G_{BSSE}(173)}{-10.10}$$

Table 2.8 Incremental solvation of N,N-cyclic lithiophenylacetonitrile dimer by THF; ΔE and ΔG reported in kcal/mol; All structures calculated at B3LYP/6-31G(d)

As shown in Chart 2.12, a linear relationship again correlates the electronic and free energy of solvation stabilization to the number of solvent molecules coordinated to the Li^+ cation. While the modeling of hexakis(THF)-solvated dimeric structures were not

attempted, this linear relationship suggests qualitatively that such a solvation pathway would indeed exhibit endothermicity, and therefore not be a likely solution structure.

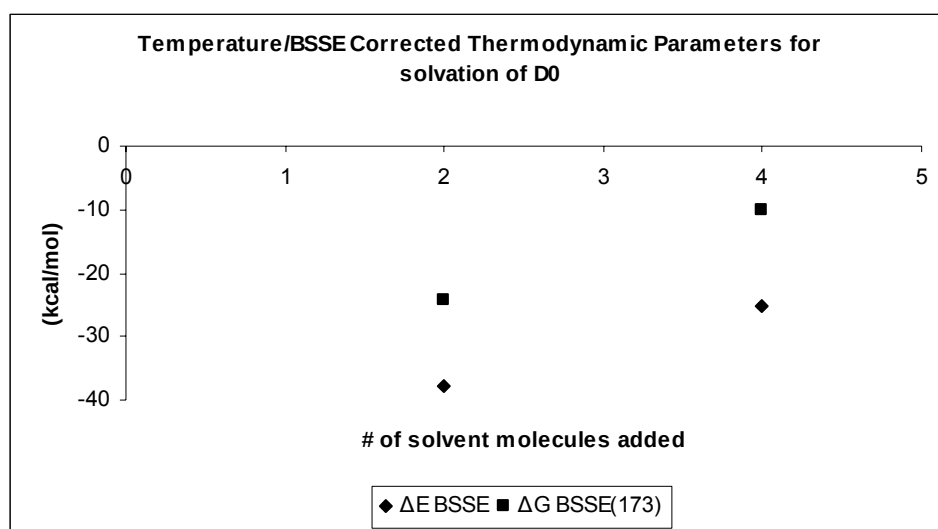


Chart 2.12 Temperature and BSSE-corrected energetic and thermodynamic parameters of solvation of dimeric PhCHCNLi by THF

In summary, the effect of basis set superposition error on solvation stabilization energy (ΔE) and free energy (ΔG) ranges from approximately 0-8 kcal/mol over the stepwise solvation of monomeric and dimeric structures. Offsetting temperature corrections typically range from 0-10 kcal/mol depending on the structure. Combining counterpoise and temperature corrections confirms the conclusion that tetrahedral coordination of lithium is optimum, as can be seen in Charts 2.11 and 2.12.

2.3.5 Redefining structural characterization by IR

As described earlier, computational investigation of the nitrile vibrational frequencies for the proposed monomeric and dimeric solution structures of **27-Li** does not provide resolution to the contradictory structural characterizations previously. The inability of theoretical modeling to resolve the apparent discrepancies between these spectral studies leads us now to re-evaluate the role of IR spectroscopy toward the structural elucidation of lithiated benzylic nitriles in THF. The important question that remains centers around what information vibrational spectroscopy can actually provide regarding solution structure. Until this point, we have inferred qualitative structural properties based on the nitrile vibrational stretch. We have correlated dual site (bridging) coordination of the Li^+ cation to the nitrile bond to an aggregate structure, and similarly single (terminal) coordination to a monomeric species, as depicted in Figure 2.2.

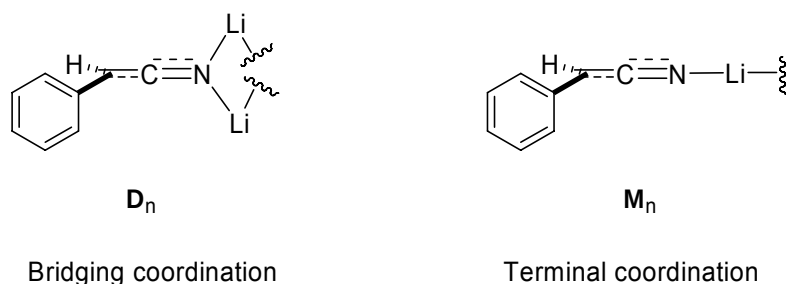


Figure 2.2 Bridging and terminal coordination of lithiophenylacetonitrile

We now propose that the nitrile vibrational frequency can indeed provide structural information regarding the nitrile, but offer that this information must be interpreted with caution. We propose that experimentally and computationally observed nitrile vibrational frequency is not inherently due to the aggregation state per se, but

rather the nature of the metal-nitrile anion coordination. From the examples shown in Figure 2.2, it may be assumed that all aggregates of **27-Li** necessarily feature bridging coordination, and that terminal coordination must be a consequence of monomeric complexation. However, this is not always the case. It is not unreasonable to envision dimeric structures which do not possess exclusive bridging linkages to the Li^+ cation. As shown in Figure 2.3, dimeric aggregates including an open-dimer and a triple ion formation each prominently feature terminal Li-coordination. We propose that the “monomeric” nitrile vibrational stretches previously reported stem not from an inherent monomeric structure, but rather terminal coordination to the nitrile anion. Similarly, bridging coordination to the nitrile terminus would give rise to nitrile vibrational stretches at much smaller relative frequencies as a result of dual coordination, not inherent aggregation phenomena.

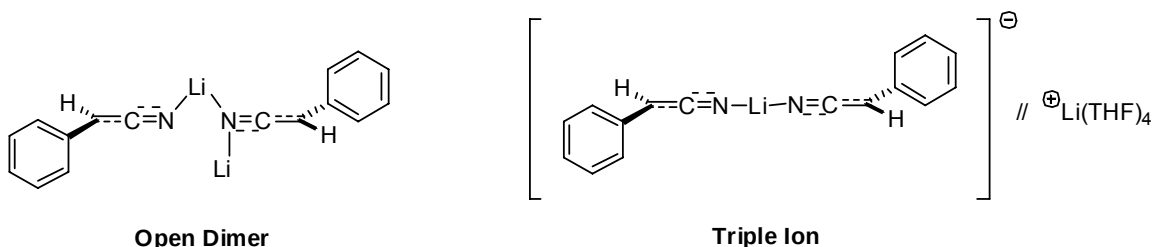


Figure 2.3 Dimeric structures featuring terminal linkage to the Li^+ cation

2.3.6 Proposal of an alternate solution structure

Under this new definition clarifying the utility of vibrational spectroscopy toward structural elucidation of lithiated benzylic nitriles, we now amend Carlier and Lo’s previous characterization of HMPA-induced **D₁** as triple-ion **TI₁** in hopes of resolving the

contradictory spectral evidence from IR and multinuclear NMR spectroscopy. As shown in Figure 2.4, the fundamentally dimeric **TI**₀ features lithium coordination to two nitrogen atoms thereby preserving the structural qualities which led to the original characterization as dimer **D**₁ by ⁷Li and ³¹P NMR spectroscopy. Due to the exclusive terminal coordination of the Li⁺ cation to the nitrile anion, **TI**₀ would be expected to exhibit nitrile vibrational stretch frequencies closely resembling those of the monomeric species described above.

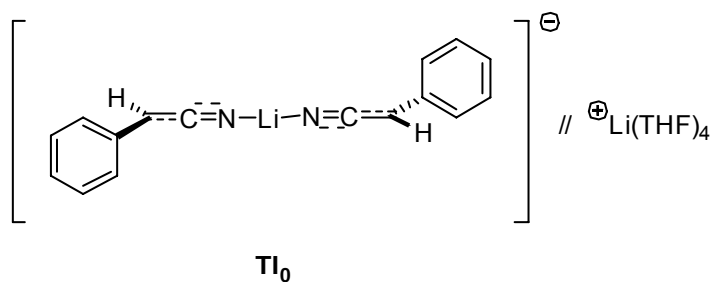


Figure 2.4 Proposed triple ion, **TI**₀ of **27-Li**

2.3.6.1 Triple ion background

Triple ions (e.g., **TI**₀) have been previously reported as viable solution structures of lithium amides in weakly polar media with highly Lewis basic co-solvents⁸⁸⁻⁹⁴. Typically, triple ions have been observed at high relative concentrations of HMPA. ¹³C NMR has suggested the generation of triple ions from principally dimeric structures lithium N-isopropylanilide⁸⁹ and lithium 2,2,3-trimethylindolenide⁹⁰ upon addition of 2-4 equivalents HMPA in diethyl ether. Similarly, anionic ion triplets have been observed at 3-4 relative equivalents HMPA in THF/hydrocarbon solutions of lithium 2,2,6,6-

tetramethylpiperidide (LiTMP).⁹³ Our proposal deviates from this motif in the formation of **TI**₁ at only 0.5 equivalents relative to **27-Li** and related lithiated benzylic nitriles.

2.3.6.2 Computational assessment of triple ion structure

To assess the validity of our proposal attributing “monomeric” IR behavior of **27-Li** solvates to terminal coordination of lithium to the nitrile anion, we now examine the theoretical anti-symmetric nitrile vibrational frequency of **TI**₀ and **TI**₁ structures (both solvated and unsolvated) at B3LYP/6-31G(d) and B3LYP/6-31+G(d). The viability of our proposed **TI**_n structure under given experimental conditions requires that these dimeric species feature $\nu(\text{C}\equiv\text{N})$ stretches comparable to that of calculated monomeric solvates.

As shown in Table 2.9, the calculated nitrile vibrational frequency for the triple-ion structures does closely resemble that of the previously monomeric species. For the unsolvated triple ion, represented by $(\text{PhCHCN})_2\text{Li}^-$, B3LYP/6-31G(d) and B3LYP/6-31+G(d) predict anti-symmetric $\nu(\text{C}\equiv\text{N})$ frequencies at 2080 cm^{-1} and 2076 cm^{-1} , respectively, with nitrile bond lengths measuring around 1.189 Å. Recall that the N-lithiated monomer exhibited predicted nitrile stretch frequencies of 2061 cm^{-1} and 2060 cm^{-1} at the two tested basis sets with somewhat longer nitrile bond lengths (1.198 Å). That the triple ion features shorter bond lengths and a higher vibrational frequency is indicative of the electronic effects resulting from a single N-terminus to two Li^+ cations. Note that is in contrast to the dual site, bridging coordination featured in the N,N-cyclic dimer structure previously described. This calculated spectroscopic behavior strongly

supports the notion that calculated nitrile stretches from experiment are more indicative of the nature of the bonding of the Li⁺ cation to the nitrile bond than of aggregation state.

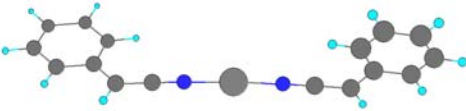
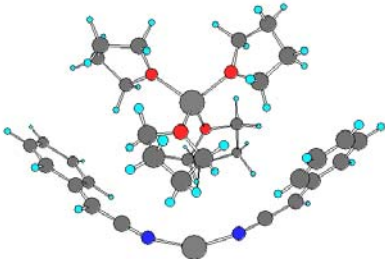
<u>Nitrile</u>	<u>Calculated Structure</u>	Calculated $\nu(\text{C}\equiv\text{N})$ cm^{-1} ; <u>CN bond length (Å)</u>	
		$^{\dagger}\text{B3LYP}/$ <u>$6-31\text{G}(d)$</u>	$^{\dagger\dagger}\text{B3LYP}/$ <u>$6-31+\text{G}(d)$</u>
$(\text{PhCHCN})_2\text{Li}^-$		2080 cm^{-1} 1.189 Å 1.189 Å	2076 ‡ cm^{-1} 1.188 Å 1.188 Å
$\text{PhCHCN})_2\text{Li}^-$ // $^+\text{Li}(\text{THF})_4$		2067 cm^{-1} (-13) 1.188 Å 1.189 Å (0.000)	2069 * cm^{-1} (-7) 1.189 Å 1.190 Å (0.001)

Table 2.9 Theoretical $\nu(\text{C}\equiv\text{N})$ frequencies for unsolvated and solvated triple ion structure of **27-Li** (relative to unsolvated species); † Calculated vibrational frequencies (reported as cm^{-1}) are scaled by 0.9495; †† Calculated vibrational frequencies are scaled by 0.9545; ‡ Anti-symmetric $\nu(\text{C}\equiv\text{N})$ for dimeric species; * Calculated at B3LYP/6-31'+G(d)

For consideration of solvation effects, it is important to realize that the triple ion, as presented, is inherently a separated ion pair structure. Therefore, consideration of solvation requires incorporation of a cationic $^+\text{Li}(\text{THF})_4$ moiety. Modeling of the fully solvated triple ion, $(\text{PhCHCN})_2\text{Li}^-/^+\text{Li}(\text{THF})_4$ at B3LYP/6-31'+G(d) predicts a calculated nitrile stretch frequency at 2069 cm^{-1} with an average CN bond length of 1.189

Å. At B3LYP/6-31G(d), this frequency is 0.2 cm^{-1} smaller with a negligible difference in nitrile bond lengths. Recall from Table 2.3 that similar trends were observed upon solvation of the N-lithiated monomer.

The modeling of HMPA-solvated **TI**₀ brings about the possibility for the existence of two potential solvates as shown in Figure 2.5. **TI**_{1a} features HMPA solvation of the Li^+ cation, and **TI**_{1b} exhibits HMPA coordination to the anionic portion of the triple ion structure.

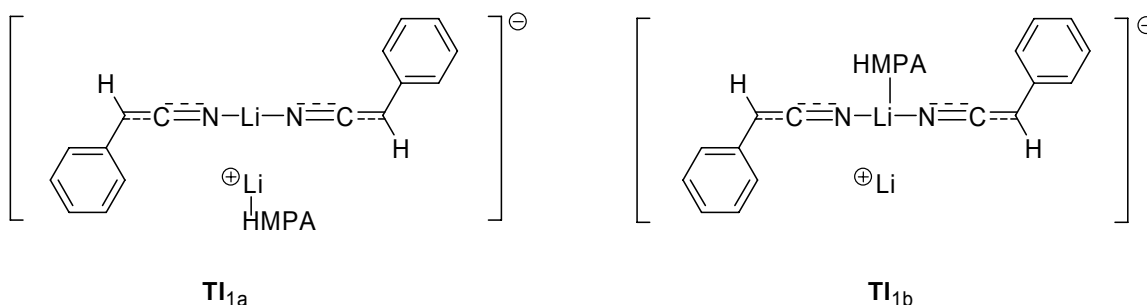


Figure 2.5 **TI**₀ HMPA solvates

As shown in Table 2.10, explicit modeling of HMPA solvated **TI**_{1a} and **TI**_{1b} reveals that both possible solvates boast predicted $\nu(\text{C}\equiv\text{N})$ stretches which again are in close agreement the previously reported calculated monomeric frequencies at B3LYP/6-31'+G(d). While triple ion structure **TI**_{1b} was not calculated at B3LYP/6-31G(d), modeling at the higher 6-31'+G(d) basis set predicts an anti-symmetric nitrile stretch frequency at 2079 cm^{-1} . **TI**_{1a} reports a similar frequency at 2069 cm^{-1} . Again, as seen with the THF-solvate, only minor changes in nitrile bond length are observed. These

results further support the proposed existence of a triple ion under experimental conditions.

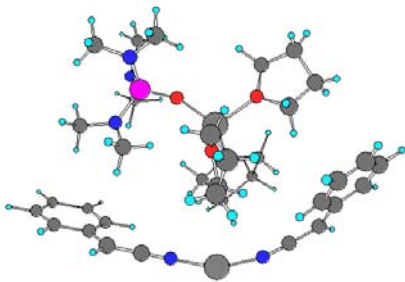
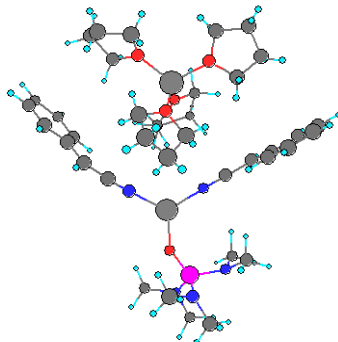
<u>Nitrile</u>	<u>Calculated Structure</u>	Calculated $\nu(\text{C}\equiv\text{N})$ cm^{-1} ; CN bond length ($\text{\AA}$)	
		${}^{\dagger}\text{B3LYP}/$ $6\text{-}31\text{G}(\text{d})$	${}^{\dagger\dagger}\text{B3LYP}/$ $6\text{-}31+\text{G}(\text{d})$
(PhCHCN)$_2$Li$^-$ //${}^+\text{Li}(\text{THF})_3(\text{HMPA})$		2070 cm^{-1} (-10)	2069 ** cm^{-1} (-7)
		1.189 $\text{\AA}$ 1.189 $\text{\AA}$ (0.000)	1.189 $\text{\AA}$ 1.189 $\text{\AA}$ (0.001)
(PhCHCN)$_2$Li$^-$(HMPA) //${}^+\text{Li}(\text{THF})_4$			2079 ** cm^{-1} (+3)
		--	1.186 $\text{\AA}$ 1.186 $\text{\AA}$ (-0.002)

Table 2.10 Scaled $\nu(\text{C}\equiv\text{N})$ frequencies for HMPA-solvated triple ion structures of **27-Li**; † Calculated vibrational frequencies (reported as cm^{-1}) are scaled by 0.9494; †† Calculated vibrational frequencies are scaled by 0.9546; ‡ Anti-symmetric $\nu(\text{C}\equiv\text{N})$ for dimeric species; *Calculated at B3LYP/6-31'+G(d)

In conclusion, the proposed triple ion potentially satisfies the requirements necessary to resolve the contradicting structural assessments brought about by

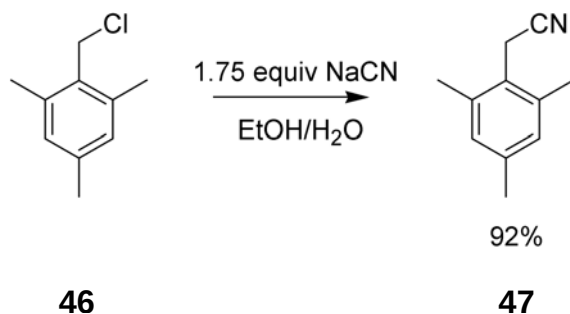
experimental studies. This triple ion structure exhibits vibrational frequencies slightly larger than those of the N-lithiated monomer and retain CN bond lengths in close agreement. Additionally, the triple ion maintains a fundamentally aggregate arrangement which could explain the apparent dimeric qualities observed by $^7\text{Li}/^{31}\text{P}$ NMR spectroscopy. We observe here that nitrile vibrational frequency does not inherently give qualitative structural information regarding aggregation state, but rather information regarding the nitrile coordination to the Li^+ cation.

2.4 Spectroscopic identification of the triple ion in solution

The most significant hurdle in the unambiguous determination of triple ion structure **TI₀**, is the necessity for observation of two separate lithium resonances by ^7Li NMR. The observed broad ^7Li signals corresponding to our proposed triple ion of **27-Li** in 20:1 THF/Hexane (Chart 2.5 A) provide little structural detail, presumably due to signal averaging consequent of rapid Li-N exchange. In order to provide conclusive evidence for the existence of a triple ion **TI_{1a}** or **TI_{1b}** in solution under given experimental conditions, we must develop a strategy which will slow the rapid Li-N exchange rate to a point at which differentiation of the individual ^7Li resonances by ^7Li NMR is possible.

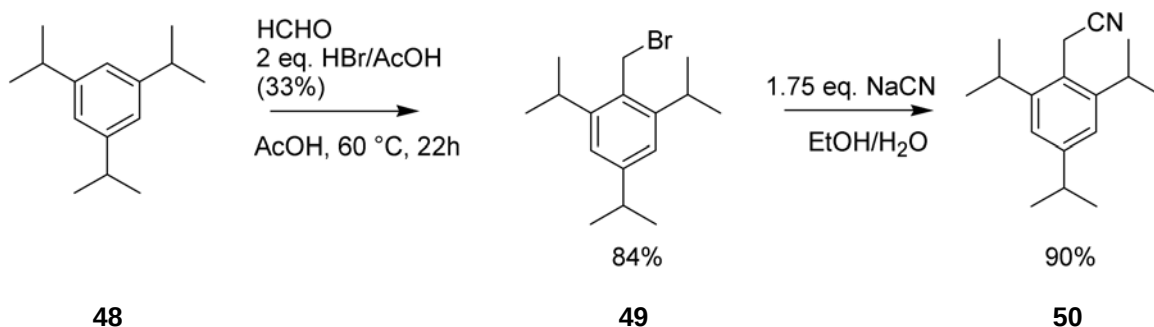
2.4.1 Synthesis of hindered benzylic nitriles

In order to effectively slow the Li-N exchange and potentially permit the observation of **TI_{1a}** or **TI_{1b}** in solution, we will introduce steric hindrance around the nitrile functional group. Our approach centers on the successive addition of bulkier alkyl groups to the *ortho*-position of phenylacetonitrile. Our synthetic targets center around *o*-substituted benzylic nitriles including mesitylcyanide **47** and triisopropylbenzylcyanide **50**. 2,4,6-trimethylphenylacetonitrile **47** is synthesized in 92% yield from the S_N2 substitution reaction of commercially available α²-chloroisodurene **46** and excess sodium cyanide as shown in Scheme 2.1.



Scheme 2.1 Synthesis of 2,4,6-trimethylphenylacetonitrile, **47**

2,4,6-Triisopropylbenzylcyanide is synthesized in two steps from 1,3,5-triisopropylbenzene **48** following a modified procedure from van der Made.⁹⁵ Bromomethylation of **48** in 33% HBr/AcOH produces **59** in 84% yield. Substitution of the halogen by sodium cyanide then proceeds in 90% yield to give product **50**, as shown in Scheme 2.2.



Scheme 2.2 Synthesis of 2,4,6-triisopropylphenylacetonitrile, **50**

2.4.2 ^7Li and ^{31}P NMR of Lithiated 2,4,6-trimethylphenylacetonitrile

The HMPA titration of **47-Li** supports the assessment that lithiated benzylic nitriles exist in 20:1 THF/Hexane as contact ion pairs, as evidenced by the appearance of free HMPA (^{31}P , δ 26.1 ppm) at relative concentrations as low as 2 equivalents per Li^+ cation, as illustrated in Chart 2.13 C. Furthering this determination is the measurement of the ^7Li linewidth ($\nu_{1/2} = 3.74$ Hz).

^{31}P NMR of the **47-Li** titration experiment suggests the presence of three independent species at one equivalent added HMPA with multiplicity and chemical shifts similar to those observed in the titration of **27-Li**: δ 27.40 ppm (q, $J_{\text{Li-P}}=7.8$ Hz), δ 26.89 ppm (q, $J_{\text{Li-P}}=7.8$ Hz), and δ 26.65 ppm (q, $J_{\text{Li-P}}=8.5$ Hz), as illustrated in Chart 2.13 B. Corresponding **47-Li** dilution comparisons at fixed HMPA concentration (Chart 2.14) one equivalent per Li^+ cation confirm the concentration dependence of the relative intensity of the δ 27.40 ppm and δ 26.89 ppm ^{31}P NMR resonances, mirroring the

behavior of **27-Li** (recall Chart 2.6). The concentration dependence of the intensities of the signals strongly suggests aggregate behavior of **47-Li** under these experimental conditions. Based on our revised assessment, we now characterize the ^{31}P δ 27.40 ppm 1:1:1:1 quartet as triple-ion **TI₁**. At the 2:1 stoichiometric ratio of phosphorus to lithium achieved at 0.5 equivalents added HMPA (Chart 2.13 A), the proposed **TI₁** signal dominates the ^{31}P spectra providing further evidence for the aggregative effect of sub-stoichiometric addition of HMPA; however there is no indication by ^7Li NMR for the existence of two separate ^7Li signals, a requirement for definitive characterization of the **TI₁** structure.

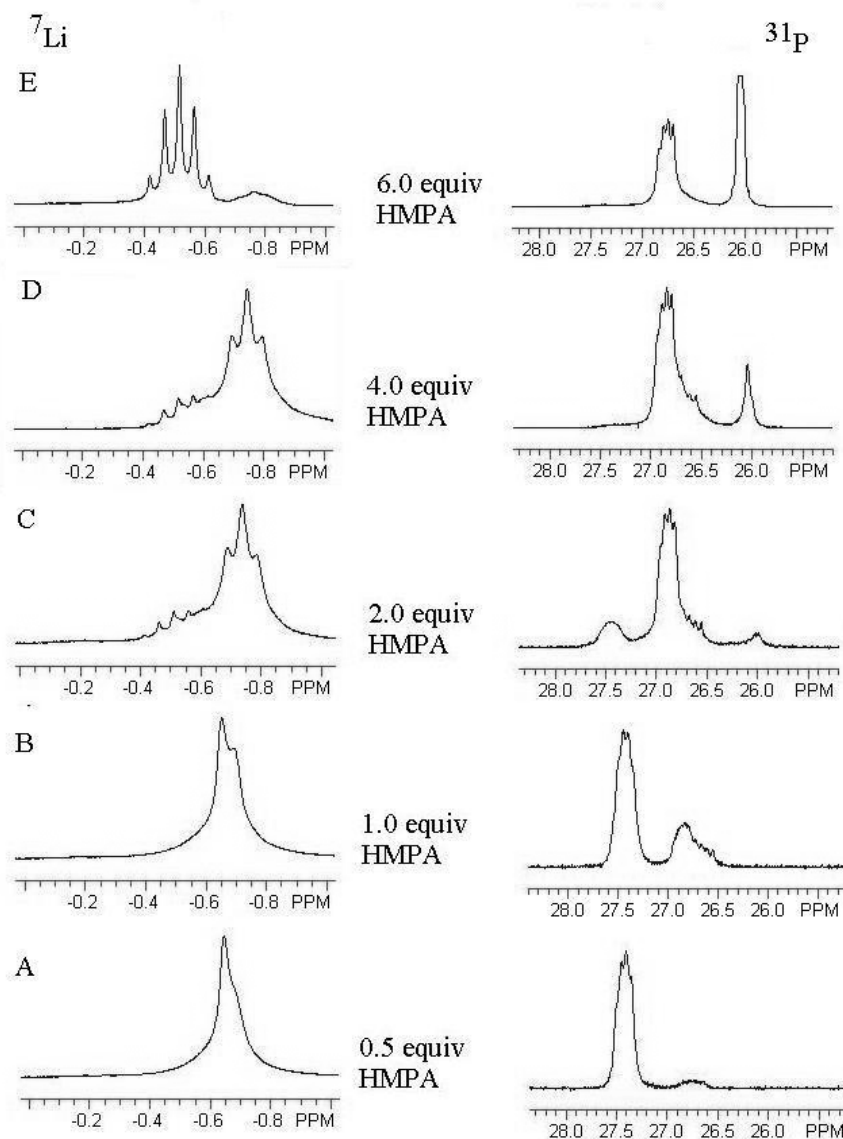


Chart 2.13 HMPA titration of lithiated mesitylacetonitrile in 20:1 THF/Hexane

At two added equivalents HMPA, a triplet by ^7Li NMR (δ -0.73 ppm, $J_{\text{Li-P}}=7.4$ Hz) indicates Li^+ cation coordination to two HMPA molecules, suggesting the primary species in solution is bis-HMPA solvated monomer, $\mathbf{M}_2$, as shown in Chart 2.13 C. By ^{31}P NMR it is interesting to note the retention of a small amount of the proposed $\mathbf{TI}_1$

resonance at this concentration. While this minor contribution may be an artifact of small variability in solution concentration, it could also be the result of the increase in basicity of **47-Li** relative to **27-Li**. The steric hindrance introduced by the addition of ortho-methyl groups to the benzylic nitrile can effectively force bond rotation of the benzylic nitrile, thus disrupting π -delocalization into the phenyl ring. The resulting increase in basicity could serve to stabilize the dimeric **TI₁** structure more so than the analogous **27-Li**, promoting the retention of the aggregate structure at slightly higher HMPA concentrations. This notion of dimeric stabilization of the moderately hindered **47-Li** is perpetuated by the concentration dependence of the monomeric and aggregate structure. Recall that for phenylacetonitrile, **27-Li**, approximately equal proportions of the dimeric species (retroactively recharacterized as **TI₁**) and monomer **M₁** is achieved at approximately 0.1 M **27-Li** (recall Chart 2.5 B). It is interesting to note that for **47-Li**, approximately equal proportions of these identifiable solvates are not observed until further dilution to 0.05 M (Chart 2.14 B). This behavior lends credence to the increased tendency of **47-Li** to aggregate upon addition of HMPA to solutions of THF/Hexane.

Similar retentive properties are observed in the addition of four equivalents HMPA (Chart 2.13 D). ⁷Li NMR suggests a strong proportion of **M₂** whereas the same concentration of HMPA in the **27-Li** analysis prompted the formation of proposed separated ion pair, **S₃**. At six equivalents added HMPA, ⁷Li NMR shows a sharp quintet characteristic for **S₄** (δ -0.52 ppm, $J_{\text{Li-P}}$ =7.6 Hz) signifying lithium coordination to four HMPA molecules (Chart 2.13 E). ³¹P NMR reveals a complementary quartet (δ 26.76, $J_{\text{Li-P}}$ =7.2 Hz).

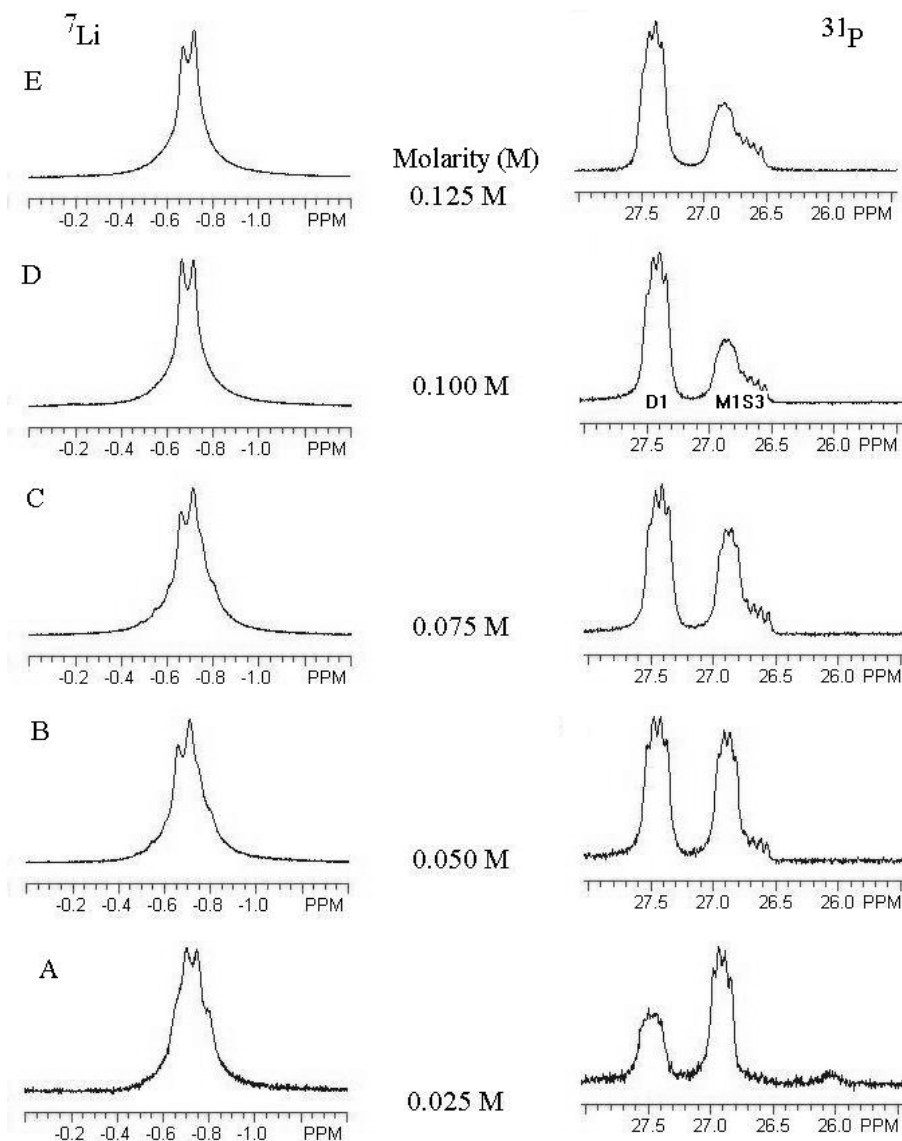
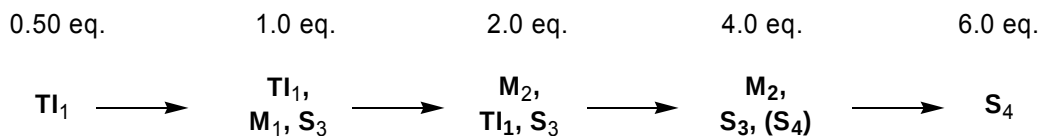


Chart 2.14 Dilution study of **47-Li** at one equivalent added HMPA

These multinuclear NMR data lead us to propose the following progression for the formation of **47-Li** HMPA-solvates as a function of HMPA concentration (Scheme 2.3). In cases with more than one identifiable solvate in solution, species are listed in order of decreasing intensity. Parenthetical listings reference solvates barely identifiable by NMR.



Scheme 2.3 Progression of HMPA solvates of **47-Li** as a function of HMPA concentration

2.4.3 NMR of lithiated 2,4,6-triisopropylphenylacetonitrile

Determination of the contact ion pair structure of **50-Li** reinforces the commonality of this structural property among lithiated benzylic nitriles in 20:1 THF/Hexane solution. An emerging trend is substantiated as the titration of **50-Li** reveals unbound HMPA by ^{31}P NMR (δ 26.10 ppm, singlet) in solution at two equivalents per Li^+ cation (Chart 2.15 C). ^7Li NMR linewidth analysis of **50-Li** in the absence of HMPA once again reinforces the contact ion pair status of lithiated benzylic nitriles ($\nu_{1/2} = 4.32$ Hz).

At first glance, the recorded ^7Li and ^{31}P NMR spectra of **50-Li** in 20:1 THF/Hexane (Chart 2.15) exhibit striking similarities to the analogous nitriles **27-Li** and **47-Li**. Upon addition of one equivalent HMPA, the three HMPA-coordinated solvates are observable by ^{31}P NMR: 1:1:1:1 quartets at δ 27.38 ppm ($J_{\text{Li-P}}=8.6$ Hz), δ 26.84 ppm ($J_{\text{Li-P}}=7.3$ Hz), and δ 26.66 ppm ($J_{\text{Li-P}}=9.8$ Hz). Dilutions at fixed HMPA concentration (one equivalent per Li^+ cation), describe familiar concentration dependence on the relative distribution of the species at δ 27.38 and δ 26.84 ppm. Chart 2.16 illustrates the effect of dilution on the relative abundance of these two species. Increased solution concentration of **50-Li** fosters an increase in the relative population of the solvate

responsible for the quartet at δ 27.38 ppm. Similarly, dilution reduces the intensity of this ^{31}P NMR resonance at the expense of the peak at δ 26.84 ppm. This information, in concert with the presence of only one solvate at 0.5 equivalents HMPA (Chart 2.15 A), strongly suggests that the signal at δ 27.38 ppm is attributed to an aggregate species, which we propose to be triple ion **TI₁**. Similarly the ^{31}P NMR quartet δ 26.84 ppm is assigned the mono-HMPA solvated monomer **M₁**.

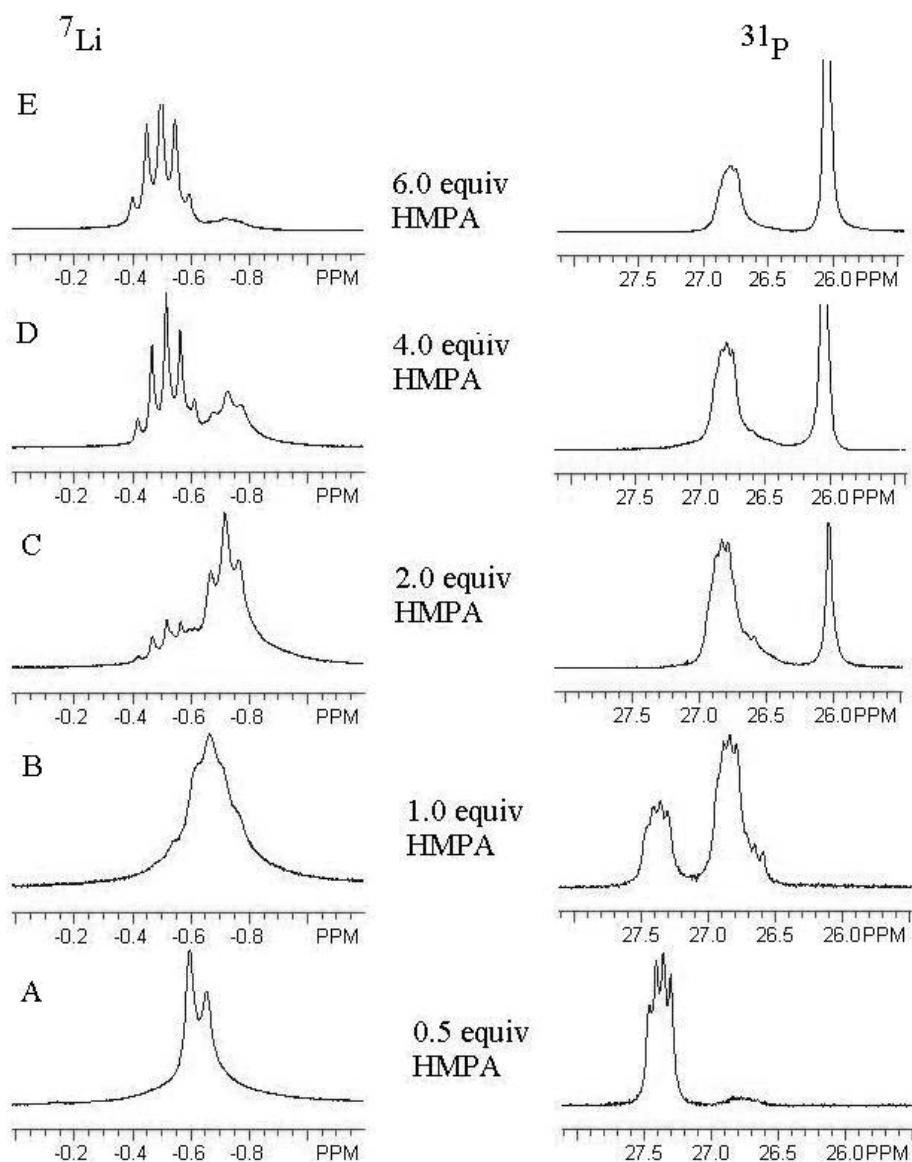


Chart 2.15 HMPA titration of lithiated triisopropylacetonitrile in 20:1 THF/Hexane

Addition of excess HMPA to 0.10 M **50-Li** in THF/Hexane yields similar observed behavior to that of **27-Li** and **47-Li** by ^7Li and ^{31}P NMR. At two equivalents added HMPA (Chart 2.15 C), a triplet corresponding **M₂** is observable by ^7Li NMR (δ - 0.71 ppm, $J_{\text{Li-P}}=7.4$ Hz). Complementary ^{31}P NMR depicts one principal quartet with identical chemical shift to the assigned **M₁** solvate (δ 26.84 ppm, $J_{\text{Li-P}}=7.3$ Hz). At

higher concentrations HMPA, the formation of separated ion pair **S**₄ is observed by the ⁷Li quintet at δ -0.50 ppm (J_{Li-P}=7.6 Hz), as seen in Chart 2.15 E.

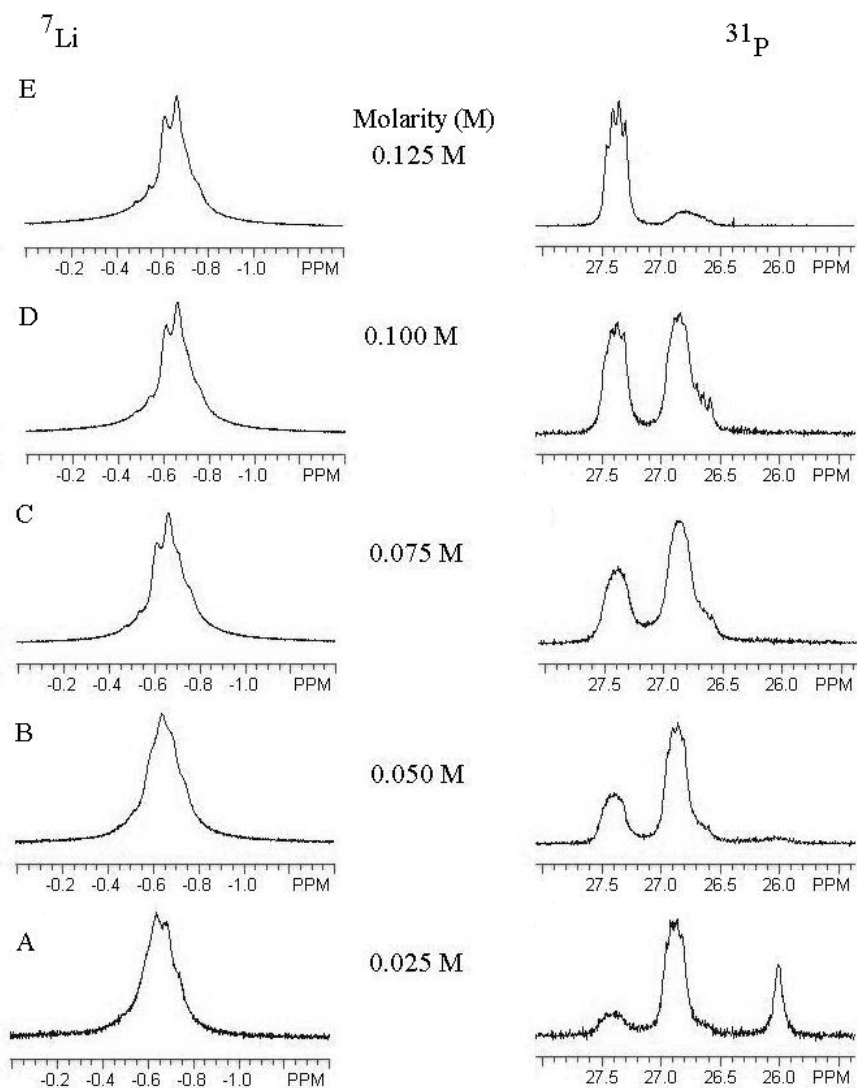
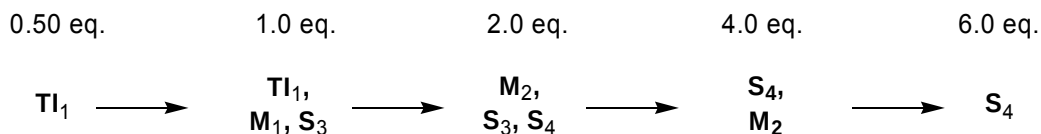


Chart 2.16 Dilution study of **50-Li** at 1 equivalent HMPA

It is worthwhile to note that the observed persistence of dimeric **TI**₁ at dilute concentrations for **47-Li** is not mirrored in the structural assessment of **50-Li**. We had

drawn the conclusion that the steric hindrance introduced by the presence of methyl substituents *ortho*- to the nitrile increases the basicity of **47-Li** in solution thereby encouraging stabilization by aggregative behavior in dilute solution. This trend is not duplicated in **50-Li**. We rationalize this discrepancy as the result of the larger steric hindrance structurally limiting the formation of aggregate structures. We suggest that the potential stabilization earned by aggregation in dilute solution is offset by the energetic penalty associated with the dimerization of isopropyl substituted benzylic nitriles. The summation of these contrasting effects results in ^{31}P NMR behavior of **50-Li** which more closely resembles that of **27-Li**.

These multinuclear NMR data lead to the proposition of the following progression for the formation of **50-Li** HMPA solvates as a function of HMPA concentration (Scheme 2.4), which closely resembles the assessment drawn from spectroscopic studies of **27-Li**. Again, in cases with more than one identifiable solvate in solution, species are listed in order of decreasing intensity.



Scheme 2.4 Progression of HMPA solvates of **50-Li** as a function of HMPA concentration

Table 2.12 summarizes the ^7Li and ^{31}P NMR spectral data obtained from the HMPA titration of nitriles **27-Li**, **47-Li**, and **50-Li** acquired at $-125\text{ }^\circ\text{C}$.

<u>Solvate</u>	<u>Nitrile</u>	<u>^7Li $\delta(\text{mult.}, J(\text{Hz}))$</u>	<u>^{31}P $\delta(\text{mult.}, J(\text{Hz}))$</u>
TI₁	27-Li	-0.53 (br)	27.43 (q, 8.4)
	47-Li	-0.65 (br)	27.40 (q, 7.8)
	50-Li	-0.59 (br), -0.65 (br)	27.38 (q, 8.6)
M₁	27-Li	-0.58 (br)	26.88 (q, 7.5)
	47-Li	-0.66 (br)	26.89 (q, 7.8)
	50-Li	-0.67 (br)	26.84 (q, 7.3)
M₂	27-Li	-0.63 (t, 7.5)	26.87 (q, 8.4)
	47-Li	-0.73 (t, 7.4)	
	50-Li	-0.73 (t, 7.4)	26.84 (q, 7.3)
S₃	27-Li	not resolved	26.75 (q, 9.3)
	47-Li	not resolved	26.65 (q, 8.5)
	50-Li	not resolved	26.66 (q, 9.8)
S₄	27-Li	-0.50 (qn, 7.6)	26.75 (q, 7.5)
	47-Li	-0.52 (qn, 7.6)	26.76 (q, 7.2)
	50-Li	-0.50 (qn, 7.6)	26.79 (q, 6.6)

Table 2.11 ^7Li and ^{31}P NMR data for HMPA-solvated ion pairs

2.4.4 Identification of a triple ion

The most important piece of information obtained from the HMPA titration of **50-Li**, is the observation of two ^7Li resonances at 0.5 equivalents added HMPA (Chart 2.15 A). This result indicates that under conditions supporting the formation of a dimeric

HMPA-solvate of **50-Li**, dynamic lithium-nitrogen exchange is adequately slowed to an extent which permits the resolution of two different ^7Li nuclei which was previously unattainable for lithiated benzylic nitriles **27-Li** and **47-Li**. Comparison of the ^7Li NMR data of **27-Li**, **47-Li**, and **50-Li** at 0.5 equivalents added HMPA provides evidence for the sterically-controlled emergence of two ^7Li resonances (Chart 2.17).

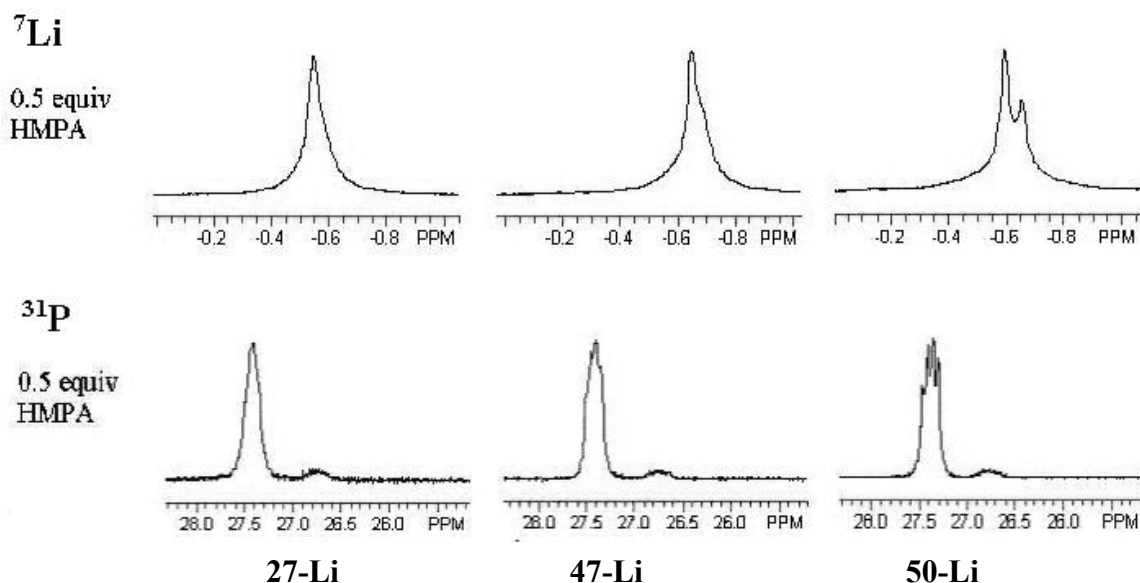


Chart 2.17 ^7Li and ^{31}P NMR evidence for sterically controlled slowing of Li-N exchange rates for **27-Li**, **47-Li**, and **50-Li**

It is evident that increased steric bulk around the nitrile assists in slowing the dynamic lithium-nitrogen rate of exchange. The ^7Li NMR for **27-Li** is best characterized as a broad singlet. The corresponding signal for **47-Li** is also a broad singlet, but there is a broadening at the base suggesting the emergence of a separate ^7Li resonance. As the steric bulk around the nitrile increases to **50-Li**, the appearance of a separate ^7Li

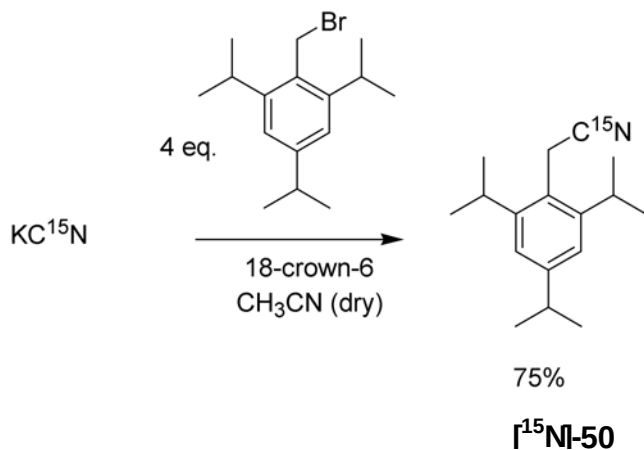
resonance strongly indicates that the lithium-nitrogen exchange rate has been sufficiently slowed to resolve the separate resonances. Secondly, ^{31}P NMR exhibits the general trend of improved resolution over the progression of sterically hindered species, which provides further, albeit subtle evidence for the slowing of exchange.

2.5 Characterization of HMPA-solvated triple ion, TI_1

Consequent of the sterically facilitated slowing of Li-N exchange, it should be possible to resolve $J_{\text{Li-N}}$ coupling for the isotopically enriched benzylic nitrile $[^{15}\text{N}]\mathbf{50-Li}$ in 20:1 THF/Hexane solution by both ^7Li and ^{15}N NMR. ^{15}N NMR (42.667 MHz) spectra of HMPA-solvated $[^{15}\text{N}]\mathbf{50-Li}$ in 20:1 THF/Hexane was acquired unlocked at $-125\text{ }^\circ\text{C}$. Chemical shifts (δ) are measured relative to external reference dimethylethylamine (natural abundance) (δ 25.7 ppm).

2.5.1 ^{15}N -2,4,6-Triisopropylphenylacetonitrile synthesis

$[^{15}\text{N}]\mathbf{-50}$ is synthesized through reaction of excess **49** with ^{15}N -labeled potassium cyanide in anhydrous acetonitrile with equimolar 18-crown-6 either in 75% yield (Scheme 2.5).



Scheme 2.5 Synthesis of [^{15}N]-2,4,6-triisopropylphenylacetonitrile

2.5.2 NMR investigation of Lithiated [^{15}N]-2,4,6-triisopropylacetonitrile

HMPA titration experiment is conducted on [^{15}N]**50-Li**, specifically targeting 0.5 equivalents added HMPA, conditions which yield a discernibly dimeric structure. Chart 2.18 illustrates that at 0.4-0.5 equivalents added HMPA (relative to Li^+ cation concentration), ^{31}P NMR reveals a 1:1:1:1 quartet (δ 27.36 ppm, $J_{\text{Li-P}} = 8.6$ Hz), mirroring the corresponding ^{31}P signal for **50-Li**. ^7Li NMR, however indicates a substantial increase in complexity relative to **50-Li** (δ -0.57 ppm) providing spectral support for slowed Li-N exchange through Li-N coupling. Due to peak overlap and the large ^7Li linewidth ($\nu_{1/2}$), direct conclusions regarding the multiplicity of these signals cannot be deduced at this time. At 0.6 equivalents added HMPA, ^{31}P NMR indicates the presence of three species closely resembling the spectra of **50-Li** at 1.0 equivalent added HMPA (recall Chart 2.15 B). This result suggests that at concentrations exceeding the 2:1 concentration stoichiometry, small amounts of monomer **M₁** and **S₃** become observable.

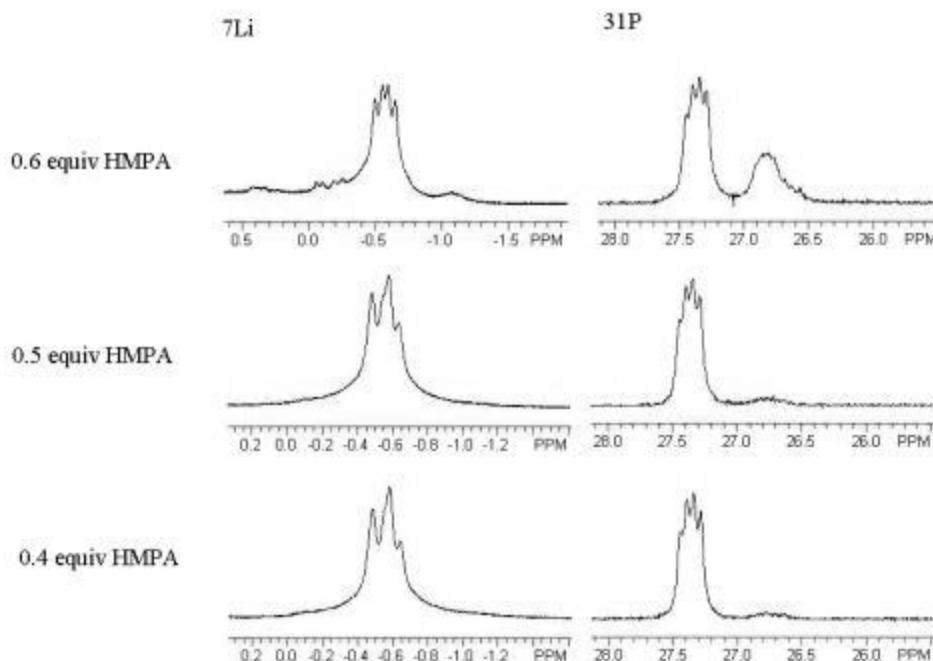


Chart 2.18 ^7Li and ^{31}P NMR spectra of Lithiated ^{15}N -2,4,6-triisopropylacetonitrile at 0.4-0.6 equivalents added HMPA

Observed multiplicity from ^{15}N NMR spectroscopy ($I=1/2^{77}$) can assist in the differentiation between dimeric species **D₁** and **TI₁** in solution. Predicted ^{15}N NMR multiplicity indicates that **D₁** would produce a septet indicating a nitrile bridged by two ^7Li nuclei. By virtue of the terminal linkage of the $^7\text{Li}^+$ cation to the nitrile terminus, ^{15}N NMR of **TI₁** would show a quartet. As shown in Chart 2.19, ^{15}N NMR of ^{15}N [**50-Li**] at 0.5 equivalents added HMPA confirms Li-N coupling (δ 222.16 ppm, q, $J_{\text{Li-N}} = 12.8$ Hz). The observation of a quartet by ^{15}N NMR strongly supports the assessment of dual terminal linkages, providing significant spectral evidence for the existence of a **TI₁** structure. For additional support of a non-cyclic dimeric structure, consider the $J_{\text{Li-N}}$ coupling constants. Confirmed cyclic dimer species TMEDA- and Et_2O -solvated $[\text{Li}]$,

$^{15}\text{N}[\text{27-Li}]$ have been reported to exhibit the following ^{15}N signals: δ 222.08 ppm (q, $J_{\text{Li-N}} = 3.4$ Hz) and δ 218.47 ppm (q, $J_{\text{Li-N}} = 3.5$ Hz), respectively.⁷⁸ The coupling constants for terminally coordinated amides, however, typically longer than those of bridged lithium amides. Examples of monomeric lithium amides and triple ions are reveal $J_{\text{Li-N}}$ constants around 6.1 Hz⁷⁸ and 7.0 Hz⁹⁰, respectively. The higher $J_{\text{Li-N}}$ coupling constant seen in $^{15}\text{N}[\text{50-Li}]$ ($J_{\text{Li-N}}=12.8$ Hz) is at least in part attributable the 2.64-fold gyromagnetic ratio of ^7Li to ^6Li .

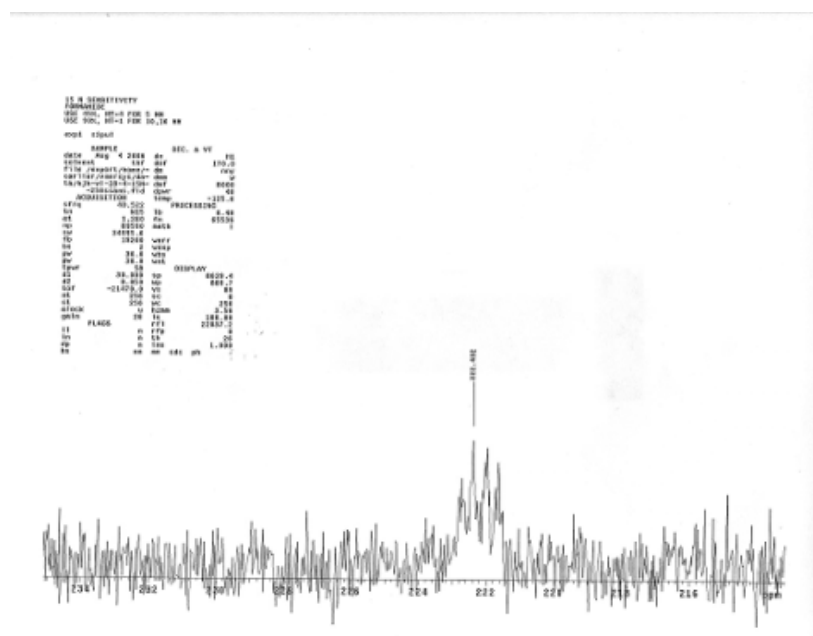


Chart 2.19 ^{15}N NMR of Lithiated ^{15}N -2,4,6-triisopropylphenylacetonitrile at 0.5 equivalents HMPA

2.6 Conclusions

In our continued efforts to confidently characterize the solution structure of lithiated benzylic nitriles in 20:1 THF/hexane we reinvestigate both the spectroscopic

data from IR and multinuclear NMR. After independent confirmation of both conflicting sets of data, we focus our efforts on data interpretation. With the support of theoretical nitrile vibrational analysis, we redefine the investigative utility of IR spectroscopy toward the elucidation of aggregate structure.

With the view that IR spectroscopy provides structural details about the nature of coordinative binding to the nitrile functional group rather than aggregation state, we amend our prior conclusion that **27-Li** and related lithiated benzylic nitriles exist as HMPA-induced **D₁** dimers. In order to find resolution to the conflicting conclusions drawn regarding this structure it was necessary to identify a principally dimeric structure featuring only terminal metal coordination to the nitrile anion. Thus we propose that our previously characterized **D₁** aggregate is actually triple ion **TI₁**. ³¹P NMR confirms the dimeric nature of this species in solution while computational analysis supports the required “monomeric” IR signature. Lastly, multinuclear NMR studies of [¹⁵N]**50-Li** indicate that the systematic introduction of steric hindrance around the benzylic nitrile significantly slows Li-N exchange, thereby allowing ¹⁵N-⁷Li coupling to be observed. This coupling strongly supports our assessment of a dimeric **TI₁** structure in solution.

Chapter 3 Experimental and Computational Details for Chapter 2

3.1 Experimental methodologies

3.1.1 Low temperature multinuclear NMR spectroscopic information

Low temperature ^7Li , ^{31}P , and ^{15}N NMR (at $-125\text{ }^\circ\text{C}$) were recorded on a UNITY Varian 400 spectrometer (^7Li at 155.435 MHz; ^{31}P at 161.907 MHz; and ^{15}N at 40.522 MHz). Shimming was performed on the ^{31}P external reference sample (0.1 M HMPA in 20:1 THF/Hexane) at $-125\text{ }^\circ\text{C}$ by maximization of the ^1H lock signal of THF; however all spectra were acquired unlocked, as there are no deuterated solvents present within the sample. Encountered spectral drift of each unlocked sample was minimal (less than 0.10 ppm) after 15 minutes equilibration time at the desired temperature, but as a safeguard spectra were periodically re-referenced over the duration of the multinuclear NMR experiments. All chemical shifts reported are relative to external reference standards listed in Table 3.1.

<u>Nuclei</u>	<u>Standard</u>	<u>Chemical shift (ppm)</u>	<u>Reference</u>
^1H	TMS	0.00	Internal
	CDCl_3	7.26	Internal
^{13}C	CDCl_3	77.0	Internal
^7Li	LiCl	0.00	External
^{31}P	HMPA	26.1	External
^{15}N	DMEA	25.7	External

Table 3.1 Chemical shift references for NMR nuclei

3.1.1.1 Sample Preparation

All glassware necessary for sample preparation were oven dried at 120 °C overnight and stored in a dessicator until ready for use. Gas-tight syringes, rubber septa, and Teflon stopcocks were also stored over desiccant. 0.3 M stock solutions of the substituted benzylic nitriles and LiHMDS were prepared using a combination of glove box and syringe techniques (5.00 ml total volume). 2.09 M stock solution HMPA (5.00 ml) was also prepared in this fashion. The solvents THF and hexane were freshly distilled under vacuum from blue/purple solutions containing the sodium benzophenone ketyl. Up to 5% tetraglyme was added to hexane to dissolve the ketyl. HMPA was distilled under reduced pressure and stored over molecular sieves.

NMR sample tubes were prepared on a Schlenk line at -78 °C. Appropriate volumes from each stock solution were injected into the septa-capped NMR tubes under a positive pressure of argon gas (Table 3.2). After sample preparation, all septa were sealed with silicon grease and wrapped with parafilm to prevent air flow into the NMR tube. Each sample tube was prepared in duplicate, and each complete experiment was performed at least two times.

	<i>Description</i>	<i>ArCN</i>	<i>LiHMDS</i>	<i>HPMA</i>	<i>THF</i>	<i>Hexane</i>
<i>Tube</i>	<i>(eq. HMPA)</i>	<i>(μl)</i>	<i>(μl)</i>	<i>(μl)</i>	<i>(μl)</i>	<i>(μl)</i>
1	0.0	250	250	0	215	35
2	0.5	250	250	18	197	35
3	1.0	250	250	36	179	35
4	2.0	250	250	72	143	35
5	4.0	250	250	144	71	35
6	6.0	250	250	215	0	35

Table 3.2 Sample HMPA titration experiment

3.1.2 Infrared spectroscopy

IR spectra were recorded using an open-compartment MIDAC M1700 FT-IR. An International Crystal Labs CaF_2 FT-IR flow cell (0.05 mm path length, Model SL-2) was used for in situ IR experiments. The IR apparatus assembled to ensure anhydrous experimental conditions in the HMPA titration of lithiophenylacetonitrile is described in Figure 3.1.

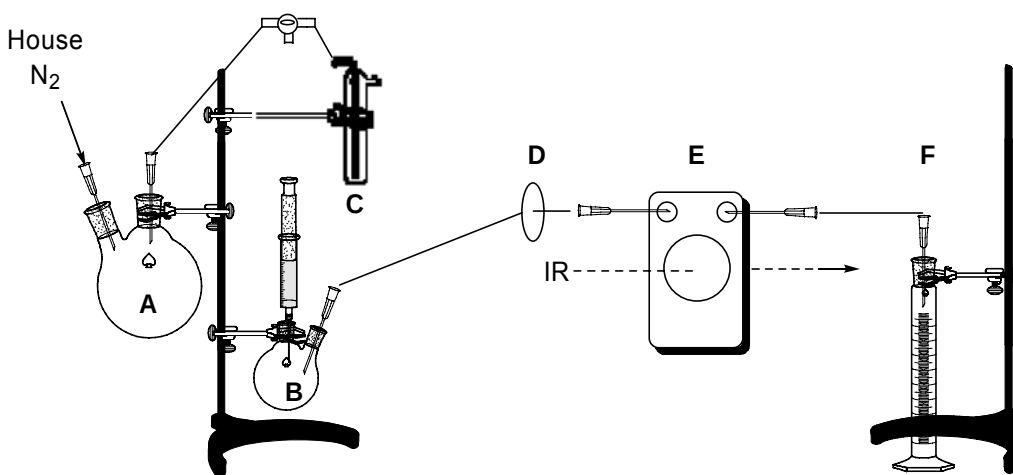


Figure 3.1 IR flow cell apparatus

3.1.2.1 General experimental

Reservoir **A** is filled with house-supplied N₂ gas and pressure is equalized via bubbler **C**. A syringe is filled with N₂ from reservoir **A** and used to cannulate 0.1 M LiHMDS in THF from reaction flask **B** into a Whatman 0.2 μm PTFE inline filter **D** to remove trace particulates. The filtered contents of are pushed through the CaF₂ flow cell **E** and into the waste receptacle **F**. The 0.1 M LiHMDS solution is then subtracted from all subsequent spectra. The remaining volume of **B** is calculated based on **F** and the estimated volume of the entire apparatus. Phenylacetonitrile is then added via syringe to be equimolar to LiHMDS, and the system is flushed with 5x the volume of the apparatus. The same technique is thereby employed to create varying concentrations of HMPA in solution.

3.1.3 Synthetic methodologies

3.1.3.1 Synthesis of organolithium base

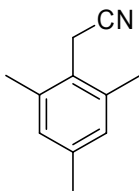
Lithium hexamethyldisilazide (LiHMDS) is synthesized under inert atmosphere from modification of Collum's published method.⁹² To both ends of a swivel frit were attached 100 mL round bottom flasks with stir bars inside each flask. About 50 mL of hexane is vacuum transferred to one of the flasks. The stopcock of the swivel frit is replaced by rubber septa, and under positive argon pressure, 5.0 ml hexamethyldisilazane (HMDS) was added via syringe. The solution was then cooled to 0 °C and 9.6 ml *n*-butyllithium (2.5M in hexanes) was added and allowed to stir for 3 hours. Concentration in vacuo was performed until crystallizing product was just visible, at which time the

temperature was decreased to -78 °C to affect the crystallization of the remaining crude LiHMDS product. Under vacuum, the swivel frit was inverted to collect crude product by filtration. The supernatant was then evaporated to dryness and the swivel frit was transferred to a dry box. Crude LiHMDS was scraped from the assembly and transferred to another swivel frit for recrystallization from hexanes following the same protocol.

3.1.3.2 Synthesis of arylacetonitriles

^1H and ^{13}C NMR spectra were recorded on either a JEOL Eclipse +500 (^1H at 500.162 MHz, ^{13}C at 125.041 MHz) or an INOVA Varian 400 (^1H at 399.946 MHz; ^{13}C at 100.466 MHz). Chemical shifts are reported relative to internal reference standards as reported in Table 3.1. Melting point ranges were determined using an Electrothermal 9100 melting point apparatus and are reported uncorrected. Mass spectra were obtained via positive ion high resolution FAB+ on a JEOL HX110 dual focusing mass spectrometer using a direct inlet with 3-Nitrobenzyl alcohol as the matrix. Thin-layer chromatography was performed on EMD silica gel 60 F₂₅₄ coated onto aluminum sheets. Flash column chromatography was performed using EMD silica gel 60 (230-400 mesh).

(2,4,6-Trimethyl-phenyl)-acetonitrile



To a 3-neck, 250 mL round bottom flask equipped with reflux condenser was added 5.4114g NaCN (112.5 mmol), 7.8 mL H₂O, and 11.4 mL EtOH. The mixture was brought to reflux temperature, and upon complete dissolution of NaCN, 10.8387g α -chloroisodurene (64.3 mmol) was added via spatula. Reaction was stirred at reflux for 3 hours, at which time the orange solution was cooled to 40 °C and extracted with toluene (6 x 20 mL). Toluene extracts were combined, washed with H₂O (3 x 20 mL), dried with anhydrous Na₂SO₄, concentrated on a rotary evaporator leaving a brown, oily mass (92% crude yield). Crude product decolorized with activated charcoal in dichloromethane, producing translucent crystals upon drying (74% yield). The analytically pure sample was prepared by recrystallization from hexanes.

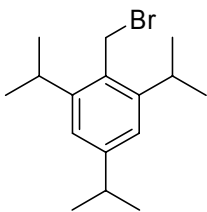
¹H NMR (CDCl₃): δ 2.27 (s, 3H), 2.33 (s, 6H), 3.60 (s, 2H), 6.89 (s, 2H)

¹³C NMR (CDCl₃): δ 17.50, 20.01, 20.94, 117.57, 124.49, 129.46, 136.57, 137.99

MS (FAB⁺): 160.1048 (M⁺)

mp: 79.9 °C – 80.4 °C

2-Bromomethyl-1,3,5-triisopropyl-benzene



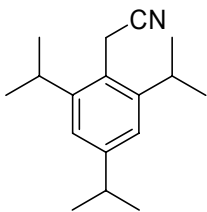
To a 100 mL round bottom flask was added 10.016 g 1,3,5-triisopropylbenzene (48.9 mmol), 1.4685 g paraformaldehyde (48.9 mmol, insoluble), and 50 mL glacial acetic acid. The mixture was heated to 50 °C at which time 16.9 ml 33% HBr/AcOH (97.8 mmol) was added via pipette, affecting complete dissolution of paraformaldehyde. Reaction maintained at 50 °C and monitored by TLC. After 18 hours, reaction mixture was quenched by addition to 100 mL H₂O. Acidic aqueous phase extracted with chloroform (5 x 40 mL). Organic extracts were combined and washed with NaHCO₃ (5 x 30 mL), once with H₂O (30 mL), and once with brine solution (1 x 50 mL). Organic phase was then dried with anhydrous Na₂SO₄, filtered, and concentrated on a rotary evaporator leaving 11.85 g yellow lachrymating oil (90%). Crude product purified by bulb-to-bulb distillation at 135 °C producing 10.79 g of colorless, viscous oil (82 %).

¹H NMR (CDCl₃): δ 1.29 (d, *J* = 6.9 Hz, 6H), 1.34 (d, *J* = 6.8 Hz, 12 H), 2.87-2.96 (m, *J* = 6.8 Hz, 1 H), 3.31-3.39 (m, *J* = 7.0 Hz, 2 H), 4.72 (s, 2H), 7.05 (s, 2H)

¹³C NMR (CDCl₃): δ 23.86, 24.15, 28.08, 29.25, 121.46, 128.52, 148.01, 149.56

MS (FAB+): 295.10493 (M⁺);

(2,4,6-Triisopropylphenyl)-acetonitrile



To a 25 mL round bottom flask was added 0.2837 g sodium cyanide (5.8 mmol) and 2 mL H₂O. 0.9854 g 2-bromomethyl-1,3,5-triisopropyl-benzene (3.3 mmol) was dissolved in 4 mL ethanol and added to the reaction flask via pipette. Temperature is maintained at reflux for two hours, at which time no remaining starting material is visible by TLC. The Heat source is removed and the flask is allowed to cool to room temperature at which point crystalline solid forms. Solid is filtered and recrystallized from hexanes: 90% yield.

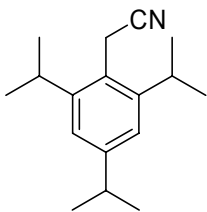
¹H NMR (CDCl₃): δ 1.25 (d, *J* = 7.10 Hz, 6H), 1.29 (d, *J* = 6.65 Hz, 12 H), 2.90-2.86 (m, *J* = 6.90 Hz, 1H), 3.16-3.12 (m, *J* = 6.90 Hz), 3.73 (s, 2H), 7.04 (s, 2H);

¹³C NMR (CDCl₃): δ 15.99, 23.96, 24.07, 30.22, 34.36, 118.67, 121.69, 122.22, 147.07, 149.27;

MS (FAB⁺): 244.20436 (M⁺);

mp: 81.3 °C-82.0 °C;

[¹⁵N]-(2,4,6-Triisopropylphenyl)-acetonitrile



To a 100 mL round bottom flask was added 2.9608 g 2-bromomethyl-1,3,5-triisopropylbenzene (10.0 mmol), 0.6621 g 18-crown-6 ether (2.5 mmol), 0.1659 g [¹⁵N]-potassium cyanide and 15 mL acetonitrile (freshly distilled). The reaction flask was capped and stirred at room temperature for 3 hours. Excess starting material was removed by addition of triethylamine (20.0 mmol) and flask was allowed to stir overnight. Contents of round bottom flask were transferred to a 250 mL separatory funnel, at which time 30 mL each of H₂O and diethyl ether were added, shaken, and separated. Organic phases was washed with H₂O (1 x 30 mL) and 0.1 M HCl (2 x 30 mL), then dried with Na₂SO₄ and concentrated by rotary evaporation. Resulting solid was recrystallized from hexane to give 75% yield purified product.

¹H NMR (CDCl₃): δ 1.25 (d, *J* = 6.85 Hz, 6H), 1.29 (d, *J* = 6.90 Hz, 12 H), 2.88 (qn, *J* = 7.10 Hz, 1H), 3.14 (qn, *J* = 6.65 Hz), 3.73 (s, 2H), 7.03 (s, 2H);

¹³C NMR (CDCl₃): δ 15.99, 23.95, 24.05, 30.21, 34.36, 118.58, 121.69, 122.21, 147.07, 149.27;

MS (FAB⁺): 245.20209 (M⁺);

mp: 81.5 °C-82.1 °C;

3.2 Computational details

All calculation data presented in Chapter 2 were obtained from Gaussian '03 Rev. B.05.⁹⁶ This software package is accessible through Inferno2, an SGI ALTIX 3700 server hosted exclusively for computational research at Virginia Polytechnic Institute and State University. At the time of this writing, Inferno2 is a 128-node 1600 MHz Itanium 2.5 processor supercluster offering 4.5 Terabytes (TB) total disk space and an additional 320 Gigabytes (GB) available memory running on a 2.6.5-7 Linux kernel. Final optimized geometries and calculated frequencies are visualized with GaussView 2.1⁹⁷ or Molden.⁹⁸

3.2.1 Counterpoise corrections

As described in Chapter 2, basis set superposition error (BSSE) is incurred in the calculation of the relative energies of molecular clusters relative to its component fragments. In order to correct for the BSSE imposed when calculating clusters of molecular fragments (i.e., dimers, solvates), a counterpoise correction must be implemented.

In the course of calculating the counterpoise correction of a molecular cluster, Gaussian '03 calculates five separate single point energies at the given basis set. First, the electronic energy of the complex (E_0) is determined. Then the energy of each respective fragment is calculated using all available orbitals from the aggregate species (defined as DCBS₁, DCBS₂, etc.). Finally the energies of each fragment are determined in the absence of the extended orbital structure of the higher order complex (MCBS₁,

MCBS₂, etc.). The counterpoise correction is calculated from these energies as follows in Equation 3.1. The counterpoise correction is added to the electronic energy E₀, giving the BSSE-corrected energy for the molecular cluster.

$$\text{Counterpoise correction} = (MCBS_1 + MCBS_2) - (DCBS_1 + DCBS_2)$$

Equation 3.1 Calculation of counterpoise correction for molecular assemblies

Application of this correction factor requires specification in the Gaussian job file (.gjf), as detailed below in the sample calculation for the BSSE error associated with mono-THF solvated lithiophenylacetonitrile (Figure 3.2). In the step-wise calculation of solvation energy described in Chapter 2, this particular example represents pathway A, Scheme 2.4.

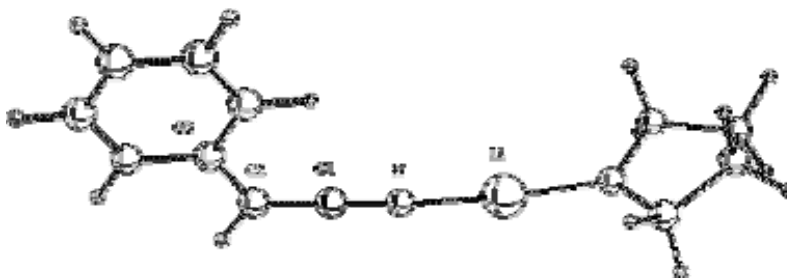


Figure 3.2 mono-THF solvated lithiophenylacetonitrile

The counterpoise correction is specified by the addition of the **Counterpoise=X** keyword to the route section (#P) of the input file, where X is the number of fragments comprising the aggregate structure as shown in Figure 3.3.

#P rb31yp/6-31g(d) **Counterpoise=2**

0 1 0 1 0 1

Li	0.000000	0.000000	0.000000, 1
N	0.000000	0.000000	1.838866, 1
C	0.250044	0.000000	3.006203, 1
C	0.527437	0.006536	4.336412, 1
C	1.865121	-0.047155	4.874550, 1
C	3.018825	-0.130549	4.058165, 1
C	4.297233	-0.177964	4.611169, 1
C	4.483443	-0.142649	5.996099, 1
C	3.356934	-0.063132	6.821993, 1
C	2.076085	-0.016409	6.274953, 1
H	1.207569	0.042617	6.930407, 1
H	3.482370	-0.036091	7.903564, 1
H	5.482389	-0.178374	6.423658, 1
H	5.164776	-0.242902	3.953457, 1
H	2.891833	-0.162422	2.977073, 1
H	-0.312877	0.055381	5.024531, 1
O	-1.526404	0.122779	-1.240059, 1
C	-1.535935	-0.207008	-2.646192, 1
C	-2.501413	0.754357	-3.357301, 1
C	-3.116570	1.637097	-2.246354, 1
H	-2.972805	2.701390	-2.459951, 1
H	-4.196012	1.476928	-2.164815, 1
C	-2.404964	1.239134	-0.941788, 1
H	-1.795614	2.052214	-0.529454, 1
H	-3.095947	0.903960	-0.162806, 1
H	-1.972911	1.359720	-4.101016, 1
H	-3.272638	0.198980	-3.899904, 1
H	-1.841147	-1.256293	-2.734051, 1
H	-0.507296	-0.118175	-3.019066, 1
O	1.732118	0.075900	-0.934418, 2
C	2.939263	0.513674	-0.261063, 2
C	4.057227	0.536355	-1.317219, 2
C	3.477130	-0.192392	-2.555123, 2
H	3.437492	0.470435	-3.425960, 2
H	4.091796	-1.051421	-2.840843, 2
C	2.070476	-0.647224	-2.135454, 2
H	1.293451	-0.410185	-2.869549, 2
H	2.027468	-1.726686	-1.933520, 2
H	4.350117	1.561571	-1.561840, 2
H	4.953301	0.033639	-0.941003, 2
H	3.151746	-0.172337	0.567664, 2
H	2.716704	1.497574	0.160740, 2

Figure 3.3 Specification of a counterpoise calculation

The total charge and multiplicity of the complex as well as each fragment must also be specified in the following format **0 1 0 1 0 1**; corresponding to charge and multiplicity of the aggregate, and the charge and multiplicity of fragments one and two, respectively. To define which atoms comprise each respective molecular fragment, atomic labels can be conveniently viewed by molecular visualization software including gOpenMol and Molden. Once the respective fragments have been defined, they are delineated within the input file by the addition of the fragment number at the terminus of the line defining that particular atom in space. In the example above, the two fragments are defined as 1 or 2.

The magnitude of the BSSE error is determined by examination of the output file by the following Unix based search command:

grep SCF filename.out

In the preceding example, the following energetic properties are calculated:

	<u>Energy (hartrees)</u>
Electronic Energy	-835.697
DCBS ₁	-603.221
DCBS ₂	-232.450
MCBS ₁	-603.220
MCBS ₂	-232.446

Table 3.3 Energetic data from counterpoise correction

Calculation of the counterpoise correction to the electronic energy of 3.3 kcal/mol as shown in Equation 3.2, giving a corrected energy $E^{\text{CP}} = -835.692$ hartrees.

$$\text{Counterpoise correction} = (MCBS_1 + MCBS_2) - (DCBS_1 + DCBS_2)$$

$$\text{Counterpoise correction} = (-603.220 - 232.446) - (-603.221 - 232.450) = 0.0053 \text{ hartrees}$$

Equation 3.2 Calculation of the BSSE error for mono-THF lithiophenylacetonitrile

Application of this protocol for more complicated aggregates or higher order solvates such as tris-THF solvated lithiophenylacetonitrile (Figure 3.4) introduces the possibility for multiple fragmentation patterns. For example, the tris-THF solvated lithiophenylacetonitrile solvate can be envisioned as three separate descriptions for Fragment 1 and 2. In these cases, the respective counterpoise corrections are reported as an average from each possible combination.

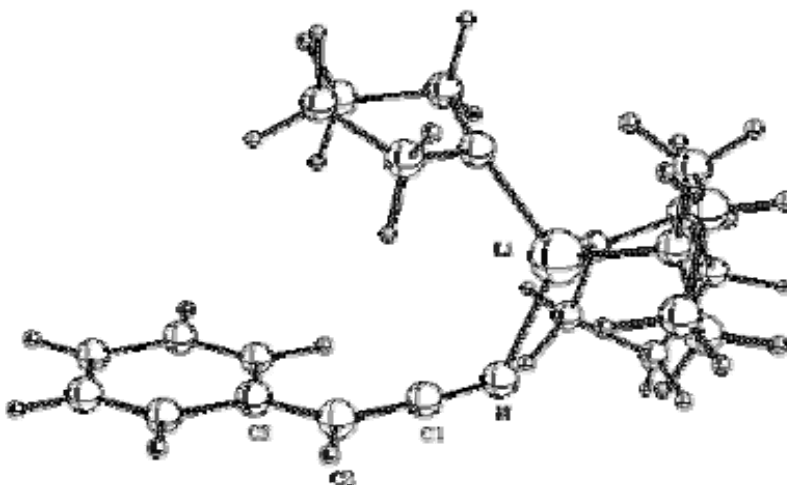


Figure 3.4 Tris-THF solvated lithiophenylacetonitrile

3.2.2 Temperature corrections to thermodynamic parameters

The thermodynamic parameters H, and G are calculated based on correction factors to the electronic energy as shown in Equation 3.3.

$$G = \text{electronic energy} + \text{thermal correction to G}$$

$$H = \text{electronic energy} + \text{thermal correction to H}$$

Equation 3.3 Calculation of thermodynamic parameters

The addition of temperature corrections to the calculated thermodynamic parameters for the solvation pathways defined in Scheme 2.4 is achieved through use of the freqchk utility of Gaussian '03. Thermodynamic parameters, normally calculated at standard temperature and pressure (298.15K, 1 atm) are stored within the checkpoint file (.chk). These calculated corrections are readily extracted from the .out file using the following search command:

grep correction filename.out

The freqchk utility allows these parameters to be manipulated for user-defined temperature and pressure considerations, and is implemented with the following command:

freqchk filename.chk

3.2.3 Absolute energies, bond lengths and nitrile frequencies for calculated structures

Reported below in Table 3.4 are the absolute energies, CN bond lengths, and vibrational frequencies calculated at both B3LYP/6-31G(d) and B3LYP/6-31+G(d). For cases where in calculations were completed at B3LYP/6-31'+G(d), those structures will be substituted.

<i>Nitrile</i>	<i>Basis set</i>	<i>Energy (hartrees)</i>	<i>CN Bond Length ($\text{\AA}$)</i>	<i>$\nu(\text{CN})$ (cm^{-1})</i>
PhCH ₂ CN	6-31G(d)	-363.8018608	1.471	2371.8009
	6-31+G(d)	-363.8164355	1.161	2359.4258
PhCHCN ⁻	6-31G(d)	-363.2200664	1.181	2223.3557
	6-31+G(d)	-363.2522215	1.183	2189.7354
PhCHCNLi	6-31G(d)	-370.7372463	1.198	2170.9843
	6-31+G(d)	-370.7560260	1.198	2158.0629
PhCH(Li)CN	6-31G(d)	-370.7417785	1.188	2153.6827
	6-31+G(d)	-370.7560260	1.187	2143.9842
[PhCHCNLi] ₂	6-31G(d)	-741.5601649	1.210	2112.5260
	6-31'+G(d)	-741.5898693	1.210	2101.2963
PhCH(Li(THF) ₃)CN	6-31G(d)	-1068.175198	1.179	2189.0721
	6-31+G(d)	-1068.190452	1.179	2206.6141
PhCHCNLi(THF) ₃	6-31G(d)	-1068.187092	1.194	2156.8273
	6-31+G(d)	-1068.218502	1.192	2157.3527
[PhCHCNLi(THF) ₂] ₂	6-31G(d)	-1671.478991	1.196	2140.8213
	6-31'+G(d)	-1671.516925	1.196	2134.1563
PhCHCNLi ⁻ / ⁺ Li(HMPA) ₄	6-31G(d)	-3652.201979	1.186	2189.0721
	6-31'+G(d)	-3652.235826	1.185	2174.1424
PhCHCNLi(THF) ₂ HMPA	6-31G(d)	-1656.083712	1.189	2176.7506
[PhCHCNLi] ₂ (THF) ₃ (HMPA)	6-31'+G(d)	-2259.376079	1.189	2167.6316
PhCHCNLi(THF)	6-31G(d)	-603.2314985	1.195	2176.0506
PhCHCNLi(THF) ₂	6-31G(d)	-835.7145102	1.193	2153.9310
PhCHCN ⁻ //Li(THF) ₄	6-31G(d)	-1300.637127	1.190	2172.1753
[PhCHCNLi(THF)] ₂	6-31G(d)	-1206.535477	1.202	2129.7139
(PhCHCN) ₂ Li ⁻	6-31G(d)	-734.0559468	1.189	2190.2190
	6-31'+G(d)	-734.0994903	1.188	2175.1282
(PhCHCN) ₂ Li ⁻ / ⁺ Li(THF) ₄	6-31G(d)	-1671.446434	1.189	2176.6879
	6-31'+G(d)	-1671.487487	1.190	2166.4713
(PhCHCN) ₂ Li ⁻ // ⁺ Li(THF) ₃ (HMPA)	6-31G(d)	-2259.376079	1.195	2145.0548
	6-31'+G(d)	-2259.414405	1.194	214.4493
(PhCHCN) ₂ Li ⁻ (HMPA)// ⁺ Li(THF) ₄	6-31G(d)	-2491.816369	1.185	2187.7828
	6-31'+G(d)	-2491.8606	1.185	2178.0706

Table 3.4 Raw energy, CN bond length, and nitrile vibrational stretch for 27-Li monomeric and dimeric isomers in Chapter 2

3.2.4 Calculated structures

The Cartesian coordinates (x,y,z) in angstroms from each of the optimized geometries are reported below. These coordinates are generated from the .chk file for each respective structure using the command line shown below.

```
newzmat -ichk -oxyz file.chk file.xyz
```

3.2.4.1 PhCH₂CN at B3LYP/6-31G(d)

H	0.187800022395	1.107283153224	-2.210750177874
C	0.190049046071	1.131955172729	-1.123085245510
C	0.182874145203	1.206274184566	1.660691117336
C	0.141145646090	-0.066272104380	-0.401293210504
C	0.240258557125	2.357355077358	-0.459064509995
C	0.236931343580	2.397611129294	0.936492075415
C	0.136088161026	-0.020506117976	0.996178082102
H	0.275320894667	3.279763903344	-1.032413886603
H	0.271094483086	3.351623265865	1.455297612336
H	0.084166693090	-0.943937359062	1.566438803792
H	0.173772928720	1.227901324982	2.747003036254
C	0.140461506311	-1.386768999837	-1.165607539433
H	1.169383158497	-1.677043402029	-1.422522926795
H	-0.388893605709	-1.269144295725	-2.118930992637
C	-0.467907097149	-2.506658622406	-0.440272650982
N	-0.938864632040	-3.393483558098	0.141664260135

3.2.4.2 PhCH₂CN at B3LYP/6-31+G(d)

C	-0.797085538374	-0.000242350436	-1.891734649589
C	-0.842873186507	0.000336031155	-0.493148341639
C	0.340804373788	-0.000078574254	0.251325760989
C	1.571060466801	-0.001080915464	-0.422392535767
C	1.616718811103	-0.001657240558	-1.816984031673
C	0.429714223500	-0.001238343042	-2.557507404621
H	-1.725434321252	0.000089209117	-2.456979144594
H	-1.803580949662	0.001108366277	0.014590896929
H	2.499077339397	-0.001413440070	0.146773567448
H	2.577842554293	-0.002433879988	-2.324726874412
H	0.463484321153	-0.001687381137	-3.643794438902
C	0.356583855445	0.000527219990	1.778221887836
H	0.903155879866	-0.877595434419	2.147934501090
H	0.904053172096	0.878388541476	2.147228660087
C	-0.965180800188	0.001458839864	2.411660193737
N	-2.011007318471	0.002199430745	2.916046793818

3.2.4.3 PhCHCN⁻ at B3LYP/6-31G(d)

C	-1.572972887522	-0.000657193004	-1.825409513382

C	-1.542884204002	0.000214284842	-0.437374510748
C	-0.317249742283	0.000295673908	0.301127561360
C	0.871520886940	-0.000607588686	-0.496808628283
C	0.825315975435	-0.001473549411	-1.883335015507
C	-0.392456156638	-0.001519446620	-2.582332008563
H	-2.539645021589	-0.000667732003	-2.332149393630
H	-2.480231720682	0.000866362934	0.119422344319
H	1.832378591878	-0.000601643104	0.013390065104
H	1.764284782267	-0.002135296291	-2.439362407859
H	-0.419312292073	-0.002201780851	-3.669942190320
C	-0.310971207199	0.001172040363	1.720946806790
H	-1.264836926884	0.001679643078	2.244445284659
C	0.842334848790	0.001341656809	2.506144311407
N	1.813076786566	0.001495025290	3.178063182756

3.2.4.4 PhCHCN⁻ at B3LYP/6-31+G(d)

H	0.911737277951	-1.591538309894	0.000000000000
C	0.866037805273	-0.504485201628	0.000000000000
C	0.783538574532	2.281640569089	0.000000000000
C	-0.420703052056	0.123597908938	0.000000000000
C	2.044051161036	0.234255604748	0.000000000000
C	2.034248732079	1.640106667528	0.000000000000
C	-0.401909271833	1.555084505688	0.000000000000
H	2.996816229158	-0.297017469259	0.000000000000
H	2.960421251664	2.211044460509	0.000000000000
H	-1.354807485801	2.084825969625	0.000000000000
H	0.735317466280	3.371603512619	0.000000000000
C	-1.648360809316	-0.597777921665	0.000000000000
H	-2.583409705043	-0.041605555898	0.000000000000
C	-1.740612039570	-1.990395135350	0.000000000000
N	-1.823403090726	-3.169924941684	0.000000000000

3.2.4.5 PhCHCNLi at B3LYP/6-31G(d)

C	0.023010844731	1.180453577824	-1.092937015382
C	0.188297748366	2.344592568977	-0.430284130266
N	0.332265039667	3.376376408175	0.162104191250
Li	0.550514818268	4.836597935696	1.129218724989
H	-0.059214371542	1.236693120584	-2.174812794458
C	-0.048430461242	-0.122165318835	-0.454593059897
C	-0.197354594680	-2.704155376806	0.727126614540
C	0.048626620293	-0.300327357622	0.944753148730
C	-0.222605442011	-1.284788753585	-1.238237456433
C	-0.295322992382	-2.548027436310	-0.657855414298
C	-0.024634271432	-1.564980393095	1.519582377205
H	0.183263026067	0.572110015112	1.580941349603
H	-0.300949549770	-1.183117243162	-2.318781684456
H	-0.429967065012	-3.419741455480	-1.294962325610
H	0.054093996777	-1.663426999432	2.600546119290
H	-0.254150478858	-3.690555165222	1.179353436723

3.2.4.6 PhCHCNLi at B3LYP/6-31+G(d)

C	0.031193797511	1.180163550669	-1.094226668607
C	0.194779788050	2.347174396670	-0.429234282705
N	0.338298025283	3.376160889068	0.167438572723
Li	0.555246012267	4.862674834788	1.087684954079
H	-0.045081610657	1.236309407418	-2.176939114958
C	-0.046138365454	-0.121968090839	-0.453325240350
C	-0.206797681802	-2.708429513804	0.730465833502
C	0.043588734998	-0.300862181443	0.948118635329
C	-0.219104990565	-1.286672470290	-1.238028639406
C	-0.297518602521	-2.551286093871	-0.657526096665
C	-0.035428529398	-1.567625361586	1.523913734270
H	0.176978995717	0.569309775276	1.587753652096

H	-0.291969406779	-1.186326813927	-2.319409104528
H	-0.430842143521	-3.422821683822	-1.295565047351
H	0.037684151878	-1.665627693276	2.605569778191
H	-0.268039105343	-3.694959132546	1.182521313056

3.2.4.7 PhCH(Li)CN at B3LYP/6-31G(d)

H	-0.399396490012	-1.165844834973	-2.698569552513
C	-0.399396490012	-1.165844834973	-1.611006552513
C	-0.308093928237	-1.165844834973	1.178407598645
C	0.164771824832	-0.072966551769	-0.935003136847
C	-0.921291806296	-2.247730864584	-0.912655501640
C	-0.855185574027	-2.236623719821	0.491764584068
C	0.215571869140	-0.034250419753	0.492098783591
H	0.681110915499	0.695158384934	-1.511367043857
H	-1.354104746549	-3.093182910975	-1.438401623644
H	-1.241181798270	-3.083328264550	1.054817551986
H	-0.274257423509	-1.177635446176	2.265200063251
C	0.645746619036	1.141148164835	1.223561863829
H	0.678441138742	1.133395647352	2.306081505468
C	1.008212628510	2.279498945194	0.514227347545
N	1.023153438772	3.150582645572	-0.292645682103
Li	-0.851565508326	1.884347866818	-0.192537015347

3.2.4.8 PhCH(Li)CN at B3LYP/6-31+G(d)

H	-0.402629392994	-1.171792662178	-2.701275737765
C	-0.402723147283	-1.170353640984	-1.613394387641
C	-0.313406897515	-1.166400562506	1.177887147429
C	0.151229123768	-0.071856080192	-0.937007186995
C	-0.918290899730	-2.257338358329	-0.913542077977
C	-0.853023500889	-2.244262739298	0.492102112949
C	0.204341565230	-0.031976119272	0.489806913101
H	0.659957775353	0.699675851933	-1.516687240566
H	-1.343075396252	-3.107394372745	-1.439283574918
H	-1.232486377532	-3.093537732264	1.056247636351
H	-0.278178698448	-1.178309881196	2.264991131606
C	0.639457555991	1.141825362897	1.222737245426
H	0.681655009787	1.129211190957	2.305498315393
C	1.017433469245	2.278092385822	0.518243193236
N	1.039449873819	3.157468251467	-0.279774130462
Li	-0.837165216517	1.917829452133	-0.210689791343

3.2.4.9 [PhCHCNLi]₂ at B3LYP/6-31G(d)

Li	0.942082244015	0.125196303271	-0.780470463008
N	0.944227839626	0.117864161938	1.157262608338
C	1.719574450893	0.119680932756	2.085946692619
C	2.580045536750	0.104920433172	3.113758631348
H	2.832897552596	1.062387065643	3.560930945947
C	3.187967717328	-1.106320634244	3.658960458816
C	4.082956824988	-1.012821530128	4.744007422934
C	4.680395086767	-2.147305166388	5.288200124822
C	4.405859259702	-3.414224114458	4.769051528244
C	3.520509709892	-3.524988413807	3.692995061850
C	2.921440459156	-2.393891066170	3.146343684978
H	2.235046129560	-2.502518293002	2.308761662853
H	3.293852702221	-4.503143578056	3.274632531905
H	4.872106421782	-4.298773558095	5.193875123691
H	5.366318791217	-2.039170852186	6.125259517524
H	4.307408854690	-0.033044439914	5.160026214034
Li	-0.944517773968	-0.112100475701	0.791312171111
N	-0.946766468201	-0.105698971465	-1.146236308806
C	-1.719573941014	-0.112001645655	-2.077020540621
C	-2.576950491185	-0.102491883707	-3.107475313699

C	-3.186461143752	1.105385305799	-3.658311852777
C	-4.077489266067	1.006064976447	-4.746091330472
C	-4.676325487284	2.137207232008	-5.295706973266
C	-4.407202057707	3.406447444702	-4.779425824137
C	-3.525868246547	3.522963333180	-3.700671197275
C	-2.925433042991	2.395230283077	-3.148610002882
H	-2.242311228227	2.508314506418	-2.308941994995
H	-3.303484373269	4.502999564060	-3.284436893279
H	-4.874540927829	4.288381037582	-5.208472550685
H	-5.359077960458	2.024588308439	-6.134761799546
H	-4.297733434555	0.024419386370	-5.159950664309
H	-2.826077751415	-1.062015882789	-3.552334737073

3.2.4.10 [PhCHCNLi]₂ at B3LYP/6-31'+G(d)

Li	0.925094044535	0.105532834960	-0.772946036235
N	0.946263310321	0.040452105913	1.149130948964
C	1.719263569797	0.053505753620	2.079385994795
C	2.578317821168	0.055051496676	3.111255270006
H	2.826571619017	1.021173525591	3.543581683667
C	3.190198254314	-1.145223347292	3.679278139738
C	4.082252616249	-1.027400250925	4.766355903160
C	4.685161645650	-2.149310230628	5.334431270790
C	4.419363019858	-3.429284363766	4.837874680687
C	3.537188922349	-3.564111976424	3.760321340969
C	2.932708209282	-2.444492569843	3.190048429549
H	2.250162051155	-2.575529305543	2.352701331870
H	3.317029267806	-4.551312929174	3.359176919926
H	4.889162716830	-4.303056437744	5.280589041439
H	5.367960591745	-2.021579041585	6.171700094002
H	4.300684502276	-0.039087861479	5.165602675881
Li	-0.933526423192	-0.109193098026	0.771663189100
N	-0.955417305091	-0.047758887608	-1.151409170331
C	-1.726493192729	-0.061077149284	-2.082803629088
C	-2.584022183381	-0.059124011980	-3.116439028540
C	-3.190874903302	1.144148578470	-3.680802882019
C	-4.081378949384	1.033096383923	-4.770477932948
C	-4.679497458861	2.158961447507	-5.335133298355
C	-4.410568571702	3.436361675600	-4.832765661875
C	-3.530041750799	3.564499935926	-3.752722412060
C	-2.930152677545	2.441233570549	-3.185563367993
H	-2.249005819321	2.567326555138	-2.346242690520
H	-3.307761194289	4.549142120582	-3.347382341223
H	-4.876890266823	4.313703654884	-5.273063763955
H	-5.360790690913	2.036532363815	-6.174035938896
H	-4.302212025725	0.047007017241	-5.174240811488
H	-2.834081878169	-1.023201053434	-3.552047010628

3.2.4.11 PhCHCNLi(THF)₃ at B3LYP/6-31G(d)

O	0.463044	-0.685609	1.669716
Li	1.309977	0.039781	0.014619
N	0.185332	0.011608	-1.590654
C	-0.912906	-0.432944	-1.734490
C	-2.177234	-0.935982	-1.855295
C	-3.337574	-0.320106	-1.253185
C	-3.283050	0.901848	-0.533046
C	-4.419535	1.456568	0.049006
C	-5.664515	0.828259	-0.057598
C	-5.742646	-0.372022	-0.771583
C	-4.611518	-0.933314	-1.354899
H	-4.698096	-1.868695	-1.904821
H	-6.700376	-0.878790	-0.876346
H	-6.549983	1.265468	0.395676
H	-4.333550	2.400151	0.585760
H	-2.331220	1.423959	-0.455874
H	-2.307743	-1.837133	-2.447267
O	1.856495	1.929961	0.367067

C	3.235709	2.280673	0.642172
C	3.518904	3.576490	-0.136471
C	2.432187	3.566593	-1.224472
C	1.255372	2.936065	-0.487784
H	0.731693	3.670867	0.139548
H	0.542385	2.419766	-1.132916
H	2.729219	2.931311	-2.066803
H	2.202022	4.563811	-1.611188
H	3.396787	4.450397	0.513649
H	4.535191	3.600318	-0.540822
H	3.360850	2.400090	1.724381
H	3.858029	1.445105	0.306117
O	2.982582	-1.018148	-0.297878
C	3.426599	-2.039865	0.626618
C	3.536463	-3.353024	-0.182167
C	2.895394	-3.000713	-1.539671
C	3.165563	-1.503548	-1.646403
H	4.196742	-1.298967	-1.970602
H	2.460599	-0.960623	-2.277838
H	1.814380	-3.175136	-1.520290
H	3.320722	-3.569687	-2.371745
H	4.586901	-3.633482	-0.314688
H	3.033243	-4.186568	0.316057
H	4.391226	-1.740091	1.054401
H	2.685023	-2.081917	1.428427
C	0.109118	0.198679	2.756964
C	-1.404714	0.066915	2.894851
C	-1.616942	-1.428416	2.607592
C	-0.552025	-1.728543	1.542081
H	-0.066221	-2.699799	1.689886
H	-0.957947	-1.675227	0.528341
H	-2.623844	-1.647180	2.243255
H	-1.441363	-2.021146	3.513156
H	-1.765381	0.370131	3.882644
H	-1.914278	0.670589	2.136388
H	0.626162	-0.127835	3.671523
H	0.458706	1.198398	2.488144

3.2.4.12 PhCHCNLi(THF)₃ at B3LYP/6-31+G(d)

O	1.595532511517	-0.442958952820	1.286843172017
Li	1.216678974517	0.089351738604	-0.608530396854
N	-0.634246083666	-0.233746679514	-1.071733366011
C	-1.682485532733	-0.698656078769	-0.746304014669
C	-2.874973915387	-1.226389724545	-0.332688026091
C	-3.695157091388	-0.629986118229	0.697882438738
C	-3.367711016976	0.592008876763	1.343470437552
C	-4.176823103242	1.129997088778	2.342715466698
C	-5.351186276179	0.483269993182	2.748334904945
C	-5.697277584097	-0.720099385860	2.118945385037
C	-4.893258987266	-1.263265143787	1.119992470592
H	-5.184430150754	-2.199739366710	0.646896253819
H	-6.607414313474	-1.241858126016	2.410325599500
H	-5.980775960388	0.906645726110	3.526679811770
H	-3.890018575047	2.072199683345	2.808022021803
H	-2.468161037134	1.124260200978	1.039527540976
H	-3.210749757686	-2.143278769455	-0.809404185967
O	1.646260948057	2.023043396797	-0.835463809983
C	2.876803505250	2.504457423296	-1.431401643799
C	2.522652224030	3.813890154529	-2.152066970615
C	1.016124140384	3.655782146546	-2.421495075814
C	0.548112441963	2.912300253421	-1.173290035741
H	0.382724302125	3.600820771259	-0.332657081044
H	-0.336099625102	2.288173852843	-1.317935161810
H	0.841755086659	3.043119938556	-3.314154012750
H	0.501436767857	4.612322179835	-2.557078727167
H	2.703222207938	4.675356571589	-1.497738316163
H	3.112968884988	3.955408990118	-3.063029365510

H	3.619070014403	2.638986929505	-0.636290889848
H	3.235357719867	1.732009058864	-2.121272302326
O	2.429058608307	-0.958231968288	-1.805274463615
C	3.509084199140	-1.807561059777	-1.342883527374
C	3.428259164120	-3.109016931858	-2.166877901492
C	2.017057537754	-3.054393803091	-2.782203804097
C	1.813753796029	-1.554450808586	-2.971931393040
H	2.325502010016	-1.188351140240	-3.874692530302
H	0.770868421539	-1.232231220737	-2.981853135506
H	1.267884865106	-3.445678976572	-2.084398358770
H	1.938959500782	-3.613940060042	-3.719916852438
H	4.187506883856	-3.110330571251	-2.957710302622
H	3.590854494807	-3.997655218569	-1.549085157790
H	4.459610219244	-1.279278386909	-1.485731126377
H	3.356864931919	-1.967622878319	-0.271019334462
C	1.831156098897	0.543192175437	2.317428886858
C	0.711696654347	0.332482192202	3.334310649617
C	0.546265726375	-1.196609707783	3.306069512318
C	0.801336201432	-1.540989577398	1.831774879144
H	1.369944391683	-2.468856008792	1.702072261861
H	-0.122038277071	-1.598741440872	1.249739489379
H	-0.445013548883	-1.523035579832	3.633123665144
H	1.293667315533	-1.672362973877	3.953031290878
H	0.967151467018	0.719222296717	4.326389357695
H	-0.208637243476	0.822589029853	2.997313795587
H	2.820592878498	0.364523709894	2.764540657139
H	1.829696149529	1.524901727165	1.836494827973

3.2.4.13 [PhCHCNLi(THF)₂]₂ at B3LYP/6-31G(d)

C	-3.595749993195	-0.012529828292	-3.037267139867
C	-3.627515330942	-0.007876686497	-1.588709804529
C	-2.508004259704	-0.004538483523	-0.815706982848
N	-1.505859798332	-0.001687039221	-0.162796900901
Li	-0.000928265417	1.373948506284	-0.004701432150
N	1.505928085193	0.001675122093	0.162757921066
C	2.508080868156	0.004285911242	0.815656421041
C	3.627569937272	0.007369670469	1.588692353454
H	4.589027969027	0.006153922194	1.084216403520
C	3.595743717389	0.012220722209	3.037247672285
C	2.391203404281	0.014141287611	3.786428733988
C	2.399822364009	0.018827425061	5.179895735569
C	3.603210283361	0.021816311220	5.892193090166
C	4.801520343291	0.019985954572	5.171603868439
C	4.800786311731	0.015309882018	3.780179867524
H	5.746656265800	0.013970050296	3.242286266418
H	5.752023382091	0.022234792908	5.701370462049
H	3.606746285903	0.025469027093	6.978512314377
H	1.452517909799	0.020163749190	5.717232512591
H	1.441995565595	0.011889090415	3.254251581073
Li	0.000978101862	-1.374014863435	0.004723348800
O	-0.041166242537	-2.613872889206	1.542665939072
C	-0.888817208139	-2.511160743206	2.710630896046
H	-1.803909576593	-3.086962707082	2.522650440393
H	-1.161727968757	-1.460402058130	2.847572088421
C	-0.075081311897	-3.091364060451	3.871649854410
H	-0.711048883522	-3.543479982934	4.638746535400
H	0.533706009971	-2.311548050920	4.341068617677
C	0.835703177646	-4.104456028548	3.159853548962
C	1.153452063545	-3.376224275658	1.854877197620
H	1.995165953192	-2.683320673158	1.969734532862
H	1.350701028750	-4.042521272817	1.010487340608
H	1.737396341810	-4.343777079858	3.730672895167
H	0.295876093003	-5.037978126908	2.959696374386
O	0.045198499620	-2.624253010188	-1.524698607747
C	0.893427727417	-2.528540032827	-2.692830830457
H	1.166136273522	-1.478571752033	-2.836030764023
C	0.080414666041	-3.116145395853	-3.850590039948
C	-0.829744464287	-4.125694803556	-3.132992713635

C	-1.148432236640	-3.390003239822	-1.832413763372
H	-1.990984126367	-2.698833866349	-1.951437975338
H	-1.344934142973	-4.051509754264	-0.984085658242
H	-1.731109539486	-4.369123052411	-3.702589917415
H	-0.289218369253	-5.057582412079	-2.927189679034
H	0.716888186495	-3.572315614059	-4.614862980101
H	-0.528851471006	-2.339569706877	-4.324739666066
H	1.808581716873	-3.102959702039	-2.500906427916
O	0.040978235417	2.613836724475	-1.542686345399
C	-1.153774478840	3.375946152422	-1.855025622590
H	-1.995314357459	2.682832128214	-1.969824908835
C	-0.836168267792	4.104165276727	-3.160062304179
H	-1.737893878696	4.342877488689	-3.731083914398
C	0.075355988102	3.091530312721	-3.871555360215
C	0.889218330263	2.512062972020	-2.710288871744
H	1.163242298924	1.461585517140	-2.847125135780
H	1.803662655905	3.088796745409	-2.521963296561
H	-0.532859579283	2.311253075059	-4.340950900520
H	0.711175470994	3.543925565283	-4.638610958432
H	-0.296927284651	5.038035910206	-2.959952801972
H	-1.351221143753	4.042308457923	-1.010728024790
O	-0.044922924550	2.624215593132	1.524766935934
C	1.148781480982	3.389817056677	1.832612580775
C	0.830149468019	4.125524299851	3.133214257563
H	0.290131811549	5.057705681062	2.927408187723
H	1.731516182875	4.368449530957	3.703022655242
C	-0.080673958393	3.116374580829	3.850525448001
C	-0.893743959900	2.529395087467	2.692515761621
H	-1.808305823473	3.104647451247	2.500213866466
H	-1.167467249523	1.479685954792	2.835653508385
H	0.528081191963	2.339397515768	4.324676831843
H	-0.717048802500	3.572788151240	4.614735349633
H	1.345462725259	4.051361305486	0.984351264622
H	1.991198854006	2.698492241358	1.951639874847
H	-4.588952854614	-0.006984105339	-1.084192661699
C	-2.391240063967	-0.013998176525	-3.786496054253
C	-2.399913262861	-0.018514470868	-5.179963416525
C	-3.603329007432	-0.021766401431	-5.892211105229
C	-4.801611081883	-0.020372762720	-5.171573473765
C	-4.800822544558	-0.015872020575	-3.780149076689
H	-5.746670486478	-0.014872235297	-3.242216222846
H	-5.752134134138	-0.022828931365	-5.701303105708
H	-3.606909019751	-0.025285934218	-6.978530619945
H	-1.452630123022	-0.019513823898	-5.717338213555
H	-1.442011625414	-0.011504320828	-3.254356702225

3.2.4.14 [PhCHCNLi(THF)₂]₂ at B3LYP/6-31++G(d)

C	0.165958270734	-0.028326979152	-4.875447875276
C	-0.936837959537	-0.021085607258	-3.934806624342
C	-0.773466803920	-0.013566394353	-2.582828759372
N	-0.605045018376	-0.007030480025	-1.398987585413
Li	0.002251031871	1.350052575988	-0.007762834658
N	0.605045033795	0.007042666839	1.398986683611
C	0.773468125120	0.013547796073	2.582827821952
C	0.936840789296	0.021032158136	3.934805717364
H	1.953842414030	0.021507564122	4.317194041229
C	-0.165954329451	0.028282548362	4.875448216267
C	-1.527671640032	0.028317947743	4.476897918896
C	-2.561289326703	0.035418375038	5.412704652401
C	-2.290257171378	0.042806294965	6.786113743044
C	-0.951981484643	0.042905365644	7.200458808262
C	0.084754475455	0.035832457883	6.270577316462
H	1.116613838558	0.036062343881	6.617187947175
H	-0.713192940028	0.048568023062	8.262105361070
H	-3.098078008978	0.048330929333	7.513128102251
H	-3.593520885435	0.035189537565	5.065959863467
H	-1.767235623175	0.022664907877	3.415095237816
Li	-0.002251585001	-1.350043635546	0.007761856693

O	-1.401534022145	-2.555855713814	0.685757843165
C	-2.817413603206	-2.443565688816	0.414729012924
H	-3.082788537910	-3.160006747003	-0.374493861402
H	-3.007618348800	-1.431653161160	0.046568812728
C	-3.511030724841	-2.776660049137	1.735317561085
H	-4.527664041449	-3.154563484643	1.589689249673
H	-3.562058333062	-1.889605947642	2.377243697133
C	-2.557160648243	-3.818357231697	2.342514039252
C	-1.182454920886	-3.290212199668	1.921877933831
H	-0.764276079292	-2.597781716709	2.660256191133
H	-0.453090814239	-4.080503344854	1.719312558412
H	-2.64885146480	-3.902782866139	3.428967798155
H	-2.743782506762	-4.806504451451	1.905168592865
O	1.392944473296	-2.568269255757	-0.656319163133
C	2.809211002375	-2.457635459752	-0.386635216753
H	3.002840144808	-1.442209348704	-0.030116468695
C	3.501622838189	-2.808182876988	-1.703334002999
C	2.544220310476	-3.853558648588	-2.298530779543
C	1.171317886309	-3.316038975656	-1.883914762173
H	0.755378307877	-2.630743113640	-2.630172011178
H	0.439347210828	-4.101520975032	-1.672250588631
H	2.635548839684	-3.950717126128	-3.383950800244
H	2.727566034388	-4.837256421961	-1.849915325335
H	4.516988438372	-3.187809630455	-1.553407222858
H	3.555592061237	-1.928720131035	-2.355384748352
H	3.072227089271	-3.165863619520	0.410747660233
O	1.401513215473	2.555860116149	-0.685809319138
C	1.182390772804	3.290212115477	-1.921924283155
H	0.764201632075	2.597773337869	-2.660288746874
C	2.557076176252	3.818381561211	-2.342600302950
H	2.648745013591	3.902787474405	-3.429057724020
C	3.510988243695	2.776721605557	-1.735406075217
C	2.817400529159	2.443609853796	-0.414805676564
H	3.007641634050	1.431701845859	-0.046650760967
H	3.082767670485	3.160058153608	0.374413114273
H	3.562037078827	1.889663824104	-2.377325188470
H	4.527610508217	3.154661157203	-1.589794573353
H	2.743681803021	4.806542514035	-1.905279512777
H	0.453021008932	4.080493177367	-1.719339403361
O	-1.392927344545	2.568269426947	0.656371474700
C	-1.171260971945	3.316029436355	1.883965751541
C	-2.544144610050	3.853570184245	2.298621940293
H	-2.727472190833	4.837286254930	1.850039804274
H	-2.635451086101	3.950698673209	3.384046457675
C	-3.501587960111	2.808237998858	1.703414318254
C	-2.809200268655	2.457682133888	0.386704336872
H	-3.072202922322	3.165924999694	-0.410669840631
H	-3.002866657874	1.442264219735	0.030181388274
H	-3.555582987433	1.928766446569	2.355450815284
H	-4.516941054739	3.187903967113	1.553502324073
H	-0.439285815425	4.101503634548	1.672287261409
H	-0.755311093210	2.630722024768	2.630206306418
H	-1.953839211205	-0.021603396473	-4.317195859002
C	1.527675211848	-0.028297032487	-4.476896342119
C	2.561294034781	-0.035393137927	-5.412701815047
C	2.290263443014	-0.042839210778	-6.786110903948
C	0.951988139432	-0.043000501901	-7.200457218210
C	-0.084748952218	-0.035932876135	-6.270576942277
H	-1.116607974672	-0.036212462078	-6.617188551662
H	0.713200795077	-0.048708403895	-8.262103799397
H	3.098085176961	-0.048360348060	-7.513124297406
H	3.593525276452	-0.035114161202	-5.065956098120
H	1.767238018636	-0.022592745094	-3.415093692512

3.2.4.15 PhCHCNLi⁺/Li⁺Li(HMPA)₄ at B3LYP/6-31G(d)

Li	-0.889998067655	0.038611210547	-0.026477012652
H	6.908054374397	1.575840150864	-1.428863772318

C	6.861753990621	0.599861737362	-0.945568565561
C	6.766498948664	-1.857109431337	0.344489340345
C	6.087535466717	0.452428996793	0.199875725109
C	7.593892676315	-0.471251578133	-1.475250491896
C	7.539160149343	-1.697936782545	-0.799933279421
C	5.987760590137	-0.793188707456	0.886471522311
H	5.556151084231	1.310286898058	0.604949434877
H	8.202066841990	-0.348893358688	-2.367616265851
H	8.113239213800	-2.545925066412	-1.172335084853
H	6.742384018197	-2.824424147687	0.844884935238
C	5.155894885674	-0.999001436286	2.031034800715
H	5.206783366377	-1.954560746248	2.547200259688
C	4.300693763482	-0.043150291076	2.559148027473
N	3.544333330342	0.753575827799	3.003736821652
O	0.063810300153	1.742179884423	-0.105482201173
O	-2.719346184285	0.335028123519	-0.828643462376
O	-1.249632181480	-0.588785492605	1.793210415792
O	-0.085479441012	-1.371304117082	-1.169642178359
P	0.287207438643	3.206916996799	-0.366194008710
P	-4.200987832431	0.084254018645	-0.797145729698
P	-0.744484149227	-1.193630827347	3.084259219332
P	0.915954049205	-1.770522676007	-2.227452546703
N	-0.366377859949	3.671102590944	-1.841635129749
N	1.919640385900	3.555611436580	-0.346896836221
N	-0.475593425852	4.271932608032	0.703541830427
N	0.170133776871	-0.131418287379	3.968065360786
N	-2.097404456835	-1.685797034907	3.973881070872
N	0.523055290854	-2.544745370993	2.972618621587
N	-4.503232629208	-1.550024724983	-0.559868884185
N	-5.048877526370	0.540683130671	-2.194316268519
N	-4.979388926046	0.987339688978	0.378849259285
N	0.469913109614	-1.045690815015	-3.694740857591
N	0.959734660130	-3.454550362151	-2.301276048475
N	2.524071736244	-1.348650235977	-2.101855817994
C	-5.120416247389	-0.392294929966	-3.318791074464
H	-4.207148340180	-0.383092351817	-3.934965331863
H	-5.963668421600	-0.112633213559	-3.961963169437
H	-5.287954356218	-1.409382334122	-2.961790456850
C	-6.383256275661	1.381631313261	0.362292197018
H	-6.818360738515	1.193869021704	-0.619643354469
H	-6.475541510705	2.453043363944	0.589581183568
H	-6.962547355607	0.832058335884	1.120634086651
C	-4.330894721045	1.151976562836	1.681708883353
H	-4.352124143389	2.210412729360	1.973332880224
H	-3.292907044518	0.817181419697	1.644692360721
H	-4.857698165480	0.575742004799	2.456388186221
C	-4.879718549215	1.929611119544	-2.635230122593
H	-3.962243542645	2.063339238644	-3.227954669255
H	-4.830337970046	2.594918595648	-1.771054232406
H	-5.738480278602	2.222719843456	-3.251620370143
C	-0.804590447276	5.013612175207	-2.194805919513
H	-1.822103312195	4.981937296302	-2.611408899618
H	-0.149711093680	5.466714755046	-2.955910820420
H	-0.810016001584	5.651800426282	-1.310882493967
C	-0.290483585117	2.749460351982	-2.970526878116
H	-1.269299658020	2.687578051533	-3.466292756562
H	-0.020915547429	1.751615784156	-2.625374593234
H	0.448482594518	3.085253901444	-3.714615778176
C	-1.902133711058	4.064557774003	0.955671602127
H	-2.374216704461	3.593558708941	0.090699946476
H	-2.389770096739	5.031185302901	1.140588997904
H	-2.070359514913	3.418966464532	1.829873322242
C	0.234847345235	4.839688980589	1.847593513086
H	-0.228646560433	5.797000553055	2.118902012627
H	1.278919504598	5.026389387363	1.595698710153
H	0.202644108033	4.183648355849	2.730274898579
C	2.827712160048	2.865074100573	0.579042697163
H	3.712777232142	2.519016192724	0.033490194290
H	2.350366093656	1.995921649847	1.028676119463
H	3.161245851231	3.528762528076	1.388751521222
C	2.488842503741	4.733997870610	-0.985232312314

H	1.824634128970	5.114418987730	-1.763523430517
H	3.443904752184	4.465751760292	-1.454469441488
H	2.686366633046	5.546778912987	-0.267819534823
C	-0.043422125027	-4.266564544907	-1.625317739147
H	-0.545361862790	-3.668193030557	-0.865476161284
H	0.441399084416	-5.123980102274	-1.137506769208
H	-0.795493691432	-4.660942049845	-2.327990711576
C	-3.318907158502	-2.128616674987	3.316712243894
H	-3.311957556580	-1.810817375976	2.273534820978
H	-4.192725867224	-1.681772210004	3.812827008524
H	-3.440496494080	-3.224608711813	3.356765966178
C	-2.011554215555	-2.027762971556	5.385556898043
H	-1.925079764337	-3.113818108665	5.555295515512
H	-2.915289236742	-1.679051447754	5.903696538801
H	-1.152991275947	-1.538028085794	5.846637930492
C	-0.323312057001	-3.872927179921	2.794512561406
H	-1.221911368705	-3.989739257749	3.403382671137
H	0.407123419274	-4.623867648907	3.119700874957
H	-0.579346479297	-4.086829624287	1.744055557148
C	1.543453350702	-2.379299987556	2.282825948971
H	1.945902882232	-1.378087807449	2.447189565120
H	1.439172367192	-2.542994632911	1.202022699759
H	2.260896974923	-3.105311031453	2.682590472875
C	1.125271998194	-0.496369146669	5.018451203828
H	1.196501050131	-1.581435305857	5.102853939821
H	0.805644684207	-0.083981221087	5.987871269851
H	2.111291420928	-0.092186652079	4.763852814092
C	0.093594780160	1.309282415881	3.720237204622
H	-0.493919350449	1.500260420135	2.821764225328
H	1.109962529421	1.687519672378	3.564116066178
H	-0.364967765297	1.830042703852	4.575123624667
C	-3.515329999808	-2.565419105060	-0.918703165283
H	-3.813549171581	-3.117922809527	-1.824381054651
H	-3.418484821757	-3.288786278478	-0.098341380760
H	-2.543197592270	-2.100565505126	-1.083799396185
C	-5.826649319306	-2.069312128855	-0.244855399380
H	-6.483349826784	-1.272797013463	0.108519989585
H	-5.750562097912	-2.823078765263	0.550046294687
H	-6.303892776628	-2.546742210882	-1.115561006747
C	-0.953610920676	-0.832280435719	-3.948619738801
H	-1.070450396118	0.009244436120	-4.643874323515
H	-1.465351301476	-0.588320867713	-3.017096794040
H	-1.432169364173	-1.714279795647	-4.407946409462
C	1.250800596889	-1.234448105103	-4.914971153195
H	1.143819954578	-0.348847222683	-5.554958903775
H	0.917024026128	-2.109535539632	-5.496053891527
H	2.307465192404	-1.355729080808	-4.672614827909
C	1.772680417242	-4.184183083933	-3.266546936518
H	2.561553798134	-3.544558598191	-3.664833904936
H	1.170260350542	-4.568387491125	-4.104763495170
H	2.252426257438	-5.042628430456	-2.776706623543
C	3.409750562580	-2.077452950512	-1.170883694163
H	3.085860592157	-3.114916660615	-1.082979347743
H	3.425972412453	-1.619524404567	-0.174757994875
H	4.431582159372	-2.053394571984	-1.560856894645
C	2.895519413906	0.073756993950	-2.206831953090
H	2.356342389092	0.548012305738	-3.028285059132
H	3.971882554677	0.136836620599	-2.394397299428
H	2.675966322649	0.615095802919	-1.279351285068

3.2.4.16 PhCHCNLi⁻/⁺Li(HMPA)₄ at B3LYP/6-31⁺'G(d)

Li	-1.056035204526	0.006543909485	-0.046945615170
H	6.917308781292	2.291965829851	-1.106507281788
C	7.040827192983	1.246026594023	-0.825843087279
C	7.369410338059	-1.404371620240	-0.052679154603

C	6.303001887277	0.742828145642	0.242459339850
C	7.947770171291	0.441852550442	-1.532158423879
C	8.101354466787	-0.891487820060	-1.118141168210
C	6.428733263793	-0.612564934850	0.672826109896
H	5.630410392181	1.401390792401	0.787612249885
H	8.526884037817	0.842173466356	-2.360718859771
H	8.808452611662	-1.539493629256	-1.634800292550
H	7.513398174948	-2.442384737883	0.245568131556
C	5.669029953613	-1.174113271146	1.746975786877
H	5.879375783776	-2.193249204960	2.062620055025
C	4.678414255997	-0.488582649850	2.437204150417
N	3.809852174767	0.086304895636	3.002627353075
O	-0.484456736716	1.869025517371	0.123369570661
O	-2.846179367694	0.079863085111	-0.942445968841
O	-1.321639530965	-0.780662017531	1.711638824529
O	-0.011910853642	-1.096948292930	-1.249134382054
P	0.139211368911	3.193855436396	-0.227520346428
P	-4.343260500967	0.021306184292	-0.823475432638
P	-0.827325199227	-1.351428490166	3.021969751118
P	0.965153729580	-1.658432153162	-2.249722530323
N	-0.313581709566	3.687026749137	-1.768924069400
N	1.803033734343	3.098472110081	-0.095747516381
N	-0.364865790896	4.517351730635	0.705670649299
N	0.117713332492	-0.276183889690	3.862312896499
N	-2.188176424298	-1.777968772062	3.930198913946
N	0.142590765628	-2.725947110071	2.956656677643
N	-4.807077800719	-1.545926086878	-0.424914543785
N	-5.211928553061	0.443588140591	-2.217632114216
N	-4.943019128810	1.112487181498	0.296075524763
N	0.440051187920	-1.241180650034	-3.804949600053
N	1.100342113385	-3.323458983400	-2.000666058049
N	2.558190974556	-1.155297639266	-2.247474556436
C	-5.384003469303	-0.561633551532	-3.267596976007
H	-4.492494191035	-0.658759478606	-3.907232234273
H	-6.228195731343	-0.271539810591	-3.904605080954
H	-5.606489561597	-1.536446599694	-2.831582133157
C	-6.308761005493	1.623647570442	0.335837224162
H	-6.825285859363	1.404322550190	-0.599174850755
H	-6.294705299794	2.712846375361	0.481510659948
H	-6.878512274822	1.185542465571	1.170254767095
C	-4.187362204729	1.343741399019	1.529601053823
H	-4.114544942896	2.422987351017	1.717455969525
H	-3.179273059014	0.936340071429	1.449569604814
H	-4.689182724637	0.877789876126	2.390543208313
C	-4.963802844288	1.781227336613	-2.769272159547
H	-4.066145584837	1.801580494053	-3.405241106216
H	-4.828416375367	2.502705449781	-1.961682311783
H	-5.825947295699	2.089582846821	-3.373442828429
C	-0.234323269267	5.052403689166	-2.274792244700
H	-1.162375813274	5.306436581742	-2.806650711044
H	0.598755076373	5.176489549851	-2.984305143674
H	-0.103348485746	5.754385624481	-1.450590943939
C	-0.453646636163	2.674197566601	-2.812910203841
H	-1.333726178133	2.904272056267	-3.428763413873
H	-0.597304302378	1.691485393490	-2.364585833920
H	0.427839624151	2.645557486471	-3.471463271335
C	-1.800286061839	4.806681744519	0.749978112114
H	-2.259409347058	4.581115426532	-0.214378464632
H	-1.951132727732	5.871459161266	0.969460232935
H	-2.313759632071	4.217572573275	1.525217047104
C	0.297505945874	4.782011848615	1.984032490347
H	0.140730860397	5.832668411355	2.257392489031
H	1.370849150743	4.607753465630	1.904488290066
H	-0.098073119626	4.154748454046	2.797758713730
C	2.439358038700	2.170681778849	0.852500531531
H	3.308804928159	1.705616171324	0.378717099073
H	1.744468286897	1.383843171981	1.138838932780
H	2.787435487967	2.681924271626	1.760374862020
C	2.688370321915	4.150943062342	-0.584179172476
H	2.206112170324	4.736768448994	-1.368430290443
H	3.591994495065	3.695279376985	-1.006607918617

H	3.002119114886	4.837473313402	0.217771138808
C	-0.009330755304	-4.052981799366	-1.396485284208
H	-0.601057759955	-3.375342692862	-0.780766082071
H	0.385686582649	-4.854792800559	-0.758516681472
H	-0.662671403238	-4.517325984476	-2.154029655318
C	-3.457927151739	-2.116407349992	3.302810055046
H	-3.469122357685	-1.757743416002	2.273070087109
H	-4.281978798727	-1.636403707317	3.850010309265
H	-3.645776001954	-3.204025236634	3.307623515561
C	-2.087919212201	-2.152502080333	5.333693592666
H	-2.108560268562	-3.245060606174	5.479942114222
H	-2.931031104660	-1.723772658415	5.892333393656
H	-1.165614108149	-1.767279802810	5.770311433603
C	-0.474597148405	-4.038194359335	2.786553242040
H	-1.410805416546	-4.101039718858	3.344197042862
H	0.205705171340	-4.805987423155	3.175132458217
H	-0.678922103666	-4.272484207448	1.729815882913
C	1.457150007154	-2.622452333420	2.300499655995
H	1.917548836847	-1.650527108853	2.488712308950
H	1.375738782841	-2.770971765087	1.214766874815
H	2.119057395343	-3.393837839025	2.711957395793
C	1.072093746441	-0.617469051698	4.923234659287
H	1.159575436558	-1.700435992528	5.017225613293
H	0.737438237035	-0.203095361956	5.886821357546
H	2.057158910887	-0.209236960100	4.669991682779
C	-0.099224200481	1.159880487462	3.701090620443
H	-0.648108978268	1.357319712381	2.779152307034
H	0.875036694659	1.657261451303	3.637821795150
H	-0.651245984926	1.580113142849	4.557261343838
C	-3.936453637452	-2.685749127528	-0.703871730201
H	-4.286158358242	-3.264416191452	-1.574180056902
H	-3.920071544430	-3.356275141601	0.165185229980
H	-2.921806948129	-2.333299138541	-0.889234388122
C	-6.175625305129	-1.893323555015	-0.067372496962
H	-6.737020345409	-1.005095386558	0.226352912869
H	-6.172104912467	-2.587749525822	0.783024446961
H	-6.712506586892	-2.379364963674	-0.897709428214
C	-0.981043703569	-0.984365957029	-4.030173538381
H	-1.091008244140	-0.215502993110	-4.807282391456
H	-1.449075661997	-0.628729208169	-3.111196286818
H	-1.512501709319	-1.887248041083	-4.376165208135
C	1.144582918642	-1.704568051426	-4.997093646494
H	1.037123083456	-0.960031021533	-5.797026252771
H	0.745885746194	-2.660642792312	-5.373154358067
H	2.208676185871	-1.826849001268	-4.788083132385
C	2.008829154260	-4.167397413464	-2.772070051665
H	2.842602539015	-3.579030874544	-3.157028371036
H	1.500040515882	-4.659319531060	-3.616202677642
H	2.418386663959	-4.952373265891	-2.122756876995
C	3.428015116607	-1.557552234239	-1.121019122421
H	3.185246960873	-2.569420258367	-0.797986433955
H	3.324767575334	-0.882577652768	-0.264280339552
H	4.471330812801	-1.529060863543	-1.448049422794
C	2.883441809662	0.195537828065	-2.729663280391
H	2.291610475333	0.437861736361	-3.613188414031
H	3.946890593648	0.224424204973	-2.989772645141
H	2.696565445557	0.957252733056	-1.960334216595

3.2.4.17 PhCHCNLi(THF)₃(HMPA) at B3LYP/6-31G(d)

C	-3.069009274868	-1.573810769363	-1.046459722972
C	-1.763840736403	-1.319491470065	-1.372675547685
N	-0.629553827028	-1.072834922619	-1.634396276845
H	-3.411979853396	-2.602771173373	-1.101612092846
C	-4.001657729091	-0.545504744610	-0.653509956243
C	-5.885644329245	1.442730783208	0.168166183641
C	-3.664461910388	0.833318471245	-0.606250947565
C	-5.328426899818	-0.878546380219	-0.278168950839

C	-6.242292305003	0.090638852405	0.121190402754
C	-4.584813499618	1.796954867865	-0.204830213317
H	-2.663707801216	1.137861318364	-0.906039836577
H	-5.631058461883	-1.923883334122	-0.304876902981
H	-7.249747011452	-0.213637434191	0.400072701892
H	-4.284663823824	2.844085720535	-0.191052817727
H	-6.602251798752	2.198102448115	0.479126816528
Li	1.131798111385	-0.280849280782	-1.242750155943
O	1.632716869161	0.198393516946	0.538086401268
P	1.103954841796	0.131638503909	1.952979606416
N	2.388137324863	-0.076251138240	3.014242746748
N	0.096073346072	-1.147055964164	2.352447476571
N	0.292104241732	1.556034116750	2.306531812664
C	3.664116440385	0.571035656073	2.718981870974
H	4.487165022660	-0.135233426807	2.892988277740
H	3.829902472557	1.451699739336	3.357873360691
H	3.688261006196	0.877688678167	1.672934596546
C	2.290223730908	-0.618559650591	4.363332976995
H	1.307504785641	-1.065405675112	4.516480602062
H	2.452466212491	0.159291377742	5.125818912253
H	3.054835990279	-1.393904772263	4.513362975197
C	-0.046114353608	1.949282522011	3.668651507640
H	0.601763913685	1.445880605284	4.388303610502
H	-1.092059605648	1.720668007972	3.924546864743
H	0.099544505954	3.031413531897	3.783058909256
C	-0.432972546048	2.286544685267	1.265583256552
H	-1.516891920839	2.107256759215	1.310615894479
H	-0.070671521153	1.981998234942	0.283475690518
H	-0.253863205820	3.363219596583	1.389260897001
C	0.566234036335	-2.501688203856	2.042740551014
H	0.129937430514	-3.209556974052	2.758503302306
H	1.654393708095	-2.553694020491	2.129437861103
H	0.272139217682	-2.803126954104	1.028123813973
C	-1.369216284698	-1.031049951083	2.291556415146
H	-1.803707893934	-1.685281673376	3.057987225927
H	-1.770349307608	-1.324147122518	1.313133722019
H	-1.682211707057	-0.009051188088	2.504106292903
O	2.546677120671	-1.464225069525	-2.039990699483
C	3.508089379981	-2.181579625027	-1.234218459587
C	3.734879745468	-3.530680834828	-1.932322578344
C	2.436305298734	-3.715845324018	-2.734498863877
C	2.123740548734	-2.281863968087	-3.155271386413
H	3.085510177019	-2.298664510782	-0.230226852674
H	4.420531479691	-1.580478345323	-1.156507905057
H	4.594361140814	-3.473469892656	-2.610607180903
H	3.923882497939	-4.339808022916	-1.220276465551
H	1.635450554160	-4.101164959394	-2.093164391170
H	2.548359349861	-4.391614021873	-3.587781562997
H	1.062208381973	-2.082356741442	-3.315822864309
H	2.694871308183	-1.991922979596	-4.048793724412
O	1.145985700824	1.416619432167	-2.310929353151
C	1.924501556602	2.599147619213	-2.066623720719
C	1.035842841253	3.800139343106	-2.483066653804
C	-0.255021320868	3.139843754611	-3.026433825466
C	0.204103022409	1.718611436552	-3.352684888155
H	2.846400497831	2.557949663552	-2.662695632248
H	2.191904113683	2.587587087615	-1.007459413293
H	0.828961880284	4.468280074576	-1.642034830900
H	1.532108130541	4.393588521072	-3.257704549105
H	-0.666432667214	3.661965715595	-3.895377998905
H	-1.030459578350	3.106337898283	-2.254080676401
H	0.708393465313	1.674261261700	-4.330821097949
H	-0.573275637636	0.954697167993	-3.306954961460

3.2.4.18 [PhCNCNLi]₂(THF)₃(HMPA) at B3LYP/6-31G(d)

C	-3.432307876250	-2.477996572440	-1.781668608165
C	-2.137610759103	-2.129885564387	-2.328646996273

C	-1.149070932775	-1.540965825518	-1.600854914691
N	-0.297661689596	-1.024768324122	-0.939639740324
Li	1.045608341401	-1.794738827286	0.387654111749
N	1.624137186673	-0.027125434816	1.206867816313
C	2.678919592713	0.365156366813	1.608230998651
C	3.894569863110	0.809113956285	2.032620158503
H	3.983364289184	1.124074375586	3.067976965000
C	5.064905238416	0.858430828663	1.182340174406
C	5.055428797231	0.444131934784	-0.174811221898
C	6.201772387543	0.506240511804	-0.964312676950
C	7.410422928047	0.978506752459	-0.443146110568
C	7.441111712768	1.389708096881	0.893202476257
C	6.300070314228	1.332928305499	1.687107737030
H	6.349983481967	1.659508349730	2.723944019953
H	8.368836418348	1.761242225093	1.324117074207
H	8.302812040321	1.025202128194	-1.060943973125
H	6.149755865338	0.181934573147	-2.002762280460
H	4.127627517143	0.067741697077	-0.601046709850
Li	0.129381668789	0.773734869145	0.011901641695
O	1.005171380878	2.082125414696	-1.252421410189
C	1.711155919437	1.650950125858	-2.441899520410
H	1.010767848975	1.712956561116	-3.283165630901
H	2.006830608940	0.605021215639	-2.314179442607
C	2.908070172366	2.600614170663	-2.603685596757
H	3.127131052841	2.813293252571	-3.654572927981
H	3.804289090262	2.167738039515	-2.147606656306
C	2.468400948659	3.843612962241	-1.812967612416
C	1.686815540994	3.214538207750	-0.662627492371
H	2.354426046083	2.862334226882	0.134123832298
H	0.922004723968	3.864892041813	-0.230216284328
H	3.311242281042	4.447862402996	-1.464930218663
H	1.812072872779	4.480744791091	-2.418406712718
O	0.268717460395	-3.066324876032	1.689929709585
C	-0.682902659989	-4.071876413365	1.251528302814
H	-1.068725204976	-3.753918523209	0.279347897987
C	-1.781410923476	-4.137975891446	2.331141186256
H	-2.779448233616	-4.178113653963	1.886775989732
C	-1.549122079699	-2.858658367230	3.157103888058
C	-0.038974000831	-2.672217185596	3.040483122835
H	0.309705638779	-1.644286536752	3.162533272493
H	0.500756219522	-3.322686520663	3.744829908422
H	-2.064942654010	-2.006704067359	2.700927572799
H	-1.886067688585	-2.950973897715	4.194319906190
H	-1.652473025421	-5.025894681327	2.960113180998
H	-0.157474864958	-5.025833164879	1.130219812259
O	2.559954845758	-2.815466530310	-0.363374511318
C	3.646142553145	-3.204468077749	0.515328806292
C	4.615694216771	-3.989076957807	-0.367750864459
H	4.306275213198	-5.038526650494	-0.444157294896
H	5.640491605074	-3.958872373868	0.013256135907
C	4.454201239049	-3.276665727359	-1.720142394087
C	2.954303670231	-2.965765998412	-1.745719133946
H	2.373481076781	-3.787129491751	-2.184012848203
H	2.706183833054	-2.042332033174	-2.277699003089
H	5.038619891768	-2.350257260644	-1.723920090026
H	4.766707217176	-3.88633777528	-2.573345906405
H	3.216262019527	-3.787678681080	1.334027336959
H	4.111248510860	-2.299253863942	0.922243715740
H	-1.929785991810	-2.357062564643	-3.370077491584
C	-3.802779622738	-2.211924189275	-0.438169478767
C	-5.057418461505	-2.564967910955	0.053930227703
C	-6.002167620965	-3.193091393836	-0.763665149432
C	-5.657425157567	-3.459855179538	-2.092513507823
C	-4.405849045416	-3.112420359707	-2.590928690076
H	-4.160523167634	-3.333127815153	-3.627932753248
H	-6.373938320499	-3.947530995924	-2.750599401022
H	-6.979256686616	-3.467797505419	-0.376114079346
H	-5.301116494074	-2.347956859699	1.093226120907
H	-3.088289872681	-1.716963101530	0.216066384195
O	-1.292335170697	1.718403990324	0.871162652816
P	-2.558230489550	2.456283400749	0.507992318959

N	-3.007798775268	2.613065588988	-1.099325056770
N	-2.389922110353	4.067473560631	0.997059035375
N	-3.870762025903	1.661758112573	1.190460834444
C	-2.244762155816	3.515625685362	-1.970817433659
H	-1.939246223465	4.405599113982	-1.420240519459
H	-2.881328414791	3.818856592596	-2.810694509743
H	-1.346617041750	3.024021974539	-2.368881991637
C	-3.485561772279	1.423435902503	-1.825796762948
H	-4.187984223876	1.742760163230	-2.605102905620
H	-3.997510524579	0.735718073564	-1.153647217355
H	-2.659899517858	0.877906972262	-2.299732254349
C	-5.260894499545	2.039688536301	0.958162297431
H	-5.864033196596	1.138052290106	0.787758433229
H	-5.341661164528	2.673665906736	0.074311423278
H	-5.686390971018	2.576861292024	1.819552878624
C	-3.678176375472	0.766096197556	2.327836500776
H	-2.625281674927	0.496151834174	2.407891898864
H	-4.269231699574	-0.147088435206	2.178947922304
H	-4.001961247147	1.233648813331	3.270644487122
C	-3.501501598842	5.008155876790	0.880848929719
H	-3.104942832960	6.026108586870	0.777614748882
H	-4.160147772857	4.991802944417	1.763942064671
H	-4.098198047553	4.784902752511	-0.005671027806
C	-1.482889995452	4.374586725480	2.104704070105
H	-1.068358157365	5.380835457809	1.962616979902
H	-0.665846949787	3.653637393035	2.123555083730
H	-1.996679756205	4.355025590851	3.079223022120

3.2.4.19 [PhCNCNLi]₂(THF)₃(HMPA) at B3LYP/6-31'+G(d)

C	-3.413200384406	-2.443241455071	-2.118177370684
C	-2.075678626795	-2.054668503312	-2.512329400763
C	-1.171021910950	-1.489855023135	-1.662050474989
N	-0.390095097375	-0.995260781402	-0.905683506975
Li	0.897542101982	-1.735700624105	0.488757692313
N	1.700866745851	0.006347278261	1.095002811895
C	2.728142757044	0.416615748402	1.543753318290
C	3.915406526661	0.883616808845	2.027862369372
H	3.935102854973	1.233967613893	3.056178391374
C	5.137092078003	0.919047337813	1.251874076996
C	5.221486539586	0.460619648436	-0.089151473859
C	6.417575796905	0.509789814776	-0.803898961079
C	7.586068262650	1.015490316755	-0.221569075436
C	7.524756090861	1.472502608878	1.101667411744
C	6.333254821288	1.426662986417	1.820767684780
H	6.312174995407	1.787303116815	2.847714825834
H	8.418153115946	1.869918566272	1.579527441190
H	8.516997133169	1.052196544027	-0.781233818327
H	6.438796761655	0.147306033955	-1.830562957360
H	4.329002825271	0.060261533210	-0.566611230486
Li	0.193157904731	0.815729275523	-0.088302919013
O	1.091953510811	2.021052489997	-1.419272831523
C	1.777676854839	1.543942064197	-2.603515357794
H	1.066483281399	1.588787398915	-3.436958628048
H	2.061578423008	0.498519482553	-2.444390577923
C	2.982989745466	2.473394226550	-2.809928318590
H	3.193431483696	2.647137796354	-3.869752355615
H	3.880486970300	2.047514380724	-2.348976270143
C	2.565377175233	3.748889441400	-2.058594792363
C	1.786821327313	3.171822048274	-0.879348450476
H	2.455557039615	2.844496968346	-0.072988869931
H	1.027723939762	3.841009213511	-0.465933231673
H	3.419148051573	4.353861221554	-1.739605278939
H	1.912459018579	4.372474232112	-2.681709033901
O	0.019946970567	-2.705048273700	1.955611603109
C	-0.826152309899	-3.862937628007	1.734938457576
H	-1.621746618676	-3.574731965938	1.038931714367
C	-1.373127666161	-4.249230130008	3.113678690883

H	-2.369972182470	-4.695315286020	3.051088661195
C	-1.351958664401	-2.908924601483	3.867103849657
C	-0.074778741961	-2.264953591247	3.328788987138
H	-0.079160578653	-1.172080483761	3.327983914003
H	0.812939707287	-2.612336886772	3.874950716151
H	-2.226963313643	-2.304662482080	3.599370743015
H	-1.336279484073	-3.024836663369	4.955152571926
H	-0.709279953754	-4.970479445588	3.604972994169
H	-0.218268189332	-4.646118826922	1.271308840178
O	2.227581608893	-3.004258319906	-0.231180286851
C	3.477458979713	-3.243293139997	0.472625092830
C	4.402015841937	-3.935358685601	-0.535547561061
H	4.304725972854	-5.025419554753	-0.466298285558
H	5.451863406109	-3.676021307659	-0.372904816937
C	3.857247824013	-3.437698554992	-1.884636840279
C	2.353839933437	-3.391665091511	-1.618284886846
H	1.888340940260	-4.377348897056	-1.756187088620
H	1.806771791371	-2.659544018474	-2.217633275438
H	4.237928846804	-2.432895809456	-2.102285722145
H	4.115014246199	-4.092447083083	-2.722762691222
H	3.259524148641	-3.855341940657	1.353817714501
H	3.871389562892	-2.275503237678	0.799211462449
H	-1.759379084311	-2.226538706259	-3.537775290936
C	-3.914644469840	-2.271576191237	-0.801377522340
C	-5.209746989527	-2.657221321378	-0.458615050374
C	-6.068066732520	-3.228352586508	-1.406040516642
C	-5.592424166950	-3.405974298561	-2.712020771630
C	-4.299246822921	-3.024474237932	-3.060707284719
H	-3.952931533248	-3.174206458771	-4.081888860725
H	-6.237629455634	-3.848939966688	-3.468223490755
H	-7.076816413485	-3.528820799506	-1.134971860744
H	-5.555030824534	-2.512005276157	0.564101802429
H	-3.269706771037	-1.826237514088	-0.046822875294
O	-1.126898696154	1.867698612761	0.776075967237
P	-2.481808810731	2.486851255653	0.529862968059
N	-3.000079523478	2.746455865207	-1.044868106545
N	-2.472140825513	4.048448008489	1.175828649625
N	-3.671194533884	1.479151379970	1.156708004256
C	-2.359911032316	3.803172917078	-1.838393764493
H	-2.111815382593	4.655656761409	-1.205685854561
H	-3.056220487931	4.132130587496	-2.619202802697
H	-1.440740383684	3.441630771299	-2.321675210512
C	-3.362265530952	1.582519316621	-1.872900041091
H	-4.075117935918	1.904241824029	-2.641188366541
H	-3.827436807514	0.804508919278	-1.268734951351
H	-2.483597873652	1.148715646212	-2.367460017668
C	-5.101327172132	1.746653976058	1.032403296049
H	-5.631959344314	0.809212110111	0.821048288422
H	-5.291308785899	2.434793724867	0.207520489114
H	-5.519519874582	2.175708030743	1.956008806961
C	-3.334414461024	0.509505710697	2.196249702718
H	-2.265386332233	0.297380947923	2.169094747717
H	-3.884304035382	-0.422829847991	2.013040894161
H	-3.605664571640	0.874595136782	3.199619448054
C	-3.677889235015	4.873425095948	1.178811634073
H	-3.392882475086	5.932303642005	1.132979085806
H	-4.282986454410	4.726661109280	2.087439267187
H	-4.294469255420	4.649401491637	0.306396201401
C	-1.549991584291	4.358681892667	2.270212580225
H	-1.247152336654	5.411171204495	2.198321800353
H	-0.662960610767	3.729437234074	2.196837100265
H	-2.014223854889	4.206394579897	3.257810948531

3.2.4.20 PhCHCNLi(THF) at B3LYP/6-31G(d)

Li	-1.372152159092	0.267034441629	-1.662782337031
N	-1.352732869027	0.183091205586	0.135932052614
C	-1.223128465794	0.116920981969	1.322452613838

C	-1.069687878293	0.041327445592	2.666452902920
C	0.201548059924	-0.168833340300	3.328516207642
C	1.422394383541	-0.322390669236	2.628256251955
C	2.623558005870	-0.523160047964	3.300268905222
C	2.665939604836	-0.580239322800	4.697221071090
C	1.471252259756	-0.430706318332	5.407161401988
C	0.266416263985	-0.229629832090	4.740528880297
H	-0.652561109894	-0.115405650513	5.312328442748
H	1.477081323625	-0.471095609332	6.494803616347
H	3.606397408219	-0.737400341524	5.218600641096
H	3.541156370109	-0.636989659150	2.725573460327
H	1.414915644985	-0.281698224096	1.540829444512
H	-1.964302268105	0.146774483957	3.273604391904
O	-1.155935900291	0.308064524259	-3.524711756943
C	-1.005810784694	-0.878073091058	-4.356547101566
C	-0.246487479184	-0.403644156010	-5.593277433773
C	-0.755719774364	1.038066548615	-5.750331928505
H	-0.084736089657	1.670233672609	-6.338096221775
H	-1.740548277507	1.047311602957	-6.230531885673
C	-0.863324264391	1.507809515425	-4.299450874721
H	0.079676123138	1.928644291335	-3.931841507555
H	-1.667770472100	2.228034634131	-4.126656064549
H	0.833159532825	-0.413690453739	-5.406816414860
H	-0.448680971370	-1.029371607345	-6.466743201205
H	-2.005558720139	-1.252034850104	-4.607015767127
H	-0.476854318482	-1.635256530115	-3.771027614174

3.2.4.21 PhCHCN⁻/Li⁺(THF)₄ at B3LYP/6-31G(d)

Li	0.850796466758	0.438496697030	0.574286947488
O	-0.119716326597	-1.311091398283	1.418635247181
C	-1.253458850532	-1.022045673386	2.272026451393
H	-1.001841005934	-1.346737626359	3.291729457561
H	-1.416408303450	0.059112208872	2.267426681334
C	-2.438647981684	-1.803843370238	1.697956724448
H	-2.962417067034	-1.197702557077	0.951474898824
H	-3.151923176487	-2.103445323436	2.472279483764
C	-1.746514521614	-2.995623763490	1.018888051467
H	-1.494568209691	-3.773224699860	1.750758958960
H	-2.352539024318	-3.445868083004	0.227792756572
C	-0.479003202323	-2.342340008665	0.469265272350
H	-0.670865404765	-1.877206764482	-0.504743762017
H	0.370268234651	-3.028976933247	0.382159552417
O	2.042288351214	0.762343141905	-1.163668499408
C	2.040342409274	-0.310241751646	-2.128944575183
H	3.068412526862	-0.682339011461	-2.247455847546
H	1.419809422932	-1.124139066644	-1.741627061426
C	1.506219857238	0.293488202937	-3.428607195929
H	0.411666245975	0.277126209856	-3.430577915057
H	1.863489195213	-0.238616670123	-4.315639055819
C	2.015292923986	1.739727764684	-3.335627746017
H	3.067709086087	1.798593059158	-3.639613339494
H	1.442393501362	2.436779690489	-3.954192234915
C	1.861120675400	2.032400162116	-1.840781601515
H	0.856649154787	2.394330748876	-1.600024661802
H	2.610983137393	2.731286623500	-1.454678372624
O	1.028482657025	2.006107183881	1.907446674495
C	0.266581986175	3.220360279765	1.719334493741
H	0.956063951818	4.048444875395	1.498244286211
H	-0.391149523255	3.050824019995	0.865917017569
C	-0.449570799201	3.438941850289	3.048496394784
H	-1.341802506659	2.804468284889	3.103358581285
H	-0.758557175308	4.477870537533	3.198126301761
C	0.615336714521	2.973111665691	4.055025661406
H	1.330410421783	3.780773064179	4.249661339661
H	0.196906680460	2.659256504471	5.016045284750
C	1.301751690314	1.813313813748	3.312313381275
H	0.894579039368	0.838544763252	3.603453594747

H	2.386070975611	1.793638263438	3.469235691270
O	2.699967415996	-0.453723975193	1.405371298635
C	2.850948342166	-1.542768607874	2.335649354277
H	2.403346783785	-1.259000052105	3.298422033330
H	2.304172210322	-2.405609486641	1.949549144258
C	4.358218669518	-1.770211535164	2.469050591537
H	4.718984004555	-2.426837219884	1.668230776247
H	4.632680350407	-2.221858440306	3.427270497232
C	4.906720150348	-0.347701572901	2.281341179073
H	4.816907051220	0.220229562237	3.215600950461
H	5.955789735162	-0.321386636737	1.971230135252
C	3.964491985103	0.215455390611	1.212637962123
H	4.324603620440	0.002156273871	0.199579488848
H	3.796463814008	1.292988437550	1.296325118959
H	-2.125052635709	-2.616064800189	-4.402902261438
C	-2.913555959861	-2.045537343956	-3.914086316604
C	-4.899561863447	-0.565814785053	-2.655869449484
C	-2.572616815649	-1.128909656428	-2.924087535138
C	-4.246301669997	-2.238545022985	-4.290643577607
C	-5.232239033106	-1.482256013047	-3.646966804811
C	-3.555710821753	-0.355033139887	-2.252885080523
H	-1.526015657682	-0.992003123727	-2.658517727314
H	-4.509199147320	-2.953964900519	-5.065125885095
H	-6.277884665378	-1.609225783586	-3.922293654584
H	-5.685673461612	0.009277957597	-2.169736728287
C	-3.242461915871	0.593229397735	-1.211751880311
H	-4.048492962286	1.170866856385	-0.768438452109
C	-1.969200506865	0.838745471266	-0.769562738791
N	-0.857660595933	1.026522714795	-0.388067111028

3.2.4.22 [PhCHCNLi(THF)]₂ at B3LYP/6-31G(d)

Li	0.812724241110	-0.814196319562	-1.037827085133
N	0.973816863246	-0.533112367097	0.893588937199
C	1.571096139630	-0.307069878176	1.911683165513
C	2.216572752469	-0.066317342287	3.073921546322
H	2.436473180938	0.970189382420	3.314467064614
C	2.672938851500	-1.108326957046	3.984096794331
C	3.342166774215	-0.759751926562	5.177311756666
C	3.784127926260	-1.730932205065	6.072056120495
C	3.576102901100	-3.087628712196	5.812119304947
C	2.917360020481	-3.452094238523	4.633914226006
C	2.474513489428	-2.485551347836	3.735875917898
H	1.971014906541	-2.792999424239	2.821417505830
H	2.748667295934	-4.503276998320	4.409454779559
H	3.921779442396	-3.844986742464	6.510289526456
H	4.297073783753	-1.423798579894	6.981024379438
H	3.513484571132	0.292305960308	5.396549104529
Li	-1.026866058454	-0.661719602785	0.770071172918
N	-1.192409729184	-0.849026497959	-1.174442446764
C	-1.786984839565	-0.656008585182	-2.199974604694
C	-2.419547983088	-0.409017217274	-3.368783877582
C	-2.473883549532	0.908052944837	-3.985990232371
C	-3.128523674144	1.084702224371	-5.225098551948
C	-3.186646428927	2.329942285921	-5.845183981660
C	-2.594923308551	3.450666166534	-5.256560536564
C	-1.945926870005	3.297871483237	-4.027667370089
C	-1.885662324493	2.055037362757	-3.402111524225
H	-1.389157803317	1.963686470797	-2.437752923367
H	-1.487172937348	4.158800031371	-3.545450481877
H	-2.642036559574	4.421714567840	-5.741453574248
H	-3.700747799487	2.425468652954	-6.799184391159
H	-3.594856271783	0.224171297609	-5.700313382169
H	-2.922587791227	-1.239758589362	-3.854593937603
O	-2.196179691601	-0.392324182207	2.232577056900
C	-1.735283013660	-0.340222206095	3.612435802476
H	-0.673933152773	-0.078719346151	3.602141398735
H	-1.854855043940	-1.335548947809	4.058630576574

C	-2.642605803114	0.686975775469	4.281604191799
H	-2.696542975696	0.550386483802	5.365353970765
C	-3.983380953399	0.436451594171	3.571778169861
C	-3.549872876937	0.128634298809	2.134195031040
H	-4.175140355824	-0.620025375554	1.639369262747
H	-3.519995550307	1.029845401604	1.510995482801
H	-4.666031717604	1.289486415656	3.621167668018
H	-4.491052967029	-0.428731093757	4.013218679583
H	-2.281820555760	1.702747537268	4.081656600909
O	1.957514483048	-0.507431991275	-2.514290066280
C	1.505763726687	-0.380550957387	-3.885496629743
H	1.995699037476	-1.161718986409	-4.481372653849
C	1.936931143763	1.031311266352	-4.327986649505
H	2.329403520464	1.016185845532	-5.348759813366
C	3.017413134054	1.447941022762	-3.289821349826
C	3.219917138247	0.185652156990	-2.441040312365
H	4.004236693261	-0.462665274057	-2.855347853357
H	3.431609606411	0.371448882460	-1.385660388753
H	3.951498518388	1.773067347963	-3.756752293496
H	2.653904675280	2.270030046147	-2.665881207378
H	1.086861193826	1.717861082835	-4.309045549238
H	0.426148003407	-0.542998889760	-3.892879612744

3.2.4.23 (PhCHCN)₂Li⁻ at B3LYP/6-31G(d)

H	2.914118017173	6.515450780791	0.688128634921
C	2.523540275556	6.239218487643	-0.290221309691
C	1.539192220902	5.555953111981	-2.794299212360
C	1.826906533737	5.009105102096	-0.420206739653
C	2.717861805987	7.090814497150	-1.372601908496
C	2.229962147823	6.764619946057	-2.642475744024
C	1.340518820223	4.699056851030	-1.718391264843
H	3.259430774276	8.024265236036	-1.222491164043
H	2.382751826568	7.430857343930	-3.488040076969
H	0.800932170524	3.766024577226	-1.866086468527
H	1.147707946966	5.275531754058	-3.771434218241
C	1.643216442188	4.148391198346	0.718255570174
H	2.046028083638	4.458631359925	1.678615634073
C	0.992744244849	2.946580191735	0.680018436001
N	0.428112644581	1.901373672419	0.653622165091
Li	-0.480988809607	0.266402683901	0.642444775849
N	-1.413212456915	-1.355300135539	0.677616239373
C	-2.010692762600	-2.381576531149	0.720478399570
C	-2.704070172619	-3.558682539485	0.771289078390
H	-3.788293891672	-3.489968501557	0.794932367037
C	-2.092422014075	-4.860984382137	0.799269164409
C	-0.942801359686	-7.479765791572	0.857776191989
C	-0.686687477352	-5.063397342089	0.770490155341
C	-2.892160815174	-6.032398465330	0.858865741368
C	-2.330282640219	-7.304430551287	0.887199101849
C	-0.133849711061	-6.338161671219	0.798805889996
H	-0.033638629324	-4.194514276654	0.724656035665
H	-3.975404000403	-5.922564609252	0.882550030762
H	-2.986338461842	-8.173160137193	0.932919529617
H	0.950101085685	-6.443751167339	0.774749954855
H	-0.504583037297	-8.474577840445	0.879987281926

3.2.4.24 (PhCHCN)₂Li⁻ at B3LYP/6-31+G(d)

H	2.906478662356	6.521553142852	0.698683675176
C	2.511954141581	6.254962480914	-0.281000000304
C	1.514671648638	5.598588880378	-2.791544268580
C	1.831046123443	5.015343108966	-0.426048339886
C	2.685019502425	7.128825727001	-1.351172268659
C	2.189603345661	6.816586224547	-2.624972991158

C	1.337447762995	4.719296089943	-1.726531043138
H	3.214084172460	8.067621487039	-1.189909063524
H	2.324965392389	7.499589080643	-3.460371308204
H	0.809427213166	3.781935857536	-1.888305355822
H	1.119155486630	5.328942859884	-3.770188529994
C	1.669344737135	4.135647908682	0.702818853351
H	2.077079682087	4.435587504737	1.664814914746
C	1.025745286015	2.926549921743	0.654177021954
N	0.467925076678	1.878516616599	0.615833621990
Li	-0.425587106452	0.244374810349	0.609615769340
N	-1.350858057702	-1.371548372287	0.648423557472
C	-1.967269952192	-2.385977100090	0.692888747836
C	-2.682139046622	-3.554203510525	0.745028108465
H	-3.765602241882	-3.466197930226	0.748178534233
C	-2.090610433115	-4.866362625387	0.796823631788
C	-0.985850622368	-7.507670818006	0.903313001003
C	-0.686613765383	-5.092910871681	0.796766866089
C	-2.912684478641	-6.024999745509	0.852338286791
C	-2.373484139199	-7.307754746575	0.904037710131
C	-0.155329697550	-6.378935054638	0.848675340494
H	-0.015485732594	-4.237659074389	0.754903104700
H	-3.994419341590	-5.897138854825	0.854256660262
H	-3.045097918994	-8.164764297624	0.945565570857
H	0.926965605186	-6.503493213680	0.846287813164
H	-0.565361269626	-8.509793921748	0.943844483082

3.2.4.25 (PhCHCN)₂Li⁺/Li(THF)₃(HMPA) at B3LYP/6-31++G(d)

H	3.180988421723	1.386512260289	6.108103934333
C	3.566131348719	0.675967400594	5.378549821388
C	4.582284326719	-1.147720076010	3.540377047241
C	3.536402754530	1.026849108280	4.002402452220
C	4.086610151999	-0.540101235868	5.814701493078
C	4.599807257118	-1.473362560868	4.903272820620
C	4.062878010211	0.066660263924	3.096660492121
H	4.097791004051	-0.760574381478	6.880588104105
H	5.014215858202	-2.417913132004	5.246169029919
H	4.079902576266	0.298503094174	2.033857720444
H	4.990791134840	-1.846809318637	2.812319898779
C	2.990487619109	2.295886412533	3.582866876537
H	2.643138181421	2.995367513422	4.338462580431
C	2.946358642770	2.714532786492	2.280950829548
N	2.897134101276	3.064578778806	1.145228882220
N	2.377476433636	3.439780946089	-2.440633905522
C	1.926104574954	3.097873390593	-3.486082372070
C	1.388321086252	2.669296676737	-4.670086048644
H	2.067496666432	2.220447692833	-5.389964789783
C	-0.007317594484	2.804348516249	-5.012991489558
C	-2.765598011624	3.022362097043	-5.746796595572
C	-0.943443947266	3.509377624728	-4.208901460106
C	-0.515531580749	2.220687740542	-6.204557072670
C	-1.857380108996	2.329819648304	-6.560137554034
C	-2.284956934459	3.613624414402	-4.570939379650
H	-0.592522256944	4.006600692651	-3.307106159302
H	0.170291939491	1.682887898559	-6.857215165707
H	-2.198805918917	1.875197317083	-7.488451337343
H	-2.963233186132	4.180506199211	-3.934970684883
H	-3.809839261869	3.118287852926	-6.033309936393
Li	-0.984664325970	-0.541421507427	-0.543278016820
O	-1.487577619290	1.301507693720	-0.015093404722
C	-2.838308110687	1.672655405538	0.337172234411
C	-2.971902657323	3.142330416223	-0.059059061790
C	-1.555523295111	3.672857040893	0.216195063915
C	-0.670574605406	2.495002226656	-0.201390348301
O	0.830230532383	-0.549678757150	-1.298876537112
C	1.137049196971	-0.717533309753	-2.709518222061
C	2.619079929303	-1.083047864655	-2.760599143312
C	3.180497817633	-0.291249556403	-1.569120224649

C	2.059305125352	-0.414036834259	-0.534789838967
O	-2.177944971870	-0.979431305781	-2.076768575176
C	-2.560419031574	-2.338632999654	-2.390602516298
C	-3.535205280529	-2.233398072733	-3.564746495657
C	-3.019045718130	-0.986000418157	-4.299125487472
C	-2.595076017578	-0.079964369891	-3.143932588135
H	4.131485504152	-0.683825124136	-1.196474520907
H	2.758828017737	-2.161112905134	-2.611408138378
H	3.077504900892	-0.805220031614	-3.714051704287
H	0.476261355412	-1.495714765221	-3.102132959272
H	2.170957315852	-1.309349770666	0.088434227868
H	-2.975714880962	1.531122059303	1.418149102888
H	-3.747618471135	3.660635123838	0.512916268204
H	-3.519516522658	1.001779254633	-0.194497933314
H	-3.213193561400	3.228690010988	-1.124845222041
H	-0.387352978262	2.544606055481	-1.256907820917
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H	-3.769439083270	-0.512864060276	-4.937957362207
H	-4.556966342918	-2.070101173726	-3.200862970209
H	0.940992063511	0.226731723551	-3.231225502867
H	-1.658164725300	-2.902933872611	-2.664506156837
H	-2.989829574083	-2.784933242959	-1.489408591799
H	-3.536694900939	-3.134350000608	-4.185661250138
H	-2.154633767878	-1.235873445738	-4.924956611396
H	1.968860011723	0.460313114519	0.114898434827
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H	-1.428678585945	3.892126698892	1.282800224549
H	-1.320704914622	4.581865117810	-0.345278480539
H	0.231417450195	2.392147032469	0.408130034548
O	-1.284657006834	-1.716459904383	0.882316232272
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N	-2.589643996102	-2.687187692576	2.886588854945
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H	-1.017650463152	0.404435742987	3.972056455233
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H	-0.049731471131	-1.533671870978	5.357852995315
H	1.513406042450	-1.429109504115	4.519300995008
H	0.584848350608	-2.945161974923	4.473274387478
C	-2.761167036133	-3.166526708071	4.252899190357
H	-3.049693419525	-4.228946377531	4.279108557920
H	-3.548195698356	-2.590167599327	4.757148570627
H	-1.839263458125	-3.051937489753	4.824217470452
C	-3.796885913685	-2.734098910203	2.069137643036
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H	-3.591267710057	-2.306721436867	1.087607120849
H	-4.594589564769	-2.149726307502	2.547396114113
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H	-1.951540597147	-5.037986612015	2.242853920137
H	-0.407749097510	-5.905227933625	2.317590888419
H	-0.948232743798	-5.194674995830	0.779773315750
C	1.173812109346	-3.813021573966	1.817711576188
H	1.700684064692	-4.648789210197	2.293595107174
H	1.661282942563	-2.883967156662	2.116615057596
H	1.261994489084	-3.924034543137	0.726024044083
Li	2.865925419050	3.543618580885	-0.648645308803

3.2.4.26 (PhCHCN)₂Li(HMPA)/⁺Li(THF)₄ at B3LYP/6-31'+G(d)

H	-0.034815081512	4.861753494036	3.485350606022
C	-0.507757500815	3.963575622575	3.880227078208
C	-1.712984839572	1.686709831086	4.928414439996
C	-0.128040695836	2.701367811483	3.345854415535
C	-1.453151737497	4.077586145119	4.895922530659

C	-2.076000303776	2.942438786659	5.434505535197
C	-0.766996815546	1.563817709723	3.912952700210
H	-1.703594595662	5.065834126453	5.278228747458
H	-2.807286313966	3.032669863371	6.233650256184
H	-0.496886635550	0.573576000045	3.551756525546
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C	0.848720410359	2.616952884624	2.289783602937
H	1.330541671751	3.529276815281	1.947281523358
C	1.265482247978	1.435335653521	1.720119295943
N	1.615528217238	0.416635342740	1.222333957349
N	1.317470826214	-2.113568384997	-1.108237304115
C	0.646596734837	-2.608723579630	-1.950617132788
C	-0.171573727002	-3.174708258076	-2.904267851056
H	-0.617977716993	-4.135107363075	-2.658270868743
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C	-0.984732573035	-1.525191626593	-6.798765109843
C	0.241696022337	-1.448831925418	-4.695452862542
C	-1.372878962558	-3.202774268802	-5.079327231615
C	-1.641646455621	-2.676971380439	-6.339899102926
C	-0.036404201581	-0.927102399781	-5.956997128101
H	1.010216366099	-0.983055870729	-4.082491824999
H	-1.892669217638	-4.102365648874	-4.752322589414
H	-2.368311091165	-3.177122903336	-6.978476951480
H	0.508977438831	-0.047905860677	-6.297022991501
H	-1.186134926448	-1.123379130049	-7.788634079539
Li	-3.019445916678	1.143054415702	-1.152893476219
O	-2.839251739215	-0.583208522531	-0.265553456130
C	-2.118400722199	-0.762179538213	0.988799949463
C	-1.805953973448	-2.256968829068	1.081261979292
C	-2.948738599409	-2.888476499515	0.269908733794
C	-3.125129149486	-1.878575882703	-0.861183313836
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C	-5.428237466598	-0.334021937079	-4.303019247356
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O	-1.299844357442	1.936155340432	-1.563047899033
C	-0.916236413960	3.323069190534	-1.388501987725
C	0.583767052574	3.399501528803	-1.709672889755
C	0.820845528239	2.147157706774	-2.570374945461
C	-0.132942945350	1.144055800520	-1.932583940254
O	-3.971479264762	2.430278500377	-0.006001686144
C	-4.896555464129	3.458211189735	-0.435454313493
C	-5.290252329481	4.224165146446	0.831006783960
C	-4.041395506916	4.064745943979	1.711910419029
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H	-2.411573913882	-2.062705424088	-1.673199800583
H	-2.527995367337	2.473975612732	1.490955638918
H	-4.13655774292	1.901382220821	2.000054651783
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H	1.858791181297	1.802872740704	-2.543627197699
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H	-5.158029579083	-1.382171498270	-4.130492652197
H	-3.862786394836	-2.959749856502	0.872815304418
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P	4.782893558157	-1.921919159937	2.202754473528
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N	4.736303503010	-3.208498131742	3.291451424185
N	6.231047280505	-1.765682650359	1.355726571034
C	5.098155510531	0.739751700905	2.642372748829
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H	5.826679424985	0.648768896563	1.836148983446
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H	3.579555727922	-1.485623941000	4.686812479778
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H	4.204080091502	0.128111881257	5.097176294880
C	4.103958912561	-4.467022314398	2.893607726531
H	3.600073944891	-4.909018727337	3.763068823489
H	4.840182607931	-5.195741883098	2.519582495661
H	3.364768685149	-4.279444674088	2.114904584189
C	5.712286604657	-3.353232935305	4.367270228971
H	5.229466580348	-3.816751659786	5.237500994145
H	6.092573527199	-2.376463843270	4.671541270779
H	6.562528871103	-3.989854475925	4.075669323228
C	6.338841970482	-2.298133012275	-0.003954369545
H	5.348861691255	-2.375085075105	-0.453768619527
H	6.814767019586	-3.291083186883	-0.016919690696
H	6.952448135175	-1.619895481569	-0.611227300784
C	7.516614393757	-1.599161505718	2.026648601583
H	8.043172602928	-2.557405537672	2.158398604696
H	7.379992700090	-1.135537674756	3.005197793493
H	8.160448275614	-0.943567535542	1.425469863296

Chapter 4 Comparative assessment of basis sets for the calculation of lithiated benzylic nitriles

4.1 Basis set economy

Computational chemistry is becoming increasingly more important for the organic chemist. The calculation of equilibrium and transition-state geometries, spectroscopic data, and reaction thermodynamic parameters can serve as a powerful predictive tool for experimental design or as a means of rationalizing complex experimental data.⁹⁹ Although available software packages and current technology allow for calculations to be run at high levels of theory for maximum accuracy, these processes are often too expensive in terms of time and computer resources to be used in a practical setting—particularly in models possessing greater than a few atoms. Chemists must routinely choose between what is possible and what is practical, balancing their desired level of accuracy versus computational time and hardware capabilities.

4.1.1 Project scope

Because the central theme of the research contained within this thesis hinges primarily on the accurate determination of the structure of lithiated benzylic nitriles in solution, computational chemistry (in concert with raw experimental data), offers the potential for critical insight into these structural determinations. Unfortunately, as described, the reliable modeling of these nitriles can become somewhat limited by current technology given the restraints of inherent molecular size.

This portion of our research focuses on the comparative assessment of several levels of computational theory to model the structures of a small series of structurally proven lithiated benzylic nitriles. In this effort we are immediately faced with a conundrum: our experimental data come from X-ray crystallography in the solid-state, but our calculations will be performed on isolated (albeit explicitly solvated) molecules in the gas phase. Because intermolecular interactions and crystal-packing considerations in the solid state will to some degree affect bond lengths, angles, and dihedrals, it is not reasonable to expect perfect agreement between calculated gas-phase and experimental solid-state structures.

In light of this situation we will therefore take the following approach. We will adopt B3LYP/6-31+G(d) as the desirable “accurate” protocol for prediction of lithiated benzylic nitrile equilibrium geometry. The B3LYP density functional^{100, 101} has been widely used to describe organolithium structure.^{46, 69, 70, 102-113} For most applications, 6-31G(d)^{114, 115} is often viewed as the minimally acceptable basis set.^{106, 108, 109} However for the anionic species, larger basis sets such as 6-31+G(d)¹¹⁶ are often preferred, since they include diffuse functions on second row atoms.

First, we will show calculated B3LYP/6-31+G(d) gas phase structures to reasonably model the experimental solid state structures. We will then calculate the bond lengths of each molecule within the sample set using smaller basis sets and alternative density functionals. Bond length comparisons will be conducted between these optimized geometries and those obtained at our target level of theory, B3LYP/6-31+G(d). Again we emphasize that our research deals *not* with the ability of computation to model these species in the solid-state *per se*, but rather the ability of lower, less expensive levels

of theory to approximate the structural parameters observed at higher levels. This goal defines the notion of “basis set economy”—achieving higher accuracy without the time and resource expense of larger basis sets.

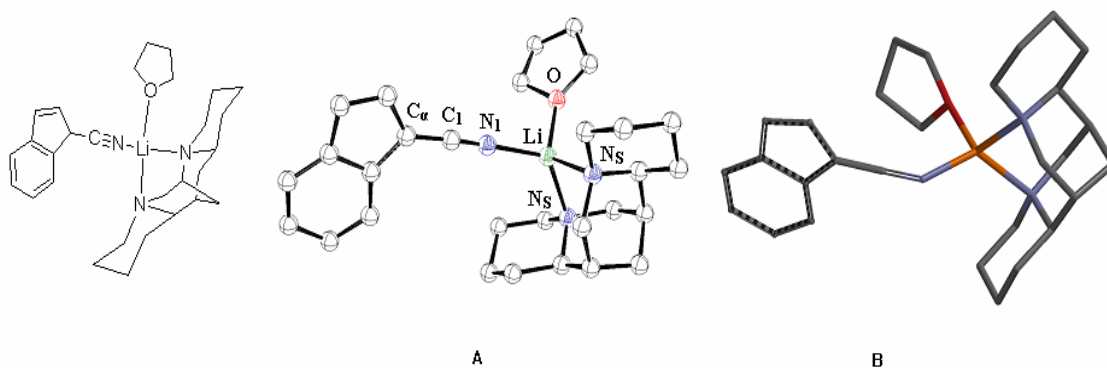
4.1.2 Sample set and B3LYP/6-31+G(d) calculated structures

The crystal structures for many metalated acetonitrile derivatives have been solved,¹¹⁷ showcasing the broad array of possible aggregation states previously observed in the solid state. Our comparative analysis, however, focuses solely on the subset of lithiated benzylic nitriles which are most relevant to our primary area of research (see Chapter 4). To date, the solid-state structures of four lithiated benzylic nitriles have been reported in the literature, shown in Figures 4.1-4.4, respectively.

- DEVJAP:⁶⁰ (1-Cyano-indenyl-*N*)-((-)-sparteine-*N,N'*)(tetrahydrofuran-*O*)-lithium
- DEVJUI:⁶¹ (Benzylcyano-*N*)(1,4,7,10-tetraoxacyclodecane-*O,O',O'',O'''*)-lithium
- JAYFIY:⁵⁹ (μ_2 -Di-isopropylamide-*N,N*)-(μ_2 -phenylacetonitrile-*N*)-bis(tetramethylene-1,2-diamine)-di-lithium
- FAHBEV:⁶³ bis((μ_2 -Benzylcyano-*N*)-(N,N,N',N'-tetramethyl-ethylenediamine-*N,N'*)-lithium)

Hereafter, each of the aforementioned lithiated benzylic nitriles comprising the sample set will be referred to solely by their corresponding Cambridge Crystallographic Data Center (CCDC) identification tags. Included within each of the Figures 4.1-4.4 is an Oak Ridge Thermal-Ellipsoid Plot (ORTEP) representation¹¹⁸ of the solved X-ray structure

(A) and the resulting B3LYP/6-31+G(d) optimized geometry of that X-ray structure (B) as calculated from the Gaussian '03 modeling software package⁹⁶ (for full details of computational methodologies see Chapter 5). Also included within each figure is a sample of tabulated structural parameters allowing for direct comparison of the B3LYP/6-31+G(d) optimized geometry to the experimentally reported solid-state species. The specific bond lengths and angles listed in this comparison concentrate primarily around the lithiated nitrile moiety, including any metal-coordinated heteroatoms. It may also be worthwhile to mention that “experimentally observed” C-H bond lengths cannot directly be compared to those derived from calculated structures. Modern X-ray crystallographic instrumentation does not typically have the resolution necessary to accurately locate hydrogen atoms within a crystal lattice. The positions of hydrogen atoms are generally approximated, and therefore bond lengths to these atoms should not be quantitatively compared to theoretical structures.



Structure	Bond lengths (Å)					Bond angle (°)
	Li-N_1	Li-N_2	Li-O	$\text{C}_1\text{-N}_1$	$\text{C}_\alpha\text{-C}_1$	$\angle\text{C}_1\text{N}_1\text{Li}$
X-ray	1.985	2.078, 2.036	1.950	1.163	1.399	176.1
B3LYP/6-31+G(d)	1.973	2.114, 2.098	2.046	1.183	1.381	132.9

Figure 4.1 DEVJAP: A) ORTEP depiction; B) B3LYP/6-31+G(d) optimized geometry

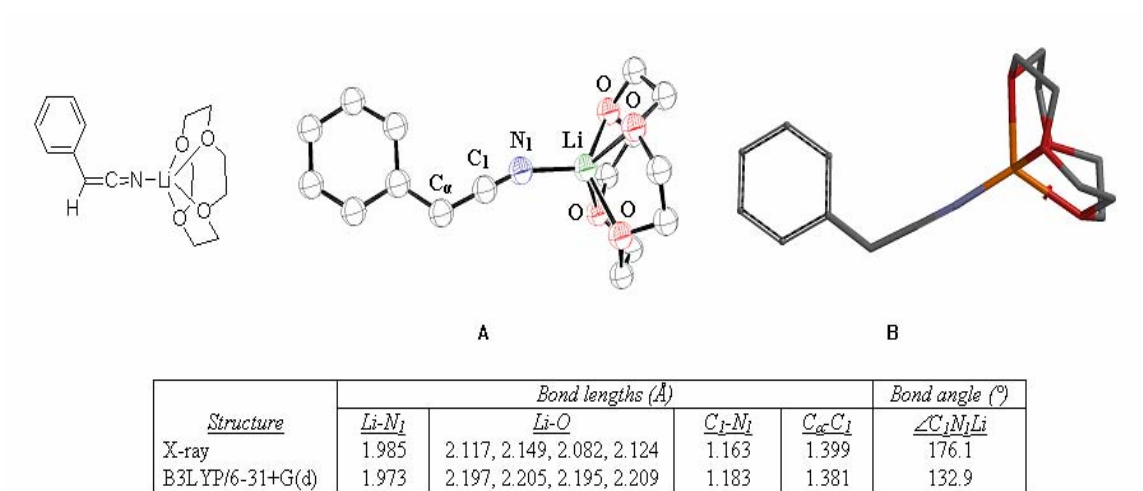


Figure 4.2 DEVJUI: A) ORTEP depiction; B) B3LYP/6-31+G(d) optimized geometry

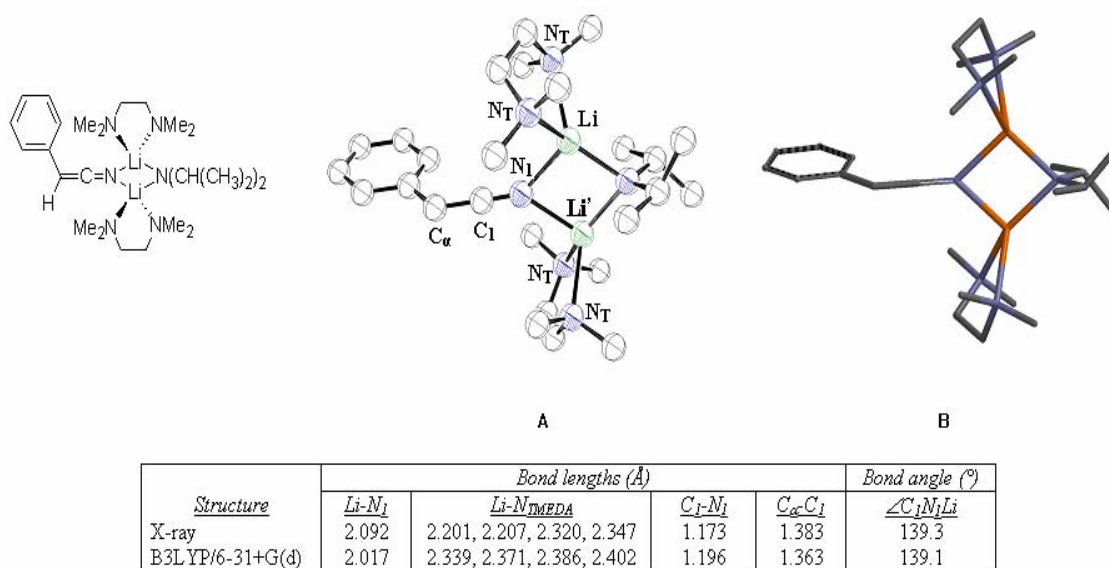
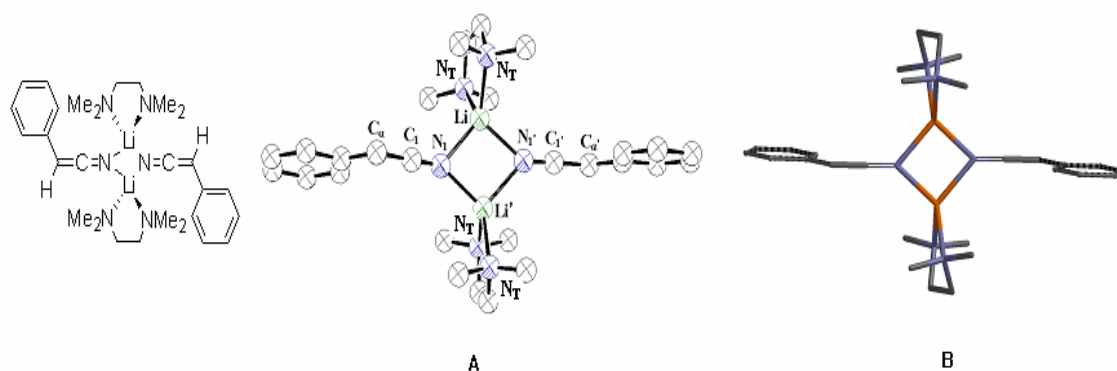


Figure 4.3 JAYFIY: A) ORTEP depiction; B) B3LYP/6-31+G(d) optimized geometry



<i>Structure</i>	<i>Bond lengths (Å)</i>				<i>Bond angle (°)</i>
	<i>Li-N₁</i>	<i>Li-N_{TMEDA}</i>	<i>C₁-N₁</i>	<i>C₆-C₁</i>	<i>∠C₁N₁Li</i>
X-ray	2.023	2.013, 2.019, 2.088, 2.090	1.173	1.375	139.6
B3LYP/6-31+G(d)	2.017	2.145, 2.146, 2.148, 2.148	1.198	1.359	138.9

Figure 4.4 FAHBEV: A) ORTEP depiction; B) B3LYP/6-31+G(d) optimized structure

As previously noted, it is not feasible to expect gas phase calculations to predict solid-state structures with high accuracy. Crystal packing effects notwithstanding, select bond length comparisons between the experimental and theoretical structures of DEVJAP, DEVJUI, JAYFIY, and FAHBEV confirm that the B3LYP/6-31+G(d) optimized geometries provide acceptable approximations of the key bond lengths within the lithiated benzylic nitrile series. Over the sample set, the B3LYP/6-31+G(d) optimized geometries uniformly exhibit an average underestimation of Li-N₁ bond lengths less than 0.03 Å, while overestimating C₁-N₁ by a slightly smaller margin (0.02 Å). The net result of these comparisons show the B3LYP/6-31+G(d) optimized geometries to provide a reasonable estimation of the lithiated nitrile moiety observed in the solid state.

Calculated bond lengths for the lithium-coordinated solvent ligands introduce larger deviations from the experimentally confirmed solid-state structures. The B3LYP/6-31+G(d) optimized geometries of JAYFIY and FAHBEV exhibit Li-N_{TMEDA} bond lengths typically 0.10 Å longer than those observed experimentally (Figures 4.3 and 4.4, respectively). The calculated Li-O bond lengths of DEVJAP and DEVJUI are also predicted to be longer than the analogous bond lengths within the X-ray structures by approximately the same margin (Figures 4.1 and 4.2). The errors associated with the bond lengths of the coordinated solvating ligands reinforce the direct effect of intermolecular interactions within the crystal lattice.

The largest structural deviations observed between theoretical and experimental structures can be seen in the monomeric DEVJAP and DEVJUI models (Figures 4.1 and 4.2, respectively). These species inherently exhibit greater structural flexibility than their more rigid dimeric counterparts. In these cases, the theoretical model fails to accurately predict the structurally observed $\angle C_1N_1Li$ bond angles, predicting an average $\angle C_1N_1Li$ bond angle deviation of 29.7°. As will be shown later (Section 4.4.1.3), the energetic penalty imposed by this bond angle deformation is minimal. As such, these observed changes in $\angle C_1N_1Li$ bond angle have little impact on the stability of the structure. Due to the rigidity of the dimeric complexes, the B3LYP/6-31+G(d) optimized geometries of JAYFIY and FAHBEV exhibit only 0.5° (average) deviation in the $\angle C_1N_1Li$ bond angle observed in the solid-state structures (Figures 4.3 and 4.4, respectively). These comparisons are meant to serve only as illustrative examples of the general reliability of our “accurate” method. Again, it is important to note that the observed deviations from

experimentally determined structures are not unexpected due to the inherent absence of intermolecular interactions in the theoretical model.

4.1.3 Theoretical modeling of lithiated phenylacetonitrile

The theoretical structures of lithiated phenylacetonitrile derivatives have received substantial attention in the recent literature.^{40, 46, 69, 70} Early computational effort on these lithiated phenylacetonitrile analogues failed to successfully account for the experimentally observed preference for N-lithiation (X-ray and $^6\text{Li}/^7\text{Li}/^{31}\text{P}/^{15}\text{N}$ NMR^{78, 84} studies), generally predicting a preference for a bridged C-lithiated structure when utilizing the HF/3-21+G basis set ($\Delta E = 0.40$ kcal/mol).⁴⁰ It may be interesting to note, however, that while employing the smaller 3-21G basis set, N-lithiation was preferred (by 5.63 kcal/mol), but these results were discarded in favor of the higher level of theory and corroboration with previous results pertaining simpler lithiated acetonitrile derivatives. C-lithiation of phenylacetonitrile supported the trends seen with the ab initio calculations of other lithiated acetonitrile derivatives: LiCH_2CN at HF/3-21+G and HF/6-31G(d),⁶⁷ and also $\text{LiCH}(\text{NH}_2)\text{CN}$ at HF/6-31G(d).⁶⁸ More recent work by Carlier and Madura, however, definitively shows that explicit solvation (albeit still inherently gas-phase) is key to correctly predicting the experimentally observed N- versus C-lithiation, and that these results can be achieved even with the low-cost HF/3-21G//PM3 protocol.⁷⁰

4.1.4 Experimental goals

Having shown B3LYP/6-31+G(d) to be a reasonable target model, we will compare the structural parameters of the optimized equilibrium geometries of DEVJAP, DEVJUI, JAYFIY, and FAHBEV optimized at PM3,¹¹⁹ the 3-21G,^{120, 121} and the 6-31G(d)¹¹⁴ basis sets to those parameters seen at 6-31+G(d). In addition to these well known Pople split-valence basis sets, we will also include the Huzinaga basis sets, Midi!¹²²⁻¹²⁴ (pronounced Midi ‘bang’) and Midi!+¹²²⁻¹²⁵ optimized by Truhlar *et al.* These basis sets reportedly boast highly accurate calculation of barrier heights, reaction energies, and equilibrium geometries, particularly with respect to organolithiums structures.^{124, 125} Finally, we will explore the use of customized Pople split-valence basis sets incorporating diffuse functions to select second row atoms giving the user-defined 6-31(+LiX)G(d) and 6-31’+’G(d) basis sets.

In addition to B3LYP, two alternate density functionals will also be used in the study: MPWLYP^{101, 126} and MPW1PW91.^{127, 128} The modified Perdew-Wang functional MPWLYP has achieved a certain measure of success in the recent literature, particularly in the calculation of weakly bound complexes, such as water clusters¹²⁹ and other systems with hydrogen bonding.^{130, 131} MPW1PW91 has enjoyed success in the calculation of metal coordination complexes including lithium.^{132, 133} The ability of these methods to adequately model non-covalent interactions could be useful in our prediction of solvated lithiophenylacetonitrile derivatives. The question we hope to address is whether these functionals could potentially offer superior performance to B3LYP when smaller basis sets (3-21G, Midi!, and Midi!+) are utilized. To further understand the importance of

electron correlation of the theoretical models, we will also carry out calculations at HF/6-31G(d).^{134, 135}

Our primary goal is to identify a less expensive computational protocol that can adequately approximate the structural parameters of lithiated benzylic nitriles seen at B3LYP/6-31+G(d). The target basis set in question is relatively large and consequently, optimization and frequency calculations on large molecules are often very difficult or even impossible to complete. An accurate, less expensive method is very appealing in that it could be confidently used as a suitable substitute in cases where calculations at B3LYP/6-31+G(d) become impractical.

The comparative assessment of the geometries optimized at these test functional/basis set combinations over the sample set will center around a mean signed/unsigned difference analysis of the bond lengths relative to B3LYP/6-31+G(d). As shown in Chapter 2, bond lengths (particularly those specific to the nitrile moiety) play a vital role in the prediction of simulated IR nitrile stretches ($\nu(\text{CN})$). The ability to accurately predict bond lengths (e.g., nitrile bond lengths) is of paramount importance in this basis set comparison. Because bond length deviations alone cannot adequately differentiate the reliability of one test computational method over another, a root mean square (RMS) structural deviation analysis will follow up the bond length comparison to quantitatively compare the overall shape of the test-method optimized geometries to the B3LYP/6-31+G(d) structure. The compounded effects of geometric variations over the sample set are notably observable through energetic destabilization relative to that of the target structure. As a tertiary means of the accuracy of the test-method structural matching, we will assess the B3LYP/6-31+G(d) single point energy for each optimized

geometry relative to the target structure. Additionally, we will address the reliability of the lower-level predictive power of the nitrile vibrational stretches compared to our accurate model. Finally, and most important to the principles of basis set economy, computational time will be examined for comparison in terms of accuracy versus time of these test methods/basis sets compared to the B3LYP/6-31+G(d) models.

4.2 Basis set primer

4.2.1 Basis set contractions

In principle, as basis sets increase in size, the attainable accuracy (and by extension the computational expense) should increase. The driving force behind both increases is the addition of more mathematical functions to describe each atom. Computational cost does not scale linearly with an increase in basis functions.¹³⁶ As can be seen in Table 4.1, DFT methods scale N^3 , where N is the number of basis functions.^{99, 136, 137} The reason for this scaling is three-fold: the electronic coulomb problem, the exchange-correlation quadrature, and the Hamiltonian diagonalization.¹³⁶ HF methods formally scale at N^4 due to the bottle-neck incurred during the calculation of repulsion integrals.^{99, 136, 137} There are, however, several viable options commonly used to improve this scaling to at least N^2 and in some cases to near-linearity.¹³⁶ Higher-level methods such as MP2 and Dunning basis sets (CCSD, CCSD(T), etc.) scale even more poorly making calculations on even relatively small molecules very impractical given modern technology. Despite the “favorable” formal scaling behavior of DFT and HF methods,

basis function scale-up still produces a dramatic effect in the computational cost of a calculation.

<u>Method</u>	<u>Scaling behavior</u>
DFT	N^3
HF	N^4
MP2	N^5
CCSD	N^6
CCSD(T)	N^8
CCSDTQ	N^{10}

Table 4.1 Formal scaling behavior of computational methods

As an illustrative example, refer to the DEVJUI molecule depicted in Figure 4.2. On Inferno2 (multi-processor server hosting Gaussian '03 for Virginia Tech; see Chapter 5 for a complete description of Inferno2), a complete optimization and frequency determination (utilizing 1 processor and 4GB memory; see Chapter 5 for detailed computational methodologies) at the B3LYP/3-21G basis set took approximately 11 hours to complete when starting from a PM3 geometry.¹³⁸ The same calculation (with identical processor and memory allotments as well as initial starting geometry) at the B3LYP/6-31G(d) basis set required approximately 30 hours.¹³⁸ Because both calculations referred to above utilize the B3LYP functional, the only difference between the two processes is the number of basis functions as defined by each basis set. The 3-21G basis set defines the DEVJUI molecule with 242 basis functions, whereas the corresponding 6-31G(d) basis set uses 374 basis functions. A complete summary of the

number of basis functions utilized by each basis set to describe the sample set can be found in Table 4.3, page 176.

4.2.1.1 Core and valence electrons^{99, 121}

A basis set is defined as the mathematical functions from which a wavefunction is constructed, the coefficients of which are solved iteratively during a calculation.⁹⁹ Basis functions are Gaussian-Type Orbitals (GTOs). For computational economy, these are often reduced (contracted) to linear combinations of primitive Gaussian functions, as defined by the particular basis set. The number of basis functions utilized by a computational method to fully describe a molecule for calculation is relatively straightforward. In the cases of the Pople split-valence basis sets (3-21G, 6-31G, etc.), the orbital contraction scheme for a given basis set is coded into the name. We will use the basis set 6-31G as a comprehensive example of the basis function formalism. The numbers shown in the basis set are intuitive descriptors of the manner in which the basis set defines atomic orbitals. The first digit (six) pertains to the core (non-valence) orbitals for a given atom. In this case, the single digit indicates that each of an atom's non-valence orbitals are described by one contracted GTO, or basis function. The numerical value indicates that each GTO is comprised of six primitive functions. The second term, 31, dictates the basis set contraction for valence electron orbitals. The two-digit number indicates that this method is a double-zeta (or split-valence) method wherein each valence orbital is described by two contracted GTOs. The numerical values of these numbers define the respective number of primitive functions comprising each GTO. In the 6-31G

example, one contracted GTO is made up of three primitive functions; the other is made up of a single primitive function.

By definition, first row atoms have zero core orbitals and only one valence orbital, 1s. By the application of the rules stated above, the 1s orbital would be defined by 2 contracted GTOs. Second row atoms have one core orbital (1s), and four valence shells: 2s, 2p_x, 2p_y, and 2p_z. The 1s orbital is treated by one contracted GTO, and each of the four valence orbitals are described by two contracted GTOs for a total of nine basis functions per second row atom as shown in Figure 4.5.

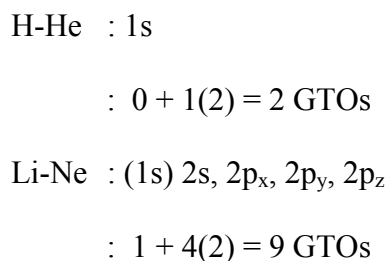


Figure 4.5 Orbital contraction schemes for first and second row elements at 6-31G

4.2.1.2 Polarization and diffuse functions^{99, 114-116}

The addition of polarization and diffuse functions is very common in computational chemistry and can profoundly increase the total number of basis functions. It is often the case that classical s and p functions do not provide the mathematical flexibility to describe the wave function for pyramidalized geometries.⁹⁹ The polarization function, commonly called ‘*’ (pronounced ‘star’) or (d), incorporates higher angular momentum for the valence orbitals of atoms in the second row and below. For a second

row atom this amounts to the inclusion of d-type orbitals. With the addition of this polarization function, second row atoms are now defined as 1s, 2s, 2p_x, 2p_y, 2p_z, d_{x²}, d_{y²}, d_{z²}, d_{xy}, d_{xz}, d_{yz} for a total of 15 basis functions as shown in Figure 4.6.

H-He : [1s]

: [0 + 1(2)] + 0 = 2 GTOs

Li-Ne : [1s, 2s, 2p_x, 2p_y, 2p_z] d_{x²}, d_{y²}, d_{z²}, d_{xy}, d_{xz}, d_{yz}

: [1 + 4(2)] + 6 = 9 GTOs + 6 GTOs = 15 GTOs

Figure 4.6 Orbital contraction schemes for first and second row elements at 6-31G(d)

It is worthwhile to note that polarization functions added to first row atoms take the form of additional p orbitals, and indeed there are cases (such as hydrogen-bonding) that warrant such descriptions of hydrogen atoms. The nomenclature for such additions take the form of 6-31G(d,p) or 6-31G**.

Diffuse functions (+) are commonly used for anionic species and/or species with high charge-delocalization. Standard atomic orbitals do not have the flexibility necessary to allow weakly bound electrons to delocalize to a significant extent from the bulk of the electron density. In order to accommodate these charge distributions, an extra set of s- and p-type GTOs with small exponents are added to each non-first row atom as shown in Figure 4.7

H-He : [1s]

: [0 + 1(2)] + 0 = 2 GTOs

Li-Ne : [1s, 2s, 2px, 2py, 2pz, d_x², d_y², d_z², d_{xy}, d_{xz}, d_{yz},] s, p_x, p_y, p_z

: [1 + 4(2) + 6] + 4 = 15 GTOs + 4 GTOs = 19 GTOs

Figure 4.7 Orbital contraction schemes for first and second row elements at 6-31+G(d)

Diffuse functions can also be added to first row atoms: the nomenclature associated with such a model takes the form of 6-31++G(d) or 6-31++G*, and is accompanied by the addition of a small-exponent s-type orbital to first row atoms. Table 4.2 shows a summary of contributions of first and second row atoms to the number of basis functions for a given basis set.

<u>Atoms</u>	<u>6-31G</u>	<u>6-31G(d)</u>	<u>6-31+G(d)</u>	<u>6-31++G(d)</u>	<u>6-31+G(d,p)</u>	<u>6-31++G(d,p)</u>
H-He	2	2	2	3	5	6
Li-Ne	9	15	19	19	19	19

Table 4.2 First and second row atomic contributions to basis functions as a function of basis set

4.2.2 Non-Pople basis sets

The Huzinaga basis sets,^{99, 122, 124, 125} Midi! and Midi!+, were developed with computational economy in mind. Rather than uniformly adding polarizing functions to all second row atoms, d functions are added to all atoms heavier than hydrogen with the

exception of carbon. Effectively, this approach localizes extra d orbitals strictly on heteroatoms. Furthermore, this basis set employs only five spherical d functions (d_{xy} , d_{xz} , d_{yz} , $d_{x^2-y^2}$ and d_{z^2}) as opposed to the six cartesian d orbitals (previously shown) typically utilized by the Pople basis sets. The result of such a technique is a smaller basis set which reportedly boasts high accuracy for some systems.^{124, 125} For sake of clarity it may be worthwhile to mention that the Midi! and Midi!+ basis sets are commonly called MidiX and MidiX+, respectively. The two naming conventions are synonymous and completely interchangeable. This alteration of nomenclature is necessary because several of the leading computational software packages do not recognize the (!) symbol as a valid input character.

4.2.3 Mixed basis sets

One strategy to minimize the computational cost of calculations is to apply user-defined basis sets. Gaussian '03 allows for the assignment of basis set on a per atom basis. Chemical intuition can be used to choose key atoms in a structure and apply higher levels of theory to those atoms while not applying them to atoms less important to the structure.

By placing diffuse functions only on selected atoms, one could hope to adequately model the electronic characteristics of the molecule while minimizing the inherent cost of the calculation. The success of such a method relies on the selection of the atoms upon which diffuse functions are added. As a conceptually illustrative example of this technique, refer to *N*-lithiophenylacetonitrile, Figure 4.8.

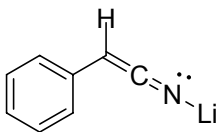


Figure 4.8 *N*-lithiophenylacetonitrile

One could add diffuse functions to the heteroatoms (in this case, only nitrogen) and to lithium while calculating all other atoms at the smaller 6-31G(d) basis. This approach applies the extra basis functions to a minimum number of atoms, while ensuring that the (arguably) two most important atoms in terms of electronic interactions are adequately described. In this case, a full 6-31+G(d) optimization would require 202 basis functions, whereas the 6-31(+LiX)G(d) approach, as defined, requires only 170 basis functions.

A more rigorous (albeit inherently more expensive) approach is to use chemical intuition to expand the diffuse functions to each atom directly and indirectly involved in electron delocalization. Figure 4.9 illustrates a resonance theory-based assessment of *N*-lithiophenylacetonitrile. It can be easily seen that charge delocalization includes the α -, *ortho*-, and *para*- carbon atoms.

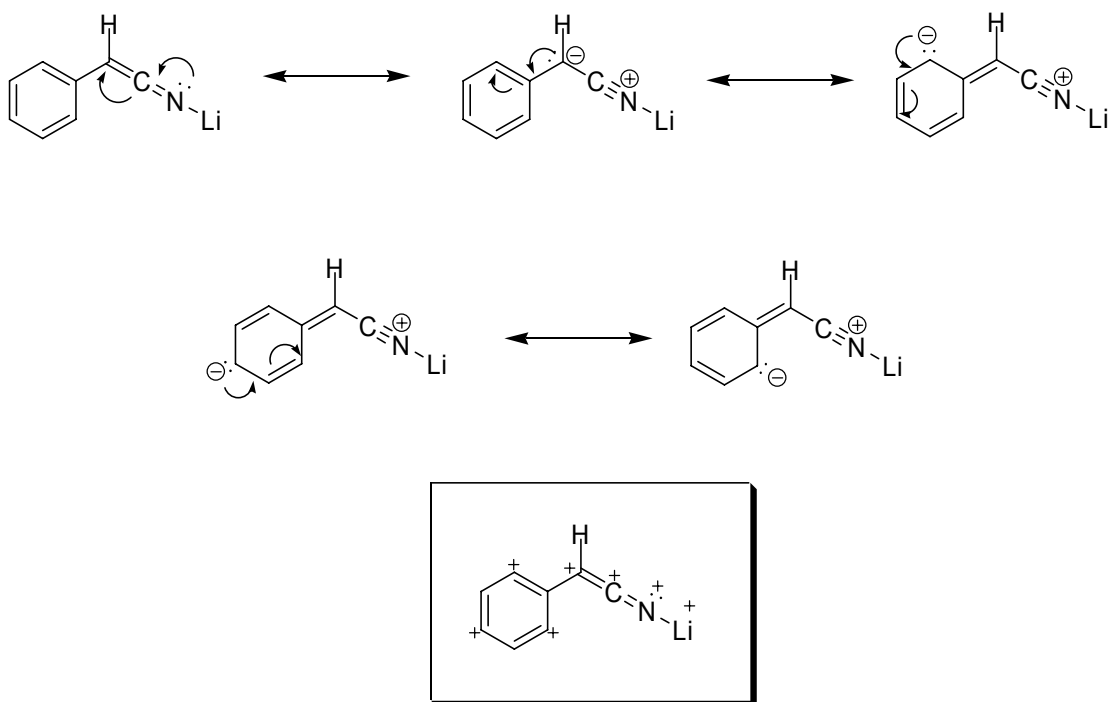


Figure 4.9 Resonance stabilized *N*-lithiophenylacetonitrile; and definition of the 6-31'+G(d) basis set. Atoms possessing diffuse functions are marked with (+)

These two approaches define the two customized basis sets employed in this comparative analysis. The first, 6-31(+LiX)G(d), applies extra diffuse functions only to the lithium and heteroatoms. The second approach, 6-31'+G(d), utilizes a resonance theory argument to include all atoms involved in electron delocalization, as shown above. It is important to note that diffuse functions are also added to the nitrile carbon, primarily due to the intimate association with the metalated nitrogen. This custom basis set would require 190 basis functions. The direct effect of these approaches for basis function minimization can be seen in Table 4.3.

4.3 Experimental assessment

The sample set used in this analysis of basis set economy consists of relatively large molecules (44-86 atoms), which can become very computationally intensive with small changes to the basis set due to the formal scaling issues mentioned earlier. Table 4.3 shows the total number of basis functions for each of the four model compounds for each basis set examined in the analysis.

	<i>DEVJUU</i>	<i>DEVJAP</i>	<i>JAYFIY</i>	<i>FAHBEV</i>
<i>Basis set</i>	<i>(44 atoms)</i>	<i>(74 atoms)</i>	<i>(86 atoms)</i>	<i>(80 atoms)</i>
PM3	110	176	188	188
3-21G	242	386	410	412
Midi!	264	403	434	436
Midi!+	352	539	570	580
6-31G(d)	374	590	614	628
6-31(+LiX)G(d)	398	610	646	660
6-31'+G(d)	422	650	678	708
6-31+G(d)	462	726	750	772

Table 4.3 Summary of basis functions for model compounds

4.3.1 Mean bond difference

The first method of analysis we employ to explore the relationship between basis set and calculated structural parameters is a mean signed/unsigned difference¹³⁹⁻¹⁴¹ comparison of bond length (R). Deviation in bond length is calculated as the difference between the length of a specific bond in the test geometry (R_i) versus the same bond in

the target B3LYP/6-31+G(d) structure (R_i^+), as shown in Equations 4.1 A and B. Both signed (ΔR_i) and unsigned ($|\Delta R_i|$) differences are considered. For the signed difference cases, positive values of ΔR_i indicate overestimation of a particular bond length relative to the target structure. Likewise, negative values of ΔR_i reflect bond length underestimation. All calculated unsigned differences are inherently positive.

$$\text{A) Signed difference} = R_i - R_i^+ = \Delta R_i$$

$$\text{B) Unsigned difference} = |R_i - R_i^+| = |\Delta R_i|$$

Equation 4.1 Calculation of A) signed differences and B) unsigned differences in bond length

For this analysis, bond lengths are categorically defined as: long ($R_i > 1.500 \text{ \AA}$); intermediate ($1.100 \text{ \AA} < R_i < 1.500 \text{ \AA}$); and short ($R_i < 1.100 \text{ \AA}$). It should be noted that only bonds between Li and heteroatoms comprise the long bonds, while C-C, C-O, and C-N bonds make up the intermediate bonds. Short bonds include only C-H bonds. It is worthwhile to note that the problem associated with the comparison of calculated C-H bonds to those seen in X-ray structures does not apply in these analyses since we are comparing the bond lengths between two calculated structures.

Mean unsigned difference (MUD) allows for a sense of the overall performance of each method/basis set basis set relative to B3LYP/6-31+G(d) over multiple bonds (N), specifically over the bond length ranges previously defined (long, intermediate, and short) as shown in Equations 4.2 A and B. Because unsigned differences are inherently

obtained as absolute values, all errors are additive; greater MUD indicates larger average deviations from what is seen in the target structure. In contrast, these deviations are not additive when comparing geometries via a mean signed difference (MSD) analysis. Signed difference allows negative deviations (underestimations) to effectively cancel out positive deviations (overestimations). MSD permits us to assess the performance of the test basis set in terms of average over- or under-estimation of particular bond lengths or types of bonds relative to the target. Negative values indicate an average underestimation of bond lengths, whereas positive values reflect an average overestimation of bond length over a particular bond length range.

$$\text{A)} \quad MSD = \overline{\Delta R_i} = \frac{1}{N} \sum_{i=1}^N (R_i - R_i^+) = \frac{1}{N} \sum_{i=1}^N \Delta R_i$$

$$\text{B)} \quad MUD = \left| \overline{\Delta R_i} \right| = \frac{1}{N} \sum_{i=1}^N \left| R_i - R_i^+ \right| = \frac{1}{N} \sum_{i=1}^N |\Delta R_i|$$

Equation 4.2 Determination of Mean A) Signed and B) Unsigned difference in bond lengths. Separate MSD and MUD values are calculated for long, intermediate, and short bonds (see text).

To assess whether differences in the MSD and MUD between the two levels of theory are significant, we determined the standard deviations of the mean signed and unsigned differences. Reported standard deviations (σ) of the mean differences over specified bond length ranges are calculated as shown in Equations 4.3 A and B.

$$\text{A)} \quad \sigma_{MSD} = \sqrt{\frac{1}{N} \sum_{i=1}^N (\Delta R_i - \overline{\Delta R_i})^2}$$

$$\text{B)} \quad \sigma_{MUD} = \sqrt{\frac{1}{N} \sum_{i=1}^N (|\Delta R_i| - \overline{|\Delta R_i|})^2}$$

Equation 4.3 Standard deviation of bond length analysis

In addition to the individual assessment of each bond length range, an ‘average’ MUD/MSD is also reported. $\overline{MSD}$ and $\overline{MUD}$ are reported as an average of the long bond, intermediate bond, and short bond error, as shown in Equations 4.4 A and B. Each bond length range is granted equal weighting so as not to unintentionally obscure the error of the longer bonds by the numerous short bonds.

$$\text{A)} \quad \text{Average MSD} = \overline{MSD} = \frac{1}{3} (MSD_{long} + MSD_{int} + MSD_{short})$$

$$\text{B)} \quad \text{Average MUD} = \overline{MUD} = \frac{1}{3} (MUD_{long} + MUD_{int} + MUD_{short})$$

Equation 4.4 Average A) MSD and B) MUD. For definition of long, intermediate, and short bonds, see text.

Uncertainty associated with the average is calculated from Equation 4.5.

$$\sigma_{MSD} = \pm \sqrt{\left(\frac{1}{3}\right)^2 \sigma_{long}^2 + \left(\frac{1}{3}\right)^2 \sigma_{int}^2 + \left(\frac{1}{3}\right)^2 \sigma_{short}^2} = \pm \sqrt{\frac{1}{9}(\sigma_{long}^2 + \sigma_{int}^2 + \sigma_{short}^2)}$$

Equation 4.5 Error propagation for Average MUD/MSD

4.3.2 RMS deviation

While measuring changes in bond length can be an effective tool for the assessment of the overall ability of a computational method to reproduce structural parameters seen with other methods or basis sets, this type of analysis cannot fully describe molecular shape. Bond lengths alone cannot account for atomic arrangements. Relative spatial positioning of individual atoms can provide a quantitative measure of changes in molecular shape as we explore alternate functionals and basis sets. In order to determine structural deviations on this scale, a root mean square (RMS)¹⁴² difference relative to the target structure must be examined (Equation 4.6). RMS difference is commonly used by protein crystallographers and target-based synthetic chemists to compare the shape of two or more enzymes, or more specifically binding pockets within enzymes.¹⁴³⁻¹⁴⁶ Using the pair-fitting functionality of PyMol,¹⁴⁷ we overlay the structure of target basis set and the test basis set to compare inter-atomic spatial distances ($\Delta\chi_i$) between the paired atoms of the test structure (χ_i) and the target B3LYP/6-31+G(d) structure (χ_i^+). Three RMS comparisons are examined: the lithiated arylacetonitrile and

all Li-coordinated heteroatoms (“backbone”); all atoms excluding hydrogen atoms; and finally all atoms.

$$RMS = \sqrt{\frac{1}{N} \sum_{i=1}^N (\chi_i - \chi_i^+)^2} = \sqrt{\frac{1}{N} \sum_{i=1}^N (\Delta\chi_i)^2}$$

Equation 4.6 Root mean square analysis of atomic spatial arrangement

Unlike the MUD/MSD analysis, the motivation to subdivide the RMS analysis is based not in purely quantitative comparisons, but rather as a descriptive means to better understand deviations in molecular shape. Large errors introduced by the “backbone” of the structure are indicative of major changes in bond angles or other structural parameters within the metalated nitrile and coordinated heteroatoms. Error introduced by the incorporation of solvating ligands (minus hydrogen atoms) suggests variability in the arrangement or orientation of these species. For overall performance ranking, only total RMS will be considered, as errors specifically stemming from structural deformations within backbone or solvating ligands are reflected in the total.

4.3.3 Energetics and frequencies

A very important consequence of structural inconsistencies relative to the target structure manifests itself in the form of energetic penalties. Despite a method’s ability to duplicate geometric results, calculated energies cannot be compared directly where the numbers of basis functions are not equal. To make direct comparisons, we calculate B3LYP/6-31+G(d) single point energies at each optimized geometry. Reported as

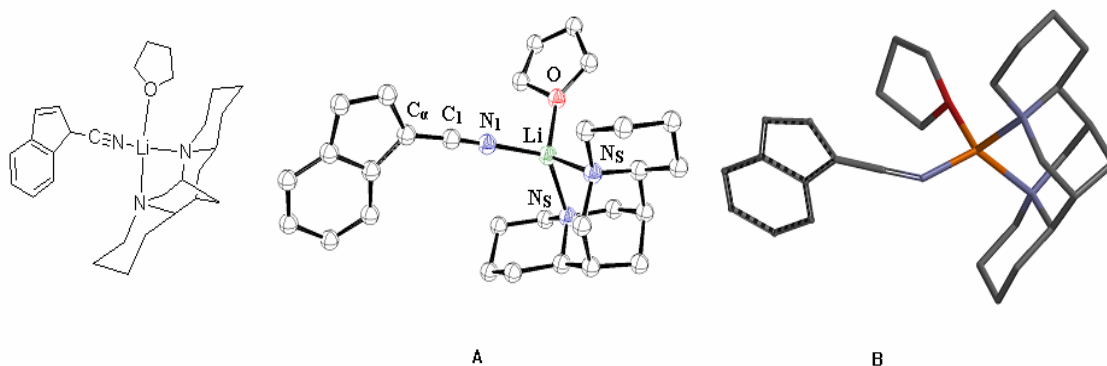
B3LYP/6-31+G(d)//X where X is the geometry in question, these values provide a secondary measure of a method's ability to replicate the structure optimized by the target basis set. The ideal functional/basis set would show minimal deviation from the energy determined at the B3LYP/6-31+G(d).

4.4 Data analysis

For a complete description of computational methodologies and data analysis procedures, and also comprehensive data tables of bond length and Cartesian coordinates for each optimized structure, refer to Chapter 5.

4.4.1 DEVJAP

It is important to mention that the optimizations of DEVJAP with the Midi!+ basis set repeatedly failed at default convergence thresholds and could only be completed through modification of the SCF optimization criteria.¹⁴⁸ The resulting geometries, however, are still included within the structural and energetic analyses.



Structure	Bond lengths (Å)					Bond angle (°)
	Li-N_1	Li-N_2	Li-O	$\text{C}_1\text{-N}_1$	$\text{C}_\alpha\text{-C}_1$	$\angle\text{C}_1\text{N}_1\text{Li}$
X-ray	1.985	2.078, 2.036	1.950	1.163	1.399	176.1
B3LYP/6-31+G(d)	1.973	2.114, 2.098	2.046	1.183	1.381	132.9

Figure 4.1 DEVJAP (repeated)

4.4.1.1 Mean bond difference

Table 4.4 reports the average (and bond length range specific) MUD and MSD for each of the tested DEVJAP geometries. It can be argued that all test functionals/basis sets perform remarkably well in the prediction of short bond lengths (notable exceptions being PM3 and HF/6-31G(d)). Typical error in the matching of C-H bond lengths is 0.002 Å. Intermediate bonds, consisting of carbon-carbon and carbon-heteroatom connections, also feature relatively small error over the set of tested methods/basis sets, but basis set dependence can be observed. Including standard deviations, intermediate bond MUD is typically 0.000-0.020 Å, with larger basis sets exhibiting smaller deviations relative to the target structure. The highest variability in bond length error exists for lithium contacts (long bonds). The success of a potential alternative computational protocol will hinge greatly on its ability to model these bonds properly. The high error in long bond length prediction is offset considerably in the average MUD

determination by the relative accuracy of intermediate and short bond lengths. Nevertheless, average MUD will serve as our marker for the evaluation of overall performance of bond length prediction.

<u>Geometry</u>	<i>Mean Unsigned Difference ($\text{\AA}$)</i>			
	<i>Long bonds</i>	<i>Intermediate bonds</i>	<i>Short bonds</i>	<i>Average MUD</i>
PM3	0.088 ± 0.060	0.012 ± 0.008	0.012 ± 0.005	0.037 ± 0.020
B3LYP/3-21G	0.067 ± 0.029	0.010 ± 0.010	0.002 ± 0.001	0.026 ± 0.010
MPWLYP/3-21G	0.054 ± 0.024	0.021 ± 0.014	0.005 ± 0.001	0.027 ± 0.009
B3LYP/Midi!	0.061 ± 0.013	0.007 ± 0.005	0.002 ± 0.001	0.023 ± 0.005
*B3LYP/Midi!+	0.028 ± 0.014	0.007 ± 0.005	0.002 ± 0.001	0.012 ± 0.005
*MPW1PW91/ Midi!+	0.033 ± 0.018	0.003 ± 0.002	0.002 ± 0.001	0.013 ± 0.006
B3LYP/6-31G(d)	0.011 ± 0.009	0.002 ± 0.002	0.001 ± 0.000	0.005 ± 0.003
HF/6-31G(d)	0.016 ± 0.009	0.011 ± 0.007	0.012 ± 0.001	0.013 ± 0.004
B3LYP/ 6-31(+LiX)G(d)	0.012 ± 0.012	0.002 ± 0.002	0.001 ± 0.000	0.005 ± 0.004
B3LYP/ 6-31'+G(d)	0.004 ± 0.002	0.000 ± 0.000	0.000 ± 0.000	0.001 ± 0.001
<u>Geometry</u>	<i>Mean Signed Difference ($\text{\AA}$)</i>			
	<i>Long bonds</i>	<i>Intermediate bonds</i>	<i>Short bonds</i>	<i>Average MSD</i>
PM3	0.061 ± 0.088	-0.003 ± 0.014	0.012 ± 0.005	0.023 ± 0.030
B3LYP/3-21G	-0.067 ± 0.029	0.009 ± 0.011	-0.002 ± 0.001	-0.020 ± 0.010
MPWLYP/3-21G	-0.054 ± 0.024	0.021 ± 0.015	0.005 ± 0.001	-0.009 ± 0.009
B3LYP/Midi!	-0.061 ± 0.013	0.006 ± 0.007	0.002 ± 0.001	-0.018 ± 0.005
*B3LYP/Midi!+	-0.028 ± 0.014	0.007 ± 0.005	0.002 ± 0.001	-0.006 ± 0.005
*MPW1PW91/ Midi!+	-0.033 ± 0.018	-0.001 ± 0.003	0.002 ± 0.001	-0.011 ± 0.006
B3LYP/6-31G(d)	-0.010 ± 0.011	-0.001 ± 0.002	0.000 ± 0.001	-0.004 ± 0.004
HF/6-31G(d)	0.015 ± 0.011	-0.011 ± 0.008	-0.012 ± 0.001	-0.003 ± 0.005
B3LYP/ 6-31(+LiX)G(d)	-0.012 ± 0.012	-0.001 ± 0.002	0.000 ± 0.001	-0.004 ± 0.004
B3LYP/ 6-31'+G(d)	-0.003 ± 0.004	0.000 ± 0.000	0.000 ± 0.000	-0.001 ± 0.001

Table 4.4 Mean unsigned/signed error of bond lengths for DEVJAP relative to B3LYP/6-31+G(d); *Optimizations completed with relaxed convergence criteria

A closer look at the MUD for DEVJAP geometries (Chart 4.1) clearly shows the relationship between basis set size and the error associated with bond length prediction. Within tolerances of standard deviation, the data fall in four distinct regions on the graph. The structures predicted by PM3, 3-21G, and Midi! constitute the first region, exhibiting the highest error in prediction of bond length. There is a sizeable decrease in the average and long bond error as we consider the structures optimized at the larger Midi!+ basis set, and another decrease upon examination of the 6-31G(d) derived geometries. Expansion of the 6-31G(d) basis set to include the extensive addition of diffuse functions throughout the resonance-stabilized structure yields another significant improvement in bond length error.

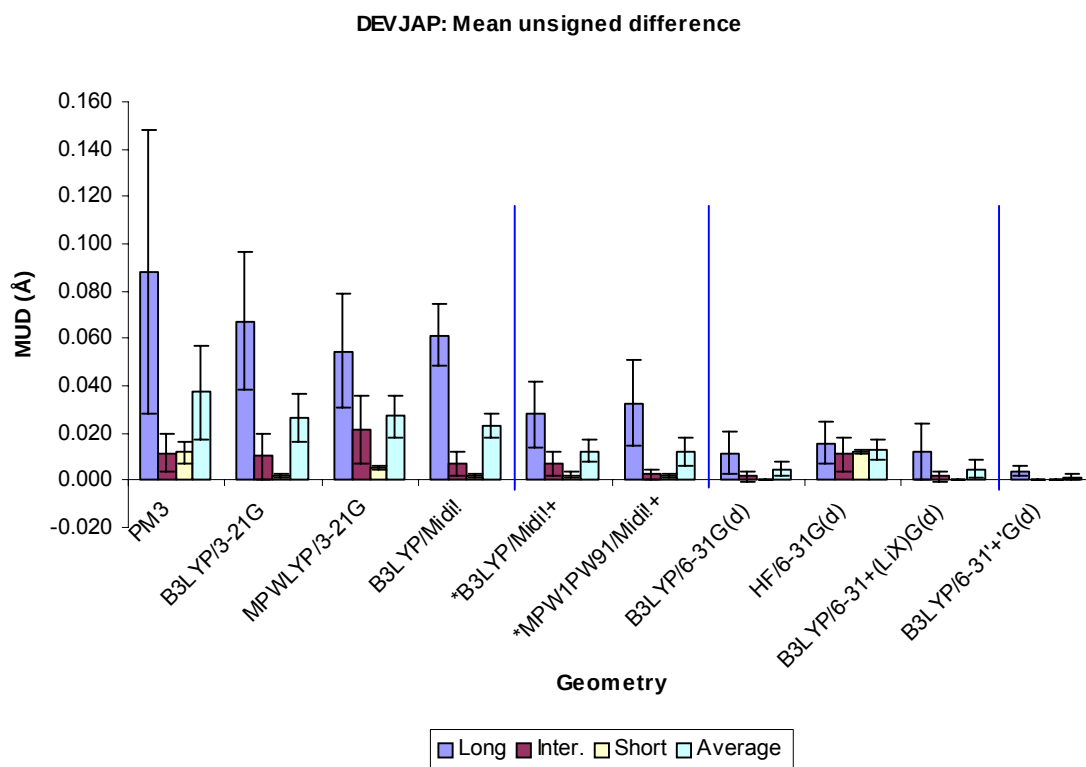


Chart 4.1 Mean unsigned differences in bond length for DEVJAP relative to B3LYP/6-31+G(d); *Optimizations completed with relaxed convergence criteria

The trends observed in Chart 4.1 hold true upon examination of the MSD analysis of bond lengths for DEVJAP geometries (Chart 4.2). For bulk comparison, an identical dependence of MSD and basis set size can be observed. PM3, 3-21G, and Midi! calculate structures with the largest bond length MSD. Error significantly decreases with the use of the Midi!+ basis set, and also again with the use of 6-31G(d). As we consider the customized 6-31'+G(d) basis set, MSD error approaches zero.

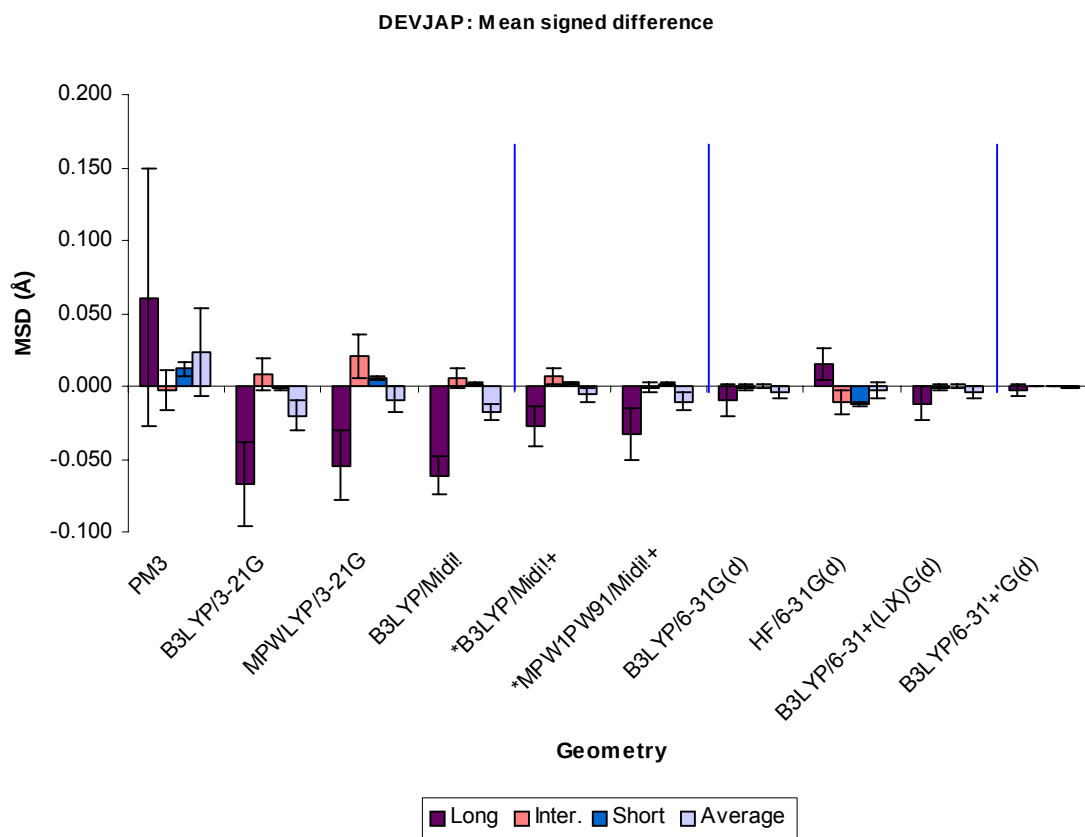


Chart 4.2 Mean signed differences in bond length for DEVJAP relative to B3LYP/6-31+G(d); *Optimizations completed with relaxed convergence criteria

Statistically there is little to distinguish the smaller methods/basis sets (PM3, 3-21G, and Midi!) in terms of overall performance in the calculation of bond length. Each structure exhibits an average MUD greater than 0.025 Å with substantial standard deviation, indicating generally poor reliability. The structures optimized at 3-21G and Midi! significantly underestimate all bonds to lithium indicating an inability to correctly model organolithium molecules. In contrast, PM3 overestimates lithium bonds (0.061 Å MSD), but within the range of standard deviation, no precise conclusions on the general ability of PM3 to approximate lithium bonds can be drawn.

The Midi! basis set offers seemingly no statistical improvement over PM3 or 3-21G geometries, but it is apparent that expansion to Midi!+ allows for a more accurate depiction of long bond lengths. Midi!+ substantially reduces the long-bond underestimation seen with B3LYP/Midi! to 0.028 Å for the B3LYP functional and 0.033 Å for the MPW1PW91 functional, however within statistical error, no meaningful comparisons between the two functionals can be deduced.

The use of the 6-31G(d) basis set offers the next step of increased accuracy for bond length predictions. B3LYP/6-31G(d) predicts a structure with an average MUD of 0.005 Å. Intermediate and short bonds exhibit predictably accurate bond lengths at this level of theory, but the real success realized through the use of 6-31G(d) is the substantial improvement of long bond length estimation. With the B3LYP density functional, this basis set exhibits a long bond MUD of 0.011 Å. The importance of electron correlation is apparent in the larger bond length errors in the HF/6-31G(d) model. Due to this neglect, larger MUDs are observed relative to the B3LYP density functional. The ab initio method also fails to correctly model intermediate and short bond lengths. Furthermore,

HF/6-31G(d) is the only method aside from PM3 that overestimates Li-X long bonds relative to B3LYP/6-31+G(d) (0.015 Å long bond MSD) .

The inclusion of diffuse functions to select atoms via the custom-defined basis sets offers somewhat mixed results. The extension of these functions to include only lithium and heteroatoms (6-31(+LiX)G(d)) provides nearly identical results to those seen at B3LYP/6-31G(d). The addition of diffuse functions throughout the resonance stabilized structure (6-31'+G(d)), however, provides excellent results relative to B3LYP/6-31+G(d), boasting an average MUD of only 0.001 Å, with intermediate and short bond MUD of 0.000 Å. This notable improvement in the performance of the customized 6-31'+G(d) basis sets strongly indicates that these extra diffuse functions are necessary for an accurate depiction of the geometry optimized at the target basis set.

4.4.1.2 RMS

The most obvious characteristic of the RMS deviation data for DEVJAP (Table 4.5 and Chart 4.3) is the extremely high error associated with nearly all optimized structures. With the exception of B3LYP/6-31'+G(d), the data show all other calculated structures to yield very poor total RMS deviations (>1.000 Å) relative to B3LYP/6-31+G(d). This RMS deviation indicates that each atom is, on average, separated in space by greater than 1 Å from the same atom in the target structure. These data clearly show the B3LYP/6-31'+G(d) customized basis set to outperform the other basis sets (total RMS equal to 0.015 Å) by a staggering amount.

<i>Method</i>	<i>RMS ($\text{\AA}$)</i>			<i>$\angle\text{C}_1\text{N}_1\text{Li}(\text{^\circ})$</i>
	<i>Backbone</i>	<i>Non -H</i>	<i>Total</i>	
PM3	1.068	1.607	1.804	170.2
B3LYP/3-21G	0.747	1.250	1.448	179.4
MPWLYP/3-21G	0.768	1.279	1.479	177.7
B3LYP/Midi!	1.010	1.422	1.589	175.3
*B3LYP/Midi!+	1.132	1.640	1.804	170.7
*MPW1PW91/Midi!+	1.122	1.593	1.779	169.5
B3LYP/6-31G(d)	0.721	1.120	1.382	177.8
HF/6-31G(d)	0.660	1.000	1.182	179.7
B3LYP/6-31(+LiX)G(d)	0.743	1.218	1.416	176.3
B3LYP/6-31'+G(d)	0.010	0.013	0.015	132.9
B3LYP/6-31+G(d)	0.000	0.000	0.000	133.0

Table 4.5 RMS deviations for DEVJAP relative to B3LYP/6-31+G(d) and calculated $\angle\text{C}_1\text{N}_1\text{Li}$ bond angle; *Optimizations completed with relaxed convergence criteria

The underlying cause to these peculiar data lies in a distinct geometric change, as evidenced by the exceptionally large error introduced by examination of the backbone of the structure. The high degree of flexibility for this monomeric species, particularly about the $\angle\text{C}_1\text{N}_1\text{Li}$ bond angle, allows for a very flat potential energy surface, and thus considerable variability in the optimized structure. As shown in Table 4.5, B3LYP/6-31+G(d) calculates the $\angle\text{C}_1\text{N}_1\text{Li}$ bond angle to be 133.0° , whereas almost all the other method/basis set predict a nearly linear orientation. The only basis set which matches the B3LYP/6-31+G(d) bond angle is 6-31'+G(d). The success of 6-31'+G(d) over 6-31(+LiX)G(d) reinforces the necessity of diffuse functions on all second-row atoms involved directly through resonance to the lithiated nitrile in order to replicate the results seen at our target basis set.

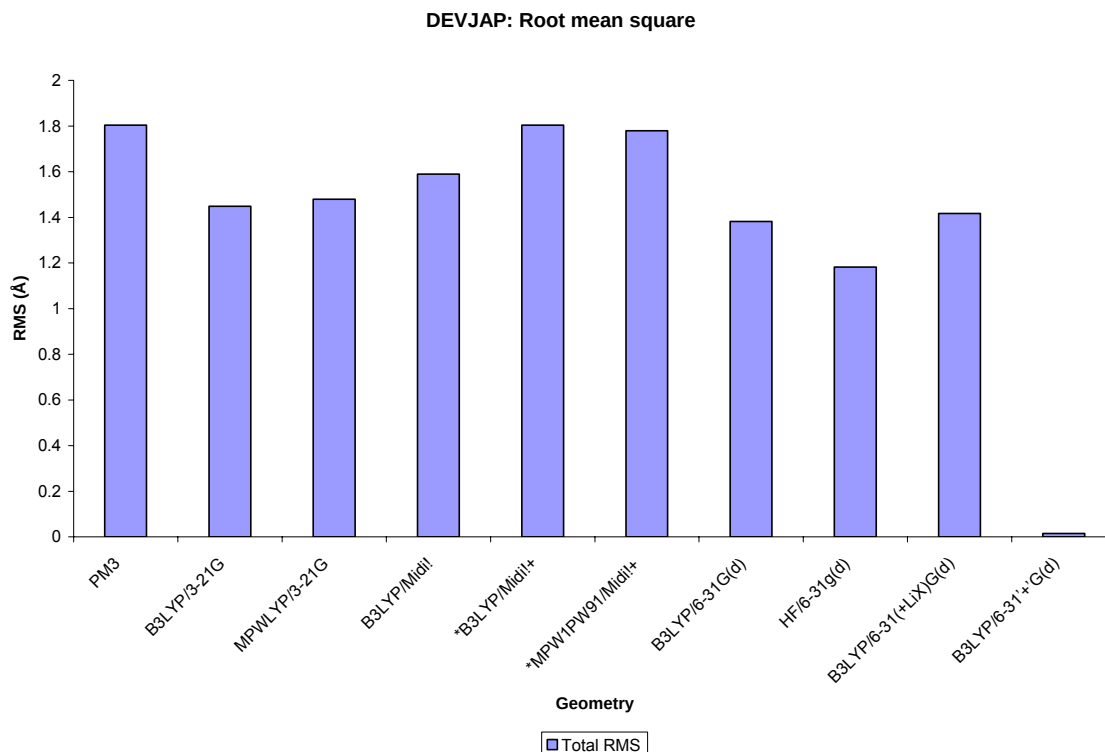


Chart 4.3 Total RMS deviations as a function of method/basis set for DEVJAP relative to B3LYP/6-31+G(d); *Optimizations completed with relaxed convergence criteria

4.4.1.3 Energetics and frequencies

A comparison of the B3LYP/6-31+G(d) single point energies for each of the optimized geometries (Table 4.6) confirms the superior ability of the customized 6-31'+G(d) basis set to match the target structure with a relative energy of 0.0 kcal/mol. The previously discussed deformation of $\angle C_1N_1Li$ bond angle appears to have little impact on the stability of the optimized geometry, as evidenced by the 0.4 kcal/mol relative energy of the 6-31G(d) and 6-31(+LiX)G(d) structures, both of which predict a nearly linear $\angle C_1N_1Li$ bond angle.

PM3 predicts the highest relative B3LYP/6-31+G(d) energy of the DEVJAP study. Due to the very high average MUD exhibited by this method (0.037 Å), the high relative energy is not unexpected. It is quite surprising, however, that both B3LYP/3-21G and B3LYP/Midi! exhibit unexpectedly low relative energy (4.3 and 3.5 kcal/mol, respectively) given the high error associated with bond length prediction. The structures optimized by the Midi!+ basis set prove to be considerably more accurate than the 3-21G structures, predicting relative B3LYP/6-31+G(d) single point energies of approximately 2 kcal/mol.

B3LYP/6-31G(d) predicts a highly accurate structure with low relative energy, but the neglect of electron correlation in the HF/6-31G(d) model results in an optimized geometry with a much higher energetic penalty. The addition of diffuse functions to lithium and heteroatoms seemingly offers no increase in accuracy, but the extensive addition of these functions results in a geometry exhibiting identical energetic matching of the target structure.

<u>Geometry</u>	<u>Relative energy (kcal/mol)</u>	<u>$\Delta v(\text{CN})$ (cm^{-1})</u>
PM3	13.4	102
B3LYP/3-21G	4.3	14
MPWLYP/3-21G	10.2	-69
B3LYP/Midi!	3.5	26
*B3LYP/Midi!+	2.1	-2
*MPW1PW91/Midi!+	1.8	33
B3LYP/6-31G(d)	0.4	11
HF/6-31G(d)	6.2	195
B3LYP/6-31(+LiX)G(d)	0.4	2
B3LYP/6-31'+G(d)	0.0	2

Table 4.6 Single point B3LYP/6-31+G(d)//geometry energies and unscaled $\Delta v(\text{CN})$ for optimized DEVJAP geometries; *Optimizations completed with relaxed convergence criteria

In order to satisfy the requirement of a potential alternative computational protocol to replace B3LYP/6-31+G(d), the test functional/basis set must also be able to accurately predict $\nu(\text{CN})$, as this is very important to other areas of our research. In addition to relative energies, Table 4.6 also shows calculated $\Delta\nu(\text{CN})$ for each geometry relative to the target structure.

These data clearly show that the variability of predicted $\Delta\nu(\text{CN})$ is high and relatively few conclusions can be definitively drawn. Most importantly, however, the 6-31+G(d)-derived custom basis sets exhibit very high accuracy in this prediction, whereas the ab initio method, HF/6-31G(d), (with its inherent neglect of electron correlation) predicts $\nu(\text{CN})$ farthest from our so-called accurate model. The Huzinaga basis sets, Midi! and Midi!+, mostly fail in the prediction of $\nu(\text{CN})$, calculating the frequency within 33 cm^{-1} . However, it is interesting to note that excellent accuracy is attained for the B3LYP/Midi!+ calculation ($\Delta\nu(\text{CN})$: -2 cm^{-1}). The structures optimized with the 3-21G basis set show considerable variation in their respective calculations of $\nu(\text{CN})$, with the most accurate value predicted by the B3LYP density functional ($\Delta\nu(\text{CN})$: 14 cm^{-1}). Examination of the $\nu(\text{CN})$ for each of the optimized geometries leads to an interesting observation. For each of the basis sets which include a means for a direct comparison of B3LYP and an alternative density functional, B3LYP uniformly predicts a much more accurate result. This suggests that the magnitude of the calculated $\nu(\text{CN})$ is in large part due to the chosen density functional, and is somewhat independent upon basis set.

4.4.1.4 DEVJAP Summary

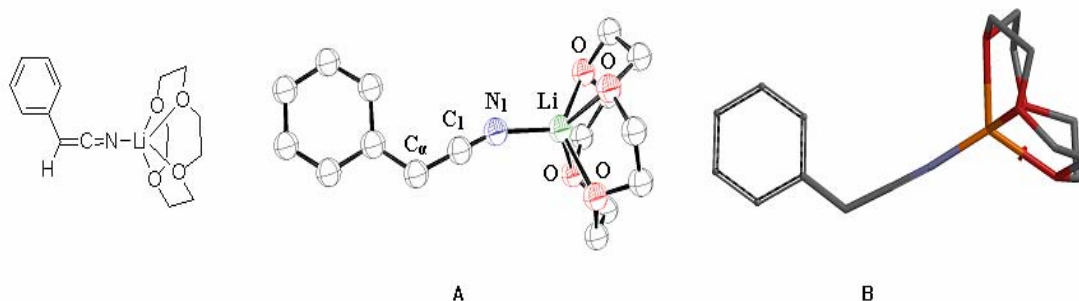
Table 4.7 summarizes the average MUD, total RMS difference, relative energy, and relative frequency of the nitrile stretch for each tested functional/basis set combination. Optimizations over several basis sets in effort to approximate structural and energetic parameters seen at B3LYP/6-31+G(d) clearly show basis set dependence. Over all comparative assessments, B3LYP/6-31'+G(d) provides the best matching of structure (average MUD: 0.001 Å; RMS: 0.015 Å), energy (relative E: 0.0 kcal/mol), and frequency of the nitrile stretch ($\Delta\nu(\text{CN})$: 2 cm^{-1}) for the DEVJAP model. While some calculations are shown to exhibit high accuracy towards calculation of the $\nu(\text{CN})$ stretch, they fail in other key respects—namely geometric considerations. For example, B3LYP/Midi!+ predicts $\nu(\text{CN})$ within 2 cm^{-1} , but shows marginal accuracy in bond length prediction and critically fails in the RMS deviation analysis of molecular shape.

<i>Geometry</i>	<i>Average MUD (Å)</i>	<i>Total RMS (Å)</i>	<i>Relative E (kcal/mol)</i>	<i>Relative $\nu(\text{CN})$ (cm^{-1})</i>
PM3	0.037 ± 0.020	1.804	13.4	102
B3LYP/3-21G	0.026 ± 0.010	1.448	4.3	14
MPWLYP/3-21G	0.027 ± 0.009	1.730	10.2	-69
B3LYP/Midi!	0.023 ± 0.005	1.589	3.45	26
*B3LYP/Midi!+	0.012 ± 0.005	1.804	2.1	-2
*MPW1PW91/Midi!	0.013 ± 0.006	1.779	1.8	33
B3LYP/6-31G(d)	0.005 ± 0.003	1.382	0.4	11
HF/6-31G(d)	0.013 ± 0.004	1.182	6.2	195
B3LYP/6-31(+LiX)G(d)	0.005 ± 0.004	1.416	0.4	2
B3LYP/6-31'+G(d)	0.001 ± 0.001	0.015	0.0	2

Table 4.7 Summary of analytical methods comparing DEVJAP test methods/basis sets to B3LYP/6-31+G(d); *Optimizations completed with relaxed convergence criteria

It is not surprising that the relative energy of the optimized structure depends greatly upon the reliability of the test basis set to duplicate structural parameters. The observation that the flat potential energy surface of the optimizations allows for energetic stability with modest structural deviation suggests that bond length plays a key role in structural stability. Most clearly, this dependence can be seen in the comparison of PM3 and B3LYP/Midi!+. Both models predict structures with total a RMS difference of 1.804 Å, but also exhibit highly varying relative energies (13.4 and 2.1 kcal/mol, respectively). An examination of the average MUD for these methods shows PM3 to exhibit the worst average bond length prediction of the series, whereas B3LYP/Midi!+ predicts significantly more accurate bond lengths (0.037 and 0.012 Å MUD, respectively). This observation, however, does not imply that RMS deviations are inconsequential to the determination of total energy. To reinforce this point, it can be seen that both B3LYP/3-21G and MPWLYP/3-21G exhibit average MUD around 0.026 Å with similar tolerances of standard deviation. The substantial difference in relative energy (4.3 and 10.2 kcal/mol, respectively) is reflected in the comparison of RMS deviations. While both calculations predict structures that exhibit very large error, B3LYP/3-21G shows slight improvement in RMS deviation over the MPW1PW91/3-21G structure. These examples show that the relative energies of the calculated structures are a complex result of structural bond length changes and alterations in molecular structure.

4.4.2 DEVJUI



Structure	Bond lengths (Å)				Bond angle (°)
	Li-N_1	Li-O		$\text{C}_1\text{-N}_1$	$\angle \text{C}_1\text{N}_1\text{Li}$
X-ray	1.985	2.117, 2.149, 2.082, 2.124	1.163	1.399	176.1
B3LYP/6-31+G(d)	1.973	2.197, 2.205, 2.195, 2.209	1.183	1.381	132.9

Figure 4.2 DEVJUI (repeated)

4.4.2.1 Mean bond difference

Much like the case for DEVJAP, the MUD/MSD bond length analysis of DEVJUI indicates basis set dependence for the accuracy of calculated bond lengths (Table 4.8). As we have already shown, modest accuracy in the prediction of C-H bond lengths is achievable at low levels of theory. For the DEVJUI study, typical short bond lengths are generally predicted within 0.002 Å of the target structure. As was the case for DEVJAP, both PM3 and HF/6-31G(d) exhibit the largest error in the estimation of short bond lengths (MUD 0.009 Å). As we consider the intermediate bond lengths, we begin to see basis set dependence. Calculated error decreases as the size of the basis set increases. These trends are amplified in the comparison of long bonds.

The primary difference in the results of the two studies relates to PM3. For DEVJAP, PM3 is among the worst methods/basis sets for bond length prediction, but proves to be one of the better models for DEVJUI. It is interesting to note the particular bonding for which these errors exist. The designated 'long bonds' of DEVJUI are comprised of four Li-O bonds (coordination of lithium to 12-crown-4 ether) and one Li-N bond (from the nitrile), whereas DEVJAP contains three Li-N bonds (two bonds to coordinated sparteine, one from the nitrile) and one Li-O bond (from the solvating THF). The average long bond MUD for DEVJAP (as reported in Table 4.4) is 0.088 Å, but the single Li-O bond exhibits an unsigned difference of only 0.007 Å. Thus, the majority of the reported error stems from Li-N bonds. In the case of DEVJUI, a much smaller long bond MUD is observed (0.017 Å). With the dramatic decrease in MUD from DEVJAP to DEVJUI, the logical conclusion is that the PM3 method is better suited to handle Li-O connectivity than Li-N connectivity.

<u>Geometry</u>	<i>Mean Unsigned Difference ($\text{\AA}$)</i>			
	<i>Long bonds</i>	<i>Intermediate bonds</i>	<i>Short bonds</i>	<i>Average MUD</i>
PM3	0.017 $\pm$ 0.004	0.010 $\pm$ 0.004	0.009 $\pm$ 0.004	0.012 $\pm$ 0.002
B3LYP/3-21G	0.098 $\pm$ 0.023	0.018 $\pm$ 0.020	0.003 $\pm$ 0.001	0.040 $\pm$ 0.010
MPWLYP/3-21G	0.084 $\pm$ 0.020	0.031 $\pm$ 0.027	0.005 $\pm$ 0.001	0.040 $\pm$ 0.011
B3LYP/Midi!	0.122 $\pm$ 0.043	0.010 $\pm$ 0.007	0.002 $\pm$ 0.001	0.045 $\pm$ 0.015
B3LYP/Midi!+	0.056 $\pm$ 0.040	0.011 $\pm$ 0.010	0.002 $\pm$ 0.001	0.023 $\pm$ 0.014
MPW1PW91/ Midi!+	0.066 $\pm$ 0.051	0.006 $\pm$ 0.006	0.002 $\pm$ 0.001	0.025 $\pm$ 0.017
B3LYP/6-31G(d)	0.008 $\pm$ 0.002	0.002 $\pm$ 0.001	0.000 $\pm$ 0.000	0.003 $\pm$ 0.001
HF/6-31G(d)	0.017 $\pm$ 0.004	0.010 $\pm$ 0.004	0.009 $\pm$ 0.004	0.012 $\pm$ 0.002
B3LYP/ 6-31(+LiX)G(d)	0.007 $\pm$ 0.003	0.001 $\pm$ 0.001	0.000 $\pm$ 0.000	0.003 $\pm$ 0.001
B3LYP/ 6-31'+G(d)	0.001 $\pm$ 0.001	0.000 $\pm$ 0.000	0.000 $\pm$ 0.000	0.001 $\pm$ 0.000
<u>Geometry</u>	<i>Mean Signed Difference ($\text{\AA}$)</i>			
	<i>Long bonds</i>	<i>Intermediate bonds</i>	<i>Short bonds</i>	<i>Average MSD</i>
PM3	-0.017 $\pm$ 0.004	-0.001 $\pm$ 0.011	0.009 $\pm$ 0.004	-0.003 $\pm$ 0.004
B3LYP/3-21G	-0.076 $\pm$ 0.067	0.017 $\pm$ 0.021	-0.003 $\pm$ 0.001	-0.021 $\pm$ 0.023
MPWLYP/3-21G	-0.060 $\pm$ 0.063	0.031 $\pm$ 0.027	0.005 $\pm$ 0.001	-0.008 $\pm$ 0.023
B3LYP/Midi!	-0.096 $\pm$ 0.087	0.008 $\pm$ 0.009	0.002 $\pm$ 0.001	-0.029 $\pm$ 0.029
B3LYP/Midi!+	-0.015 $\pm$ 0.067	0.011 $\pm$ 0.010	0.002 $\pm$ 0.001	-0.001 $\pm$ 0.023
MPW1PW91/ Midi!+	-0.021 $\pm$ 0.080	0.004 $\pm$ 0.007	0.002 $\pm$ 0.001	-0.005 $\pm$ 0.027
B3LYP/6-31G(d)	-0.004 $\pm$ 0.007	-0.001 $\pm$ 0.001	0.000 $\pm$ 0.000	-0.002 $\pm$ 0.002
HF/6-31G(d)	-0.017 $\pm$ 0.004	-0.001 $\pm$ 0.011	0.009 $\pm$ 0.004	-0.003 $\pm$ 0.004
B3LYP/ 6-31(+LiX)G(d)	0.005 $\pm$ 0.006	-0.001 $\pm$ 0.002	0.000 $\pm$ 0.000	0.001 $\pm$ 0.002
B3LYP/ 6-31'+G(d)	-0.001 $\pm$ 0.001	0.000 $\pm$ 0.000	0.000 $\pm$ 0.000	0.000 $\pm$ 0.000

Table 4.8 Mean unsigned/signed error of bond lengths for DEVJUI relative to B3LYP/6-31+G(d)

Closer examination of the MUD for the DEVJUI geometries clearly illustrates the superior performance of PM3 over the small basis sets 3-21G, Midi!, and Midi!+ (Chart 4.4). The structures optimized by these small basis sets project the greatest error in average MUD, the majority of which stems from error in long bond length prediction.

A sizeable increase in the accuracy of these bond lengths is realized through the use of the larger basis sets, starting with 6-31G(d).

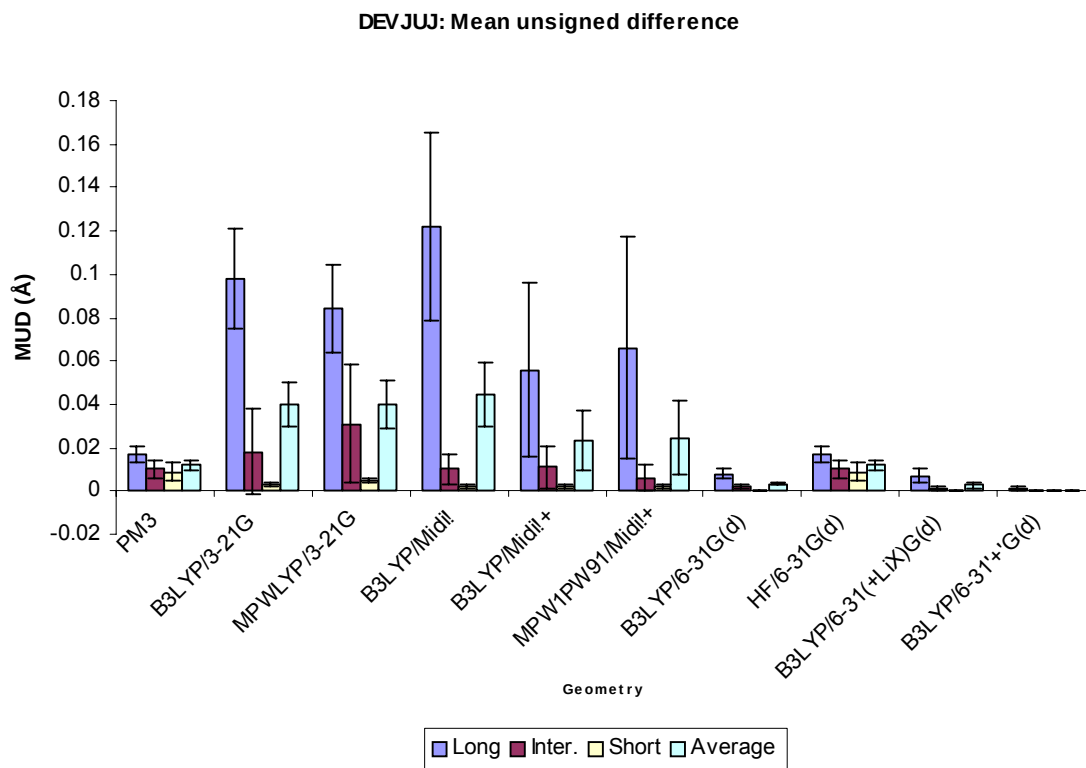


Chart 4.4 Mean unsigned differences in bond length for DEVJUU relative to B3LYP/6-31+G(d)

The MSD analysis for DEVJUU predictably shows similar trends over the tested basis sets/methods (Chart 4.5). PM3 exhibits superior accuracy over the small basis sets, while the larger basis sets predict error near zero.

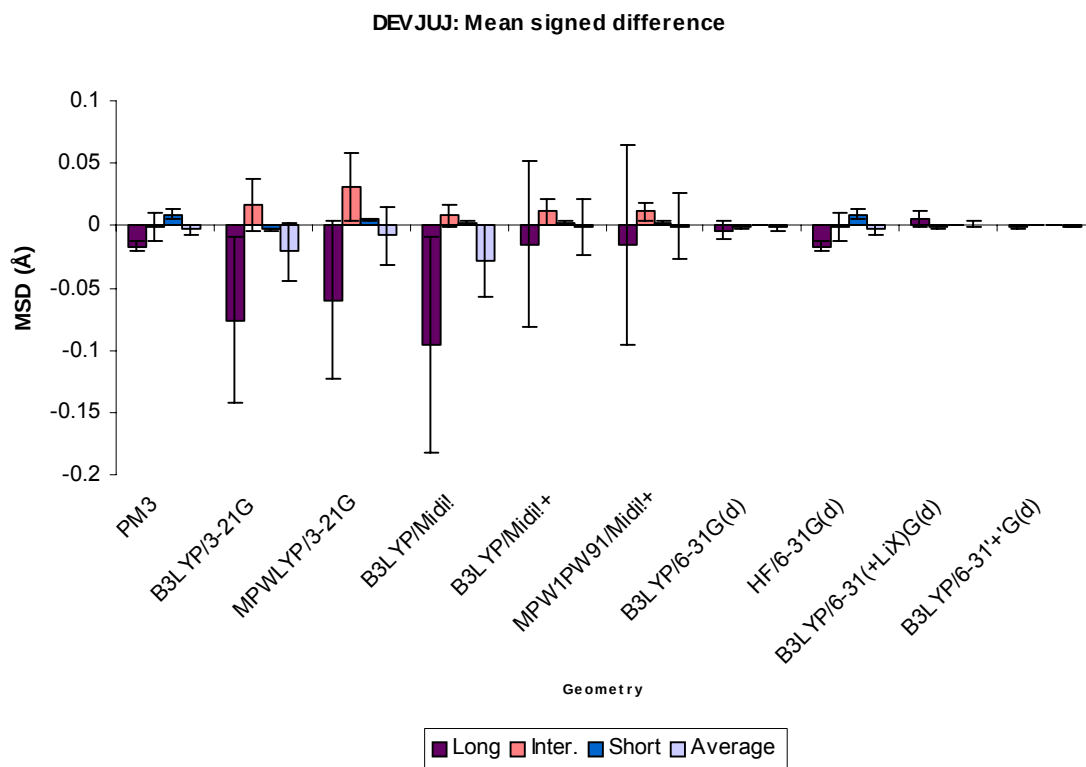


Chart 4.5 Mean signed differences in bond length for DEVJUI relative to B3LYP/6-31+G(d)

There is once again little to distinguish the performance of the smaller basis sets. The structures optimized at 3-21G and Midi! exhibit average MUD greater than 0.040 Å. Average error is seemingly reduced upon expansion of the Midi! basis set to Midi!+ (0.023 - 0.025 Å), but within statistical error, no definitive conclusions can be drawn. The MSD analysis shows 3-21G and Midi! to underestimate the long bonds of DEVJUI relative to the target method. The larger Midi!+ basis set shows these bonds to be only slightly underestimated, but the large standard deviation indicates inconsistency in these predictions. For each of the smaller basis sets, intermediate bond lengths are overestimated in comparison to B3LYP/6-31+G(d) (0.008 - 0.031 Å).

The trends seen within the 6-31G(d) basis set series are indeed identical to those seen with DEVJAP, with the exception of the underestimation of long bond lengths by the Hartree-Fock method. The structure optimized at B3LYP/6-31G(d) shows superior bond length prediction over all bond length ranges in comparison to HF/6-31G(d). As an example, the ab initio optimized structure exhibits an average MUD of 0.012 Å compared to 0.003 Å for B3LYP/6-31G(d). These relative failures of HF/6-31G(d) reinforce the importance of electron correlation for the accurate modeling of these organolithium systems.

The structures obtained from the addition of diffuse functions to select atoms are also similar to those seen in the DEVJAP study. The B3LYP/6-31(+LiX) basis set gives both average and individual MUD nearly identical to the B3LYP/6-31G(d) method, while B3LYP/6-31'+G(d) shows almost no deviation from the bond lengths seen at B3LYP/6-31+G(d) (average MUD 0.001 Å). These results strongly suggest that the addition of diffuse functions throughout the resonance-stabilized structure is key to accurately modeling the structural parameters seen by our target model.

4.4.2.2 RMS

Table 4.9 and Chart 4.6 report the RMS deviations for each optimized structure relative to the B3LYP/6-31+G(d) target geometry. In the DEVJAP example, RMS was greatly affected by a geometric change, specifically a change about the $\angle C_1N_1Li$ bond angle seen only with the addition of diffuse functions to all atoms involved in the resonance stabilization. A similar effect is observed in the case of DEVJUI. Whereas in

the case of DEVJAP, B3LYP/6-31+G(d) predicted a markedly non-linear $\angle C_1N_1Li$ bond angle, the reverse is true for the DEVJUI study. The X-ray structure for DEVJUI shows a 158.7° $\angle C_1N_1Li$ bond angle, as opposed to a nearly linear orientation predicted by our target process. The basis sets which predict a linear $\angle C_1N_1Li$ bond angle, uniformly exhibit small RMS deviations, with the customized 6-31+G(d) derivatives excelling among them.

<u>Geometry</u>	<u>RMS ($\text{\AA}$)</u>			<u>$\angle C_1N_1Li(^{\circ})$</u>
	<u>Backbone</u>	<u>Non-H</u>	<u>Total</u>	
PM3	0.203	0.214	0.265	179.9
B3LYP/3-21G	0.931	1.145	1.331	127.1
MPWLYP/3-21G	0.955	1.156	1.335	126.1
B3LYP/MidiX	1.002	1.224	1.444	112.4
B3LYP/MidiX+	1.125	1.300	1.577	111.2
MPW1PW91/MidiX+	1.174	1.370	1.661	109.7
B3LYP/6-31G(d)	0.033	0.033	0.040	172.2
HF/6-31G(d)	0.060	0.077	0.093	172.5
B3LYP/6-31(+LiX)G(d)	0.020	0.023	0.023	173.1
B3LYP/6-31'+G(d)	0.010	0.012	0.015	174.5
B3LYP/6-31+G(d)	0.000	0.000	0.000	174.8

Table 4.9 RMS deviations as a function of method/basis set for DEVJUI relative to B3LYP/6-31+G(d)

The inherent flexibility of the monomeric DEVJAP and DEVJUI molecules and the flat nature of the potential energy surface allow for the possibility of considerable geometric variability about the $\angle C_1N_1Li$ bond angle. In the case of DEVJAP, the relationship between $\angle C_1N_1Li$ bond angle and diffuse functions is clearly defined. In this case, however, the requirement of extensive diffuse functions applied to all second-row atoms does not hold true. Both the DFT and ab initio functionals in conjunction with 6-31G(d) exhibit excellent agreement between the test and target basis sets. These data

seem to indicate that correct modeling of bond angle is, in this case, dependent upon the size of the basis set; the obvious exception to this rule being PM3.

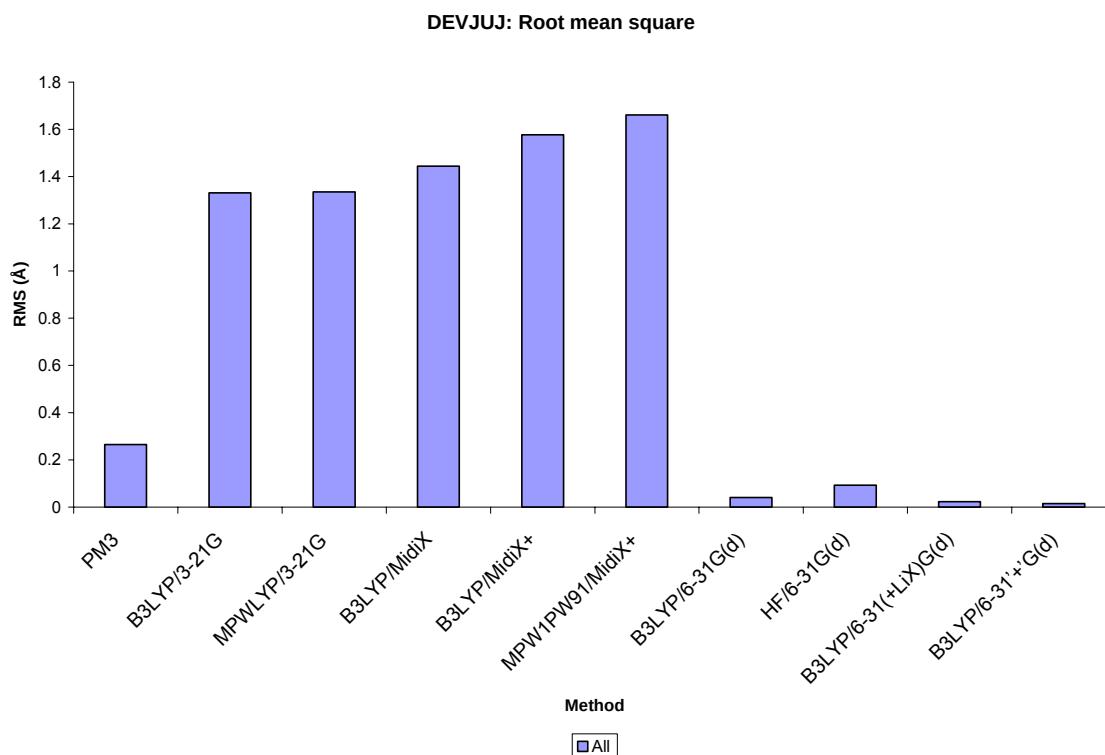


Chart 4.6 Total RMS deviations as a function of method/basis set for DEVJUU relative to B3LYP/6-31+G(d)

4.4.2.3 Energetics and frequencies

Table 4.10 details the energetic penalty associated with each optimized geometry. As was the case for DEVJAP, the B3LYP/6-31+G(d) single point energy calculated for the B3LYP/6-31'+G(d) geometry most closely matches the energy of the target structure (relative energy: 0.0 kcal/mol). Also performing very well are B3LYP/6-31G(d) and B3LYP/6-31(+LiX)G(d), both of which show a relative energy of 0.1 kcal/mol. The structures exhibiting the highest relative energy are those optimized at 3-21G (>7.0

kcal/mol), the largest of which results from the MPWLYP functional (13.5 kcal/mol). The analysis of DEVJAP led us to the conclusion that relative energy was highly dependent upon bond length deviation. Here we also see that the structures boasting the highest relative B3LYP/6-31+G(d) energies are among the structures with the highest average MUD.

The structure optimized at B3LYP/Midi! exhibits marginal accuracy (4.5 kcal/mol) but the larger basis set resulting from the expansion to Midi!+ reduces that energetic penalty to <2.5 kcal/mol. It should be noted that this reduction in energetic penalty is accompanied by a decrease in average MUD from 0.045 Å to 0.023 Å and 0.025 Å for the B3LYP and MPW1PW91 functionals, respectively.

<u>Geometry</u>	<u>Relative energy (kcal/mol)</u>	<u>$\Delta v(\text{CN})$ (cm^{-1})</u>
PM3	5.7	69
B3LYP/3-21G	7.1	-6
MPWLYP/3-21G	13.5	-89
B3LYP/Midi!	4.5	3
B3LYP/Midi!+	2.4	-54
MPW1PW91/Midi!+	2.2	-20
B3LYP/6-31G(d)	0.1	8
HF/6-31G(d)	5.0	161
B3LYP/6-31(+LiX)G(d)	0.1	-4
B3LYP/6-31'+G(d)	0.0	1

Table 4.10 Single point B3LYP/6-31+G(d)//geometry energies for DEVJUI and unscaled $\Delta v(\text{CN})$ of the optimized DEVJUI geometries relative to B3LYP/6-31+G(d)

When comparing the frequency of the nitrile stretch of the test functionals/basis sets versus that of the target basis set, similar trends to those seen with DEVJAP are observed (Table 4.10). Once again, the customized B3LYP/6-31'+G(d) calculation most

closely approximates the $\nu(\text{CN})$ predicted by B3LYP/6-31+G(d) ($\Delta\nu(\text{CN})$: 1 cm^{-1}). HF/6-31G(d) exhibits the worst prediction for the simulated IR stretch. Perhaps surprisingly, the Midi! basis set shows very good agreement with the “accurate” model ($\Delta\nu(\text{CN})$: 3 cm^{-1}), but expansion of the basis set to include diffuse functions does not improve the calculated CN stretch. In fact, B3LYP/3-21G predicts a much closer $\nu(\text{CN})$ than either of the Midi!+ calculations, contrary to the observations gathered from the DEVJAP analysis.

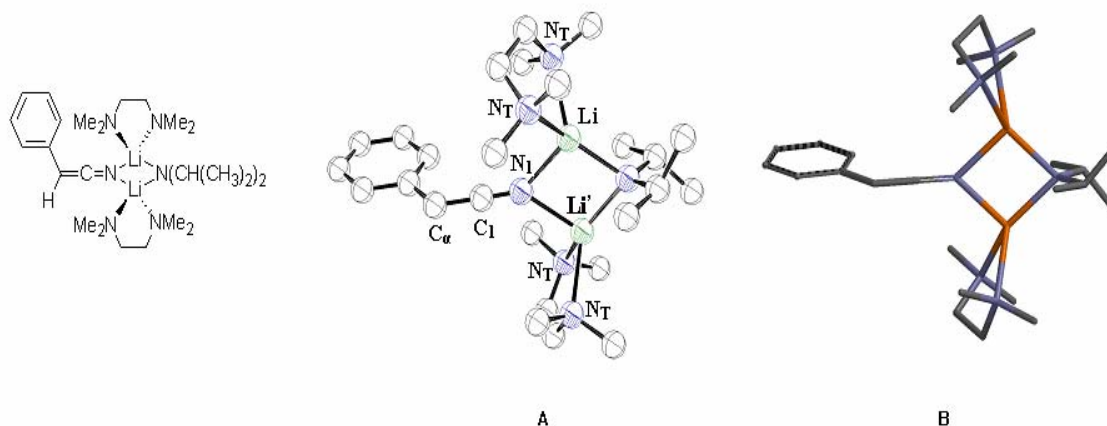
4.4.2.4 DEVJUI Summary

Table 4.11 summarizes the structural and energetic analyses of DEVJUI over the test methods/basis sets. Overall, the best performing models are B3LYP/6-31'+G(d), B3LYP/6-31(+LiX)G(d), and B3LYP/6-31G(d). Each of these protocols boast small deviations in bond length (average MUD ≤ 0.003 Å), negligible relative energy (≤ 0.1 kcal/mol), and highly accurate prediction of the frequency of the nitrile stretch ($\Delta\nu(\text{CN})$: 8 cm^{-1}). Of these three, the 6-31'+G(d) basis set clearly outperforms the others. B3LYP/Midi! and B3LYP/3-21G exhibit modest accuracy in the prediction of $\nu(\text{CN})$ ($\Delta\nu(\text{CN})$: 3 and 6, respectively), but fail to accurately predict the structural properties seen at the larger basis set (1.444 and 1.331 Å RMS). The ab initio method, HF/6-31G(d), performs moderately well in the prediction of structure, but fails to properly account for the $\nu(\text{CN})$ and also exhibits a relatively high B3LYP/6-31+G(d) energy.

<i>Geometry</i>	<i>Average MUD (Å)</i>	<i>Total RMS (Å)</i>	<i>Relative E (kcal/mol)</i>	<i>Relative $\nu(\text{CN})$ (cm^{-1})</i>
PM3	0.012 ± 0.002	0.265	5.7	69
B3LYP/3-21G	0.040 ± 0.010	1.331	7.1	-6
MPWLYP/3-21G	0.040 ± 0.011	0.132	13.5	-89
B3LYP/Midi!	0.045 ± 0.015	1.444	4.5	3
B3LYP/Midi!+	0.023 ± 0.014	1.577	2.4	-54
MPW1PW91/Midi!+	0.025 ± 0.017	1.661	2.2	-20
B3LYP/6-31G(d)	0.003 ± 0.001	0.040	0.1	8
HF/6-31G(d)	0.012 ± 0.002	0.093	5.0	161
B3LYP/6-31(+LiX)G(d)	0.003 ± 0.001	0.027	0.1	-4
B3LYP/6-31'+G(d)	0.001 ± 0.000	0.015	0.0	1

Table 4.11 Summary of analytical methods comparing DEVJUI test methods/basis sets to B3LYP/6-31+G(d)

4.4.3 JAYFIY



<i>Structure</i>	<i>Bond lengths (Å)</i>				<i>Bond angle (°)</i>
	<i>Li-N₁</i>	<i>Li-N_{TMEDA}</i>	<i>C₁-N₁</i>	<i>C_α-C₁</i>	<i>∠C₁N₁Li</i>
X-ray	2.092	2.201, 2.207, 2.320, 2.347	1.173	1.383	139.3
B3LYP/6-31+G(d)	2.017	2.339, 2.371, 2.386, 2.402	1.196	1.363	139.1

Figure 4.3 JAYFIY (repeated)

4.4.3.1 Mean bond difference

We expand our comparative analyses to include dimeric species, in this case a bis-TMEDA solvated, LDA/PhCHCNLi heterodimer. Table 4.12 shows the individual and average MUD/MSD analysis for JAYFIY.

<u>Geometry</u>	<i>Mean Unsigned Difference ($\text{\AA}$)</i>			
	<i>Long bonds</i>	<i>Intermediate bonds</i>	<i>Short bonds</i>	<i>Average MUD</i>
PM3	0.097 ± 0.071	0.019 ± 0.010	0.009 ± 0.006	0.042 ± 0.024
B3LYP/3-21G	0.063 ± 0.058	0.015 ± 0.012	0.002 ± 0.001	0.027 ± 0.020
MPWLYP/3-21G	0.059 ± 0.058	0.028 ± 0.016	0.005 ± 0.001	0.031 ± 0.020
B3LYP/Midi!	0.065 ± 0.052	0.010 ± 0.005	0.002 ± 0.001	0.026 ± 0.017
B3LYP/Midi!+	0.065 ± 0.052	0.010 ± 0.005	0.002 ± 0.001	0.026 ± 0.017
MPW1PW91/ Midi!+	0.045 ± 0.034	0.003 ± 0.002	0.002 ± 0.001	0.017 ± 0.011
B3LYP/6-31G(d)	0.014 ± 0.010	0.001 ± 0.001	0.000 ± 0.000	0.005 ± 0.003
HF/6-31G(d)	0.021 ± 0.009	0.011 ± 0.004	0.012 ± 0.001	0.015 ± 0.003
B3LYP/ 6-31(+LiX)G(d)	0.011 ± 0.010	0.001 ± 0.001	0.000 ± 0.000	0.004 ± 0.003
B3LYP/ 6-31'+G(d)	0.009 ± 0.007	0.000 ± 0.000	0.000 ± 0.000	0.003 ± 0.002
<u>Geometry</u>	<i>Mean Signed Difference ($\text{\AA}$)</i>			
	<i>Long bonds</i>	<i>Intermediate bonds</i>	<i>Short bonds</i>	<i>Average MSD</i>
PM3	-0.017 ± 0.119	0.010 ± 0.019	0.008 ± 0.007	0.000 ± 0.040
B3LYP/3-21G	-0.053 ± 0.067	0.014 ± 0.013	-0.002 ± 0.001	-0.014 ± 0.023
MPWLYP/3-21G	-0.042 ± 0.071	0.028 ± 0.016	0.005 ± 0.001	-0.003 ± 0.024
B3LYP/Midi!	-0.064 ± 0.053	0.008 ± 0.008	0.002 ± 0.001	-0.018 ± 0.018
B3LYP/Midi!+	-0.064 ± 0.053	0.008 ± 0.008	0.002 ± 0.001	-0.018 ± 0.018
MPW1PW91/ Midi!+	-0.027 ± 0.049	0.001 ± 0.004	0.002 ± 0.001	-0.008 ± 0.016
B3LYP/6-31G(d)	-0.004 ± 0.053	-0.001 ± 0.001	0.000 ± 0.000	-0.002 ± 0.006
HF/6-31G(d)	0.021 ± 0.009	-0.011 ± 0.005	-0.012 ± 0.001	-0.001 ± 0.003
B3LYP/ 6-31(+LiX)G(d)	-0.009 ± 0.012	-0.001 ± 0.001	0.000 ± 0.000	-0.003 ± 0.004
B3LYP/ 6-31'+G(d)	-0.003 ± 0.011	0.000 ± 0.000	0.000 ± 0.000	-0.001 ± 0.004

Table 4.12 Mean unsigned/signed error of bond lengths for JAYFIY relative to B3LYP/6-31+G(d)

PM3 exhibits the highest average MUD (0.042 Å) and also the highest long bond MUD (0.097 Å). Interestingly, the MSD analysis tells us that these long bonds are underestimated by an average of 0.017 Å. It is important to note that for this dimeric species that Li-Li interatomic distance is included in the ‘long-bond’ categorical assessment, a detail that plays an important role in the analysis of the MUD/MSD for long bonds. In the case of JAYFIY, the Li-Li interatomic distance is overestimated by 0.240 Å relative to the B3LYP/6-31+G(d) optimized geometry. This elongation leads to a deformation within the (Li-N)₂ cyclic structure. Our analysis of DEVJAP indicated that PM3 overestimated the predicted Li-N bond lengths to the coordinated sparteine moiety. In this model, bonds stemming from lithium to the exocyclic TMEDA nitrogen atoms are actually underestimated by 0.126 Å, whereas lithium contacts to the cyclic atoms are overestimated by 0.059 Å. These data reveal that PM3 is not particularly well suited to describing the geometry of dimeric species principally due to the failure of the model to adequately predict Li-Li interatomic distances.

As we have shown in for both DEVJAP and DEVJUI, the smaller basis sets are nearly indistinguishable within standard deviation. This fact is illustrated in Chart 4.7. Each of the structures optimized at 3-21G, Midi!, and Midi!+ predict structures with an average MUD greater than 0.026 Å and long bond MUD greater than 0.059 Å. A substantial increase in accuracy is achieved with the use of the larger basis sets, first observed with the use of 6-31G(d) and sustained through the use of the customized 6-31+G(d) derivatives.

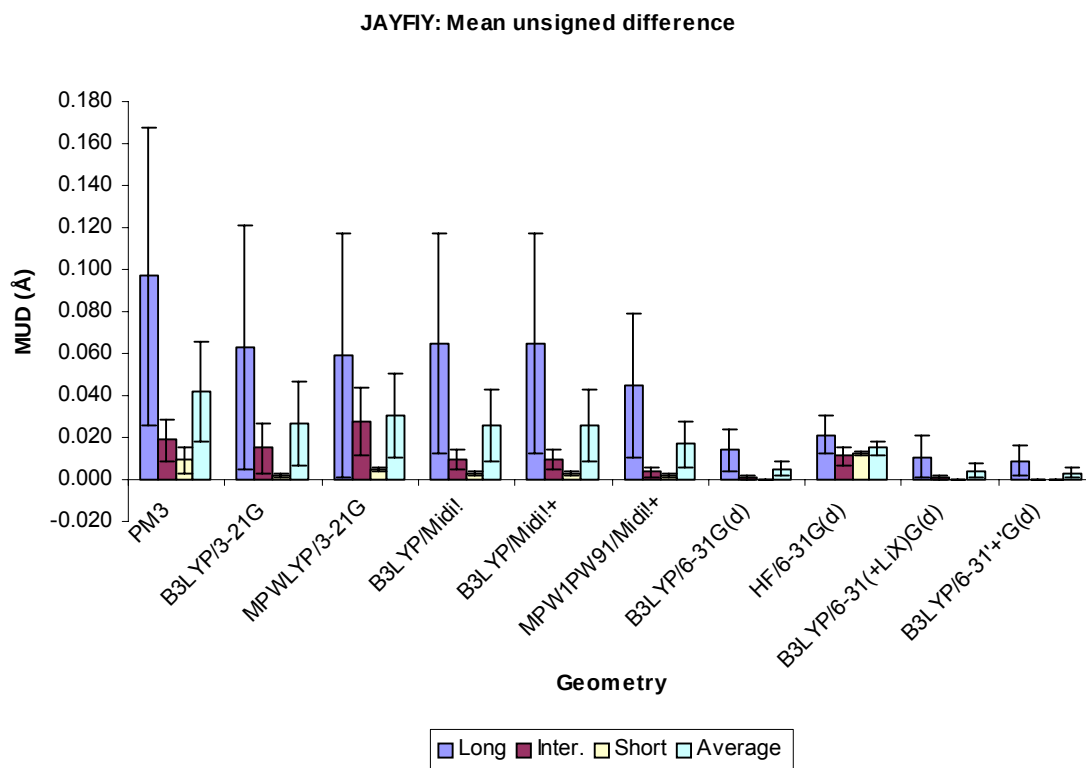


Chart 4.7 Mean unsigned differences in bond length for JAYFIY relative to B3LYP/6-31+G(d)

These trends are echoed in the MSD analysis (Chart 4.8). Each of the smaller basis sets (excluding PM3) show a significant average underestimation of long bond lengths (greater than 0.042 Å), but within tolerances of standard deviation no specific generalizations can be made to differentiate the individual sets. As we have previously noted, error approaches zero as the size of the basis set increases.

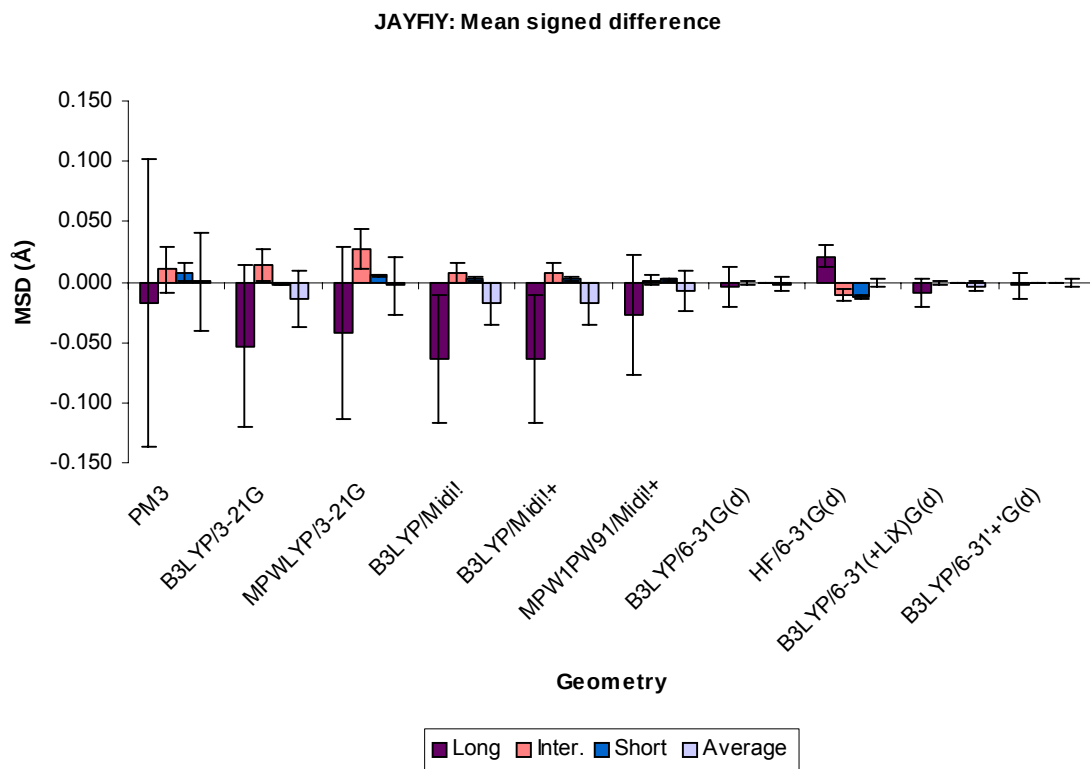


Chart 4.8 Mean signed differences in bond length for JAYFIY relative to B3LYP/6-31+G(d)

As we examine the structures optimized at 3-21G, we see a notable decrease in the long bond MUD attributed to the decrease in error associated with the Li-Li interatomic distance. The 3-21G geometries report Li-Li MSD error of 0.014 Å (for B3LYP) and 0.020 Å (for MPWLYP)—a substantial improvement over PM3. The long bond error for each of the 3-21G optimized geometries is net underestimation, and due to the decreased inaccuracy in the Li-Li distances, the standard deviations of the reported MSD are significantly smaller.

The Huzinaga basis sets yield little to no improvement in the estimation of long bond lengths over the 3-21G structures (MUD: 0.045-0.065 Å). Midi!, however, does

appear to predict intermediate bonds to a higher degree of accuracy (with smaller standard deviation) than the 3-21G structures. Expansion of the basis set to include diffuse functions does offer a marginal improvement, but only with respect to the MPW1PW91 density functional. The B3LYP/Midi!+ predicts structural parameters identical to those calculated at the cheaper B3LYP/Midi! basis set.

The use of B3LYP/6-31G(d) offers greatly increased accuracy for the system, as illustrated in Charts 4.7 and 4.8. The structure calculated at HF/6-31G(d) exhibits larger error for each of the bond length ranges. HF/6-31G(d) once again overestimates all Li-N bonds due to the neglect of electron correlation. As we apply the customized 6-31+G(d)-derived basis sets, the greatest accuracy is observed. The addition of diffuse functions to only the lithium and nitrogen atoms offers a negligible decrease in average bond MUD over 6-31G(d). The Li-Li interatomic distance is reduced to an error of only 0.002 Å, indicating the necessity of diffuse functions on the lithium atom to ensure proper structural assignments. As we increase diffuse functions to other atoms within the resonance stabilized structure, the errors are further minimized as evidenced by an average MUD of 0.003 Å.

4.4.3.2 RMS

An important consequence of the structural rigidity of dimeric species is a substantial improvement in RMS deviations analysis. Due to the structural constraints imposed by the formation of the cyclic dimer, there are less degrees of freedom associated with the bond angles. The direct effect of this higher rigidity can clearly be

seen in Table 4.13 and Chart 4.9. All RMS deviations are substantially smaller than those seen from either of the monomeric structures used in this analysis.

<u>Geometry</u>	<u>RMS (Å)</u>		
	<u>Backbone</u>	<u>Non-H</u>	<u>Total</u>
PM3	0.156	0.267	0.397
B3LYP/3-21G	0.164	0.288	0.333
MPWLYP/3-21G	0.182	0.360	0.459
B3LYP/Midi!	0.231	0.374	0.434
B3LYP/Midi!+	0.231	0.374	0.435
MPW1PW91/Midi!+	0.159	0.212	0.242
B3LYP/6-31G(d)	0.093	0.158	0.185
HF/6-31G(d)	0.044	0.059	0.071
B3LYP/6-31(+LiX)G(d)	0.074	0.131	0.156
B3LYP/6-31'+G(d)	0.031	0.040	0.047

Table 4.13 RMS deviations for JAYFIY relative to B3LYP/6-31+G(d)

The difficulties encountered in differentiating the small basis sets in the bond length analysis are mirrored in this RMS analysis of molecular shape. Each of the structures optimized at PM3, 3-21G, Midi!, and Midi!+ exhibit RMS deviations greater than 0.3 Å. While these deviations are considerably smaller than those measured for the monomeric species, they do represent the largest errors of the JAYFIY study. Within this series, B3LYP/3-21G shows the smallest error (0.333 Å), while MPWLYP/3-21G predicts the largest error (0.459 Å).

Somewhat surprising is the excellent performance of the HF/6-31G(d) method. As described in Section 2.4.3.1, the Hartree-Fock method failed in comparison to B3LYP/6-31G(d) for bond length matching, but in terms of spatial arrangement of the individual atoms, it excels with a total RMS deviation of only 0.071 Å. The B3LYP/6-

31G(d) method exhibits a total RMS deviation of 0.185 Å, thus underlining the necessity for an RMS analysis.

The addition of diffuse functions to the lithium and nitrogen atoms offers very little increase in the quality of the structure over the 6-31G model, but the extensive addition of diffuse functions to all atoms involved in the resonance boasts highly accurate molecular shapes (total RMS 0.047 Å).

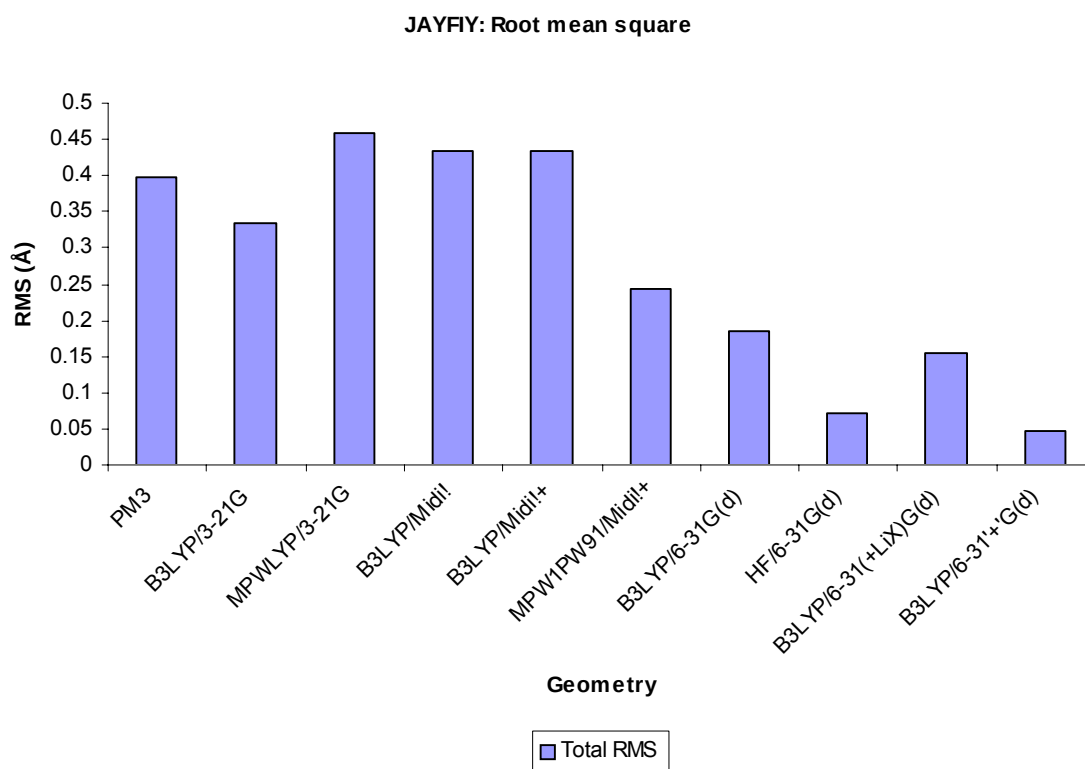


Chart 4.9 Total RMS deviations as a function of method/basis set for JAYFIY relative to B3LYP/6-31+G(d)

4.4.3.3 Energetics and frequencies

B3LYP/6-31+G(d) single point energies taken at each of the test basis set geometries once again reveal the structural dependence of energy calculations. Similar trends emerge, as it is evident that those structures yielding the largest structural deviations exhibit the highest relative B3LYP/6-31+G(d) energy (Table 4.14).

<u>Geometry</u>	<u>Relative energy (kcal/mol)</u>	<u>$\Delta v(\text{CN})$ (cm^{-1})</u>
PM3	25.6	40
B3LYP/3-21G	5.3	8
MPWLYP/3-21G	12.5	-68
B3LYP/Midi!	4.5	17
B3LYP/Midi!+	1.8	17
MPW1PW91/Midi!+	1.6	18
B3LYP/6-31G(d)	0.1	9
HF/6-31G(d)	5.9	150
B3LYP/6-31(+LiX)G(d)	0.1	3
B3LYP/6-31'+G(d)	0.0	2

Table 4.14 Single point B3LYP/6-31+G(d)//geometry energies and unscaled $\Delta v(\text{CN})$ for JAYFIY

The geometries optimized at PM3 and MPWLYP/3-21G exhibit the highest relative energies (25.6 and 12.5 kcal/mol, respectively), and not surprisingly also the highest average MUD (0.042 and 0.031 Å, respectively). Perhaps the most noteworthy result seen from the smaller basis sets is the low relative energy predicted by Midi!+. The structures optimized by B3LYP/Midi!+ and MPW1PW91/Midi!+ show no greater accuracy for bond length prediction than 3-21G or PM3, and also project very high deviations in the RMS analysis of molecular shape. Nevertheless, these two structures yield B3LYP/6-31+G(d) single point energies of 1.8 and 1.6 kcal/mol, respectively.

The structure generated from the B3LYP/6-31G(d) basis set exhibits highly accurate B3LYP/6-31+G(d) energetic performance (0.1 kcal/mol), but the analogous ab initio calculation once again results in a much higher relative energy (5.9 kcal/mol). The customized split valence basis sets excel, predicting B3LYP/6-31+G(d) energy within 0.1 kcal/mol.

With respect to prediction of key vibrational frequencies, similar trends to those seen with the DEVJAP and DEVJUI models are observed. HF/6-31G(d) performs the worst in prediction of $\nu(\text{CN})$ due to the neglect of electron correlation. Of the small basis sets, B3LYP/3-21G predicts the closest $\nu(\text{CN})$ ($\Delta\nu(\text{CN})$ 8 cm^{-1}), outperforming the Huzinaga basis, Midi! and Midi!+ ($\Delta\nu(\text{CN})$ 17-18 cm^{-1}). As has been repeatedly shown, the customized basis sets perform excellently compared to the target set. Both the 6-31(+LiX)G(d) and 6-31'+G(d) basis sets are able to predict the correct $\nu(\text{CN})$ within 3 cm^{-1} .

4.4.3.4 JAYFIY Summary

The summary of all the data analysis for JAYFIY is presented in Table 4.15. Overall the best performing functional/basis set combination (once again) is B3LYP/6-31'+G(d). This optimized structure boasts the lowest average MUD (0.003 Å), RMS deviation (0.047 Å), relative energy (0.0 kcal/mol), and relative $\nu(\text{CN})$ ($\Delta\nu(\text{CN})$ 2 cm^{-1}). The geometries optimized at B3LYP/6-31G(d) and B3LYP/6-31(+LiX)G(d) also perform very well, but are unable to match the molecular shape as well as B3LYP/6-31'+G(d). Concerning the smaller basis sets, Midi!+ is able to match the energy of the B3LYP/6-

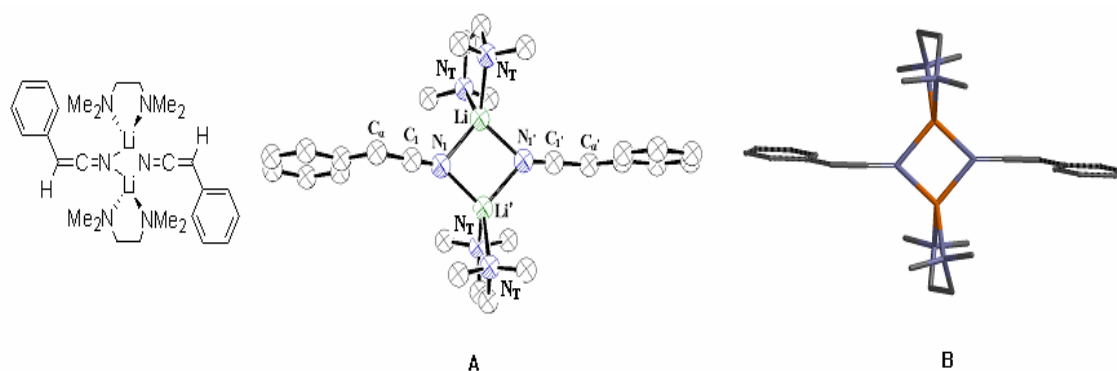
31+G(d) target structure within 2 kcal/mol, but fails with respect to geometric considerations (average MUD: 0.026 Å; total RMS: 0.435). Similarly, B3LYP/3-21G shows moderate accuracy in the estimation of $\nu(\text{CN})$ ($\Delta\nu(\text{CN})$ 8 cm^{-1}), but also fails to model the geometric parameters of the target structure (average MUD: 0.027 Å; total RMS: 0.333 Å).

<i>Geometry</i>	<i>Average MUD (Å)</i>	<i>Total RMS (Å)</i>	<i>Relative E (kcal/mol)</i>	<i>Relative $\nu(\text{CN})$ (cm^{-1})</i>
PM3	0.042 ± 0.024	0.397	25.6	40
B3LYP/3-21G	0.027 ± 0.020	0.333	5.3	8
MPWLYP/3-21G	0.031 ± 0.020	0.381	8.0	-68
B3LYP/Midi!	0.026 ± 0.017	0.435	4.5	17
B3LYP/Midi!+	0.026 ± 0.017	0.434	1.8	17
MPW1PW91/Midi!+	0.017 ± 0.011	0.242	1.6	18
B3LYP/6-31G(d)	0.005 ± 0.003	0.185	0.1	9
HF/6-31G(d)	0.015 ± 0.003	0.071	5.9	150
B3LYP/6-31(+LiX)G(d)	0.004 ± 0.003	0.156	0.1	3
B3LYP/6-31'+G(d)	0.003 ± 0.002	0.047	0.0	2

Table 4.15 Summary of analytical methods comparing JAYFIY test methods/basis sets to B3LYP/6-31+G(d)

4.4.4 FAHBEV

For the analysis of the bis-TMEDA solvated, PhCHCNLi homodimer it is important to note that we were unable to locate structural minima for either B3LYP/Midi!+ or MPW1PW91/Midi!+. As such, these structures cannot be included in the data analyses.



<i>Structure</i>	<i>Bond lengths (Å)</i>				<i>Bond angle (°)</i>
	<i>Li-N_I</i>	<i>Li-N_{TMEDA}</i>	<i>C_I-N_I</i>	<i>C₆-C_I</i>	<i>∠C_IN_ILi</i>
X-ray	2.023	2.013, 2.019, 2.088, 2.090	1.173	1.375	139.6
B3LYP/6-31+G(d)	2.017	2.145, 2.146, 2.148, 2.148	1.198	1.359	138.9

Figure 4.4 FAHBEV (repeated)

4.4.4.1 Mean bond difference

The failure of PM3 with respect to the proper calculation of Li-Li interatomic distance is again seen in study of FAHBEV, overestimating this distance by 0.157 Å (Table 4.16, Charts 4.10 and 4.11). This very large error significantly overshadows the error stemming from lithium contacts to Li-N bonds to the exocyclic TMEDA nitrogen atoms (MSD: 0.038 Å). As was seen for JAYFIY, lithium bonds to the cyclic nitrile atoms exhibit considerably smaller error (MSD: 0.022 Å).

<u>Geometry</u>	<i>Mean Unsigned Difference ($\text{\AA}$)</i>			
	<i>Long bonds</i>	<i>Intermediate bonds</i>	<i>Short bonds</i>	<i>Average MUD</i>
PM3	0.044 $\pm$ 0.041	0.017 $\pm$ 0.010	0.008 $\pm$ 0.004	0.023 $\pm$ 0.014
B3LYP/3-21G	0.055 $\pm$ 0.024	0.010 $\pm$ 0.010	0.002 $\pm$ 0.001	0.022 $\pm$ 0.009
MPWLYP/3-21G	0.041 $\pm$ 0.028	0.021 $\pm$ 0.014	0.005 $\pm$ 0.001	0.022 $\pm$ 0.010
B3LYP/Midi!	0.060 $\pm$ 0.037	0.007 $\pm$ 0.005	0.003 $\pm$ 0.001	0.023 $\pm$ 0.012
*B3LYP/Midi!+	--	--	--	--
*MPW1PW91/ Midi!+	--	--	--	--
B3LYP/6-31G(d)	0.005 $\pm$ 0.005	0.001 $\pm$ 0.001	0.000 $\pm$ 0.000	0.002 $\pm$ 0.002
HF/6-31G(d)	0.024 $\pm$ 0.015	0.012 $\pm$ 0.005	0.012 $\pm$ 0.001	0.016 $\pm$ 0.005
B3LYP/ 6-31(+LiX)G(d)	0.008 $\pm$ 0.003	0.001 $\pm$ 0.001	0.000 $\pm$ 0.000	0.003 $\pm$ 0.001
B3LYP/ 6-31'+G(d)	0.007 $\pm$ 0.004	0.000 $\pm$ 0.000	0.000 $\pm$ 0.000	0.002 $\pm$ 0.001
<u>Geometry</u>	<i>Mean Signed Difference ($\text{\AA}$)</i>			
	<i>Long bonds</i>	<i>Intermediate bonds</i>	<i>Short bonds</i>	<i>Average MSD</i>
PM3	0.044 $\pm$ 0.041	0.006 $\pm$ 0.019	0.007 $\pm$ 0.006	0.019 $\pm$ 0.015
B3LYP/3-21G	-0.042 $\pm$ 0.043	0.008 $\pm$ 0.011	-0.002 $\pm$ 0.001	-0.012 $\pm$ 0.015
MPWLYP/3-21G	-0.034 $\pm$ 0.036	0.021 $\pm$ 0.014	0.005 $\pm$ 0.001	-0.003 $\pm$ 0.013
B3LYP/Midi!	-0.056 $\pm$ 0.042	0.004 $\pm$ 0.007	0.003 $\pm$ 0.001	-0.016 $\pm$ 0.014
*B3LYP/Midi!+	--	--	--	--
*MPW1PW91/ Midi!+	--	--	--	--
B3LYP/6-31G(d)	0.003 $\pm$ 0.006	-0.001 $\pm$ 0.001	0.000 $\pm$ 0.000	0.001 $\pm$ 0.002
HF/6-31G(d)	0.024 $\pm$ 0.015	-0.012 $\pm$ 0.005	-0.012 $\pm$ 0.001	0.000 $\pm$ 0.005
B3LYP/ 6-31(+LiX)G(d)	-0.008 $\pm$ 0.003	-0.001 $\pm$ 0.001	0.000 $\pm$ 0.000	-0.003 $\pm$ 0.001
B3LYP/ 6-31'+G(d)	-0.004 $\pm$ 0.007	0.000 $\pm$ 0.000	0.000 $\pm$ 0.000	-0.001 $\pm$ 0.002

Table 4.16 Mean unsigned/signed error in bond lengths for FAHBEV relative to B3LYP/6-31+G(d); *Unable to locate equilibrium geometry

The 3-21G methods also exhibit large MUD error for long bond lengths, but these particular failures are not largely due to errors in the prediction of Li-Li interatomic distances. On the whole, this basis set significantly underestimates Li-N bond lengths. B3LYP/3-21G and MPWLYP/3-21G underestimate the Li-Li interatomic distance by 0.039 and 0.029 $\text{\AA}$, respectively. B3LYP/3-21G underestimates the lithium contacts to

the exocyclic TMEDA nitrogen atoms by 0.082 Å. MPWLYP/3-21G fares slightly better, only underestimating these bond lengths by 0.072 Å. As we have repeatedly shown, within standard deviation there is effectively no difference in the overall performance of the smaller methods/basis sets. Due to failed optimizations, a definitive trend within the Huzinaga basis sets cannot be ascertained. The B3LYP/Midi! functional/basis set combination exhibits large error in the underestimation of bonds stemming from lithium (MSD 0.056 Å). The average bond MUD, however, offers seemingly no improvement over the 3-21G basis set (0.023 Å).

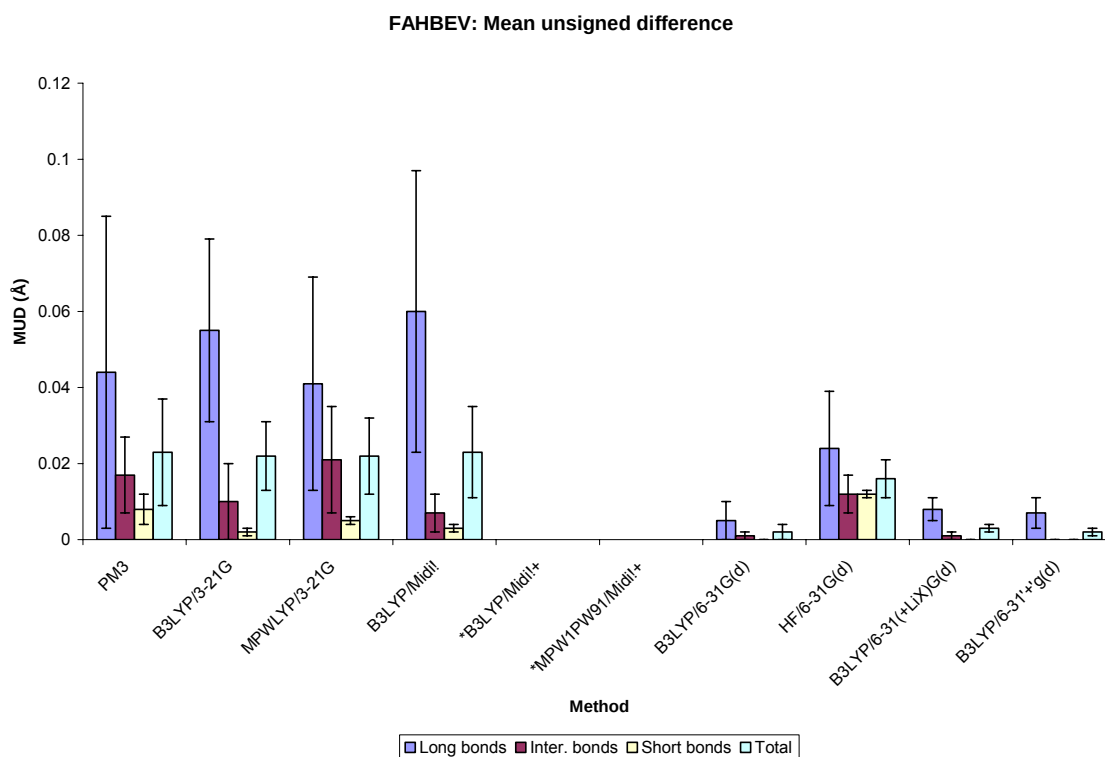


Chart 4.10 Mean unsigned difference for FAHBEV relative to B3LYP/6-31+G(d);
 *Unable to locate equilibrium geometry

Predictably, the 6-31G derived basis sets generally perform much better in the matching of the bond lengths of the structure predicted by our target basis set. B3LYP/6-31G(d) offers tremendous increases in accuracy over the smaller basis sets, boasting an average MUD of only 0.002 Å. For this particular geometry, the largest discrepancy is a 0.005 Å error in the calculation of long bond lengths. Once again, the use of HF/6-31G(d) offers no increase in accuracy. The ab initio method substantially overestimates long bonds by 0.024 Å.

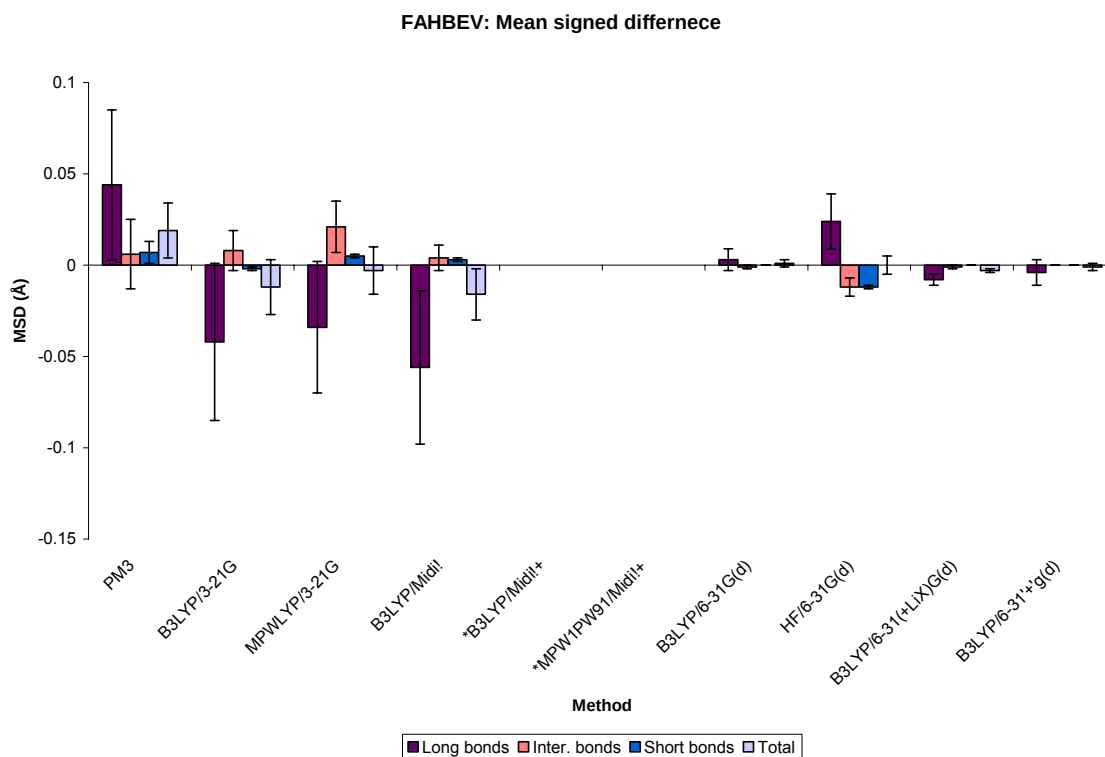


Chart 4.11 Mean signed difference for FAHBEV relative to B3LYP/6-31+G(d);
 *Unable to locate equilibrium geometry

The customized basis sets also perform well in the matching of bond lengths of the target structure, but surprisingly exhibit no significant improvement over the

B3LYP/6-31G(d) structure. Each of these geometries boast an average MUD within 0.003 Å of the target structure. The extensive addition of diffuse functions to select second-row atoms seems to offer no increases in accuracy of calculated long bond lengths for FAHBEV, and only slight improvement in prediction of intermediate bond lengths. The negligible gain observed from the use of these customized basis sets suggests that the addition of diffuse functions is essentially unimportant to the accurate modeling of FAHBEV bond lengths.

4.4.4.2 RMS

The conclusion that the higher rigidity exhibited by the cyclic dimers results in smaller RMS deviations holds true for FAHBEV (Table 4.17, Chart 4.12). The 6-31G(d) basis sets exhibit small RMS deviation, but once again the customized basis sets excel in the prediction of molecular shape. The basis set defined by diffuse functions only on lithium and nitrogen atoms exhibits a total RMS deviation of 0.046 Å. As could be predicted by the bond length analysis, this method actually performs slightly better than the expanded B3LYP/6-31'+G(d) basis set (total RMS deviation 0.047 Å).

<u>Geometry</u>	<u>RMS (Å)</u>		
	<u>Backbone</u>	<u>Non-H</u>	<u>Total</u>
PM3	0.174	0.293	0.384
B3LYP/3-21G	0.267	0.371	0.445
MPWLYP/3-21G	0.135	0.170	0.201
B3LYP/Midi!	0.354	0.437	0.510
*B3LYP/Midi!+	--	--	--
*MPW1PW91/Midi!+	--	--	--
B3LYP/6-31G(d)	0.093	0.113	0.131
HF/6-31G(d)	0.089	0.125	0.150
B3LYP/6-31(+LiX)G(d)	0.043	0.043	0.046
B3LYP/6-31'+G(d)	0.032	0.039	0.047

Table 4.17 RMS deviations for FAHBEV relative to B3LYP/6-31+G(d); *Unable to locate equilibrium geometry

The Midi! basis set exhibits the highest total RMS error, followed closely by B3LYP/3-21G (RMS 0.510 and 0.445 Å, respectively). Due to the inability to locate structural minima at the expanded Midi!+ basis set, conclusions about these particular basis sets cannot be drawn. Of the smaller basis sets, MPWLYP/3-21G seems to excel in the prediction of molecular shape, with a total RMS deviation of 0.201 Å. This result is rather unexpected given the unremarkable performance of this functional/basis set in the depiction of calculated bond lengths.

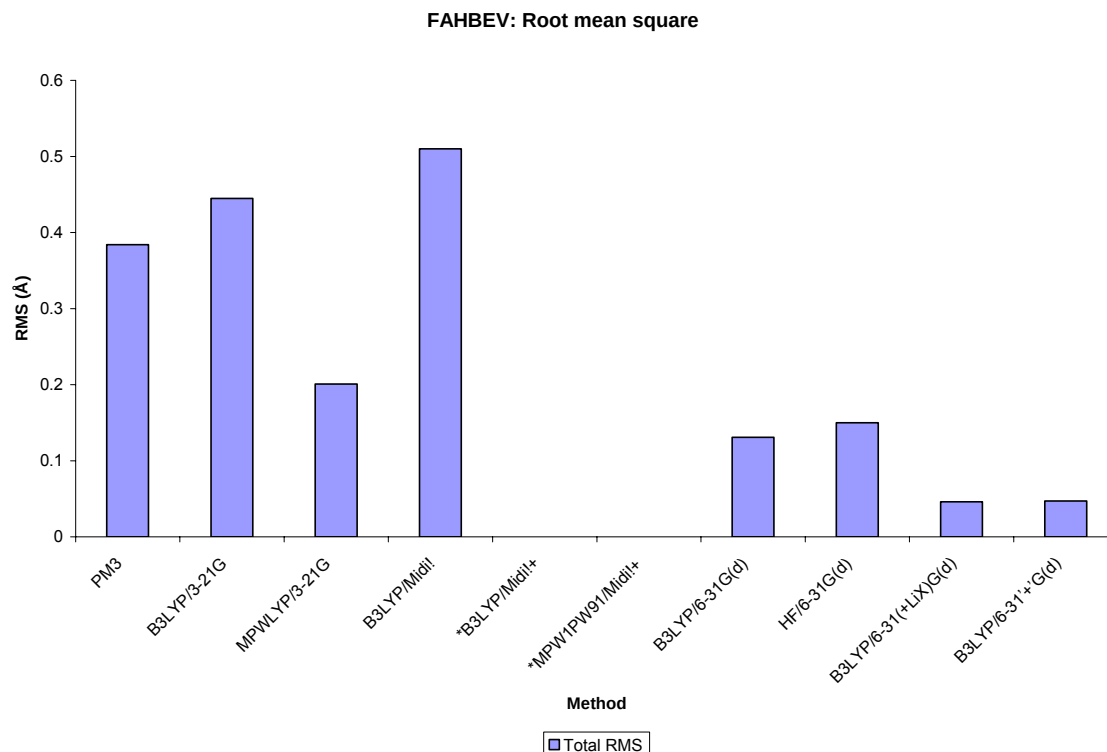


Chart 4.12 RMS deviation relative to B3LYP/6-31+G(d) for FAHBEV; *Unable to locate equilibrium geometry

4.4.4.3 Energetics and frequencies

The structures optimized at PM3 and MPWLYP/3-21G exhibit the highest overall relative energy (9.9 and 8.7 kcal/mol, respectively). In accordance with our observation that bond length deviation plays a key role in energetic matching, these two geometries are among the structures with the highest average MUD. The Midi! basis set predicts a geometry that has a relative energy of 3.9 kcal/mol, which is marginally better than that which is predicted for HF/6-31G(d). The B3LYP/6-31G(d) optimized geometry and the customized split-valence geometries each predict structures with B3LYP/6-31+G(d) single point energies of 0.1 kcal/mol relative to the target structure. The B3LYP/6-

31'+G(d) optimized structure boasts the lowest relative energy at 0.0 kcal/mol, confirming this method to accurately predict the structural parameters seen at the target basis set.

<u>Geometry</u>	<u>Relative energy (kcal/mol)</u>	<u>$\Delta \nu(\text{CN})$ (cm^{-1})</u>
PM3	9.9	43
B3LYP/3-21G	3.5	13
MPWLYP/3-21G	8.7	-60
B3LYP/MidiX	3.9	26
*B3LYP/MidiX+	--	--
*MPW1PW91/MidiX+	--	--
B3LYP/6-31G(d)	0.1	9
HF/6-31G(d)	6.6	139
B3LYP/6-31(+LiX)G(d)	0.1	2
B3LYP/6-31'+G(d)	0.0	2

Table 4.18 Single point B3LYP/6-31+G(d)//geometry energies for FAHBEV; * Unable to locate equilibrium geometry

Unlike the heterodimer shown previously, FAHBEV can exhibit both a symmetric and anti-symmetric $\nu(\text{CN})$. Because symmetric stretches are invisible by IR spectroscopy, we will exclude them from our comparison, but will mention that spacing between the symmetric and anti-symmetric $\nu(\text{CN})$ stretches is roughly independent of basis set or functional. DFT methods generally predict a 13-18 cm^{-1} spacing while PM3 and HF methods predict 21-24 cm^{-1} , with symmetric stretches exhibiting higher frequency than the anti-symmetric. Table 4.18 summarizes the $\nu_{\text{as}}(\text{CN})$ for FAHBEV as a function of chosen method.

As we have consistently shown, the B3LYP/6-31(+LiX)G(d) and B3LYP/6-31++G(d) methods clearly excel in the prediction of $\Delta v_{\text{as}}(\text{CN})$ relative to the target basis set (2 cm^{-1}). The ab initio method, HF/6-31G(d), again greatly overestimates this stretch (139 cm^{-1}), as was seen for each of the other models in the sample set. Among the smaller basis sets, B3LYP/3-21G shows high accuracy over Midi!, but due to our inability to locate equilibrium geometries for the expanded Midi!+, further comparisons cannot be made.

4.4.4.4 FAHBEV Summary

As shown in Table 4.19, a summary of the major data within this study strongly indicates that the customized basis sets excel in all areas of prediction relative to the target basis set. These methods exhibit the smallest average bond length error ($0.002 - 0.003 \text{ \AA}$), lowest RMS deviation of molecular shape ($0.046-0.047 \text{ \AA}$), lowest relative energy (0.1 and 0.0 kcal/mol), and best estimation of $v_{\text{as}}(\text{CN})$ (2 cm^{-1}). The structure optimized at B3LYP/6-31G(d) excels in the prediction of bond length (average MUD: $0.002 \text{ \AA}$) and relative energy (0.1 kcal/mol), but performs relatively poorly in the determination of overall molecular shape (total RMS: $0.131 \text{ \AA}$). Despite this particular shortcoming, B3LYP/6-31G(d) proves to be consistently more accurate and reliable than HF/6-31G(d) and the smaller basis sets.

<i>Geometry</i>	<i>Average MUD (Å)</i>	<i>Total RMS (Å)</i>	<i>Relative E (kcal/mol)</i>	<i>Relative $\nu(\text{CN})$ (cm⁻¹)</i>
PM3	0.023 ± 0.014	0.384	9.9	43
B3LYP/3-21G	0.022 ± 0.009	0.445	3.5	13
MPWLYP/3-21G	0.022 ± 0.010	0.255	8.7	-60
B3LYP/Midi!	0.023 ± 0.012	0.510	3.9	36
*B3LYP/Midi!+	--	--	--	--
*MPW1PW91/Midi!+	--	--	--	--
B3LYP/6-31G(d)	0.002 ± 0.002	0.131	0.1	9
HF/6-31G(d)	0.016 ± 0.005	0.150	6.6	139
B3LYP/6-31(+LiX)G(d)	0.003 ± 0.001	0.046	0.1	2
B3LYP/6-31'+G(d)	0.002 ± 0.001	0.047	0.0	2

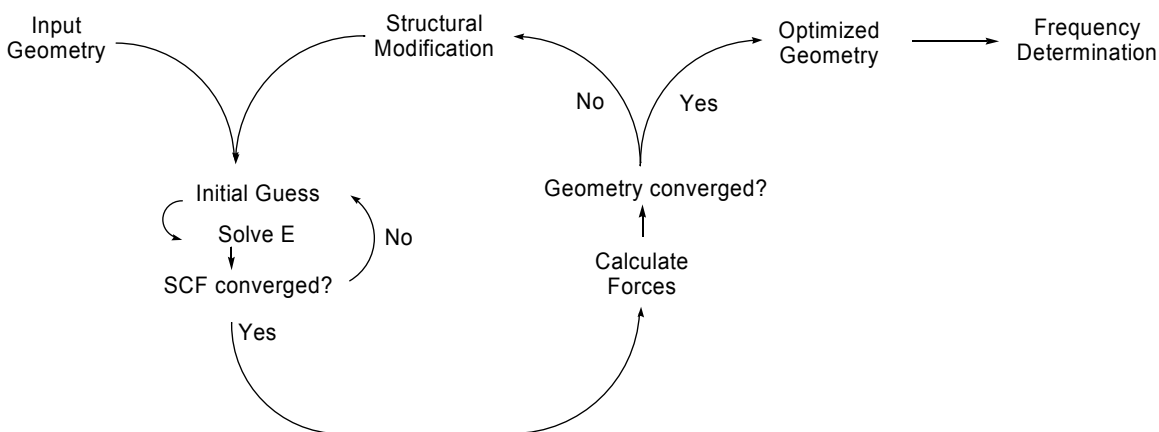
Table 4.19 Summary of the analytical methods comparing FAHBEV test methods/basis sets to B3LYP/6-31+G(d); * Unable to locate structural minima

4.5 Computational time and expense

Throughout this study to find an accurate, low-cost method to replace B3LYP/6-31+G(d) for cases in which optimizations are either impossible or impractical, numerous references are made to resource/time expense at high levels of theory and large basis sets. It is important to mention that computational time and computational expense are related, *not* identical. Expense is a product of the algorithms used to solve the energy, forces, and determine the structure, and is therefore directly affected by the chosen method as well as the efficiency of programming code utilized by the modeling software. Actual time does indeed relate to expense, but is also affected by external factors, such as the hardware employed for the calculation including: processor speed, memory allotment, and the speed with which data can be written and/or read.

At this juncture it may be important to describe how Gaussian '03 conducts a standard geometry optimization and frequency analysis. As shown in the highly simplified Scheme 2.1, the first step in a geometry optimization is the initial solution of

the SCF energy of the input structure. Energy (E) is solved from the time-independent Schrödinger equation, $H\Psi=E\Psi$. Initially, the parameters of the wavefunction, Ψ are guessed for the solution to energy. The resulting energy is then used to generate new parameters for the wavefunction, and the cycle repeats until the changes in energy are below pre-established thresholds. Once the SCF energy has converged, first derivatives of the energy with respect to displacement are calculated to measure forces acting on the molecule. These force measurements instruct Gaussian '03 on the direction and distance atoms need to move. After atomic repositioning, the new structure is subjected to the same SCF convergence criteria as the cycle repeats. The structure is considered optimized after forces and displacement have converged below default thresholds. After optimization, atomic positions are locked and one final cycle confirms the energetic and geometric convergences and calculates second derivatives (vibrational frequencies).



Scheme 4.1 Simplified flow-chart for Gaussian optimization/frequency determination

Having completed the detailed analysis of accuracy, it is now important to relate these findings to computational time. The notion of “basis set economy” hinges upon

high accuracy with decreased computational cost. Unfortunately, for many of the calculations presented in this study, an accurate measure of the total time spent optimizing the structure and calculating the second derivative vibrational frequencies cannot be determined due to repeated optimization failures and restarts.

In order to systematically compare computational expense, we conduct FORCE calculations on each of the B3LYP/6-31+G(d) optimized structures at each of the test method/basis set combinations. Our model FORCE calculations are intended to measure the time required to calculate a single convergence of the SCF energy and also the first derivative forces on that structure for each test method/basis set. These timings will provide a direct means of quantifying the computational expense for each protocol, and will also allow for general insight into the practical time required to fully optimize the structure. The first of these parameters that will be discussed is the computational time required to calculate the first derivatives forces (Table 4.20).

<i>Method</i>	<i>DEVJUL</i>		<i>DEVJAP</i>		<i>JAYFIY</i>		<i>FAHBEV</i>	
	<i>Basis Func.</i>	<i>Time (sec)</i>	<i>Basis Func.</i>	<i>Time (sec)</i>	<i>Basis Func.</i>	<i>Time (sec)</i>	<i>Basis Func.</i>	<i>Time (sec)</i>
PM3	110	0.0	176	0.2	188	0.3	188	0.2
B3LYP/3-21G	242	57.6	386	230.1	410	281.9	412	206.7
MPWLYP/ 3-21G	242	56.5	386	220.7	410	247.3	412	195.2
B3LYP/Midi!	264	77.6	403	285.1	434	341.6	436	263.9
B3LYP/Midi!+	352	288.4	539	1407.5	570	1581.4	--	--
MPW1PW91/ Midi!+	352	289.8	539	1366.5	570	1624.9	--	--
B3LYP/ 6-31G(d)	374	311.7	590	1183.6	614	1332.5	628	1105.1
HF/6-31G(d)	374	269.8	590	1069.6	614	1137.9	628	968.0
B3LYP/ 6-31(+LiX)G(d)	398	443.4	610	1593.3	646	1945.0	660	1665.6
B3LYP/ 6-31'+G(d)	422	622.6	650	2368.1	678	2703.0	700	2522.6
B3LYP/ 6-31+G(d)	462	996.6	726	4692.9	750	5055.0	772	4826.6

Table 4.20 Computational time (first derivatives calculations) vs. basis functions

These data reveal the direct dependence of the first-derivative computational time on the total number of basis functions. We observe that small increases in the number of basis functions yield a scaled increase in computational time. In fact, our experimental results suggest that the time required for the calculation of the first derivatives at a given structure scales roughly N^4 ; recall that the DFT method formally scales N^3 . Note that the HF/6-31G(d) timings for each of the models are included in Table 4.20 and Chart 4.13 for qualitative performance comparison only. The scaling behavior of ab initio methods cannot be directly compared to DFT methods, and thus HF/6-31G(d) determinations are excluded from the curve-fit. It is worthwhile to note, however, that HF/6-31G(d) does consistently require less computational time than B3LYP/6-31G(d).

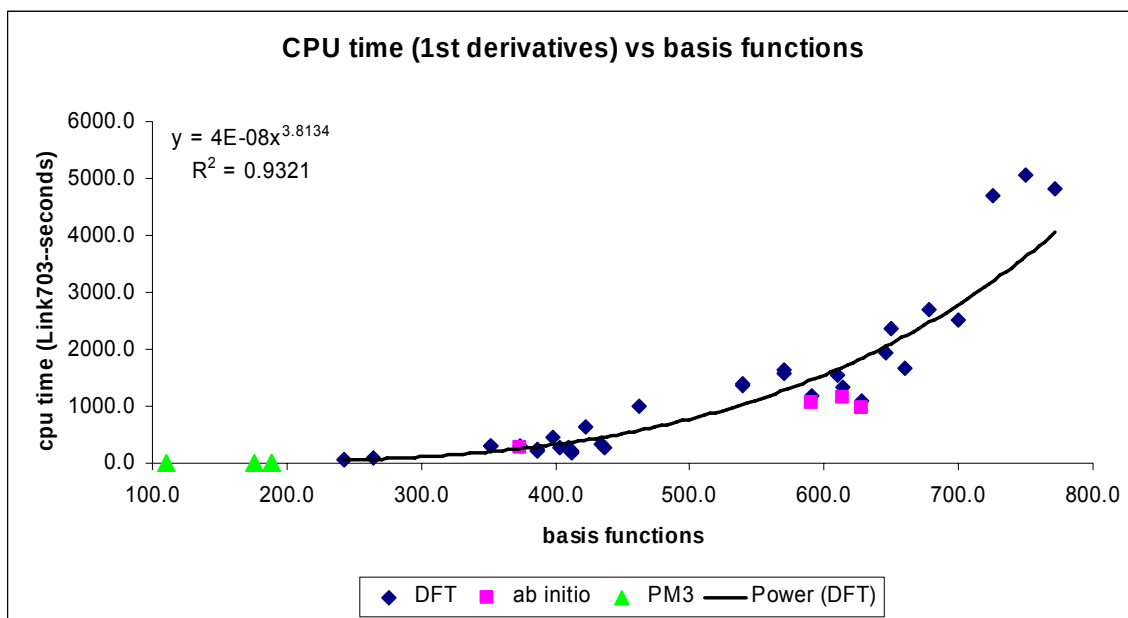


Chart 4.13 Computational time (first derivatives) vs. basis functions

The scaled increase in computational time observed with larger basis sets provides a compelling argument for the minimization of basis functions. The most accurate alternate functional/basis set combination of the study is B3LYP/6-31'+G(d). The resonance theory based approach allows for an 8-11% reduction in the total number of basis functions over the sample set relative to B3LYP/6-31+G(d). This minimization of basis functions corresponds to a 37-48% decrease in the time required to calculate the first derivatives. Not surprisingly, PM3 (the lowest-cost method) offers unparalleled speed, but has proven to be unreliable in the accurate approximation of the target B3LYP/6-31+G(d) structural and energetic parameters.

The timings of the first derivative calculations are indeed an important contributor to the total computational time for these FORCE calculations, but are not the slowest

step. Reported in Table 4.21 is the time required by each method to complete a single SCF convergence. These computational timings allow for direct comparison between the test methods/basis sets for this study, but it is important to note that in an actual optimization the SCF energy would be converged each time atoms are repositioned within the structure.

<i>Method</i>	<i>DEVJUU</i>		<i>DEVJAP</i>		<i>JAYFIY</i>		<i>FAHBEV</i>	
	<i>Basis Func.</i>	<i>Time (sec)</i>	<i>Basis Func.</i>	<i>Time (sec)</i>	<i>Basis Func.</i>	<i>Time (sec)</i>	<i>Basis Func.</i>	<i>Time (sec)</i>
PM3	110	0.2	176	0.5	188	0.6	188	0.6
B3LYP/3-21G	242	263.0	386	969.2	410	1470.9	412	975.5
MPWLYP/ 3-21G	242	244.2	386	817.0	410	1044.5	412	788.9
B3LYP/Midi!	264	481.7	403	1775.8	434	2506.4	436	1605.9
B3LYP/Midi!+	352	2350.0	539	13381.9	570	22488.3	--	--
MPW1PW91/ Midi!+	352	1884.8	539	15263.4	570	35026.7	--	--
B3LYP/ 6-31G(d)	374	812.7	590	2988.7	614	4204.0	628	2060.9
HF/6-31G(d)	374	446.9	590	2221.3	614	2451.6	628	1905.8
B3LYP/ 6-31(+LiX)G(d)	398	1021.4	610	4048.9	646	6972.5	660	4682.0
B3LYP/ 6-31'+G(d)	422	1552.7	650	7428.6	678	10478.4	700	10137.4
B3LYP/ 6-31+G(d)	462	3041.6	726	14472.6	750	18767.0	772	17284.2

Table 4.21 Computational time (SCF convergence) vs. basis functions

As illustrated in Chart 4.14, a similar scalar relationship between CPU time and the number basis functions is observed. The data show roughly N^3 scaling of time to basis functions, as is commonly accepted as the formal scaling behavior of DFT methods. Again the HF/6-31G(d) energies converge slightly faster than those at B3LYP/6-31G(d), and PM3 exhibits the fastest SCF convergences. Interestingly, the FORCE calculations

on the B3LYP/6-31+G(d) optimized structures which employ the Midi!+ basis set perform very poorly in the convergence of the SCF energy, echoing the difficulties encountered in the B3LYP/Midi!+ and MPW1PW91/Midi!+ optimizations. The problems observed in the SCF convergence at this basis set indicate that Midi!+ is not an efficiently designed basis set for the calculation of lithiated benzylic nitriles. Due to the extremely high relative computational cost, the SCF convergence timings for Midi!+ are included for comparison purposes, but are excluded from the curve-fit.

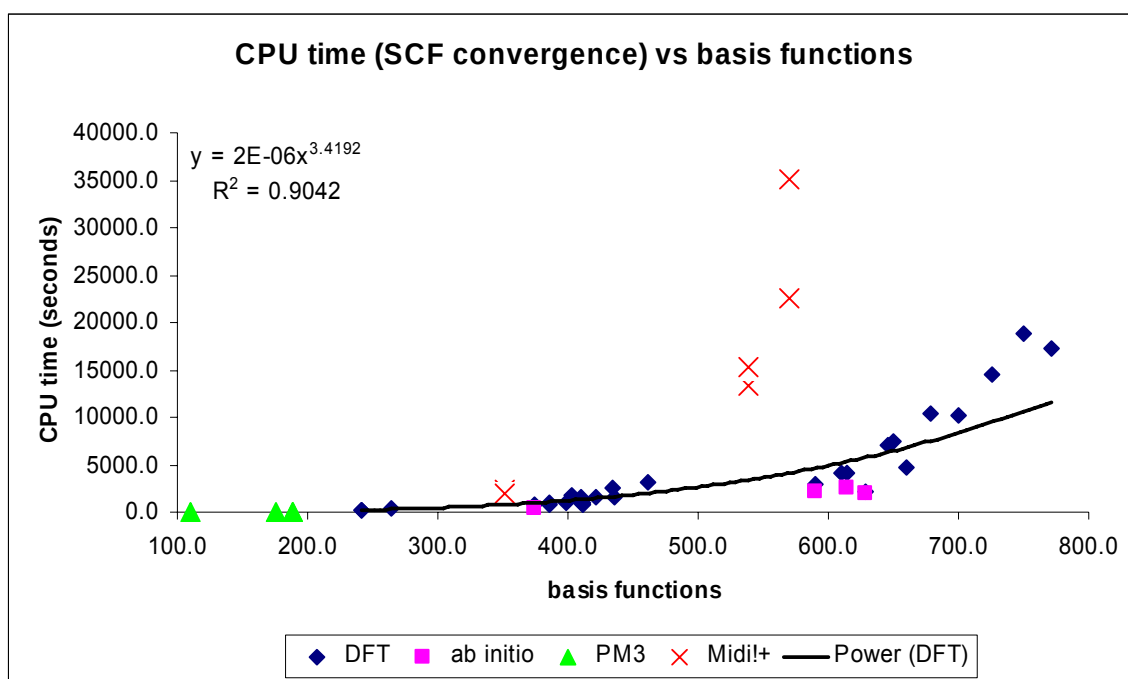


Chart 4.14 Computational time (SCF convergence) vs. basis functions

The aforementioned 8-11% decrease in the total number of basis functions achieved by use of the 6-31'+G(d) basis set again yields a substantial decrease in the

computational time. For the convergence of the SCF energy, this customized basis set offers CPU time-savings of 41-49% over B3LYP/6-31+G(d) for the sample set.

FORCE calculations allow us to evaluate the computational expense of our alternate functional/basis set combinations, but provide no information on the actual computational time for a full optimization/frequency determination. As described previously, the SCF energy and force determinations must be calculated several times throughout a full optimization. With repeated optimization failures it is difficult to ascertain the exact time required for these processes. Frequency calculations, however, cannot be restarted from a failed process, and therefore provide a reliable measure of computational time for second derivatives and their dependence upon the total number of basis functions. Reported in Table 4.22 is a summary of the computational time required to solve the second derivative vibrational frequencies for each of the compounds in the sample set at the each of the test method/basis set combinations. Again, this data reports only the computational time required to complete the frequency calculation, excluding time spent optimizing the equilibrium geometry. Note that for readability, units of time have been changed from seconds to hours.

For the comparison of second derivative frequency timings, PM3 once again exhibits the fastest performance, predicting vibrational frequencies in a fraction of the time required by other methods. The Midi!+ geometries again suffer from computational inefficiency, generally requiring a disproportionate amount of time given the smaller size of the basis set. Also, HF/6-31G(d) boasts computational times marginally faster than B3LYP/6-31G(d).

<i>Method</i>	<i>DEVJUL</i>		<i>DEVJAP</i>		<i>JAYFIY</i>		<i>FAHBEV</i>	
	<i>Basis Func.</i>	<i>Time (hours)</i>	<i>Basis Func.</i>	<i>Time (hours)</i>	<i>Basis Func.</i>	<i>Time (hours)</i>	<i>Basis Func.</i>	<i>Time (hours)</i>
PM3	110	0.0	176	0.2	188	0.3	188	0.2
B3LYP/3-21G	242	2.5	386	16.1	410	13.9	412	9.4
MPWLYP/ 3-21G	242	3.7	386	9.2	410	21.0	412	8.4
B3LYP/Midi!	264	2.4	403	20.4	434	16.8	436	14.3
B3LYP/Midi!+ MPW1PW91/ Midi!+	352	12.7	539	226.5	570	175.0	--	--
B3LYP/ 6-31G(d)	352	14.0	539	219.1	570	178.5	--	--
HF/6-31G(d)	374	4.9	590	54.1	614	42.6	628	37.6
B3LYP/ 6-31G(d)	374	3.9	590	30.5	614	40.2	628	31.6
B3LYP/ 6-31(+LiX)G(d)	398	6.0	610	38.1	646	61.4	660	62.2
B3LYP/ 6-31'+G(d)	422	10.9	650	92.0	678	112.3	700	115.0
B3LYP/ 6-31+G(d)	462	17.6	726	487.0	750	428.5	772	470.4

Table 4.22 Computational time (frequency analysis) vs. basis functions

Once again, a scalar relationship exists between CPU time and number of basis functions. These experimental timings provide the strongest evidence for the benefit of an accurate, lower-cost computational protocol in the calculation of lithiated benzylic nitriles. As an illustrative example, the frequency determination for FAHBEV at B3LYP/6-31+G(d) requires 470 hours to complete, whereas as the 9.3% reduction in basis functions results in a time savings of 75.5% when using B3LYP/6-31'+G(d)—a savings of several hundred hours.

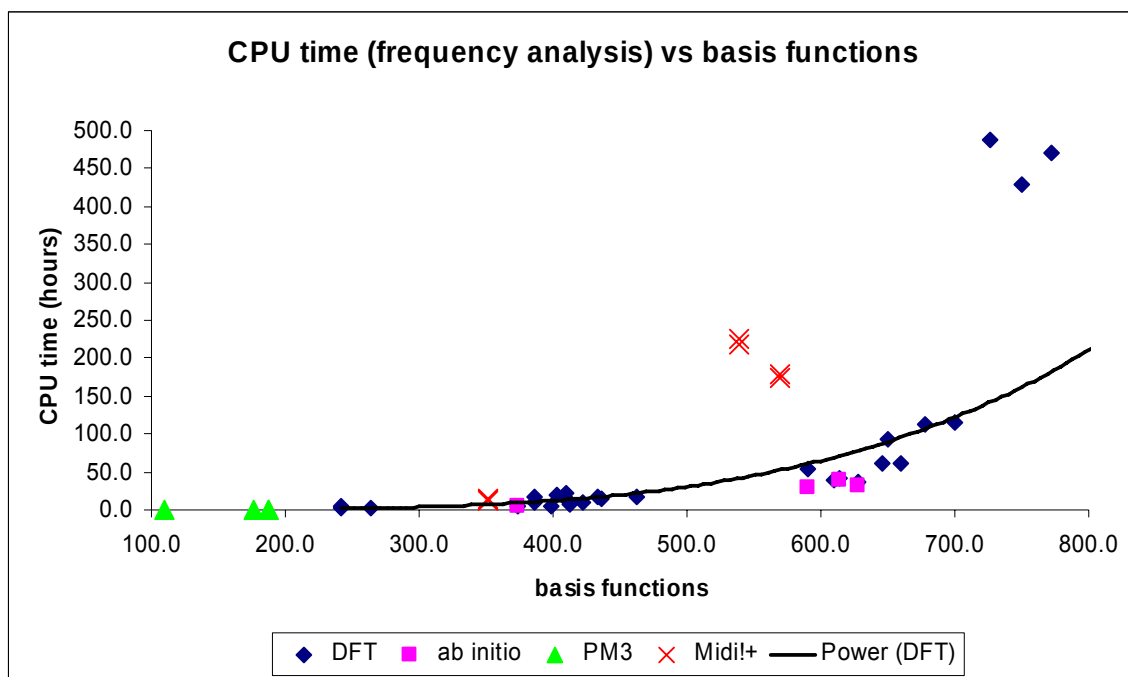


Chart 4.15 Computational time (frequency analysis) vs. basis functions

4.6 Conclusions

Throughout the course of this comparative analysis we have definitively shown that accurate approximations of B3LYP/6-31+G(d) geometries *can* be predicted by lower cost basis sets. Over the sample set of lithiated benzylic nitriles, we see considerable variability in the performance of these test methods/basis sets, but the greatest accuracy was achieved through a simple resonance theory approach to per atom basis set designation. The overwhelming evidence (Table 4.23) points to B3LYP/6-31'+G(d) as an excellent approximation of the accurate method. This functional/basis set boasts an average MUD of only 0.002 Å, relative energies which are indistinguishable from B3LYP/6-31+G(d), and $\nu(\text{CN})$ frequencies are predicted within 2 cm^{-1} . In addition to

high accuracy, this method exhibits tremendous computational cost savings relative to the B3LYP/6-31+G(d) calculation. Over the four structures examined, an 8-11% decrease in the total number of basis functions offers a 37-48% decrease in the computational time for first-derivative forces, a 41-49% decrease in time for SCF convergence, and a 38-81% decrease in the time necessary for the vibrational frequency analysis. The high accuracy as well as the decreased cost in computational resources will allow us to confidently use this basis set in cases where optimization and frequency calculations performed at B3LYP/6-31+G(d) are not feasible.

The other customized basis set, 6-31(+LiX)G(d), also proves to be highly successful in every comparison except total RMS deviation. B3LYP/6-31(+LiX)G(d) predicts bond lengths only marginally worse (average MUD: 0.004 Å) than the more computationally intensive B3LYP/6-31++G(d), and relative energies are still within 0.2 kcal/mol. The structures optimized with this basis set exhibit very similar accuracy to the geometries from the slightly smaller B3LYP/6-31G(d). The customized basis set has an advantage in the calculation of nitrile stretch frequencies, but structurally there is little to distinguish their respective optimized structures. The performance parallels between the 6-31G(d) and 6-31(+LiX)G(d) indicate that more extensive implementation of diffuse functions throughout the resonance stabilized structure is required to achieve the highest accuracy relative to B3LYP/6-31+G(d). Nevertheless, B3LYP/6-31G(d) does prove to exhibit considerable accuracy (average MUD: 0.004 Å) with time savings of 77% for first derivatives, 88% for SCF convergence, and 92% for the calculation of vibrational frequencies over B3LYP/6-31+G(d) for the largest structure (FAHBEV).

<i>Geometry</i>	<i>Average MUD ($\text{\AA}$)</i>	<i>Avg. Total RMS ($\text{\AA}$)</i>		<i>Relative E (kcal/mol)</i>	<i>Relative $\nu(\text{CN})$ (cm^{-1})</i>
		<i>Monomers</i>	<i>Dimers</i>		
PM3	0.028 ± 0.009	1.035	0.391	13.7 ± 7.4	64 ± 25
B3LYP/3-21G	0.029 ± 0.006	1.390	0.389	5.1 ± 1.3	7 ± 8
MPWLYP/3-21G	0.030 ± 0.007	1.407	0.330	11.2 ± 1.9	-72 ± 11
B3LYP/Midi!	0.029 ± 0.007	1.517	0.472	4.1 ± 0.4	18 ± 9
[†] B3LYP/Midi!+	0.020 ± 0.006	1.691	0.435	2.1 ± 0.2	-13 ± 30
[†] MPW1PW91/Midi!+	0.018 ± 0.007	1.720	0.242	1.9 ± 0.2	10 ± 22
B3LYP/6-31G(d)	0.004 ± 0.002	0.711	0.158	0.2 ± 0.1	9 ± 1
HF/6-31G(d)	0.014 ± 0.002	0.638	0.111	5.9 ± 0.6	161 ± 21
B3LYP/ 6-31(+LiX)G(d)	0.004 ± 0.001	0.720	0.101	0.2 ± 0.1	1 ± 3
B3LYP/6-31'+G(d)	0.002 ± 0.001	0.015	0.047	0.0 ± 0.0	2 ± 0

Table 4.23 Summary of basis set economy comparisons for DEVJAP, DEVJUI, JAYFIY, and FAHBEV; [†]Average values exclude FAHBEV due to inability to locate equilibrium geometry

With the high accuracy and substantial computational economy demonstrated by the B3LYP/6-31'+G(d) method, it may be difficult to imagine looking to other basis sets for low-cost alternatives to higher levels of theory. Nevertheless, it is not hard to envision cases wherein even these less-expensive methods can become impractical to use. In cases such as these it may be beneficial to look for an accurate method among the smaller basis sets—particularly 3-21G, Midi!, and Midi!+. We excluded PM3 from this comparison because despite boasting extremely fast computational timings for first and second derivatives and SCF convergence, this method is too unreliable in the accurate prediction of structural and energetic parameters for the sample set of lithiated benzylic nitriles.

B3LYP/3-21G predicts average MUD and relative energies somewhat larger than those predicted by B3LYP/Midi!+ and MPW1PW91/Midi!+, but has a significant advantage in computational stability. B3LYP/3-21G is not plagued by the SCF

convergence issues observed with Midi!+ than Midi!+. The 3-21G basis set also exhibits demonstrably better total RMS and $v(\text{CN})$. For the largest structure (FAHBEV), B3LYP/3-21G offers computational savings greater than 90% relative to B3LYP/6-31+G(d) for determination of SCF convergence and also first and second derivatives. Furthermore, B3LYP/3-21G offers similar accuracy to B3LYP/Midi!, with the advantage of decreased computational time. Admittedly, the accuracy of B3LYP/3-21G may not compare to B3LYP/6-31'+G(d); however, a good case can be made for using this basis set for large assemblies where even the customized 6-31G(d) basis sets cannot efficiently be utilized.

Chapter 5 Computational data and methodologies for the comparative assessment of basis sets for the calculation of aromatic organolithium compounds

5.1 Computational hardware and software

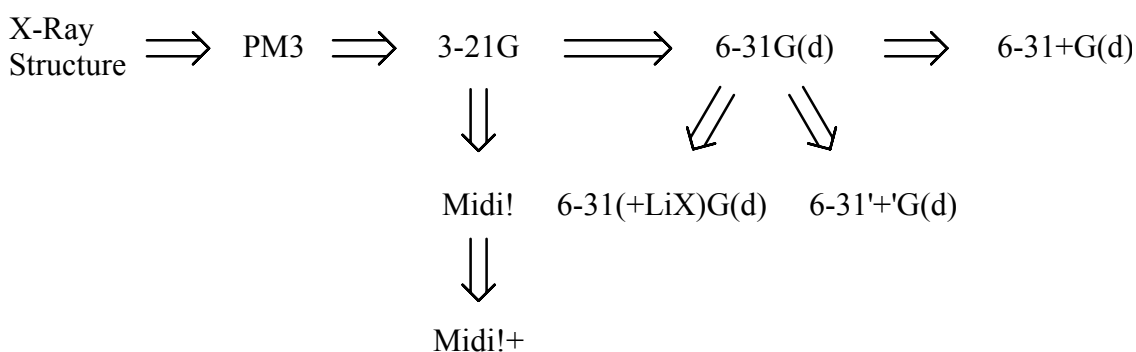
All calculation data presented in Chapter 2 were obtained from Gaussian '03 Rev. B.05.⁹⁶ This software package is accessible through Inferno2, an SGI ALTIX 3700 server hosted exclusively for computational research at Virginia Polytechnic Institute and State University. At the time of this writing, Inferno2 is a 128-node 1600 MHz Itanium 2.5 processor supercluster offering 4.5 Terabytes (TB) total disk space and an additional 320 Gigabytes (GB) available memory running on a 2.6.5-7 Linux kernel. Final optimized geometries and calculated frequencies are visualized with GaussView 2.1⁹⁷ or Molden.⁹⁸

5.2 Computational methodologies

The published X-ray structures for each of the compounds in the sample set (DEVJAP, DEVJUI, JAYFIY, and FAHBEV) were obtained in .cif and .mol2 format from the Cambridge Structural Database,⁶⁶ a repository of small molecule crystal structures. Mercury v1.4.1¹⁴⁹ (available through the CCDC) was used to convert the .cif files into .pdb format, a file-type readable by Gaussian '03. Single point energy calculations were performed on each of the structures in order to preserve their original structural parameters within a Gaussian checkpoint file (e.g. file.chk). Checkpoint files store structural parameters and other important data (force constants, thermodynamic

corrections, etc.), but most importantly allow for a convenient means to generate a variety of file-types readable by Gaussian '03 and other software applications.

Each of the X-ray structures were optimized at PM3, and then at successively higher levels of theory as shown in Scheme 5.1. This systematic ordering ensures that lower level optimizations are not compromised by the use of a higher level starting geometry.



Scheme 5.1 Optimization flow-chart for structural analysis

Starting geometries for each calculation are obtained from the appropriate .chk files (Scheme 5.1) through the use of the newzmat command as shown below:

```
newzmat -ichk -oxyz file.chk newfile.gjf
```

This command line extracts structural parameters of the optimized geometry from file.chk file and generates a new Z-matrix with atomic positions defined in Cartesian space (x,y,z coordinates). For all calculations, one processor with a maximum of four GB RAM is allotted as illustrated in the header of the sample Gaussian job file (.gjf) for

lithiophenylacetonitrile, PhCHCNLi, shown in Figure 5.1. All optimized geometries are characterized as structural minima by vibrational frequency analysis (no imaginary frequencies). In all cases, the opt(gdiis) keyword^{150, 151} is employed to assist geometric convergence for optimizations. For single point B3LYP/6-31+G(d) energy calculations, the keyword SCF=Tight is added to compensate for the unreliability of the default SP cutoffs with respect to diffuse functions. Single point 6-31+G(d) energies are by default calculated with weaker thresholds to energy and density-matrix population.¹⁴⁸ Note that during a 6-31+G(d) optimization this keyword is not required as SCF=Tight is included in the default method. Relative energies reported in Chapter 4 are *not* zero-point corrected. All calculations were completed under default thresholds unless otherwise explicitly stated.

```

%nprocshared=1
%mem=4GB
%rwf=filename
%int=filename
%scr=filename
%d2e=filename
%nosave
%chk=filename
#P rb3lyp/6-31+G(d) opt(gdiis) freq

B3LYP/6-31+G(d) optimization and frequency for
lithiophenylacetonitrile, PhCHCNLi

0 1
C      -1.07758      0.00001      1.19470
C      -0.39402      0.00101      2.35848
N       0.21666     -0.00101      3.38963
Li      1.21044      0.00011      4.84826
H      -2.16206      0.00047      1.26024
C      -0.45802      0.00013     -0.11889
C       0.68614     -0.00014     -2.72200
C       0.94304      0.00023     -0.30948
C      -1.26288     -0.00006     -1.28007
C      -0.70086     -0.00023     -2.55366
C       1.49947      0.00010     -1.58444
H       1.59531      0.00040      0.56146
H      -2.34533     -0.00013     -1.16896
H      -1.35404     -0.00040     -3.42388
H       2.58240      0.00022     -1.69231
H       1.12403     -0.00021     -3.71647

```

Figure 5.1 Sample Gaussian job file (.gjf) for lithiophenylacetonitrile, PhCHCNLi

5.2.1 User-defined basis sets

As described in Chapter 2, Gaussian '03 allows for the assignment of basis sets to groups of atoms (i.e., all carbon atoms) or to specific atoms (atom C₁, C₂, etc.) within a

given geometry. This functionality is key to the generation of the user-defined 6-31(+LiX)G(d) and 6-31'+G(d) basis sets. Customization is achieved in part through modification of the route section of the Gaussian job file (Figure 5.1, line 9). In order to specify the use of a nonstandard computational protocol, the GEN keyword must replace the basis set in the route section as shown in Figure 5.2. Note that the 6D keyword is also included to specify the use of six Cartesian d-orbitals [d_{x^2} , d_{y^2} , d_{z^2} , d_{xy} , d_{xz} , d_{yz}] rather than five spherical d-orbitals.

```
#P rb3lyp/GEN 6D opt(gdiis) freq
```

Figure 5.2 Modification of the route section to utilize customized basis sets

In addition to alteration of the route section, an extra section of input defining the atoms upon which diffuse functions are added must also be included following the molecular geometry specification. For the first approach defined in Chapter 2 (6-31(+LiX)G(d)), diffuse functions are added to all lithium and heteroatoms present within the molecule. Applying this approach to the sample Gaussian job file for lithiophenylacetonitrile (see above), diffuse functions are universally added to all lithium and nitrogen atoms as shown in Figure 5.3. For this basis set, all carbon and hydrogen atoms are calculated at 6-31G(d).

(continued. from Figure 5.1)

```

O 1
C      -1.07758      0.00001      1.19470
C      -0.39402      0.00101      2.35848
N       0.21666     -0.00101      3.38963
Li      1.21044      0.00011      4.84826
H      -2.16206      0.00047      1.26024
C      -0.45802      0.00013     -0.11889
C       0.68614     -0.00014     -2.72200
C       0.94304      0.00023     -0.30948
C      -1.26288     -0.00006     -1.28007
C      -0.70086     -0.00023     -2.55366
C       1.49947      0.00010     -1.58444
H       1.59531      0.00040      0.56146
H      -2.34533     -0.00013     -1.16896
H      -1.35404     -0.00040     -3.42388
H       2.58240      0.00022     -1.69231
H       1.12403     -0.00021     -3.71647

****
C H 0
6-31G(d)
****
Li N 0
6-31+G(d)
****

```

Figure 5.3 6-31(+LiX)G(d) basis set atomic designations for lithiophenylacetonitrile

The resonance theory based approach to basis set specification dictates that diffuse functions are added only to atoms involved in charge delocalization of the resonance stabilized structure. The GEN keyword allows the user to apply diffuse functions only to these select atoms. Of particular interest in the 6-31'+G(d) basis set are the carbon atoms involved in resonance stabilization as shown in Figure 5.4. In the lithiophenylacetonitrile example, C₁ and C₇-C₉ participate in electron delocalization

through the resonance stabilized structure, and thus are calculated at 6-31+G(d). Diffuse functions are also added to C₂ given the intimate association with the nitrogen atom.

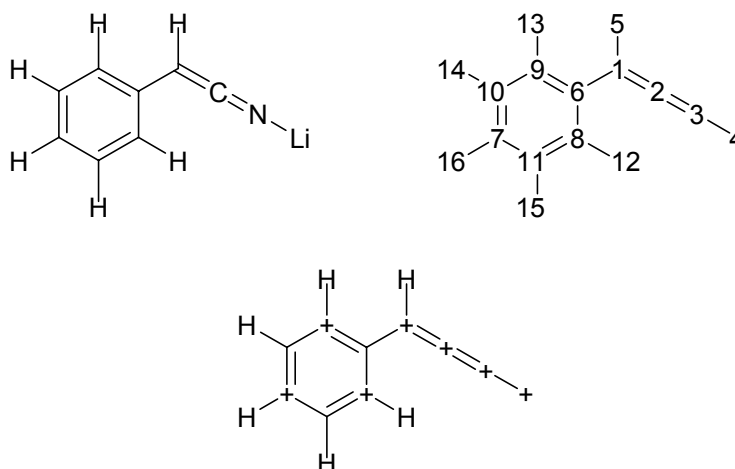


Figure 5.4 Application of diffuse functions throughout the resonance stabilized structure of lithiophenylacetonitrile

Much like the case for the 6-31(+LiX)G(d) basis set, all carbon atoms are initially designated 6-31G(d). Separately, parameters for the addition of diffuse functions for individual atoms must be explicitly added to the Gaussian job file adhering to the format detailed in Figure 5.5A. For each atom, the shell type (S, P, D, etc.), number of primitive Gaussians, and scaling factor defining diffuse functions must be stated. Following specification of the shell type (SP for the diffuse functions), the exponent for the primitive Gaussian (α) and the s- and p- contraction coefficients (d_s and d_p , respectively) must also be defined. The primitive Gaussian exponent and s- and p- contraction coefficients¹⁴⁸ are shown in Figure 5.5B.

A)	Shell type	Primitive Gaussians		Scaling Factor
	α	d_s	d_p	
B)	SP	1	1.00	
		0.4380000000D-01	0.1000000000D+01	0.1000000000D+01

Figure 5.5 A) Formatting requirements for per-atom basis set assignment; B) 6-31+G(d) exponent and contraction coefficients

Figure 5.6 outlines the required input for the atomic assignments necessary to execute the 6-31+'G(d) optimization of lithiophenylacetonitrile. In this example, all lithium and heteroatoms are designated 6-31+G(d), as are carbon atoms C₁, C₂, and C₇₋₉. The remaining carbon and hydrogen atoms are all calculated at 6-31G(d).

(continued from Figure 5.1)

```

0 1
C      -1.07758      0.00001      1.19470
C      -0.39402      0.00101      2.35848
N       0.21666     -0.00101      3.38963
Li      1.21044      0.00011      4.84826
H      -2.16206      0.00047      1.26024
C      -0.45802      0.00013     -0.11889
C       0.68614     -0.00014     -2.72200
C       0.94304      0.00023     -0.30948
C      -1.26288     -0.00006     -1.28007
C      -0.70086     -0.00023     -2.55366
C       1.49947      0.00010     -1.58444
H       1.59531      0.00040      0.56146
H      -2.34533     -0.00013     -1.16896
H      -1.35404     -0.00040     -3.42388
H       2.58240      0.00022     -1.69231
H       1.12403     -0.00021     -3.71647

****
C H 0
6-31G(d)
****
Li N 0
6-31+G(d)
****
1 0
SP 1 1.00
0.4380000000D-01 0.1000000000D+01 0.1000000000D+01
****
2 0
SP 1 1.00
0.4380000000D-01 0.1000000000D+01 0.1000000000D+01
****
7 0
SP 1 1.00
0.4380000000D-01 0.1000000000D+01 0.1000000000D+01
****
8 0
SP 1 1.00
0.4380000000D-01 0.1000000000D+01 0.1000000000D+01
****
9 0
SP 1 1.00
0.4380000000D-01 0.1000000000D+01 0.1000000000D+01
****

```

Figure 5.6 6-31'+G(d) basis set atomic designations for lithiophenylacetonitrile

5.3 Analytic methodology

5.3.1 Mean signed/unsigned differences in bond length

After the successful optimization and frequency determination of each structure, the bond length parameters of the optimized geometry are extracted from the Gaussian '03 output file (.out or .log) with a combination of Unix-based text-editing tools and two AWK (a text-processing UNIX programming language) scripts. As an illustrative example of the data collection process, the B3LYP/6-31+G(d) optimized geometry of hydrogen peroxide (H_2O_2) is detailed below.

Each atom is first assigned a numerical tag based on its listing order within the Z-matrix of the input file. These designations are for internal referencing only, and have no bearing in the outcome of the optimized parameters. In this example, the atoms of H-O-O-H are designated 1-2-3-4, respectively. It is worthwhile to mention that because each optimized geometry within the sample set is ultimately generated from its respective original X-ray structure, atomic ordering remains consistent within each model.

During the optimization process several iterative geometries are reported as the computational software attempts to locate the structural minima. After the optimization criteria are met, the 'Optimized Parameters' are tabulated as shown in Figure 5.7. The optimized parameters are divided into one of three classifications: R (bond length), A (bond angle), or D (dihedral angle). In this format, R(1,2) refers to the bond length between atoms 1 and 2. In the H_2O_2 example, this definition corresponds to an O-H bond, and is reported to be 0.9741 Å.

! Optimized Parameters !			
! (Angstroms and Degrees) !			

! Name	Definition	Value	Derivative Info.!

! R1	R(1,2)	0.9741	-DE/DX = 0.0 !
! R2	R(2,3)	1.4565	-DE/DX = 0.0001 !
! R3	R(3,4)	0.9741	-DE/DX = 0.0 !
! A1	A(1,2,3)	100.249	-DE/DX = 0.0 !
! A2	A(2,3,4)	100.249	-DE/DX = 0.0 !
! D1	D(1,2,3,4)	118.4915	-DE/DX = 0.0 !

Figure 5.7 Sample geometry optimization output for hydrogen peroxide, H₂O₂

In order to minimize the risk of transcription errors, we first extract the ‘Optimized Parameters’ table from the output file using basic UNIX file-manipulation commands. This task is accomplished using the ‘grep’ command as shown below:

```
grep -A XX Optimized file.out >file.bl
```

This command searches file.out for instances of ‘Optimized,’ and then prints all occurrences of the search string plus the following (XX) lines to a new file with the extension .bl (bond list). Note that within UNIX-based operating systems, file extensions are arbitrary, and are principally defined for convenience rather than to imply software specific formatting (i.e., bl = bond list; gjf = Gaussian job file; xyz = Cartesian coordinates, etc.).

As outlined, the ‘grep’ procedure for the extraction of optimized parameters is generalized, and in practice the number (XX) must be manually counted by visual

inspection of the output file. In the H₂O₂ example this number is seven, giving the output shown in Figure 5.8.

! Optimized Parameters ! ! (Angstroms and Degrees) !			
! Name	Definition	Value	Derivative Info.!
! R1	R(1,2)	0.9741	-DE/DX = 0.0 !
! R2	R(2,3)	1.4565	-DE/DX = 0.0001 !
! R3	R(3,4)	0.9741	-DE/DX = 0.0 !

Figure 5.8 Extraction of the table of optimized parameters from the output file

From the new file containing this data table (file.bl), the individual bond definitions and lengths are extracted using two AWK scripts (Figures 5.9A and 5.9B). The general format for the execution AWK scripts within a UNIX shell is reported below.

```
awk -f bondlist.awk file.bl >file.bla
```

A)	#Bondlist.awk	B)	#Bondlength.awk
	/R/{ print \$3		/R/{ print \$4
	}		}

Figure 5.9 Customized AWK scripts for the extraction of structural parameters

The first of these two AWK scripts (bondlist.awk), “reads” file.bl, considers only lines of text containing “R”, and prints the information contained in the third column to a new file, file.bla. For clarification, note that the exclamation point (!) counts as one column in the example shown in Figure 5.8. The second AWK script (bondlength.awk) performs a similar function, but prints only data from column four. The resulting output from each of the detailed AWK scripts is reported in Figure 5.10.

A)	R (1, 2)	B)	0.9741
	R (2, 3)		1.4565
	R (3, 4)		0.9741

Figure 5.10 AWK script output for A) bondlist.awk and B) bondlength.awk

For further analysis, these bond definitions and bond lengths are copied and pasted into Microsoft Excel where they are sorted against and compared to the same bonds within the target structure. For simple cases such as the H₂O₂ example, visual inspection can verify that all bonds are considered. As molecular size increases, however, the bonding patterns become more complex. Often is that case that exceptionally long bonds are omitted from these bond lists because they do not meet predetermined conditions to be called a bond by the computational software. To ensure that each structure within the study offers the same bonds for comparison, the .bla files must be checked for discrepancies. UNIX allows for a convenient method to compare the contents of two text files. Using the ‘diff’ command, the .bla file of one structure can

be compared to the .bla file of a reference structure, as shown below. If the two files are different (i.e., contain different bond lists), the discrepancies will be reported.

```
diff file1.bla file2.bla
```

In cases such as these, the missing bond lengths are manually measured using visualization software such as GaussView 2.1, Molden, or gOpenMol.^{152, 153}

5.3.2 RMS deviations

For the determination of RMS deviations of overall molecular shape, each of the optimized structures must be converted into a file-type readable by PyMol (.pdb). This transformation is accomplished through manipulation of the Z-matrix with the newzmat command as previously described. The pair fitting functionality of PyMol requires one structure to be defined as ‘mobile’ and the other as a ‘target’. For these comparisons, the B3LYP/6-31+G(d) structure is defined as the target geometry, while the geometries at each of the alternate methods/basis sets are designated mobile. Individual atoms are selected from the mobile structure and paired to the analogous atom within the target structure. PyMol then attempts to overlay the paired atoms while minimizing the RMS deviation over the selected pairs, as shown in Figure 5.11.

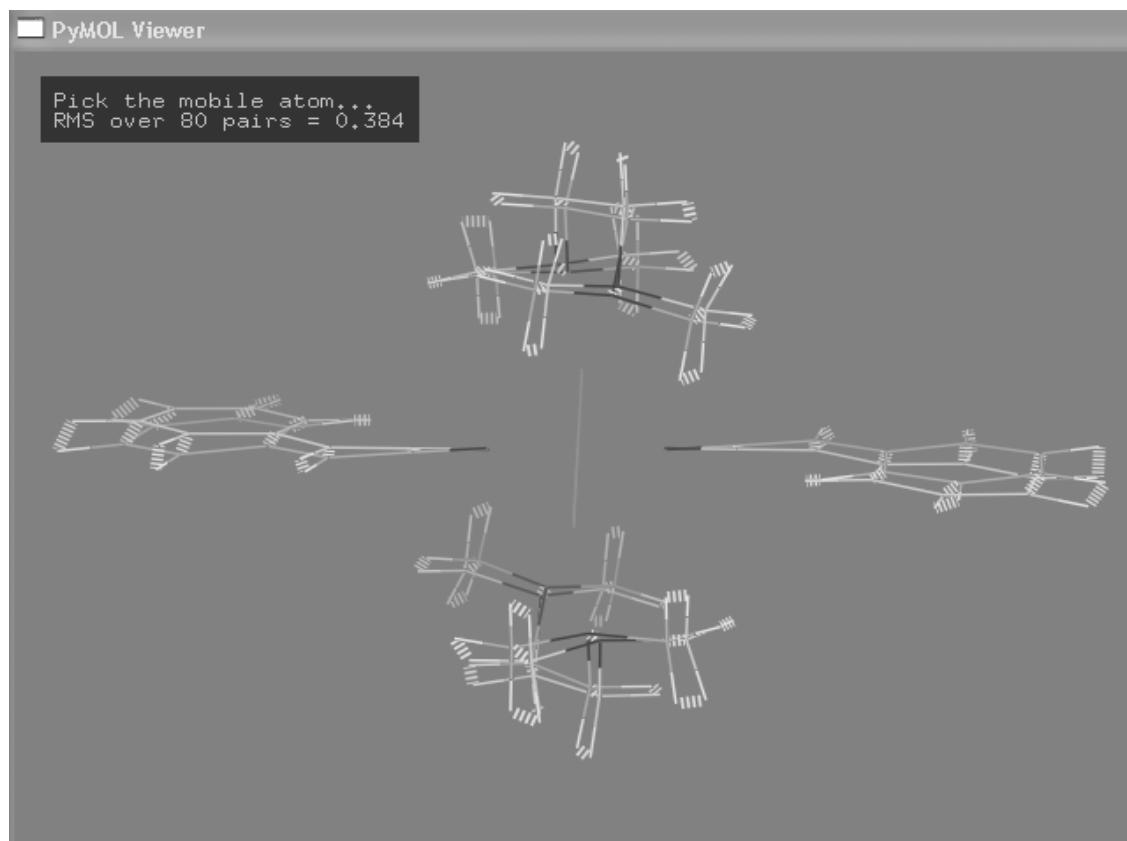


Figure 5.11 Pair-fitting functionality of PyMol

Figure 5.11 illustrates the pair-fitting functionality of PyMol. This particular example shows the total RMS deviation (covering all atoms) for FAHBEV optimized at PM3 (blue) relative to the B3LYP/6-31+G(d) target structure (green). Spatial differences in atomic positions are graphically depicted by the yellow bars connecting the paired atoms of the two structures. This figure shows the total RMS over all atoms, but is important to note that collection of these data actually occurs in three stages. The atoms of the backbone (lithiated benzylic nitrile plus coordinated heteroatoms) are first paired and the RMS deviation is recorded. This process is completed with the inclusion of non-hydrogen atoms from the solvating ligands, and then again for all atoms.

5.3.3 Computational timings

In order to systematically compare the computational time required for the convergence of SCF energy and the calculation of first derivative forces, we first generate a new input file from the checkpoint file of the B3LYP/6-31+G(d) optimized geometry as previously described. This technique allows for CPU time determinations to be compared for each method/basis set combination from an equivalent starting geometry. The FORCE keyword is added to the route section as shown in Figure 5.12.

```
#P rb3lyp/6-31G(d) FORCE
```

Figure 5.12 Specifying a FORCE calculation

Note that by default Gaussian does not report the CPU time required at specific stages (Links) of a given process. In order to view these timings, verbose output must be explicitly requested by the user. This specification is accomplished by the addition of ‘P’ to the route section as shown above.

Examination of the FORCE calculation output confirms that convergence of the SCF energy and the calculation of first derivative forces (Links 502 and 703, respectively) are in fact the most computationally expensive stages of the calculation.

```
grep cpu: file.out
```

Indeed this is also the case for full optimization sequences. Note that SCF convergence is calculated differently for PM3 calculations. SCF convergence for molecular mechanics

and semi-empirical processes is calculated at Link 402. First derivative forces are handled at Link 703 as are the standard DFT methods.

5.4 Structural data

The Cartesian coordinates (x,y,z) from each of the optimized geometries are reported below. These coordinates are generated from the .chk file for each respective structure using the command line shown below.

```
newzmat -ichk -oxyz file.chk file.xyz
```

Also included with the Cartesian coordinates for each structure are tabulated bond length deviations (both signed and unsigned).

5.4.1 DEVJAP (1-Cyano-indenyl-N)-((-)-sparteine-N,N')-(tetrahydrofuran-O)-lithium

Reported below are the raw bond length data for each of the test functional/basis set combinations for DEVJAP. For reference, Figure 5.13 defines all atomic labels for the DEVJAP structures.

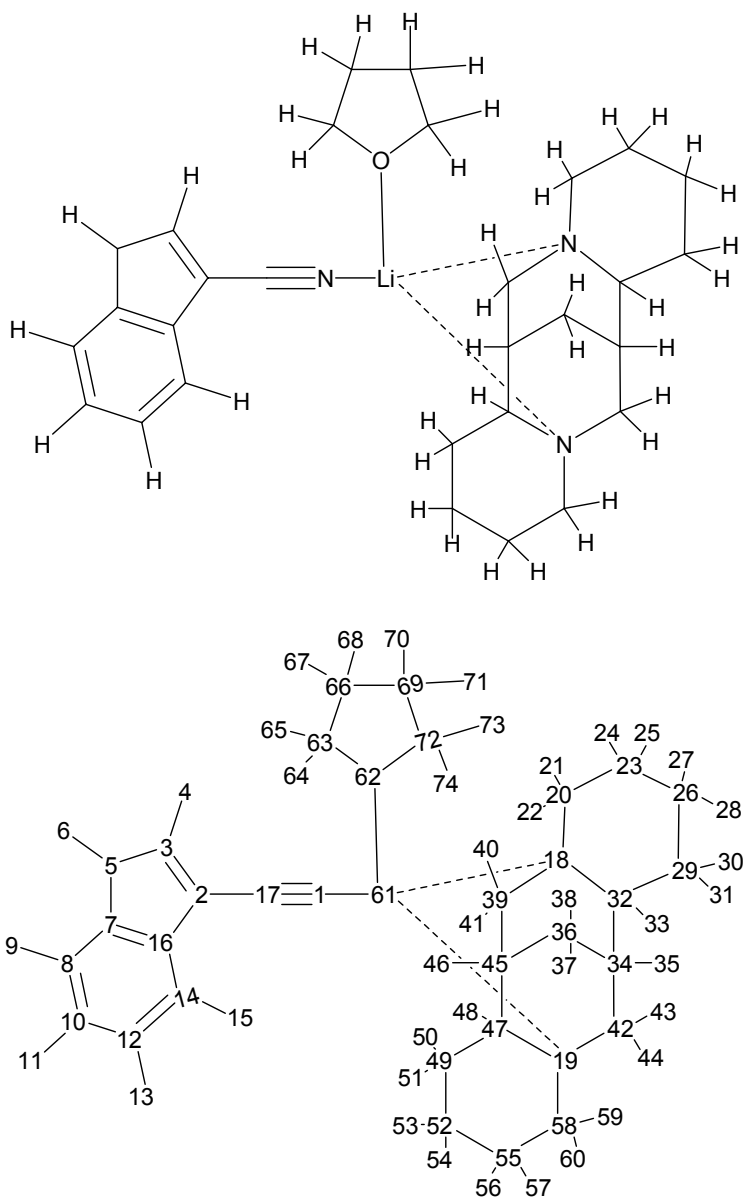


Figure 5.13 Atomic labels for DEVJAP

	Bond list	PM3	B3LYP/ 3-21G	MPW1PW91/ 3-21G	B3LYP/ M6d++	B3LYP/ M6d++	MPW1PW91/ M6d++	B3LYP/ 6-31G(d)	HF/ 6-31G(d)	B3LYP/6- 31(+LX)G(d)	B3LYP/6- 31+G(d)	B3LYP/ 6-31+G(d)
long	R(19,61)	2.2754	2.0373	2.0504	2.0413	2.0856	2.0735	2.1245	2.1475	2.1168	2.1138	2.1211
	R(18,61)	2.2396	2.0259	2.0398	2.0349	2.0701	2.0578	2.0999	2.1239	2.0953	2.0975	2.1022
	R(61,62)	2.0535	1.9553	1.9761	2.0010	2.0423	2.0443	2.0288	2.0596	2.0433	2.0461	2.0469
	R(1,61)	1.9147	1.9526	1.9564	1.9182	1.9315	1.9342	1.9484	1.9681	1.9376	1.9730	1.9703
	R(2,34)	1.5442	1.5479	1.5599	1.5526	1.5526	1.5435	1.5459	1.5392	1.5458	1.5467	1.5471
intermediate	R(29,32)	1.5382	1.5529	1.5650	1.5542	1.5541	1.5448	1.5470	1.5398	1.5471	1.5464	1.5470
	R(45,47)	1.5411	1.5476	1.5599	1.5488	1.5513	1.5417	1.5460	1.5394	1.5469	1.5454	1.5457
	R(39,45)	1.5339	1.5481	1.5603	1.5462	1.5485	1.5392	1.5438	1.5372	1.5435	1.5421	1.5425
	R(34,42)	1.5362	1.5480	1.5600	1.5488	1.5486	1.5398	1.5421	1.5359	1.5419	1.5417	1.5422
	R(66,69)	1.5276	1.5491	1.5602	1.5502	1.5480	1.5394	1.5362	1.5285	1.5364	1.5363	1.5370
	R(20,23)	1.5254	1.5422	1.5529	1.5451	1.5455	1.5370	1.5351	1.5290	1.5352	1.5350	1.5357
	R(34,36)	1.5256	1.5412	1.5527	1.5430	1.5435	1.5353	1.5351	1.5282	1.5351	1.5350	1.5355
	R(47,49)	1.5316	1.5395	1.5505	1.5445	1.5426	1.5340	1.5344	1.5299	1.5348	1.5352	1.5355
	R(26,29)	1.5178	1.5449	1.5556	1.5459	1.5442	1.5362	1.5353	1.5295	1.5350	1.5347	1.5354
	R(49,52)	1.5213	1.5433	1.5544	1.5443	1.5444	1.5359	1.5340	1.5286	1.5343	1.5345	1.5350
	R(23,26)	1.5184	1.5435	1.5543	1.5452	1.5435	1.5355	1.5339	1.5279	1.5337	1.5335	1.5342
	R(36,45)	1.5256	1.5405	1.5514	1.5420	1.5421	1.5339	1.5336	1.5268	1.5336	1.5337	1.5342
	R(52,55)	1.5207	1.5427	1.5538	1.5431	1.5433	1.5352	1.5333	1.5274	1.5336	1.5334	1.5340
	R(63,66)	1.5297	1.5340	1.5420	1.5553	1.5408	1.5336	1.5257	1.5209	1.5258	1.5308	1.5310
	R(55,58)	1.5266	1.5376	1.5483	1.5402	1.5402	1.5323	1.5300	1.5249	1.5301	1.5303	1.5306
	R(69,72)	1.5291	1.5417	1.5509	1.5350	1.5366	1.5294	1.5319	1.5272	1.5315	1.5257	1.5265
	R(19,47)	1.5192	1.5056	1.5234	1.4973	1.4995	1.4879	1.4892	1.4757	1.4895	1.4908	1.4911
	R(18,32)	1.5154	1.5027	1.5210	1.4964	1.4984	1.4863	1.4881	1.4736	1.4882	1.4903	1.4905
	R(18,20)	1.5054	1.5030	1.5199	1.4933	1.4947	1.4840	1.4822	1.4698	1.4821	1.4832	1.4833
	R(19,42)	1.5114	1.5039	1.5212	1.4930	1.4944	1.4832	1.4809	1.4685	1.4806	1.4830	1.4833
	R(18,39)	1.5103	1.5034	1.5215	1.4900	1.4933	1.4815	1.4837	1.4700	1.4832	1.4820	1.4823
	R(19,58)	1.5099	1.5041	1.5212	1.4933	1.4940	1.4834	1.4803	1.4676	1.4798	1.4810	1.4814
	R(62,63)	1.4365	1.5049	1.5280	1.4777	1.4808	1.4680	1.4567	1.4309	1.4582	1.4594	1.4589
	R(62,72)	1.4353	1.4949	1.5180	1.4620	1.4730	1.4607	1.4465	1.4228	1.4480	1.4529	1.4528
	R(2,16)	1.4385	1.4535	1.4654	1.4462	1.4485	1.4426	1.4485	1.4390	1.4492	1.4470	1.4472
	R(2,3)	1.4405	1.4499	1.4606	1.4451	1.4464	1.4409	1.4426	1.4340	1.4430	1.4418	1.4421
	R(5,7)	1.4423	1.4457	1.4531	1.4404	1.4432	1.4388	1.4396	1.4417	1.4398	1.4394	1.4396
	R(7,16)	1.4304	1.4421	1.4555	1.4376	1.4404	1.4352	1.4356	1.4154	1.4354	1.4383	1.4382
	R(10,12)	1.4012	1.4096	1.4187	1.4093	1.4128	1.4090	1.4089	1.4027	1.4088	1.4121	1.4120

Table 5.1 Raw bond length data for DEVJAP

	Bond list (cont.)	PM3	B3LYP/ 3-21G	MPWLYP/ 3-21G	B3LYP/ Midi	B3LYP/ Midi+	MPWTPW91/ Midi+	B3LYP/ 6-31G(d)	HF/ 6-31G(d)	B3LYP/6- 31(+LIX)G(d)	B3LYP/6- 31++G(d)	B3LYP/ 6-31+G(d)
Int. (cont.)	R(7,8)	1.3932	1.4034	1.4126	1.4024	1.4053	1.4017	1.4046	1.3978	1.4045	1.4071	1.4071
	R(14,16)	1.3961	1.4010	1.4090	1.4007	1.4038	1.4002	1.4014	1.3987	1.4016	1.4051	1.4050
	R(12,14)	1.3951	1.3935	1.4047	1.3916	1.3912	1.3912	1.3922	1.3765	1.3922	1.3941	1.3941
	R(8,10)	1.3862	1.3927	1.4035	1.3911	1.3948	1.3905	1.3914	1.3769	1.3914	1.3930	1.3931
	R(3,5)	1.3760	1.3797	1.3909	1.3797	1.3856	1.3823	1.3768	1.3580	1.3765	1.3824	1.3822
	R(2,17)	1.3667	1.3667	1.3723	1.3738	1.3777	1.3751	1.3747	1.3600	1.3749	1.3812	1.3809
	R(1,17)	1.1842	1.1873	1.2002	1.1802	1.1818	1.1787	1.1846	1.1564	1.1852	1.1833	1.1836
	R(47,48)	1.1266	1.1087	1.1161	1.1116	1.1131	1.1134	1.1101	1.0958	1.1104	1.1100	1.1105
	R(58,59)	1.1137	1.1052	1.1125	1.1097	1.1103	1.1098	1.1072	1.0934	1.1077	1.1074	1.1079
	R(42,44)	1.1142	1.105	1.1124	1.1089	1.1096	1.1094	1.1063	1.0927	1.1066	1.1063	1.1068
Short	R(39,41)	1.1138	1.1006	1.1076	1.1048	1.1054	1.1049	1.1025	1.0896	1.1024	1.1025	1.1032
	R(32,33)	1.1241	1.0995	1.1069	1.1034	1.1043	1.1044	1.1015	1.0886	1.1018	1.1017	1.1017
	R(26,28)	1.1089	1.0996	1.1069	1.1033	1.1037	1.1029	1.1004	1.0891	1.1006	1.1005	1.1009
	R(52,54)	1.1087	1.099	1.1060	1.1024	1.1030	1.1022	1.1002	1.0888	1.1001	1.1000	1.1006
	R(23,24)	1.1097	1.0967	1.1038	1.0999	1.1006	1.0997	1.0981	1.0868	1.0983	1.0984	1.0987
	R(34,35)	1.1079	1.0976	1.1049	1.1004	1.1013	1.1005	1.0980	1.0869	1.0980	1.0979	1.0985
	R(45,46)	1.1186	1.0985	1.1059	1.1001	1.1011	1.1008	1.0982	1.0870	1.0981	1.0980	1.0985
	R(20,22)	1.1150	1.0982	1.1057	1.0997	1.1012	1.1009	1.0978	1.0867	1.0978	1.0980	1.0985
	R(49,51)	1.1083	1.0971	1.1043	1.0997	1.1007	1.0999	1.0976	1.0873	1.1001	1.0983	1.0984
	R(36,38)	1.1069	1.0973	1.1042	1.1004	1.1009	1.1004	1.0975	1.0867	1.0976	1.0978	1.0983
	R(23,25)	1.1073	1.0965	1.1036	1.0994	1.1005	1.0996	1.0969	1.0862	1.0970	1.0970	1.0977
	R(63,65)	1.1058	1.0942	1.1017	1.0962	1.0992	1.0983	1.0981	1.0852	1.0982	1.0972	1.0976
	R(55,57)	1.1077	1.0965	1.1037	1.0991	1.1003	1.0993	1.0970	1.0863	1.0971	1.0970	1.0975
	R(29,30)	1.1151	1.0955	1.1027	1.0989	1.0993	1.0988	1.0968	1.0852	1.0969	1.0971	1.0974
	R(69,71)	1.1054	1.0948	1.1017	1.0983	1.0990	1.0982	1.0962	1.0854	1.0964	1.0969	1.0974
	R(26,27)	1.1071	1.096	1.1031	1.0990	1.0998	1.0989	1.0966	1.0857	1.0966	1.0966	1.0972
	R(42,43)	1.1130	1.0955	1.1027	1.0996	1.1000	1.0997	1.0972	1.0848	1.0972	1.0969	1.0970
	R(55,56)	1.1136	1.0952	1.1026	1.0990	1.0995	1.0992	1.0970	1.0852	1.0971	1.0970	1.0969
	R(72,74)	1.1093	1.0935	1.1011	1.1010	1.0997	1.0990	1.0975	1.0838	1.0976	1.0969	1.0969
	R(52,53)	1.1088	1.0956	1.1028	1.0984	1.0990	1.0982	1.0958	1.0847	1.0957	1.0959	1.0964
	R(58,60)	1.1124	1.0951	1.1023	1.0983	1.0993	1.0989	1.0964	1.0842	1.0964	1.0959	1.0961
	R(49,50)	1.1143	1.0936	1.1007	1.0986	1.0982	1.0981	1.0955	1.0828	1.0954	1.0959	1.0960
	R(36,37)	1.1136	1.0947	1.1019	1.0979	1.0982	1.0976	1.0955	1.0839	1.0955	1.0954	1.0959

Table 5.1 (cont.) Raw bond length data for DEVJAP

Bond list (cont.)	PM3	B3LYP/ 3-21G	MPWLYP/ 3-21G	B3LYP/ M6d!	B3LYP/ M6d!+	MPW1PW91/ M6d!+	B3LYP/ 6-31G(d)	HF/ 6-31G(d)	B3LYP/6- 31(+LX)G(d)	B3LYP/6- 31++G(d)	B3LYP/ 6-31+G(d)
R(39,40)	1.1143	1.0936	1.1007	1.0978	1.0982	1.0979	1.0947	1.0820	1.0947	1.0951	1.0952
R(72,73)	1.1059	1.0922	1.0997	1.0953	1.0963	1.0954	1.0953	1.0825	1.0953	1.0944	1.0947
R(66,67)	1.1054	1.0947	1.1019	1.0972	1.0980	1.0974	1.0959	1.0848	1.0960	1.0945	1.0946
R(66,68)	1.1052	1.0922	1.0993	1.0956	1.0965	1.0955	1.0937	1.0829	1.0938	1.0939	1.0944
R(20,21)	1.1117	1.0928	1.1002	1.0964	1.0974	1.0970	1.0937	1.0812	1.0936	1.0943	1.0943
R(69,70)	1.1051	1.0926	1.0998	1.0959	1.0965	1.0955	1.0939	1.0830	1.0940	1.0936	1.0942
R(63,64)	1.1090	1.0886	1.0962	1.0955	1.0951	1.0946	1.0910	1.0773	1.0912	1.0932	1.0933
R(14,15)	1.0951	1.087	1.0945	1.0917	1.0913	1.0903	1.0897	1.0784	1.0898	1.0896	1.0897
R(8,9)	1.0936	1.0857	1.0928	1.0905	1.0909	1.0900	1.0888	1.0776	1.0888	1.0890	1.0890
R(12,13)	1.0941	1.0852	1.0922	1.0895	1.0901	1.0893	1.0881	1.0771	1.0881	1.0882	1.0882
R(10,11)	1.0939	1.085	1.0920	1.0892	1.0897	1.0889	1.0878	1.0766	1.0878	1.0879	1.0879
R(3,4)	1.0871	1.0814	1.0880	1.0865	1.0866	1.0859	1.0852	1.0752	1.0853	1.0855	1.0855
R(5,6)	1.0860	1.0803	1.0872	1.0854	1.0859	1.0851	1.0845	1.0738	1.0846	1.0848	1.0848

Table 5.1 (cont.) Raw bond

length data for DEVJAP

5.4.1.1 X-ray⁶⁰

N	0.641586991870	0.311062195122	-0.945699593496	C	1.723986991870	-4.178137804878	-1.668299593496
C	1.181086991870	2.120762195122	-2.676299593496	H	2.295386991870	-4.184937804878	-2.438799593496
C	2.429586991870	2.638262195122	-3.049499593496	H	1.047586991870	-4.847237804878	-1.778199593496
H	3.271486991870	2.314762195122	-2.546899593496	C	2.512186991870	-4.407937804878	-0.466199593496
C	2.269186991870	3.600162195122	-4.014099593496	H	3.444686991870	-4.251337804878	-0.627899593496
H	2.873786991870	4.025762195122	-4.434499593496	H	2.399386991870	-5.315337804878	-0.178899593496
C	0.865486991870	3.722662195122	-4.284799593496	C	2.019886991870	-3.454637804878	0.554700406504
C	0.135886991870	4.504062195122	-5.186599593496	H	1.600586991870	-3.938137804878	1.268000406504
H	0.587586991870	5.130562195122	-5.756599593496	H	2.737486991870	-2.932037804878	0.916000406504
C	-1.233813008130	4.381562195122	-5.239199593496				
H	-1.731913008130	4.910962195122	-5.865599593496				
C	-1.901613008130	3.491162195122	-4.399399593496				
H	-2.858513008130	3.434962195122	-4.444699593496				
C	-1.217513008130	2.687662195122	-3.515199593496				
H	-1.691213008130	2.071362195122	-2.952499593496				
C	0.184186991870	2.794862195122	-3.440299593496				
C	0.915186991870	1.123162195122	-1.731999593496				
N	0.570586991870	-0.175837804878	2.319400406504				
N	-1.744413008130	-1.403237804878	1.152500406504				
C	1.977986991870	0.321262195122	2.156800406504				
H	1.962986991870	1.078862195122	1.566400406504				
H	2.509386991870	-0.361337804878	1.741000406504				
C	2.633886991870	0.741762195122	3.440100406504				
H	2.171786991870	1.499362195122	3.805100406504				
H	3.539286991870	1.005662195122	3.261800406504				
C	2.615286991870	-0.393737804878	4.431500406504				
H	2.973186991870	-0.077037804878	5.263900406504				
H	3.164086991870	-1.117237804878	4.122900406504				
C	1.177386991870	-0.858437804878	4.665200406504				
H	0.669086991870	-0.167337804878	5.096700406504				
H	1.180686991870	-1.624537804878	5.242700406504				
C	0.505686991870	-1.234737804878	3.345900406504				
H	0.984986991870	-1.988837804878	2.996600406504				
C	-0.949813008130	-1.690937804878	3.531600406504				
H	-0.965113008130	-2.336137804878	4.241200406504				
C	-1.816213008130	-0.512837804878	3.954700406504				
H	-1.441013008130	-0.092337804878	4.731800406504				
H	-2.709513008130	-0.798837804878	4.161700406504				
C	-0.375113008130	0.944362195122	2.580900406504				
H	-0.353313008130	1.552162195122	1.837100406504				
H	-0.087113008130	1.422762195122	3.361600406504				
C	-1.560913008130	-2.332737804878	2.295400406504				
H	-0.990513008130	-3.051137804878	2.014500406504				
H	-2.412213008130	-2.710637804878	2.529100406504				
C	-1.803213008130	0.459162195122	2.794300406504				
H	-2.333913008130	1.218462195122	3.052100406504				
C	-2.476213008130	-0.187737804878	1.592300406504				
H	-3.346513008130	-0.472037804878	1.881500406504				
C	-2.685013008130	0.745162195122	0.409600406504				
H	-1.832413008130	1.048262195122	0.090000406504				
H	-3.185713008130	1.512962195122	0.695100406504				
C	-3.422513008130	0.059162195122	-0.723099593496				
H	-3.477613008130	0.644762195122	-1.482499593496				
H	-4.315613008130	-0.153637804878	-0.442199593496				
C	-2.706013008130	-1.224437804878	-1.109299593496				
H	-1.852413008130	-1.001437804878	-1.487199593496				
H	-3.212013008130	-1.697737804878	-1.773599593496				
C	-2.506813008130	-2.102937804878	0.101100406504				
H	-3.368913008130	-2.354837804878	0.440100406504				
H	-2.037013008130	-2.903037804878	-0.150299593496				
Li	0.178586991870	-0.979337804878	0.490000406504				
O	1.061286991870	-2.622137804878	-0.079999593496				
C	1.108186991870	-2.867337804878	-1.470499593496				
H	1.650786991870	-2.191437804878	-1.878899593496				
H	0.235986991870	-2.843437804878	-1.866899593496				

5.4.1.2 PM3

N	0.865329230550	0.122193480414	-1.099584336090	H	0.654996246090	-2.879275399585	-1.914885932036
C	1.146046635592	1.851737271103	-2.953401174497	H	-0.042269916304	-4.153968212158	-0.857862665961
C	2.322333746626	2.082817075804	-3.752231648629	C	2.059299198512	-4.529377751646	-1.468253099446
H	3.249181672804	1.524244139092	-3.648462756879	H	2.355462227200	-4.408992458594	-2.526371204917
C	2.077737803661	3.103102083560	-4.642498192620	H	1.788487110556	-5.594956323210	-1.355280932963
H	2.765028843662	3.510642340712	-5.377997178408	C	3.187437336920	-4.134643256185	-0.516970002440
C	0.725491064908	3.563575219879	-4.443497762608	H	4.104781721979	-3.848899724012	-1.062877666021
C	-0.017227697382	4.561044181379	-5.071583417931	H	3.479892838845	-4.978220330287	0.134830340540
H	0.426922434155	5.156078587563	-5.874408516512	C	2.638998842543	-2.962886095246	0.298025386373
C	-1.322166712774	4.779043097083	-4.657922187733	H	2.742667660481	-3.084945299150	1.392288057672
H	-1.921698291836	5.557612183091	-5.138495443296	H	3.090516147011	-1.991314977986	0.010280378534
C	-1.891725123243	4.016082420308	-3.629851691711				
H	-2.924909720849	4.214987965414	-3.329767407389				
C	-1.172127234180	3.019667117951	-2.991284084991				
H	-1.622690192459	2.425307119885	-2.189363702447				
C	0.144290983057	2.785767344819	-3.393179645342				
C	1.003489044668	0.921776419817	-1.962099415264				
N	0.580475947792	-0.172728610087	2.356533079393				
N	-1.807856765156	-1.313657910225	1.024017609885				
C	2.008556478528	0.303119198324	2.379396318756				
H	2.105246253986	1.174136071987	1.695392627694				
H	2.632750877864	-0.510443330098	1.941474274769				
C	2.525662332817	0.662879164925	3.768628651775				
H	2.010887378903	1.565271141213	4.158637810506				
H	3.595616276919	0.939531606098	3.700091037612				
C	2.343556816687	-0.499165011858	4.728916373905				
H	2.673878155034	-0.210367818185	5.745305448092				
H	2.995606421783	-1.344783739386	4.429847855796				
C	0.894246713587	-0.948669850954	4.764452747043				
H	0.247936944468	-0.166174879841	5.226533203236				
H	0.793668940380	-1.838320763583	5.416945317554				
C	0.363770111791	-1.286743854916	3.360727738469				
H	0.942993359531	-2.165103470123	2.964939719825				
C	-1.129326193092	-1.668024228197	3.460222746830				
H	-1.222239165130	-2.442801857664	4.261646668626				
C	-1.935199081781	-0.433842990361	3.853810074035				
H	-1.519083934203	0.002726531711	4.789966460739				
H	-2.987181682930	-0.696655432370	4.076071875447				
C	-0.379348659561	0.983674466495	2.506376678356				
H	-0.288817027505	1.610772470889	1.589716967053				
H	-0.076139105993	1.628528895977	3.362369828182				
C	-1.691462040633	-2.289103930377	2.172560156456				
H	-1.044358766186	-3.130850306344	1.838496023432				
H	-2.686394258054	-2.733365649330	2.405152095895				
C	-1.842069362517	0.567585475041	2.706700976912				
H	-2.413637625601	1.492267338952	2.969220231906				
C	-2.522847572561	-0.049397382519	1.469384320773				
H	-3.569620088363	-0.329228535638	1.777899355459				
C	-2.635715706227	0.943303668615	0.308565812331				
H	-1.630761576949	1.295407139748	-0.019772300344				
H	-3.167712710039	1.851116046605	0.656600149220				
C	-3.384523357312	0.315640733463	-0.857500386114				
H	-3.414436240378	1.025355517910	-1.708884180974				
H	-4.441812177756	0.130794775804	-0.579541823859				
C	-2.719349729390	-0.982167466707	-1.288571564595				
H	-1.728854207573	-0.768545180480	-1.750620472615				
H	-3.318270427072	-1.470090238309	-2.082459064091				
C	-2.567907549582	-1.947968508470	-0.116025699961				
H	-3.570576277776	-2.295143785481	0.222271210408				
H	-2.015342048341	-2.858653054125	-0.436583245393				
Li	0.338548749834	-1.057549422302	0.313438057038				
O	1.221128648549	-2.897541080852	0.084617848965				
C	0.886740510247	-3.612383096750	-1.115625321338				

Table 5.2 Signed and Unsigned differences in bond length for the PM3 structure of DEVJAP relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(19,61)	2.1211	2.2754	0.1543	0.1543
R(18,61)	2.1022	2.2396	0.1374	0.1374
R(61,62)	2.0469	2.0535	0.0066	0.0066
R(1,61)	1.9703	1.9147	-0.0556	0.0556
R(32,34)	1.5471	1.5442	-0.0029	0.0029
R(29,32)	1.5470	1.5382	-0.0088	0.0088
R(45,47)	1.5457	1.5411	-0.0046	0.0046
R(39,45)	1.5425	1.5339	-0.0086	0.0086
R(34,42)	1.5422	1.5362	-0.0060	0.0060
R(66,69)	1.5370	1.5276	-0.0094	0.0094
R(20,23)	1.5357	1.5254	-0.0103	0.0103
R(34,36)	1.5355	1.5256	-0.0099	0.0099
R(47,49)	1.5355	1.5316	-0.0039	0.0039
R(26,29)	1.5354	1.5178	-0.0176	0.0176
R(49,52)	1.5350	1.5213	-0.0137	0.0137
R(23,26)	1.5342	1.5184	-0.0158	0.0158
R(36,45)	1.5342	1.5256	-0.0086	0.0086
R(52,55)	1.5340	1.5207	-0.0133	0.0133
R(63,66)	1.5310	1.5297	-0.0013	0.0013
R(55,58)	1.5306	1.5266	-0.0040	0.0040
R(69,72)	1.5265	1.5291	0.0026	0.0026
R(19,47)	1.4911	1.5192	0.0281	0.0281
R(18,32)	1.4905	1.5154	0.0249	0.0249
R(18,20)	1.4833	1.5054	0.0221	0.0221
R(19,42)	1.4833	1.5103	0.0280	0.0280
R(18,39)	1.4823	1.5099	0.0285	0.0285
R(19,58)	1.4814	1.4365	-0.0224	0.0224
R(62,63)	1.4589	1.4353	-0.0175	0.0175
R(62,72)	1.4528	1.4385	-0.0087	0.0087
R(2,16)	1.4472	1.4405	-0.0016	0.0016
R(2,3)	1.4421	1.4423	0.0027	0.0027
R(5,7)	1.4396	1.4304	-0.0078	0.0078
R(7,16)	1.4382	1.4012	-0.0108	0.0108
R(10,12)	1.4120	1.3932	-0.0139	0.0139
R(7,8)	1.4071	1.3961	-0.0089	0.0089
R(14,16)	1.4050	1.3851	-0.0090	0.0090
R(12,14)	1.3941	1.3862	-0.0069	0.0069
R(8,10)	1.3931	1.3760	-0.0062	0.0062
R(3,5)	1.3822	1.3667	-0.0142	0.0142
R(2,17)	1.3809	1.1842	0.0006	0.0006
R(1,17)	1.1836	1.5103	0.0280	0.0280
R(47,48)	1.1105	1.1266	0.0161	0.0161
R(58,59)	1.1079	1.1137	0.0058	0.0058
R(42,44)	1.1068	1.1142	0.0074	0.0074
R(39,41)	1.1032	1.1138	0.0106	0.0106
R(32,33)	1.1017	1.1241	0.0224	0.0224
R(26,28)	1.1009	1.1089	0.0080	0.0080
R(52,54)	1.1006	1.1087	0.0081	0.0081

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(23,24)	1.0987	1.1097	0.0110	0.0110
R(29,31)	1.0985	1.1079	0.0094	0.0094
R(34,35)	1.0985	1.1186	0.0201	0.0201
R(45,46)	1.0985	1.1183	0.0198	0.0198
R(20,22)	1.0984	1.1150	0.0166	0.0166
R(49,51)	1.0983	1.1083	0.0100	0.0100
R(36,38)	1.0981	1.1069	0.0088	0.0088
R(23,25)	1.0977	1.1073	0.0096	0.0096
R(63,65)	1.0976	1.1058	0.0082	0.0082
R(55,57)	1.0975	1.1077	0.0102	0.0102
R(29,30)	1.0974	1.1151	0.0177	0.0177
R(69,71)	1.0974	1.1054	0.0080	0.0080
R(26,27)	1.0972	1.1071	0.0099	0.0099
R(42,43)	1.0970	1.1130	0.0160	0.0160
R(55,56)	1.0969	1.1136	0.0167	0.0167
R(72,74)	1.0969	1.1093	0.0124	0.0124
R(52,53)	1.0964	1.1088	0.0124	0.0124
R(58,60)	1.0961	1.1097	0.0110	0.0110
R(49,50)	1.0960	1.1124	0.0163	0.0163
R(36,37)	1.0959	1.1143	0.0183	0.0183
R(39,40)	1.0952	1.1136	0.0177	0.0177
R(72,73)	1.0947	1.1143	0.0191	0.0191
R(66,67)	1.0946	1.1059	0.0112	0.0112
R(66,68)	1.0944	1.1054	0.0108	0.0108
R(20,21)	1.0943	1.1052	0.0108	0.0108
R(69,70)	1.0942	1.1117	0.0174	0.0174
R(63,64)	1.0933	1.1051	0.0109	0.0109
R(14,15)	1.0897	1.1090	0.0157	0.0157
R(8,9)	1.0890	1.0951	0.0054	0.0054
R(12,13)	1.0882	1.0936	0.0046	0.0046
R(10,11)	1.0879	1.0941	0.0059	0.0059
R(3,4)	1.0855	1.0939	0.0060	0.0060
R(5,6)	1.0987	1.0871	0.0016	0.0016

5.4.1.3 B3LYP/3-21G

N	0.530854365104	0.359593177627	-0.795652095990	H	-1.799290086256	-0.815838914926	-1.509727660710
C	1.076932680921	2.112562085997	-2.570857534423	H	-3.378101090253	-1.554450841678	-1.857738628090
C	2.360610410674	2.734156696797	-2.831514908693	C	-2.610360186686	-1.993769751197	0.112018342546
H	3.261736850336	2.518491920652	-2.274001136688	H	-3.602242384387	-2.292443793342	0.497151132852
C	2.240631577586	3.622350616285	-3.880408702070	H	-2.065684086519	-2.896713318770	-0.183202656101
H	3.032221105472	4.230017161191	-4.294095424367	Li	0.077892123265	-0.978096571302	0.552675286631
C	0.870300131436	3.609106018823	-4.341047568631	O	0.793232431155	-2.691375410664	-0.060558289399
C	0.206398484921	4.304186695385	-5.363643086784	C	0.905996648003	-2.789160273233	-1.558023940558
H	0.748466630003	5.014050359066	-5.980969348881	H	0.714662014440	-1.789269166953	-1.943484957712
C	-1.150281129517	4.076550348865	-5.581161578740	H	0.160322927532	-3.505733925761	-1.915567402359
H	-1.667673586049	4.611284191771	-6.370779843945	C	2.334794262259	-3.288286404122	-1.808228923850
C	-1.863213913908	3.156708815727	-4.785861953000	H	3.036643883515	-2.449854155533	-1.755200908741
H	-2.919789258965	2.995651703127	-4.973885339260	H	2.432797498329	-3.781765768227	-2.777673300062
C	-1.227531999713	2.454421111583	-3.763839868483	C	2.561108475068	-4.254656154844	-0.618791942136
H	-1.785576767492	1.746779344945	-3.155971143908	H	3.619165458565	-4.442805462339	-0.421787895271
C	0.136785029778	2.669674889457	-3.529243752047	H	2.055040363003	-5.206745561409	-0.808514831125
C	0.794036695160	1.175786214692	-1.616757927384	C	1.884656101225	-3.510525555322	0.549716717325
N	0.627136248885	-0.260934604632	2.366052592265	H	1.442617875289	-4.184202560019	1.287038595460
N	-1.816088173610	-1.340891074625	1.209813178272	H	2.585579729434	-2.829511532191	1.040213214992
C	2.058739955176	0.154464632780	2.173428363585				
H	2.063544906494	0.968120011997	1.443879369204				
H	2.580766662815	-0.699830206924	1.722036330126				
C	2.778021547132	0.540926612714	3.481784938759				
H	2.314001472689	1.433523217972	3.918364356238				
H	3.822482662129	0.786882228711	3.256302383525				
C	2.696511011711	-0.629604357867	4.484641364814				
H	3.177936707359	-0.361378139762	5.432052611350				
H	3.233814394364	-1.496361031130	4.073466934018				
C	1.219061013922	-1.009759703815	4.728479962955				
H	0.714783499804	-0.171999674892	5.222532241286				
H	1.152081170494	-1.879225826244	5.395046176906				
C	0.504081198751	-1.351111996583	3.392950445196				
H	1.018405477307	-2.223720047034	2.965295779734				
C	-0.984637016972	-1.721234153801	3.599732125143				
H	-1.020296551025	-2.495728967922	4.377990495466				
C	-1.789415730501	-0.485211243177	4.046824473100				
H	-1.372921943381	-0.050288438847	4.961063644232				
H	-2.828529050530	-0.770068419581	4.254413488593				
C	-0.267800435211	0.921182187435	2.615071752380				
H	-0.195894333242	1.553226221665	1.725469559312				
H	0.080244604761	1.508623333178	3.478254831449				
C	-1.653493863756	-2.320782688664	2.338997888966				
H	-1.058775226039	-3.155738678542	1.952768991134				
H	-2.644920355297	-2.709424312405	2.633967348001				
C	-1.739673017399	0.523874801493	2.883942345570				
H	-2.273180638355	1.442205574353	3.163331619831				
C	-2.493492217832	-0.079054289086	1.674236226844				
H	-3.508839312997	-0.342389141417	2.033179719838				
C	-2.650205937886	0.902989753702	0.499018644526				
H	-1.662088972775	1.178289939166	0.119940349107				
H	-3.150909128707	1.807888179593	0.865285075102				
C	-3.461971271451	0.265123118440	-0.648133044286				
H	-3.520364218431	0.959707307493	-1.493432482409				
H	-4.486183690893	0.056466735837	-0.308694930040				
C	-2.783073188597	-1.048374534170	-1.088224131392				

Table 5.3 Signed and Unsigned differences in bond length for the B3LYP/3-21G structure of DEVJAP relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(19,61)	2.1211	2.0373	-0.0838	0.0838
R(18,61)	2.1022	2.0259	-0.0763	0.0763
R(61,62)	2.0469	1.9553	-0.0916	0.0916
R(1,61)	1.9703	1.9526	-0.0177	0.0177
R(32,34)	1.5471	1.5479	0.0008	0.0008
R(29,32)	1.5470	1.5529	0.0059	0.0059
R(45,47)	1.5457	1.5476	0.0019	0.0019
R(39,45)	1.5425	1.5481	0.0056	0.0056
R(34,42)	1.5422	1.5480	0.0058	0.0058
R(66,69)	1.5370	1.5491	0.0121	0.0121
R(20,23)	1.5357	1.5422	0.0065	0.0065
R(34,36)	1.5355	1.5412	0.0057	0.0057
R(47,49)	1.5355	1.5395	0.0040	0.0040
R(26,29)	1.5354	1.5449	0.0095	0.0095
R(49,52)	1.5350	1.5433	0.0083	0.0083
R(23,26)	1.5342	1.5435	0.0093	0.0093
R(36,45)	1.5342	1.5405	0.0063	0.0063
R(52,55)	1.5340	1.5427	0.0087	0.0087
R(63,66)	1.5310	1.5340	0.0030	0.0030
R(55,58)	1.5306	1.5376	0.0070	0.0070
R(69,72)	1.5265	1.5417	0.0152	0.0152
R(19,47)	1.4911	1.5056	0.0145	0.0145
R(18,32)	1.4905	1.5027	0.0122	0.0122
R(18,20)	1.4833	1.5030	0.0197	0.0197
R(19,42)	1.4833	1.5039	0.0206	0.0206
R(18,39)	1.4823	1.5034	0.0211	0.0211
R(19,58)	1.4814	1.5041	0.0227	0.0227
R(62,63)	1.4589	1.5049	0.0460	0.0460
R(62,72)	1.4528	1.4949	0.0421	0.0421
R(2,16)	1.4472	1.4535	0.0063	0.0063
R(2,3)	1.4421	1.4499	0.0078	0.0078
R(5,7)	1.4396	1.4457	0.0061	0.0061
R(7,16)	1.4382	1.4421	0.0039	0.0039
R(10,12)	1.4120	1.4096	-0.0024	0.0024
R(7,8)	1.4071	1.4034	-0.0037	0.0037
R(14,16)	1.4050	1.4010	-0.0040	0.0040
R(12,14)	1.3941	1.3935	-0.0006	0.0006
R(8,10)	1.3931	1.3927	-0.0004	0.0004
R(3,5)	1.3822	1.3797	-0.0025	0.0025
R(2,17)	1.3809	1.3667	-0.0142	0.0142
R(1,17)	1.1836	1.1873	0.0037	0.0037
R(47,48)	1.1105	1.1087	-0.0018	0.0018
R(58,59)	1.1079	1.1052	-0.0027	0.0027
R(42,44)	1.1068	1.1050	-0.0018	0.0018
R(39,41)	1.1032	1.1006	-0.0026	0.0026
R(32,33)	1.1017	1.0995	-0.0022	0.0022
R(26,28)	1.1009	1.0996	-0.0013	0.0013
R(52,54)	1.1006	1.0990	-0.0016	0.0016

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(23,24)	1.0987	1.0967	-0.0020	0.0020
R(29,31)	1.0985	1.0976	-0.0009	0.0009
R(34,35)	1.0985	1.0985	0.0000	0.0000
R(45,46)	1.0985	1.0982	-0.0003	0.0003
R(20,22)	1.0984	1.0982	-0.0002	0.0002
R(49,51)	1.0983	1.0971	-0.0012	0.0012
R(36,38)	1.0981	1.0973	-0.0008	0.0008
R(23,25)	1.0977	1.0965	-0.0012	0.0012
R(63,65)	1.0976	1.0942	-0.0034	0.0034
R(55,57)	1.0975	1.0965	-0.0010	0.0010
R(29,30)	1.0974	1.0955	-0.0019	0.0019
R(69,71)	1.0974	1.0948	-0.0026	0.0026
R(26,27)	1.0972	1.096	-0.0012	0.0012
R(42,43)	1.0970	1.0955	-0.0015	0.0015
R(55,56)	1.0969	1.0952	-0.0017	0.0017
R(72,74)	1.0969	1.0935	-0.0034	0.0034
R(52,53)	1.0964	1.0956	-0.0008	0.0008
R(58,60)	1.0961	1.0951	-0.0010	0.0010
R(49,50)	1.0960	1.0936	-0.0024	0.0024
R(36,37)	1.0959	1.0947	-0.0012	0.0012
R(39,40)	1.0952	1.0936	-0.0016	0.0016
R(72,73)	1.0947	1.0922	-0.0025	0.0025
R(66,67)	1.0946	1.0947	1E-04	1E-04
R(66,68)	1.0944	1.0922	-0.0022	0.0022
R(20,21)	1.0943	1.0928	-0.0015	0.0015
R(69,70)	1.0942	1.0926	-0.0016	0.0016
R(63,64)	1.0933	1.0886	-0.0047	0.0047
R(14,15)	1.0897	1.087	-0.0027	0.0027
R(8,9)	1.0890	1.0857	-0.0033	0.0033
R(12,13)	1.0882	1.0852	-0.0030	0.0030
R(10,11)	1.0879	1.085	-0.0029	0.0029
R(3,4)	1.0855	1.0814	-0.0041	0.0041
R(5,6)	1.0987	1.0803	-0.0045	0.0045

5.4.1.4 MPWLYP/3-21G

N	0.569302014760	0.310762492736	-0.815173194509	H	-2.129116084851	-2.902015839692	-0.175938093579
C	1.087126459207	2.089251306789	-2.600104459760	Li	0.084079125913	-1.010767934512	0.543412306535
C	2.371999904897	2.723991248901	-2.882293049242	O	0.746018029460	-2.771483406419	-0.061984682826
H	3.289686099514	2.504188683448	-2.340644137281	C	0.936111041158	-2.836963397917	-1.576721147108
C	2.224899271217	3.629146612205	-3.928049888596	H	0.689956315005	-1.836116676858	-1.950038155959
H	3.010871507357	4.248134409216	-4.353516007164	H	0.257342199254	-3.605311148265	-1.980016547855
C	0.839075576275	3.615634506490	-4.364910128293	C	2.416429860701	-3.224218233724	-1.767761001087
C	0.146975564710	4.322443764896	-5.373334155137	H	3.052441163878	-2.331862087323	-1.652082103024
H	0.676813191230	5.045656009915	-5.998163256725	H	2.599804852644	-3.681157385590	-2.750673898031
C	-1.223273119109	4.088842355872	-5.567436076104	C	2.658164517036	-4.217889660452	-0.589459671180
H	-1.761605122904	4.632856224602	-6.346306085231	H	3.724396271589	-4.337016136078	-0.347729492811
C	-1.921521977476	3.151755337405	-4.763038788448	H	2.227830427072	-5.202456486759	-0.832874666907
H	-2.987701553066	2.986645671479	-4.932744111454	C	1.876019013740	-3.558858107142	0.576384247181
C	-1.257683004705	2.436098460698	-3.752901395598	H	1.439591433538	-4.290819092372	1.271505667553
H	-1.805125701523	1.714389688954	-3.138635845262	H	2.510240204918	-2.847314876577	1.127678954161
C	0.117878539810	2.656212111471	-3.541574659434				
C	0.823209433925	1.140748715667	-1.644174127048				
N	0.648066568426	-0.288285332125	2.365657320469				
N	-1.831683245671	-1.321625514912	1.204659183268				
C	2.107783675712	0.097539521101	2.191340114677				
H	2.137775496137	0.905356774744	1.445079599908				
H	2.616621304067	-0.782869269898	1.757145281924				
C	2.825369282214	0.487570397639	3.512130676861				
H	2.372843612975	1.401671054605	3.934102579593				
H	3.884520966387	0.707822010455	3.293773234968				
C	2.705681160370	-0.676232593067	4.535395693781				
H	3.186317466300	-0.405195869100	5.490553621965				
H	3.230725242857	-1.565555391106	4.137149656945				
C	1.207967029367	-1.023784548037	4.772212526543				
H	0.714354141711	-0.165903958524	5.258451622633				
H	1.117164623261	-1.891804716514	5.449746794233				
C	0.486373463410	-1.366337468862	3.426404443051				
H	0.980857856360	-2.265716946182	3.011796906735				
C	-1.025852965934	-1.691120056957	3.628932651376				
H	-1.088648477748	-2.456903558984	4.424299204540				
C	-1.802450117263	-0.416052574471	4.055435132139				
H	-1.372279047247	0.024791932966	4.969142267142				
H	-2.856602894417	-0.670004972161	4.264259491041				
C	-0.224452482910	0.936075279213	2.599552655844				
H	-0.129767221514	1.552692242530	1.692685609950				
H	0.138199465256	1.529609959952	3.461548847422				
C	-1.711420607430	-2.297321662198	2.365543019046				
H	-1.136976432803	-3.162385315115	1.994434385493				
H	-2.724454031239	-2.648596487478	2.661676099198				
C	-1.719450100415	0.579369179664	2.868333442583				
H	-2.231312924034	1.522970108207	3.132529707522				
C	-2.492227225926	-0.024982561653	1.655501117608				
H	-3.520273557959	-0.263747337145	2.018661541976				
C	-2.624093106107	0.950635198152	0.457614353021				
H	-1.621665389170	1.202771444610	0.079465661207				
H	-3.112043327940	1.875270219399	0.813248604594				
C	-3.448581588782	0.312647358807	-0.695330931786				
H	-3.477463213078	1.000692419181	-1.556741276187				
H	-4.487930140691	0.137183284333	-0.360344377383				
C	-2.800537652655	-1.035634141585	-1.115369036434				
H	-1.802764409268	-0.835855224600	-1.539840090241				
H	-3.411982906984	-1.540029837962	-1.883329395940				
C	-2.655972269422	-1.975824594098	0.106204192043				
H	-3.662105834574	-2.242304518171	0.499165075741				

Table 5.4 Signed and Unsigned differences in bond length for the MPWLYP/3-21G structure of DEVJAP relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(19,61)	2.1211	2.0504	-0.0707	0.0707
R(18,61)	2.1022	2.0398	-0.0624	0.0624
R(61,62)	2.0469	1.9761	-0.0708	0.0708
R(1,61)	1.9703	1.9564	-0.0139	0.0139
R(32,34)	1.5471	1.5599	0.0128	0.0128
R(29,32)	1.5470	1.5650	0.0180	0.0180
R(45,47)	1.5457	1.5599	0.0142	0.0142
R(39,45)	1.5425	1.5603	0.0178	0.0178
R(34,42)	1.5422	1.5600	0.0178	0.0178
R(66,69)	1.5370	1.5602	0.0232	0.0232
R(20,23)	1.5357	1.5529	0.0172	0.0172
R(34,36)	1.5355	1.5527	0.0172	0.0172
R(47,49)	1.5355	1.5505	0.0150	0.0150
R(26,29)	1.5354	1.5556	0.0202	0.0202
R(49,52)	1.5350	1.5544	0.0194	0.0194
R(23,26)	1.5342	1.5543	0.0201	0.0201
R(36,45)	1.5342	1.5514	0.0172	0.0172
R(52,55)	1.5340	1.5538	0.0198	0.0198
R(63,66)	1.5310	1.5420	0.0110	0.0110
R(55,58)	1.5306	1.5483	0.0177	0.0177
R(69,72)	1.5265	1.5509	0.0244	0.0244
R(19,47)	1.4911	1.5234	0.0323	0.0323
R(18,32)	1.4905	1.5210	0.0305	0.0305
R(18,20)	1.4833	1.5199	0.0366	0.0366
R(19,42)	1.4833	1.5212	0.0379	0.0379
R(18,39)	1.4823	1.5215	0.0392	0.0392
R(19,58)	1.4814	1.5212	0.0398	0.0398
R(62,63)	1.4589	1.5280	0.0691	0.0691
R(62,72)	1.4528	1.5180	0.0652	0.0652
R(2,16)	1.4472	1.4654	0.0182	0.0182
R(2,3)	1.4421	1.4606	0.0185	0.0185
R(5,7)	1.4396	1.4531	0.0135	0.0135
R(7,16)	1.4382	1.4555	0.0173	0.0173
R(10,12)	1.4120	1.4187	0.0067	0.0067
R(7,8)	1.4071	1.4126	0.0055	0.0055
R(14,16)	1.4050	1.4090	0.0040	0.0040
R(12,14)	1.3941	1.4047	0.0106	0.0106
R(8,10)	1.3931	1.4035	0.0104	0.0104
R(3,5)	1.3822	1.3909	0.0087	0.0087
R(2,17)	1.3809	1.3723	-0.0086	0.0086
R(1,17)	1.1836	1.2002	0.0166	0.0166
R(47,48)	1.1105	1.1161	0.0056	0.0056
R(58,59)	1.1079	1.1125	0.0046	0.0046
R(42,44)	1.1068	1.1124	0.0056	0.0056
R(39,41)	1.1032	1.1076	0.0044	0.0044
R(32,33)	1.1017	1.1069	0.0052	0.0052
R(26,28)	1.1009	1.1069	0.0060	0.0060
R(52,54)	1.1006	1.1060	0.0054	0.0054

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(23,24)	1.0987	1.1038	0.0051	0.0051
R(29,31)	1.0985	1.1049	0.0064	0.0064
R(34,35)	1.0985	1.1059	0.0074	0.0074
R(45,46)	1.0985	1.1055	0.0070	0.0070
R(20,22)	1.0984	1.1057	0.0073	0.0073
R(49,51)	1.0983	1.1043	0.0060	0.0060
R(36,38)	1.0981	1.1042	0.0061	0.0061
R(23,25)	1.0977	1.1036	0.0059	0.0059
R(63,65)	1.0976	1.1017	0.0041	0.0041
R(55,57)	1.0975	1.1037	0.0062	0.0062
R(29,30)	1.0974	1.1027	0.0053	0.0053
R(69,71)	1.0974	1.1017	0.0043	0.0043
R(26,27)	1.0972	1.1031	0.0059	0.0059
R(42,43)	1.0970	1.1027	0.0057	0.0057
R(55,56)	1.0969	1.1026	0.0057	0.0057
R(72,74)	1.0969	1.1011	0.0042	0.0042
R(52,53)	1.0964	1.1028	0.0064	0.0064
R(58,60)	1.0961	1.1023	0.0062	0.0062
R(49,50)	1.0960	1.1007	0.0047	0.0047
R(36,37)	1.0959	1.1019	0.0060	0.0060
R(39,40)	1.0952	1.1007	0.0055	0.0055
R(72,73)	1.0947	1.0997	0.0050	0.0050
R(66,67)	1.0946	1.1019	0.0073	0.0073
R(66,68)	1.0944	1.0993	0.0049	0.0049
R(20,21)	1.0943	1.1002	0.0059	0.0059
R(69,70)	1.0942	1.0998	0.0056	0.0056
R(63,64)	1.0933	1.0962	0.0029	0.0029
R(14,15)	1.0897	1.0945	0.0048	0.0048
R(8,9)	1.0890	1.0928	0.0038	0.0038
R(12,13)	1.0882	1.0922	0.0040	0.0040
R(10,11)	1.0879	1.0920	0.0041	0.0041
R(3,4)	1.0855	1.0880	0.0025	0.0025
R(5,6)	1.0987	1.0872	0.0024	0.0024

5.4.1.5 B3LYP/Midi!

N	0.554471518789	0.078966857594	-0.956573965560			
C	1.199482199671	1.720874368333	-2.803337898913	Li	0.033129734308	-1.020154240404
C	2.473821576175	1.841168696842	-3.474188359512	O	0.972791064967	-2.742442833053
H	3.336641090166	1.215831984069	-3.262337207048	C	0.612297712554	-3.234937214022
C	2.410459062667	2.859613684230	-4.402768941143	H	0.189918873949	-2.404459276194
H	3.215670450002	3.181116529728	-5.055723304281	H	-0.139455914962	-4.020165242962
C	1.090069226924	3.433959798749	-4.363534988800	C	1.918253768818	-3.777557093953
C	0.486235333195	4.479364133658	-5.077187477767	H	2.286032387519	-3.074627319101
H	1.052779736793	5.022755788078	-5.834174756208	H	1.767828957036	-4.753554970925
C	-0.836822358980	4.820253894802	-4.815365347106	C	2.905270386907	-3.844942201590
H	-1.307544051062	5.632099071706	-5.368289446504	H	3.951203141377	-3.750456165817
C	-1.578802357602	4.124668340958	-3.839814774274	H	2.781938874527	-4.783442993150
H	-2.613854964505	4.407533868613	-3.650911638416	C	2.431475388021	-2.659855543609
C	-1.002385494253	3.083423864168	-3.118634076567	H	2.722605664784	-2.725413901767
H	-1.582067588000	2.547990182648	-2.364322423789	H	2.769024505804	-1.701309371886
C	0.329211874426	2.728080404734	-3.368816329320			-0.237337305122
C	0.861336901788	0.832133920849	-1.811808906662			
N	0.437644314513	-0.135242430859	2.313795137340			
N	-1.851323738189	-1.483567149002	1.159979687358			
C	1.809654729909	0.425025296607	2.130455508963			
H	1.735178854393	1.230739127206	1.390594666283			
H	2.426074393304	-0.367196002553	1.681192224704			
C	2.490506855359	0.891600762388	3.436611205417			
H	1.948887264379	1.743227987573	3.873719953583			
H	3.507323460140	1.240174895030	3.205824658104			
C	2.531393800756	-0.279058759551	4.444308799067			
H	2.980239709606	0.041105965794	5.394953662126			
H	3.165259541518	-1.086101417909	4.039245157220			
C	1.102011597435	-0.816980497087	4.683455404888			
H	0.510831022799	-0.045567954936	5.196312218592			
H	1.130058579692	-1.697713445141	5.342554082314			
C	0.426078708466	-1.220956196787	3.343454172311			
H	1.023815594393	-2.041875609829	2.911834346804			
C	-1.020318879869	-1.744747479378	3.553376059324			
H	-0.977731577759	-2.511649496640	4.340907567054			
C	-1.955706573978	-0.595005503329	3.982349762264			
H	-1.608631254989	-0.115021853731	4.906792653506			
H	-2.967912865590	-0.982203991301	4.173362167516			
C	-0.544634491694	0.950204703911	2.591325661167			
H	-0.515485698616	1.627089557365	1.727589525134			
H	-0.268958298171	1.543496879023	3.481550173482			
C	-1.623286828031	-2.422594152600	2.298143255160			
H	-0.943970363412	-3.204769092114	1.929522233445			
H	-2.576315856494	-2.904848139472	2.596002676637			
C	-1.976501778781	0.410845572295	2.813818332350			
H	-2.612952098941	1.270423186239	3.069966254726			
C	-2.620445341725	-0.269653733557	1.580521438157			
H	-3.639535287271	-0.584349511467	1.893815997159			
C	-2.770000546257	0.684879906743	0.375576120748			
H	-1.776200511338	0.991918416378	0.021988205073			
H	-3.312404042310	1.585215045122	0.699044617665			
C	-3.516195950613	-0.006333869981	-0.786409820634			
H	-3.554537818726	0.661801024228	-1.657373215704			
H	-4.553705229747	-0.226636995002	-0.485807203857			
C	-2.785347475876	-1.315416061141	-1.151594955901			
H	-1.794201355093	-1.067127399618	-1.556363115440			
H	-3.340442681036	-1.871209804705	-1.920284504940			
C	-2.615589571656	-2.201505286975	0.096741933700			
H	-3.610138614714	-2.506729245767	0.482922339656			
H	-2.061657260427	-3.116508399535	-0.152449414998			

Table 5.5 Signed and Unsigned differences in bond length for the B3LYP/Midi! structure of DEVJAP relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(19,61)	2.1211	2.0413	-0.0798	0.0798
R(18,61)	2.1022	2.0349	-0.0673	0.0673
R(61,62)	2.0469	2.0010	-0.0459	0.0459
R(1,61)	1.9703	1.9182	-0.0521	0.0521
R(32,34)	1.5471	1.5526	0.0055	0.0055
R(29,32)	1.5470	1.5542	0.0072	0.0072
R(45,47)	1.5457	1.5488	0.0031	0.0031
R(39,45)	1.5425	1.5462	0.0037	0.0037
R(34,42)	1.5422	1.5488	0.0066	0.0066
R(66,69)	1.5370	1.5502	0.0132	0.0132
R(20,23)	1.5357	1.5451	0.0094	0.0094
R(34,36)	1.5355	1.5430	0.0075	0.0075
R(47,49)	1.5355	1.5445	0.0090	0.0090
R(26,29)	1.5354	1.5459	0.0105	0.0105
R(49,52)	1.5350	1.5443	0.0093	0.0093
R(23,26)	1.5342	1.5452	0.0110	0.0110
R(36,45)	1.5342	1.5420	0.0078	0.0078
R(52,55)	1.5340	1.5431	0.0091	0.0091
R(63,66)	1.5310	1.5553	0.0243	0.0243
R(55,58)	1.5306	1.5402	0.0096	0.0096
R(69,72)	1.5265	1.5350	0.0085	0.0085
R(19,47)	1.4911	1.4973	0.0062	0.0062
R(18,32)	1.4905	1.4964	0.0059	0.0059
R(18,20)	1.4833	1.4933	0.0100	0.0100
R(19,42)	1.4833	1.4930	0.0097	0.0097
R(18,39)	1.4823	1.4900	0.0077	0.0077
R(19,58)	1.4814	1.4933	0.0119	0.0119
R(62,63)	1.4589	1.4777	0.0188	0.0188
R(62,72)	1.4528	1.4620	0.0092	0.0092
R(2,16)	1.4472	1.4462	-0.0010	0.0010
R(2,3)	1.4421	1.4451	0.0030	0.0030
R(5,7)	1.4396	1.4404	0.0008	0.0008
R(7,16)	1.4382	1.4376	-0.0006	0.0006
R(10,12)	1.4120	1.4093	-0.0027	0.0027
R(7,8)	1.4071	1.4024	-0.0047	0.0047
R(14,16)	1.4050	1.4007	-0.0043	0.0043
R(12,14)	1.3941	1.3916	-0.0025	0.0025
R(8,10)	1.3931	1.3911	-0.0020	0.0020
R(3,5)	1.3822	1.3797	-0.0025	0.0025
R(2,17)	1.3809	1.3738	-0.0071	0.0071
R(1,17)	1.1836	1.1802	-0.0034	0.0034
R(47,48)	1.1105	1.1116	0.0011	0.0011
R(58,59)	1.1079	1.1097	0.0018	0.0018
R(42,44)	1.1068	1.1089	0.0021	0.0021
R(39,41)	1.1032	1.1048	0.0016	0.0016
R(32,33)	1.1017	1.1034	0.0017	0.0017
R(26,28)	1.1009	1.1033	0.0024	0.0024
R(52,54)	1.1006	1.1024	0.0018	0.0018

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(23,24)	1.0987	1.0999	0.0012	0.0012
R(29,31)	1.0985	1.1004	0.0019	0.0019
R(34,35)	1.0985	1.1001	0.0016	0.0016
R(45,46)	1.0985	1.0998	0.0013	0.0013
R(20,22)	1.0984	1.0997	0.0013	0.0013
R(49,51)	1.0983	1.0997	0.0014	0.0014
R(36,38)	1.0981	1.1004	0.0023	0.0023
R(23,25)	1.0977	1.0994	0.0017	0.0017
R(63,65)	1.0976	1.0962	-0.0014	0.0014
R(55,57)	1.0975	1.0991	0.0016	0.0016
R(29,30)	1.0974	1.0989	0.0015	0.0015
R(69,71)	1.0974	1.0983	0.0009	0.0009
R(26,27)	1.0972	1.0990	0.0018	0.0018
R(42,43)	1.0970	1.0996	0.0026	0.0026
R(55,56)	1.0969	1.0990	0.0021	0.0021
R(72,74)	1.0969	1.1010	0.0041	0.0041
R(52,53)	1.0964	1.0984	0.0020	0.0020
R(58,60)	1.0961	1.0983	0.0022	0.0022
R(49,50)	1.0960	1.0986	0.0026	0.0026
R(36,37)	1.0959	1.0979	0.0020	0.0020
R(39,40)	1.0952	1.0978	0.0026	0.0026
R(72,73)	1.0947	1.0953	0.0006	0.0006
R(66,67)	1.0946	1.0972	0.0026	0.0026
R(66,68)	1.0944	1.0956	0.0012	0.0012
R(20,21)	1.0943	1.0964	0.0021	0.0021
R(69,70)	1.0942	1.0959	0.0017	0.0017
R(63,64)	1.0933	1.0955	0.0022	0.0022
R(14,15)	1.0897	1.0917	0.0020	0.0020
R(8,9)	1.0890	1.0905	0.0015	0.0015
R(12,13)	1.0882	1.0895	0.0013	0.0013
R(10,11)	1.0879	1.0892	0.0013	0.0013
R(3,4)	1.0855	1.0865	0.0010	0.0010
R(5,6)	1.0987	1.0854	0.0006	0.0006

5.4.1.6 B3LYP/Midi!+

N	0.572613478529	-0.053800279877	-1.085394965565	O	1.072166129135	-2.862429801898	0.165272642829
C	1.152492256342	1.675410399640	-2.880742295148	C	0.677262198999	-3.516707446153	-1.103035305268
C	2.345641059898	1.751442217127	-3.694730054477	H	0.032906179247	-2.824510589083	-1.655297127891
H	3.171276380111	1.047075803956	-3.640762179935	H	0.117888317975	-4.426916211966	-0.844616997392
C	2.259570355482	2.849820575374	-4.535070338490	C	1.987493449141	-3.838113098884	-1.847283925619
H	3.006683511711	3.160784527723	-5.259200201225	H	2.275506196185	-2.999982103083	-2.495568779889
C	1.004241774776	3.517664669916	-4.288302086254	H	1.901207142774	-4.738232853281	-2.467555851986
C	0.410138831664	4.662189077078	-4.846788932382	C	3.000663519963	-3.999284068784	-0.688007793034
H	0.926699338263	5.222285938187	-5.627488308861	H	4.040386924432	-3.862344678522	-1.008187211570
C	-0.843035294453	5.078909554172	-4.398190859066	H	2.909653879535	-4.992078210217	-0.225458802451
H	-1.306174206777	5.966071201521	-4.829356926946	C	2.539878609043	-2.901843088578	0.283830062910
C	-1.522254452669	4.360808041464	-3.388671363773	H	2.778230382116	-3.107981345664	1.333816124154
H	-2.501564030746	4.703134288416	-3.053962826645	H	2.943978100904	-1.920672912850	-0.004692010232
C	-0.953724013048	3.220877890814	-2.819013009862				
H	-1.487561968533	2.672225602256	-2.041213615080				
C	0.307604367598	2.789574713816	-3.259001472467				
C	0.855540667547	0.734483839810	-1.919226413454				
N	0.464216492540	-0.114015569506	2.256271455833				
N	-1.843357135204	-1.502302215697	1.119063637729				
C	1.856467531555	0.406281127455	2.098344062099				
H	1.831207515053	1.184007477603	1.324533524948				
H	2.468245352390	-0.419532015624	1.702852563595				
C	2.511024714055	0.920001339117	3.400779219525				
H	1.990015693146	1.815140701821	3.772985459660				
H	3.544928234065	1.227882374156	3.183201940188				
C	2.483106889173	-0.191333279070	4.471580300237				
H	2.914203427555	0.164576220515	5.418708064913				
H	3.107783608608	-1.037565542324	4.137252975733				
C	1.031685883410	-0.671623286053	4.688718856233				
H	0.448965100046	0.142618083526	5.142444825115				
H	1.008572705458	-1.512049392789	5.400070655626				
C	0.385588857832	-1.132517700966	3.352532340701				
H	0.971412778136	-1.996941288563	2.993365663843				
C	-1.080756179772	-1.601535965433	3.553629733870				
H	-1.081544921338	-2.312422068408	4.394560371845				
C	-1.995190533430	-0.399670305693	3.872742489326				
H	-1.661512170577	0.140082269800	4.769059456627				
H	-3.021482716830	-0.745423807956	4.070524883417				
C	-0.510419275209	1.006445429847	2.413523908926				
H	-0.437343145041	1.620940294895	1.506251013198				
H	-0.250413482307	1.658982112592	3.267054689748				
C	-1.669365046571	-2.353915302449	2.334713594849				
H	-1.016914590016	-3.194292544423	2.055177789224				
H	-2.649101161350	-2.778097522887	2.636925334425				
C	-1.962287586175	0.513825353783	2.630719301973				
H	-2.583722893053	1.405682212904	2.803554401554				
C	-2.601262345428	-0.248988423452	1.440569115146				
H	-3.621328308736	-0.542860963999	1.775233726172				
C	-2.761385135986	0.616585215691	0.173723004448				
H	-1.776318861742	0.924531251442	-0.201444824180				
H	-3.315350544656	1.530443164897	0.437538511745				
C	-3.507983769139	-0.160120398992	-0.932873109878				
H	-3.558129262581	0.441466766023	-1.851193027359				
H	-4.546336737433	-0.353309179503	-0.614796975796				
C	-2.789784916531	-1.498613328525	-1.205749678298				
H	-1.809669472972	-1.295322278933	-1.660680341759				
H	-3.365001863875	-2.109484949574	-1.917561645235				
C	-2.605839076409	-2.289034770672	0.103342097831				
H	-3.597513112892	-2.568191220076	0.517313585168				
H	-2.054299764528	-3.222225033803	-0.079330367615				
Li	0.096404504731	-1.094447532124	0.470603906312				

Table 5.6 Signed and Unsigned differences in bond length for the B3LYP/Midi!+ structure of DEVJAP relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(19,61)	2.1211	2.0856	-0.0355	0.0355
R(18,61)	2.1022	2.0701	-0.0321	0.0321
R(61,62)	2.0469	2.0423	-0.0046	0.0046
R(1,61)	1.9703	1.9315	-0.0388	0.0388
R(32,34)	1.5471	1.5526	0.0055	0.0055
R(29,32)	1.5470	1.5541	0.0071	0.0071
R(45,47)	1.5457	1.5513	0.0056	0.0056
R(39,45)	1.5425	1.5485	0.0060	0.0060
R(34,42)	1.5422	1.5486	0.0064	0.0064
R(66,69)	1.5370	1.5480	0.0110	0.0110
R(20,23)	1.5357	1.5455	0.0098	0.0098
R(34,36)	1.5355	1.5435	0.0080	0.0080
R(47,49)	1.5355	1.5426	0.0071	0.0071
R(26,29)	1.5354	1.5442	0.0088	0.0088
R(49,52)	1.5350	1.5444	0.0094	0.0094
R(23,26)	1.5342	1.5435	0.0093	0.0093
R(36,45)	1.5342	1.5421	0.0079	0.0079
R(52,55)	1.5340	1.5433	0.0093	0.0093
R(63,66)	1.5310	1.5408	0.0098	0.0098
R(55,58)	1.5306	1.5402	0.0096	0.0096
R(69,72)	1.5265	1.5366	0.0101	0.0101
R(19,47)	1.4911	1.4995	0.0084	0.0084
R(18,32)	1.4905	1.4984	0.0079	0.0079
R(18,20)	1.4833	1.4947	0.0114	0.0114
R(19,42)	1.4833	1.4944	0.0111	0.0111
R(18,39)	1.4823	1.4933	0.0110	0.0110
R(19,58)	1.4814	1.494	0.0126	0.0126
R(62,63)	1.4589	1.4808	0.0219	0.0219
R(62,72)	1.4528	1.473	0.0202	0.0202
R(2,16)	1.4472	1.4485	0.0013	0.0013
R(2,3)	1.4421	1.4464	0.0043	0.0043
R(5,7)	1.4396	1.4432	0.0036	0.0036
R(7,16)	1.4382	1.4404	0.0022	0.0022
R(10,12)	1.4120	1.4128	0.0008	0.0008
R(7,8)	1.4071	1.4053	-0.0018	0.0018
R(14,16)	1.4050	1.4038	-0.0012	0.0012
R(12,14)	1.3941	1.3954	0.0013	0.0013
R(8,10)	1.3931	1.3948	0.0017	0.0017
R(3,5)	1.3822	1.3856	0.0034	0.0034
R(2,17)	1.3809	1.3777	-0.0032	0.0032
R(1,17)	1.1836	1.1818	-0.0018	0.0018
R(47,48)	1.1105	1.1131	0.0026	0.0026
R(58,59)	1.1079	1.1103	0.0024	0.0024
R(42,44)	1.1068	1.1096	0.0028	0.0028
R(39,41)	1.1032	1.1054	0.0022	0.0022
R(32,33)	1.1017	1.1043	0.0026	0.0026
R(26,28)	1.1009	1.1037	0.0028	0.0028
R(52,54)	1.1006	1.1030	0.0024	0.0024

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(23,24)	1.0987	1.1006	0.0019	0.0019
R(29,31)	1.0985	1.1013	0.0028	0.0028
R(34,35)	1.0985	1.1011	0.0026	0.0026
R(45,46)	1.0985	1.1007	0.0022	0.0022
R(20,22)	1.0984	1.1012	0.0028	0.0028
R(49,51)	1.0983	1.1007	0.0024	0.0024
R(36,38)	1.0981	1.1009	0.0028	0.0028
R(23,25)	1.0977	1.1005	0.0028	0.0028
R(63,65)	1.0976	1.0992	0.0016	0.0016
R(55,57)	1.0975	1.1003	0.0028	0.0028
R(29,30)	1.0974	1.0993	0.0019	0.0019
R(69,71)	1.0974	1.0990	0.0016	0.0016
R(26,27)	1.0972	1.0998	0.0026	0.0026
R(42,43)	1.0970	1.1000	0.0030	0.0030
R(55,56)	1.0969	1.0995	0.0026	0.0026
R(72,74)	1.0969	1.0997	0.0028	0.0028
R(52,53)	1.0964	1.0990	0.0026	0.0026
R(58,60)	1.0961	1.0993	0.0032	0.0032
R(49,50)	1.0960	1.0982	0.0022	0.0022
R(36,37)	1.0959	1.0982	0.0023	0.0023
R(39,40)	1.0952	1.0982	0.0030	0.0030
R(72,73)	1.0947	1.0963	0.0016	0.0016
R(66,67)	1.0946	1.0980	0.0034	0.0034
R(66,68)	1.0944	1.0965	0.0021	0.0021
R(20,21)	1.0943	1.0974	0.0031	0.0031
R(69,70)	1.0942	1.0965	0.0023	0.0023
R(63,64)	1.0933	1.0951	0.0018	0.0018
R(14,15)	1.0897	1.0913	0.0016	0.0016
R(8,9)	1.0890	1.0909	0.0019	0.0019
R(12,13)	1.0882	1.0901	0.0019	0.0019
R(10,11)	1.0879	1.0897	0.0018	0.0018
R(3,4)	1.0855	1.0866	0.0011	0.0011
R(5,6)	1.0987	1.0859	0.0011	0.0011

5.4.1.7 MPW1PW91/Midi!+

N	0.557945687657	-0.071148648190	-1.094709060239	C	0.668809243870	-3.514288923766	-1.120860994483
C	1.164116365443	1.688570296876	-2.843087171933	H	0.024520609071	-2.819573848983	-1.668883127551
C	2.381373992992	1.795509119734	-3.606733502654	H	0.109339283783	-4.426096061853	-0.871943070933
H	3.216667813002	1.105918509204	-3.530278070928	C	1.970475496264	-3.831284205895	-1.867285119009
C	2.306519897233	2.900063752447	-4.434526501212	H	2.264723266588	-2.985659365432	-2.501800386023
H	3.073420560072	3.233809451589	-5.125805406649	H	1.879583646689	-4.719130651688	-2.502579571765
C	1.033866138837	3.538289051257	-4.226979977455	C	2.972462479993	-4.013735299609	-0.712898252524
C	0.440620896475	4.674734331076	-4.793762715433	H	4.014881478590	-3.890331086522	-1.026305407757
H	0.975239304225	5.253279077066	-5.547151133059	H	2.865791680257	-5.006455795370	-0.255552743654
C	-0.833219815501	5.059513846848	-4.390184357779	C	2.520397079515	-2.918770138960	0.254496579400
H	-1.297425884998	5.941602439463	-4.828637853832	H	2.764531024671	-3.123455305640	1.302584484431
C	-1.533891601895	4.317768068201	-3.418481411052	H	2.929683010106	-1.941774541883	-0.038321854300
H	-2.531557562784	4.636100859774	-3.118556752924				
C	-0.966425734956	3.186265685809	-2.841318234125				
H	-1.518354712303	2.617270630846	-2.092788887894				
C	0.315941220483	2.786951888092	-3.237142648771				
C	0.850214071392	0.731915448241	-1.906567159629				
N	0.445866435079	-0.123138178206	2.228954229588				
N	-1.840223857719	-1.505237998159	1.137378157120				
C	1.827975240290	0.385830287587	2.047670292992				
H	1.801002293924	1.141348111634	1.252714226255				
H	2.435150545425	-0.451773600459	1.671306139765				
C	2.489192725990	0.928479900182	3.324678840414				
H	1.973745391484	1.832658065584	3.679781767819				
H	3.520065917077	1.232139048212	3.091951857288				
C	2.469038200107	-0.153480247177	4.414096885901				
H	2.909269012531	0.219726819272	5.349277402205				
H	3.088576118024	-1.007947665428	4.093952384546				
C	1.024702237510	-0.621019325558	4.648935047524				
H	0.445413676714	0.208231734832	5.078040843949				
H	0.999144764309	-1.437470156121	5.386348501195				
C	0.381657482153	-1.114968845555	3.334034213373				
H	0.971766297596	-1.982598949969	2.989568740139				
C	-1.072282601766	-1.584890727316	3.552086271946				
H	-1.063416077134	-2.288878458699	4.398312587252				
C	-1.981721732791	-0.388737298664	3.866982859628				
H	-1.647513311102	0.157117859348	4.758628241956				
H	-3.006484637323	-0.734052489817	4.070924110553				
C	-0.512088828111	0.994934048806	2.393653771274				
H	-0.446190656732	1.611029140375	1.487245218628				
H	-0.240398647655	1.646398596950	3.243715564528				
C	-1.666764625841	-2.341531520404	2.349981922285				
H	-1.022377925355	-3.189644603314	2.076506258361				
H	-2.646897794274	-2.757848763010	2.660927338347				
C	-1.954563160724	0.509874775134	2.624178612724				
H	-2.575597201012	1.402663139498	2.791212242866				
C	-2.591424764400	-0.259406426656	1.449707291339				
H	-3.612241375375	-0.550047456805	1.786176378287				
C	-2.744685350070	0.592737625502	0.183441743365				
H	-1.755976742933	0.881302139569	-0.197379164665				
H	-3.282444442535	1.517580076961	0.438742840650				
C	-3.500308053630	-0.183681489152	-0.905168360726				
H	-3.558768160162	0.409766803189	-1.827325683098				
H	-4.535542523532	-0.372389817983	-0.577135055787				
C	-2.787029130964	-1.517237521394	-1.168950821450				
H	-1.807368473871	-1.315937405291	-1.624990609284				
H	-3.359261846007	-2.132337891240	-1.877988347231				
C	-2.606043307952	-2.292578664355	0.140283190759				
H	-3.598243250327	-2.559845785995	0.559631946480				
H	-2.064358563510	-3.232721465303	-0.033727651011				
Li	0.081122309738	-1.114219825855	0.462753618757				
O	1.064741868849	-2.877200379387	0.141036974144				

Table 5.7 Signed and Unsigned differences in bond length for the MPW1PW91/Midi!+ structure of DEVJAP relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(19,61)	2.1211	2.0735	-0.0476	0.0476
R(18,61)	2.1022	2.0578	-0.0444	0.0444
R(61,62)	2.0469	2.0443	-0.0026	0.0026
R(1,61)	1.9703	1.9342	-0.0361	0.0361
R(32,34)	1.5471	1.5435	-0.0036	0.0036
R(29,32)	1.5470	1.5448	-0.0022	0.0022
R(45,47)	1.5457	1.5417	-0.0040	0.0040
R(39,45)	1.5425	1.5392	-0.0033	0.0033
R(34,42)	1.5422	1.5398	-0.0024	0.0024
R(66,69)	1.5370	1.5394	0.0024	0.0024
R(20,23)	1.5357	1.5370	0.0013	0.0013
R(34,36)	1.5355	1.5353	-0.0002	0.0002
R(47,49)	1.5355	1.5340	-0.0015	0.0015
R(26,29)	1.5354	1.5362	0.0008	0.0008
R(49,52)	1.5350	1.5359	0.0009	0.0009
R(23,26)	1.5342	1.5355	0.0013	0.0013
R(36,45)	1.5342	1.5339	-0.0003	0.0003
R(52,55)	1.5340	1.5352	0.0012	0.0012
R(63,66)	1.5310	1.5336	0.0026	0.0026
R(55,58)	1.5306	1.5323	0.0017	0.0017
R(69,72)	1.5265	1.5294	0.0029	0.0029
R(19,47)	1.4911	1.4879	-0.0032	0.0032
R(18,32)	1.4905	1.4863	-0.0042	0.0042
R(18,20)	1.4833	1.4840	0.0007	0.0007
R(19,42)	1.4833	1.4832	-1E-04	1E-04
R(18,39)	1.4823	1.4815	-0.0008	0.0008
R(19,58)	1.4814	1.4834	0.0020	0.0020
R(62,63)	1.4589	1.4680	0.0091	0.0091
R(62,72)	1.4528	1.4607	0.0079	0.0079
R(2,16)	1.4472	1.4426	-0.0046	0.0046
R(2,3)	1.4421	1.4409	-0.0012	0.0012
R(5,7)	1.4396	1.4388	-0.0008	0.0008
R(7,16)	1.4382	1.4352	-0.0030	0.0030
R(10,12)	1.4120	1.4090	-0.0030	0.0030
R(7,8)	1.4071	1.4017	-0.0054	0.0054
R(14,16)	1.4050	1.4002	-0.0048	0.0048
R(12,14)	1.3941	1.3912	-0.0029	0.0029
R(8,10)	1.3931	1.3905	-0.0026	0.0026
R(3,5)	1.3822	1.3823	1E-04	1E-04
R(2,17)	1.3809	1.3751	-0.0058	0.0058
R(1,17)	1.1836	1.1787	-0.0049	0.0049
R(47,48)	1.1105	1.1134	0.0029	0.0029
R(58,59)	1.1079	1.1098	0.0019	0.0019
R(42,44)	1.1068	1.1094	0.0026	0.0026
R(39,41)	1.1032	1.1049	0.0017	0.0017
R(32,33)	1.1017	1.1044	0.0027	0.0027
R(26,28)	1.1009	1.1029	0.0020	0.0020
R(52,54)	1.1006	1.1022	0.0016	0.0016

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(23,24)	1.0987	1.0997	0.001	0.001
R(29,31)	1.0985	1.1005	0.002	0.002
R(34,35)	1.0985	1.1008	0.0023	0.0023
R(45,46)	1.0985	1.1003	0.0018	0.0018
R(20,22)	1.0984	1.1009	0.0025	0.0025
R(49,51)	1.0983	1.0999	0.0016	0.0016
R(36,38)	1.0981	1.1004	0.0023	0.0023
R(23,25)	1.0977	1.0996	0.0019	0.0019
R(63,65)	1.0976	1.0983	0.0007	0.0007
R(55,57)	1.0975	1.0993	0.0018	0.0018
R(29,30)	1.0974	1.0988	0.0014	0.0014
R(69,71)	1.0974	1.0982	0.0008	0.0008
R(26,27)	1.0972	1.0989	0.0017	0.0017
R(42,43)	1.0970	1.0997	0.0027	0.0027
R(55,56)	1.0969	1.0992	0.0023	0.0023
R(72,74)	1.0969	1.0990	0.0021	0.0021
R(52,53)	1.0964	1.0982	0.0018	0.0018
R(58,60)	1.0961	1.0989	0.0028	0.0028
R(49,50)	1.0960	1.0981	0.0021	0.0021
R(36,37)	1.0959	1.0976	0.0017	0.0017
R(39,40)	1.0952	1.0979	0.0027	0.0027
R(72,73)	1.0947	1.0954	0.0007	0.0007
R(66,67)	1.0946	1.0974	0.0028	0.0028
R(66,68)	1.0944	1.0955	0.0011	0.0011
R(20,21)	1.0943	1.0970	0.0027	0.0027
R(69,70)	1.0942	1.0955	0.0013	0.0013
R(63,64)	1.0933	1.0946	0.0013	0.0013
R(14,15)	1.0897	1.0903	0.0006	0.0006
R(8,9)	1.0890	1.0900	0.0010	0.0010
R(12,13)	1.0882	1.0893	0.0011	0.0011
R(10,11)	1.0879	1.0889	0.0010	0.0010
R(3,4)	1.0855	1.0859	0.0004	0.0004
R(5,6)	1.0987	1.0851	0.0003	0.0003

5.4.1.8 B3LYP/6-31G(d)

N	0.903812271444	0.491506226785	-0.182900686931	H	0.725360058747	1.828334717702	1.949686283723
C	3.345696208983	0.820719685534	-0.874509888584	H	-0.240952890520	1.866402876544	3.457648435275
C	3.863715564491	1.767966452611	-1.831309604064	C	-0.206296577277	3.780135463737	2.407267728308
H	3.251376357989	2.472417162431	-2.384877741292	H	0.244388141423	4.158503001344	1.482733264657
C	5.230426073700	1.627577338711	-1.920693089321	H	0.320568172055	4.230487899675	3.253318877538
H	5.889990314810	2.204498774138	-2.559731612197	C	-1.719255725980	4.045968150706	2.422972444364
C	5.644640258185	0.582022382750	-1.021935763395	H	-1.993092757361	5.033099101802	2.039263174413
C	6.901707008644	0.034220970461	-0.717517873644	H	-2.112632424556	3.957142604655	3.442344458372
H	7.796115429142	0.412047945218	-1.210253796547	C	-2.254167740122	2.913443242018	1.540879774222
C	6.997685732739	-0.992682624144	0.216488965034	H	-3.248182636972	2.563590566146	1.839562221725
H	7.970142128144	-1.418632901316	0.453760874568	H	-2.290548592019	3.211823772679	0.485327097187
C	5.846868894678	-1.488297339068	0.860584608004				
H	5.942955288484	-2.291270106120	1.588501939869				
C	4.589814977097	-0.961959904453	0.575729924202				
H	3.705384495972	-1.349984927646	1.080364461855				
C	4.475402260563	0.071817563383	-0.363563825749				
C	2.030971499214	0.651419261202	-0.510292398513				
N	-2.169352331978	-0.003463630390	-1.291270918980				
N	-1.801002471317	-1.450588646366	1.251996352462				
C	-1.782069167178	1.121613395840	-2.175091227157				
H	-0.736889928517	0.972666270091	-2.460929396741				
H	-1.814325911589	2.038142017839	-1.567503891517				
C	-2.688176205748	1.318069094198	-3.398616616013				
H	-2.594568765949	0.464611454144	-4.083143719068				
H	-2.352284211958	2.202157368972	-3.954357530813				
C	-4.148034915747	1.471798827100	-2.953597107167				
H	-4.814565376526	1.559870861220	-3.819905076658				
H	-4.256421532736	2.404076841887	-2.379135261305				
C	-4.565798293472	0.280012629602	-2.080513995048				
H	-4.596139251849	-0.622411872651	-2.703104010826				
H	-5.581980062036	0.424772787194	-1.690519989196				
C	-3.599555995043	0.080331039813	-0.888969120601				
H	-3.678411388970	0.986438474740	-0.267639079945				
C	-3.986016462819	-1.131289239816	-0.010146587361				
H	-5.056257784292	-1.035088730598	0.216277374286				
C	-3.717661512483	-2.444377838892	-0.758626065866				
H	-4.257357550261	-2.485209080484	-1.711086188528				
H	-4.061477577175	-3.298842813724	-0.161895735663				
C	-1.765956161209	-1.317530098259	-1.849725774392				
H	-0.677251075446	-1.290586293859	-1.960509682234				
H	-2.185385930239	-1.477341982839	-2.856743677677				
C	-3.254830255040	-1.184833969339	1.346502798648				
H	-3.380142180181	-0.238613747337	1.887586494693				
H	-3.738576528204	-1.970623921051	1.956845353916				
C	-2.201283073174	-2.513982618865	-0.976684547020				
H	-1.943818738775	-3.422025969786	-1.537328344962				
C	-1.511920662724	-2.638394986439	0.401466445231				
H	-1.966552771059	-3.526666602390	0.887779201009				
C	-0.000764230364	-2.891819307829	0.319588914913				
H	0.493338253119	-2.052660236017	-0.182208632941				
H	0.167990305210	-3.786447115233	-0.293421017352				
C	0.611464339473	-3.074487165168	1.714220352952				
H	1.698973664425	-3.186060332332	1.638499755471				
H	0.226424638601	-3.998489649072	2.170618662375				
C	0.255710757825	-1.876952328873	2.603209861271				
H	0.767263392587	-0.981920070910	2.228186203495				
H	0.597444613283	-2.038233993704	3.633055801099				
C	-1.255319724638	-1.636933923958	2.615330894681				
H	-1.762640219944	-2.489329221604	3.107251868074				
H	-1.499802590441	-0.738589988854	3.194423595992				
Li	-0.947706406785	0.293937766493	0.390623667433				
O	-1.318512995272	1.818655724904	1.676595215964				
C	-0.153736151064	2.255543899132	2.434526277067				

Table 5.8 Signed and Unsigned differences in bond length for the B3LYP/6-31G(d) structure of DEVJAP relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(19,61)	2.1211	2.1245	0.0034	0.0034
R(18,61)	2.1022	2.0999	-0.0023	0.0023
R(61,62)	2.0469	2.0288	-0.0181	0.0181
R(1,61)	1.9703	1.9484	-0.0219	0.0219
R(32,34)	1.5471	1.5459	-0.0012	0.0012
R(29,32)	1.5470	1.5470	0.0000	0.0000
R(45,47)	1.5457	1.5460	0.0003	0.0003
R(39,45)	1.5425	1.5438	0.0013	0.0013
R(34,42)	1.5422	1.5421	-1E-04	1E-04
R(66,69)	1.5370	1.5362	-0.0008	0.0008
R(20,23)	1.5357	1.5351	-0.0006	0.0006
R(34,36)	1.5355	1.5351	-0.0004	0.0004
R(47,49)	1.5355	1.5344	-0.0011	0.0011
R(26,29)	1.5354	1.5353	-1E-04	1E-04
R(49,52)	1.5350	1.5340	-0.0010	0.0010
R(23,26)	1.5342	1.5339	-0.0003	0.0003
R(36,45)	1.5342	1.5336	-0.0006	0.0006
R(52,55)	1.5340	1.5333	-0.0007	0.0007
R(63,66)	1.5310	1.5257	-0.0053	0.0053
R(55,58)	1.5306	1.5300	-0.0006	0.0006
R(69,72)	1.5265	1.5319	0.0054	0.0054
R(19,47)	1.4911	1.4892	-0.0019	0.0019
R(18,32)	1.4905	1.4881	-0.0024	0.0024
R(18,20)	1.4833	1.4822	-0.0011	0.0011
R(19,42)	1.4833	1.4809	-0.0024	0.0024
R(18,39)	1.4823	1.4837	0.0014	0.0014
R(19,58)	1.4814	1.4803	-0.0011	0.0011
R(62,63)	1.4589	1.4567	-0.0022	0.0022
R(62,72)	1.4528	1.4465	-0.0063	0.0063
R(2,16)	1.4472	1.4485	0.0013	0.0013
R(2,3)	1.4421	1.4426	0.0005	0.0005
R(5,7)	1.4396	1.4396	0.0000	0.0000
R(7,16)	1.4382	1.4356	-0.0026	0.0026
R(10,12)	1.4120	1.4089	-0.0031	0.0031
R(7,8)	1.4071	1.4046	-0.0025	0.0025
R(14,16)	1.4050	1.4014	-0.0036	0.0036
R(12,14)	1.3941	1.3922	-0.0019	0.0019
R(8,10)	1.3931	1.3914	-0.0017	0.0017
R(3,5)	1.3822	1.3768	-0.0054	0.0054
R(2,17)	1.3809	1.3747	-0.0062	0.0062
R(1,17)	1.1836	1.1846	0.0010	0.0010
R(47,48)	1.1105	1.1101	-0.0004	0.0004
R(58,59)	1.1079	1.1072	-0.0007	0.0007
R(42,44)	1.1068	1.1063	-0.0005	0.0005
R(39,41)	1.1032	1.1025	-0.0007	0.0007
R(32,33)	1.1017	1.1015	-0.0002	0.0002
R(26,28)	1.1009	1.1004	-0.0005	0.0005
R(52,54)	1.1006	1.1002	-0.0004	0.0004

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(23,24)	1.0987	1.0981	-0.0006	0.0006
R(29,31)	1.0985	1.0980	-0.0005	0.0005
R(34,35)	1.0985	1.0982	-0.0003	0.0003
R(45,46)	1.0985	1.0978	-0.0007	0.0007
R(20,22)	1.0984	1.1001	0.0017	0.0017
R(49,51)	1.0983	1.0976	-0.0007	0.0007
R(36,38)	1.0981	1.0975	-0.0006	0.0006
R(23,25)	1.0977	1.0969	-0.0008	0.0008
R(63,65)	1.0976	1.0981	0.0005	0.0005
R(55,57)	1.0975	1.0970	-0.0005	0.0005
R(29,30)	1.0974	1.0968	-0.0006	0.0006
R(69,71)	1.0974	1.0962	-0.0012	0.0012
R(26,27)	1.0972	1.0966	-0.0006	0.0006
R(42,43)	1.0970	1.0972	0.0002	0.0002
R(55,56)	1.0969	1.0970	1E-04	1E-04
R(72,74)	1.0969	1.0975	0.0006	0.0006
R(52,53)	1.0964	1.0958	-0.0006	0.0006
R(58,60)	1.0961	1.0964	0.0003	0.0003
R(49,50)	1.0960	1.0955	-0.0005	0.0005
R(36,37)	1.0959	1.0955	-0.0004	0.0004
R(39,40)	1.0952	1.0947	-0.0005	0.0005
R(72,73)	1.0947	1.0953	0.0006	0.0006
R(66,67)	1.0946	1.0959	0.0013	0.0013
R(66,68)	1.0944	1.0937	-0.0007	0.0007
R(20,21)	1.0943	1.0937	-0.0006	0.0006
R(69,70)	1.0942	1.0939	-0.0003	0.0003
R(63,64)	1.0933	1.0910	-0.0023	0.0023
R(14,15)	1.0897	1.0897	0.0000	0.0000
R(8,9)	1.0890	1.0888	-0.0002	0.0002
R(12,13)	1.0882	1.0881	-1E-04	1E-04
R(10,11)	1.0879	1.0878	-1E-04	1E-04
R(3,4)	1.0855	1.0852	-0.0003	0.0003
R(5,6)	1.0987	1.0845	-0.0003	0.0003

5.4.1.9 HF/6-31G(d)

N	0.438536207167	0.603011107614	-0.733673804974	C	1.983333944548	-3.259194888359	-2.173932302452
C	0.935969679517	2.439471470049	-2.410696209216	H	2.756780796618	-2.502946750080	-2.255391338069
C	1.851817049529	3.531251247756	-2.250812723082	H	1.890819252821	-3.754973023261	-3.132166272101
H	2.442739816350	3.703837078958	-1.369302588341	C	2.280711077693	-4.215485231338	-1.019228984703
C	1.851716219507	4.296026866229	-3.372985871798	H	3.325432450623	-4.489359006989	-0.938606369785
H	2.438953906791	5.179681487986	-3.538659298227	H	1.701281049424	-5.127196637064	-1.124962173027
C	0.924074262438	3.718766613136	-4.313563770453	C	1.799722066453	-3.413700936842	0.188334363338
C	0.542554835591	4.093846047048	-5.604875018661	H	1.391813338987	-4.033792258307	0.976273760951
H	0.972050638768	4.969290162349	-6.063539220810	H	2.597456591615	-2.808067456033	0.602282787367
C	-0.384396453609	3.339190277867	-6.288340176923				
H	-0.682119644929	3.623024644674	-7.283297660909				
C	-0.947631956612	2.198615864152	-5.697253329449				
H	-1.671854103022	1.621095125439	-6.246959497561				
C	-0.587248598256	1.810727165144	-4.426659293510				
H	-1.029460735958	0.932867231863	-3.983164642479				
C	0.353686659912	2.567136120720	-3.720451613205				
C	0.669956707021	1.445542939813	-1.491125070614				
N	0.602781707401	-0.195958087238	2.503419925327				
N	-1.886890115678	-1.323151100843	1.378522760931				
C	1.975563646824	0.278352557287	2.278201033234				
H	1.926506299454	1.163596643917	1.659363565895				
H	2.492813906428	-0.478121720511	1.693048672293				
C	2.779648373732	0.535266639616	3.553053424084				
H	2.361861073184	1.373172540063	4.104960205330				
H	3.791866968023	0.818265932726	3.278979128037				
C	2.784468368400	-0.713718894833	4.433081286131				
H	3.304347315970	-0.526171518066	5.367605738158				
H	3.328635895590	-1.510325957464	3.927758213134				
C	1.349261908983	-1.165508202715	4.707520544779				
H	0.865747237235	-0.427693361171	5.339534471218				
H	1.346732606778	-2.100050287834	5.262570080407				
C	0.562039351997	-1.365240772661	3.399351539740				
H	1.061979559148	-2.169076166516	2.861844632466				
C	-0.890429300095	-1.806186592262	3.654098436117				
H	-0.855093998058	-2.631624644455	4.360423106992				
C	-1.709939968190	-0.652089689611	4.230174916842				
H	-1.277565837838	-0.268942262247	5.147295614015				
H	-2.713638039234	-0.987957990293	4.474517485994				
C	-0.312891897668	0.894504602193	2.868731097202				
H	-0.294125070355	1.611861519909	2.058935629832				
H	0.029630192962	1.419804723403	3.759826010374				
C	-1.612013724746	-2.335817806950	2.405940633026				
H	-1.030762194782	-3.126393398484	1.943421160216				
H	-2.550371683162	-2.787167361108	2.737262557235				
C	-1.749474477470	0.423759900362	3.147484502784				
H	-2.296879194495	1.290695639765	3.507486776576				
C	-2.537463634845	-0.125539339132	1.944467832751				
H	-3.512941726158	-0.425315221876	2.343605473697				
C	-2.804291019740	0.914611229841	0.854796606427				
H	-1.871278163368	1.275274521656	0.440124890659				
H	-3.309007422643	1.764558810352	1.306249277968				
C	-3.659732459247	0.329619263404	-0.268855631711				
H	-3.779634025894	1.055935189163	-1.065457873741				
H	-4.655821177568	0.102941024148	0.107896191747				
C	-3.013180296885	-0.946215761206	-0.804619232623				
H	-2.092771337437	-0.694491128890	-1.321388005342				
H	-3.662717009652	-1.432873022817	-1.526680281129				
C	-2.718631857171	-1.923043777742	0.328685292080				
H	-3.660306849841	-2.274282830375	0.759284706413				
H	-2.198079832005	-2.794939025755	-0.051102498570				
Li	0.034106817620	-0.826909213378	0.556784102758				
O	0.777692460962	-2.549110593255	-0.293634492208				
C	0.677427725946	-2.626116912612	-1.718900503698				
H	0.518105085779	-1.630410991366	-2.097938079978				
H	-0.173738070277	-3.250411296084	-1.970823535117				

Table 5.9 Signed and Unsigned differences in bond length for the HF/6-31G(d) structure of DEVJAP relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(19,61)	2.1211	2.1475	0.0264	0.0264
R(18,61)	2.1022	2.1239	0.0217	0.0217
R(61,62)	2.0469	2.0596	0.0127	0.0127
R(1,61)	1.9703	1.9681	-0.0022	0.0022
R(32,34)	1.5471	1.5392	-0.0079	0.0079
R(29,32)	1.5470	1.5398	-0.0072	0.0072
R(45,47)	1.5457	1.5394	-0.0063	0.0063
R(39,45)	1.5425	1.5372	-0.0053	0.0053
R(34,42)	1.5422	1.5359	-0.0063	0.0063
R(66,69)	1.5370	1.5285	-0.0085	0.0085
R(20,23)	1.5357	1.5290	-0.0067	0.0067
R(34,36)	1.5355	1.5282	-0.0073	0.0073
R(47,49)	1.5355	1.5299	-0.0056	0.0056
R(26,29)	1.5354	1.5295	-0.0059	0.0059
R(49,52)	1.5350	1.5286	-0.0064	0.0064
R(23,26)	1.5342	1.5279	-0.0063	0.0063
R(36,45)	1.5342	1.5268	-0.0074	0.0074
R(52,55)	1.5340	1.5274	-0.0066	0.0066
R(63,66)	1.5310	1.5209	-0.0101	0.0101
R(55,58)	1.5306	1.5249	-0.0057	0.0057
R(69,72)	1.5265	1.5272	0.0007	0.0007
R(19,47)	1.4911	1.4757	-0.0154	0.0154
R(18,32)	1.4905	1.4736	-0.0169	0.0169
R(18,20)	1.4833	1.4698	-0.0135	0.0135
R(19,42)	1.4833	1.4685	-0.0148	0.0148
R(18,39)	1.4823	1.4700	-0.0123	0.0123
R(19,58)	1.4814	1.4676	-0.0138	0.0138
R(62,63)	1.4589	1.4309	-0.0280	0.0280
R(62,72)	1.4528	1.4228	-0.0300	0.0300
R(2,16)	1.4472	1.4390	-0.0082	0.0082
R(2,3)	1.4421	1.4340	-0.0081	0.0081
R(5,7)	1.4396	1.4417	0.0021	0.0021
R(7,16)	1.4382	1.4154	-0.0228	0.0228
R(10,12)	1.4120	1.4027	-0.0093	0.0093
R(7,8)	1.4071	1.3978	-0.0093	0.0093
R(14,16)	1.4050	1.3987	-0.0063	0.0063
R(12,14)	1.3941	1.3765	-0.0176	0.0176
R(8,10)	1.3931	1.3769	-0.0162	0.0162
R(3,5)	1.3822	1.3580	-0.0242	0.0242
R(2,17)	1.3809	1.3800	-0.0009	0.0009
R(1,17)	1.1836	1.1564	-0.0272	0.0272
R(47,48)	1.1105	1.0958	-0.0147	0.0147
R(58,59)	1.1079	1.0934	-0.0145	0.0145
R(42,44)	1.1068	1.0927	-0.0141	0.0141
R(39,41)	1.1032	1.0896	-0.0136	0.0136
R(32,33)	1.1017	1.0886	-0.0131	0.0131
R(26,28)	1.1009	1.0891	-0.0118	0.0118
R(52,54)	1.1006	1.0888	-0.0118	0.0118

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(23,24)	1.0987	1.0868	-0.0119	0.0119
R(29,31)	1.0985	1.0869	-0.0116	0.0116
R(34,35)	1.0985	1.0870	-0.0115	0.0115
R(45,46)	1.0985	1.0867	-0.0118	0.0118
R(20,22)	1.0984	1.0873	-0.0111	0.0111
R(49,51)	1.0983	1.0867	-0.0116	0.0116
R(36,38)	1.0981	1.0862	-0.0119	0.0119
R(23,25)	1.0977	1.0862	-0.0115	0.0115
R(63,65)	1.0976	1.0852	-0.0124	0.0124
R(55,57)	1.0975	1.0863	-0.0112	0.0112
R(29,30)	1.0974	1.0852	-0.0122	0.0122
R(69,71)	1.0974	1.0854	-0.0120	0.0120
R(26,27)	1.0972	1.0857	-0.0115	0.0115
R(42,43)	1.0970	1.0848	-0.0122	0.0122
R(55,56)	1.0969	1.0852	-0.0117	0.0117
R(72,74)	1.0969	1.0838	-0.0131	0.0131
R(52,53)	1.0964	1.0847	-0.0117	0.0117
R(58,60)	1.0961	1.0842	-0.0119	0.0119
R(49,50)	1.0960	1.0828	-0.0132	0.0132
R(36,37)	1.0959	1.0839	-0.0120	0.0120
R(39,40)	1.0952	1.0820	-0.0132	0.0132
R(72,73)	1.0947	1.0825	-0.0122	0.0122
R(66,67)	1.0946	1.0848	-0.0098	0.0098
R(66,68)	1.0944	1.0829	-0.0115	0.0115
R(20,21)	1.0943	1.0812	-0.0131	0.0131
R(69,70)	1.0942	1.0830	-0.0112	0.0112
R(63,64)	1.0933	1.0773	-0.0160	0.0160
R(14,15)	1.0897	1.0784	-0.0113	0.0113
R(8,9)	1.0890	1.0776	-0.0114	0.0114
R(12,13)	1.0882	1.0771	-0.0111	0.0111
R(10,11)	1.0879	1.0766	-0.0113	0.0113
R(3,4)	1.0855	1.0752	-0.0103	0.0103
R(5,6)	1.0987	1.0738	-0.011	0.011

5.4.1.10 B3LYP/6-31(+LiX)G(d)

N	0.892778264912	0.553550651203	-0.127958464820	H	-0.277023707872	1.844137231469	3.512254417131
C	3.309501287338	0.733352060195	-0.953019271342	C	-0.276040213825	3.790333126193	2.521389694442
C	3.795189043223	1.491821553927	-2.080493064971	H	0.174467946472	4.206341752399	1.612988031097
H	3.166608047847	2.101545643508	-2.721532081814	H	0.235207370079	4.223992497109	3.385673909619
C	5.154849258663	1.313724949123	-2.200183003301	C	-1.793971201153	4.027428882436	2.534007859530
H	5.792081769377	1.760615830378	-2.955520951103	H	-2.083394205851	5.020224057359	2.177155555192
C	5.597341493464	0.432476799847	-1.151118213837	H	-2.192263231630	3.901932021107	3.547731728168
C	6.861196584338	-0.075558066854	-0.808668319078	C	-2.302936723107	2.912295801609	1.615882267252
H	7.736604469350	0.196128680373	-1.396333292851	H	-3.291631465865	2.534487611226	1.897656865292
C	6.988265003783	-0.926529757254	0.284847751153	H	-2.334474862603	3.237391000151	0.568048174989
H	7.966115115134	-1.321043511078	0.552248857662				
C	5.862118013192	-1.283161411497	1.052474523004				
H	5.982460271874	-1.948806557695	1.904769270805				
C	4.598611274457	-0.793166658366	0.732807025154				
H	3.734461383739	-1.072823074557	1.334982698960				
C	4.453336397620	0.064507492760	-0.366179815141				
C	2.008693584399	0.646157819413	-0.516488946951				
N	-2.135068158058	0.030530531264	-1.281804935825				
N	-1.787234334815	-1.453807813515	1.240594094243				
C	-1.747617718797	1.174759795074	-2.140391500590				
H	-0.699837331775	1.036994084763	-2.421870532912				
H	-1.788001665462	2.079362275595	-1.515659582929				
C	-2.643678862982	1.390355352615	-3.368226407337				
H	-2.537420811529	0.551760386674	-4.069392493731				
H	-2.308407834041	2.288156429504	-3.901963452397				
C	-4.108908642244	1.523955175251	-2.935398031843				
H	-4.767144815059	1.624999989869	-3.806656830070				
H	-4.231006898612	2.442910346267	-2.342174642477				
C	-4.524919750669	0.310028280987	-2.093118979813				
H	-4.537565512314	-0.579155716912	-2.735326452175				
H	-5.546961518662	0.435919549303	-1.712009600458				
C	-3.570624106317	0.094758665875	-0.894617546332				
H	-3.664043467323	0.987701400165	-0.255997417379				
C	-3.958171760058	-1.136815159495	-0.044597454017				
H	-5.032343343619	-1.054746776014	0.168343695435				
C	-3.666744723356	-2.433269915019	-0.813324797929				
H	-4.191958502756	-2.460983694528	-1.774312685237				
H	-4.011191514956	-3.301745534655	-0.237535131111				
C	-1.714295376634	-1.269191985357	-1.859430891402				
H	-0.624839763950	-1.230673303792	-1.959595610752				
H	-2.123959797605	-1.415144377429	-2.872436164503				
C	-3.245489595333	-1.210206952106	1.320688550972				
H	-3.392214060963	-0.278529961259	1.881396621402				
H	-3.725712908430	-2.017105087944	1.906320984389				
C	-2.146837257251	-2.484386792602	-1.011678164211				
H	-1.872264067868	-3.380720924893	-1.582952595976				
C	-1.472749233463	-2.623478213102	0.373603640527				
H	-1.922901926565	-3.525348794663	0.839368586975				
C	0.042754463729	-2.856292160082	0.306358009748				
H	0.531305578747	-2.004894127617	-0.179768720783				
H	0.229859818155	-3.740931905408	-0.315843736281				
C	0.644393583773	-3.049585227558	1.704447166557				
H	1.734494311451	-3.137726703666	1.636789769990				
H	0.273482224140	-3.988594737774	2.141499715833				
C	0.256895921433	-1.875622572908	2.611963329049				
H	0.758706994035	-0.964131833552	2.264031760111				
H	0.586485934461	-2.053363011538	3.643127704641				
C	-1.257964071311	-1.659960708079	2.607078036387				
H	-1.758477563475	-2.531952537281	3.071877297596				
H	-1.526081624402	-0.779186675706	3.202424314175				
Li	-0.948816387986	0.309417009544	0.422688462931				
O	-1.349438955315	1.828506975056	1.729182759030				
C	-0.193353416448	2.266877294138	2.502181245248				
H	0.694352031731	1.871142834003	2.006081553687				

Table 5.10 Signed and Unsigned differences in bond length for the B3LYP/6-31(+LiX)G(d) structure of DEVJAP relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(19,61)	2.1211	2.1168	-0.0043	0.0043
R(18,61)	2.1022	2.0953	-0.0069	0.0069
R(61,62)	2.0469	2.0433	-0.0036	0.0036
R(1,61)	1.9703	1.9376	-0.0327	0.0327
R(32,34)	1.5471	1.5458	-0.0013	0.0013
R(29,32)	1.5470	1.5471	1E-04	1E-04
R(45,47)	1.5457	1.5469	0.0012	0.0012
R(39,45)	1.5425	1.5435	0.0010	0.0010
R(34,42)	1.5422	1.5419	-0.0003	0.0003
R(66,69)	1.5370	1.5364	-0.0006	0.0006
R(20,23)	1.5357	1.5352	-0.0005	0.0005
R(34,36)	1.5355	1.5351	-0.0004	0.0004
R(47,49)	1.5355	1.5348	-0.0007	0.0007
R(26,29)	1.5354	1.5350	-0.0004	0.0004
R(49,52)	1.5350	1.5343	-0.0007	0.0007
R(23,26)	1.5342	1.5337	-0.0005	0.0005
R(36,45)	1.5342	1.5336	-0.0006	0.0006
R(52,55)	1.5340	1.5336	-0.0004	0.0004
R(63,66)	1.5310	1.5258	-0.0052	0.0052
R(55,58)	1.5306	1.5301	-0.0005	0.0005
R(69,72)	1.5265	1.5315	0.0050	0.0050
R(19,47)	1.4911	1.4895	-0.0016	0.0016
R(18,32)	1.4905	1.4882	-0.0023	0.0023
R(18,20)	1.4833	1.4821	-0.0012	0.0012
R(19,42)	1.4833	1.4806	-0.0027	0.0027
R(18,39)	1.4823	1.4832	0.0009	0.0009
R(19,58)	1.4814	1.4798	-0.0016	0.0016
R(62,63)	1.4589	1.4582	-0.0007	0.0007
R(62,72)	1.4528	1.4480	-0.0048	0.0048
R(2,16)	1.4472	1.4492	0.0020	0.0020
R(2,3)	1.4421	1.4430	0.0009	0.0009
R(5,7)	1.4396	1.4398	0.0002	0.0002
R(7,16)	1.4382	1.4354	-0.0028	0.0028
R(10,12)	1.4120	1.4088	-0.0032	0.0032
R(7,8)	1.4071	1.4045	-0.0026	0.0026
R(14,16)	1.4050	1.4016	-0.0034	0.0034
R(12,14)	1.3941	1.3924	-0.0017	0.0017
R(8,10)	1.3931	1.3914	-0.0017	0.0017
R(3,5)	1.3822	1.3765	-0.0057	0.0057
R(2,17)	1.3809	1.3749	-0.0060	0.0060
R(1,17)	1.1836	1.1852	0.0016	0.0016
R(47,48)	1.1105	1.1104	-1E-04	1E-04
R(58,59)	1.1079	1.1077	-0.0002	0.0002
R(42,44)	1.1068	1.1066	-0.0002	0.0002
R(39,41)	1.1032	1.1024	-0.0008	0.0008
R(32,33)	1.1017	1.1018	1E-04	1E-04
R(26,28)	1.1009	1.1006	-0.0003	0.0003
R(52,54)	1.1006	1.1001	-0.0005	0.0005

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(23,24)	1.0987	1.0983	-0.0004	0.0004
R(29,31)	1.0985	1.0980	-0.0005	0.0005
R(34,35)	1.0985	1.0981	-0.0004	0.0004
R(45,46)	1.0985	1.0978	-0.0007	0.0007
R(20,22)	1.0984	1.1001	0.0017	0.0017
R(49,51)	1.0983	1.0976	-0.0007	0.0007
R(36,38)	1.0981	1.0975	-0.0006	0.0006
R(23,25)	1.0977	1.0970	-0.0007	0.0007
R(63,65)	1.0976	1.0982	0.0006	0.0006
R(55,57)	1.0975	1.0971	-0.0004	0.0004
R(29,30)	1.0974	1.0969	-0.0005	0.0005
R(69,71)	1.0974	1.0964	-0.0010	0.0010
R(26,27)	1.0972	1.0966	-0.0006	0.0006
R(42,43)	1.0970	1.0972	0.0002	0.0002
R(55,56)	1.0969	1.0971	0.0002	0.0002
R(72,74)	1.0969	1.0976	0.0007	0.0007
R(52,53)	1.0964	1.0957	-0.0007	0.0007
R(58,60)	1.0961	1.0964	0.0003	0.0003
R(49,50)	1.0960	1.0954	-0.0006	0.0006
R(36,37)	1.0959	1.0955	-0.0004	0.0004
R(39,40)	1.0952	1.0947	-0.0005	0.0005
R(72,73)	1.0947	1.0953	0.0006	0.0006
R(66,67)	1.0946	1.0960	0.0014	0.0014
R(66,68)	1.0944	1.0938	-0.0006	0.0006
R(20,21)	1.0943	1.0936	-0.0007	0.0007
R(69,70)	1.0942	1.0940	-0.0002	0.0002
R(63,64)	1.0933	1.0912	-0.0021	0.0021
R(14,15)	1.0897	1.0898	0.0001	0.0001
R(8,9)	1.0890	1.0888	-0.0002	0.0002
R(12,13)	1.0882	1.0881	-1E-04	1E-04
R(10,11)	1.0879	1.0878	-1E-04	1E-04
R(3,4)	1.0855	1.0853	-0.0002	0.0002
R(5,6)	1.0987	1.0846	-0.0002	0.0002

5.4.1.11 B3LYP/6-31'+G(d)

N	0.956105498276	-0.579114388726	-0.923361192545	C	0.518642889358	1.312554841948	2.218543006180
C	3.103786130498	0.819494911328	-0.997699715952	H	1.118901381936	0.408612054251	2.085743285850
C	3.439445023043	1.857807710794	-1.940043656294	H	-0.041717446643	1.242551325693	3.159239757909
H	2.841946561859	2.111604220044	-2.810040089321	C	1.351774931792	2.594038369226	2.134282089660
C	4.628174214085	2.454036289424	-1.562599870619	H	2.234254374091	2.432022624768	1.507401115689
H	5.130684749110	3.260521547960	-2.085988459826	H	1.688927630850	2.928267559549	3.119741096079
C	5.097013021814	1.816174178211	-0.360416065268	C	0.381946974601	3.577551907304	1.461633061072
C	6.231056414936	2.024508133461	0.446173997211	H	0.892465190598	4.405817150467	0.962373804115
H	6.953577598093	2.796346886708	0.184927516730	H	-0.324463777798	3.994258973832	2.190069291035
C	6.425765542438	1.237699741128	1.579120747681	C	-0.343158275972	2.670043249651	0.472442722034
H	7.302907540149	1.395402020535	2.203126351198	H	-1.356293014833	3.001883532796	0.225030148492
C	5.499342126641	0.229172412768	1.923500659096	H	0.238288581548	2.543839578332	-0.449068796605
H	5.675329131732	-0.382475062205	2.806137897354				
C	4.369083255084	0.001655564397	1.139728270400				
H	3.671251268268	-0.792190170289	1.404453187086				
C	4.154437673775	0.790201266437	-0.003205642671				
C	1.953439199853	0.055156832397	-0.980956269673				
N	-2.325223368962	-0.283347898487	-1.386424809060				
N	-1.815105275299	-1.735937184697	1.147560815409				
C	-1.861894915444	0.664124770135	-2.429249043983				
H	-0.998554407527	0.211984383369	-2.926967018111				
H	-1.493867715179	1.562121828758	-1.915060101670				
C	-2.938652107362	1.091870401332	-3.436222792811				
H	-3.252763436649	0.237002051481	-4.050236826711				
H	-2.508225475526	1.829165107890	-4.125139955636				
C	-4.148608828714	1.674486917421	-2.695857789249				
H	-4.947944663756	1.939130739120	-3.398424464250				
H	-3.852069575774	2.607022543751	-2.192363951061				
C	-4.665194046868	0.671456162282	-1.655534777762				
H	-5.093692552245	-0.192577505600	-2.178539533840				
H	-5.478060278356	1.113529608163	-1.064606372740				
C	-3.544988015798	0.216745904904	-0.691282050658				
H	-3.220278572840	1.111445592646	-0.136561734006				
C	-4.047666573109	-0.822804396101	0.337806382638				
H	-4.972435972901	-0.420176250261	0.771745844558				
C	-4.325347297790	-2.168609529364	-0.346261699670				
H	-5.051981772894	-2.067674457245	-1.159754917051				
H	-4.749929493271	-2.879795676610	0.373824725932				
C	-2.440945554693	-1.664889008864	-1.910257587146				
H	-1.443845799950	-1.954463010231	-2.258432936994				
H	-3.110671981450	-1.713600081364	-2.784645589147				
C	-3.085429322651	-1.066177588772	1.517541438204				
H	-2.827241102946	-0.116738433608	2.002466630255				
H	-3.622739431515	-1.679180392077	2.265442827879				
C	-2.974793830087	-2.671414606964	-0.871104323539				
H	-3.108031534592	-3.626129366964	-1.396758050137				
C	-2.052796670224	-2.962570294951	0.334410829788				
H	-2.606544649083	-3.687760482516	0.966521732597				
C	-0.719345248862	-3.620905286307	-0.046921288367				
H	-0.134914300509	-2.948114840195	-0.684707099964				
H	-0.934299097131	-4.524901256251	-0.631601755771				
C	0.102833818280	-3.973894034678	1.199700376238				
H	1.079633766855	-4.377420745363	0.909832394169				
H	-0.411243975975	-4.760732031841	1.771198275251				
C	0.277684620591	-2.731831989088	2.081779420583				
H	0.926221911294	-2.011042544272	1.568728422086				
H	0.766091093319	-2.989996467511	3.029560411187				
C	-1.074747707045	-2.082124172015	2.382672451301				
H	-1.686511259957	-2.767678056363	3.000767903384				
H	-0.942956768513	-1.162164968518	2.963465396754				
Li	-0.759898484920	-0.300652543076	0.009664307236				
O	-0.455636237280	1.381460557138	1.134168218545				

Table 5.11 Signed and Unsigned differences in bond length for the B3LYP/6-31'+G(d) structure of DEVJAP relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(19,61)	2.1211	2.1138	-0.0073	0.0073
R(18,61)	2.1022	2.0975	-0.0047	0.0047
R(61,62)	2.0469	2.0461	-0.0008	0.0008
R(1,61)	1.9703	1.9730	0.0027	0.0027
R(32,34)	1.5471	1.5467	-0.0004	0.0004
R(29,32)	1.5470	1.5464	-0.0006	0.0006
R(45,47)	1.5457	1.5454	-0.0003	0.0003
R(39,45)	1.5425	1.5421	-0.0004	0.0004
R(34,42)	1.5422	1.5417	-0.0005	0.0005
R(66,69)	1.5370	1.5363	-0.0007	0.0007
R(20,23)	1.5357	1.5350	-0.0007	0.0007
R(34,36)	1.5355	1.5350	-0.0005	0.0005
R(47,49)	1.5355	1.5352	-0.0003	0.0003
R(26,29)	1.5354	1.5347	-0.0007	0.0007
R(49,52)	1.5350	1.5345	-0.0005	0.0005
R(23,26)	1.5342	1.5335	-0.0007	0.0007
R(36,45)	1.5342	1.5337	-0.0005	0.0005
R(52,55)	1.5340	1.5334	-0.0006	0.0006
R(63,66)	1.5310	1.5308	-0.0002	0.0002
R(55,58)	1.5306	1.5303	-0.0003	0.0003
R(69,72)	1.5265	1.5257	-0.0008	0.0008
R(19,47)	1.4911	1.4908	-0.0003	0.0003
R(18,32)	1.4905	1.4903	-0.0002	0.0002
R(18,20)	1.4833	1.4832	-1E-04	1E-04
R(19,42)	1.4833	1.4830	-0.0003	0.0003
R(18,39)	1.4823	1.4820	-0.0003	0.0003
R(19,58)	1.4814	1.4810	-0.0004	0.0004
R(62,63)	1.4589	1.4594	0.0005	0.0005
R(62,72)	1.4528	1.4529	1E-04	1E-04
R(2,16)	1.4472	1.4470	-0.0002	0.0002
R(2,3)	1.4421	1.4418	-0.0003	0.0003
R(5,7)	1.4396	1.4394	-0.0002	0.0002
R(7,16)	1.4382	1.4383	1E-04	1E-04
R(10,12)	1.4120	1.4121	1E-04	1E-04
R(7,8)	1.4071	1.4071	0.0000	0.0000
R(14,16)	1.4050	1.4051	1E-04	1E-04
R(12,14)	1.3941	1.3941	0.0000	0.0000
R(8,10)	1.3931	1.3930	-1E-04	1E-04
R(3,5)	1.3822	1.3824	0.0002	0.0002
R(2,17)	1.3809	1.3812	0.0003	0.0003
R(1,17)	1.1836	1.1833	-0.0003	0.0003
R(47,48)	1.1105	1.1100	-0.0005	0.0005
R(58,59)	1.1079	1.1074	-0.0005	0.0005
R(42,44)	1.1068	1.1063	-0.0005	0.0005
R(39,41)	1.1032	1.1025	-0.0007	0.0007
R(32,33)	1.1017	1.1017	0.0000	0.0000
R(26,28)	1.1009	1.1005	-0.0004	0.0004
R(52,54)	1.1006	1.1000	-0.0006	0.0006

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(23,24)	1.0987	1.0984	-0.0003	0.0003
R(29,31)	1.0985	1.0979	-0.0006	0.0006
R(34,35)	1.0985	1.0980	-0.0005	0.0005
R(45,46)	1.0985	1.0980	-0.0005	0.0005
R(20,22)	1.0984	1.0983	-1E-04	1E-04
R(49,51)	1.0983	1.0978	-0.0005	0.0005
R(36,38)	1.0981	1.0975	-0.0006	0.0006
R(23,25)	1.0977	1.0970	-0.0007	0.0007
R(63,65)	1.0976	1.0972	-0.0004	0.0004
R(55,57)	1.0975	1.0970	-0.0005	0.0005
R(29,30)	1.0974	1.0971	-0.0003	0.0003
R(69,71)	1.0974	1.0969	-0.0005	0.0005
R(26,27)	1.0972	1.0966	-0.0006	0.0006
R(42,43)	1.0970	1.0969	-1E-04	1E-04
R(55,56)	1.0969	1.0970	1E-04	1E-04
R(72,74)	1.0969	1.0969	0.0000	0.0000
R(52,53)	1.0964	1.0959	-0.0005	0.0005
R(58,60)	1.0961	1.0959	-0.0002	0.0002
R(49,50)	1.0960	1.0959	-1E-04	1E-04
R(36,37)	1.0959	1.0954	-0.0005	0.0005
R(39,40)	1.0952	1.0951	-1E-04	1E-04
R(72,73)	1.0947	1.0944	-0.0003	0.0003
R(66,67)	1.0946	1.0945	-1E-04	1E-04
R(66,68)	1.0944	1.0939	-0.0005	0.0005
R(20,21)	1.0943	1.0943	0.0000	0.0000
R(69,70)	1.0942	1.0936	-0.0006	0.0006
R(63,64)	1.0933	1.0932	-1E-04	1E-04
R(14,15)	1.0897	1.0896	-1E-04	1E-04
R(8,9)	1.0890	1.089	0.0000	0.0000
R(12,13)	1.0882	1.0882	0.0000	0.0000
R(10,11)	1.0879	1.0879	0.0000	0.0000
R(3,4)	1.0855	1.0855	0.0000	0.0000
R(5,6)	1.0987	1.0848	0.0000	0.0000

5.4.1.12 B3LYP/6-31+G(d)

N	0.956983407969	-0.581373607522	-0.917683759705	H	-0.053822672493	1.245955287180	3.168626083734
C	3.106915505731	0.812975170519	-1.003325542855	C	1.350601773856	2.593400791105	2.152374715538
C	3.448452600029	1.837343825508	-1.959164213499	H	2.236359011961	2.429605839269	1.530466564359
H	2.853834313500	2.081251882891	-2.833956026325	H	1.683110810920	2.926691219308	3.140324780654
C	4.638262351951	2.434355204913	-1.587086546967	C	0.386306461395	3.579742405375	1.474520525863
H	5.144494381781	3.232237037316	-2.119997455473	H	0.902772294631	4.406115154508	0.976959799142
C	5.102391896167	1.811237795323	-0.375217544145	H	-0.322099629569	4.000190307587	2.199620500504
C	6.235778432528	2.026158779275	0.430539456795	C	-0.337315764374	2.673802370941	0.481671499962
H	6.961448086648	2.791960455560	0.160448009646	H	-1.349760724233	3.007059333769	0.232354836364
C	6.426084867253	1.253137813655	1.573736431563	H	0.246298126125	2.550005825648	-0.438844392866
H	7.302720194334	1.415845402366	2.197127686309				
C	5.495799795187	0.252258468339	1.929505570033				
H	5.668465666128	-0.349048675738	2.819878158646				
C	4.365805997057	0.018877443942	1.147020315874				
H	3.664800294294	-0.769188859125	1.420711862920				
C	4.155552701760	0.793574397899	-0.006093380944				
C	1.955623034468	0.050811611036	-0.980472263464				
N	-2.327130859881	-0.281218572709	-1.385838283255				
N	-1.818584630181	-1.739123285886	1.148004053515				
C	-1.863237739234	0.670114372838	-2.425102008781				
H	-0.998136479194	0.221307835828	-2.922838386192				
H	-1.497846163917	1.567446110859	-1.907646140827				
C	-2.938730916194	1.100136109580	-3.433397305053				
H	-3.250015309362	0.247635061814	-4.052741259222				
H	-2.507235646749	1.841708576606	-4.118050848648				
C	-4.152046535170	1.678645467963	-2.693828713443				
H	-4.951067773040	1.942467143411	-3.398021262354				
H	-3.858980558856	2.611453402439	-2.187881361551				
C	-4.668720525535	0.671592053961	-1.656393549888				
H	-5.096881837577	-0.190953441987	-2.182663250390				
H	-5.482657372500	1.112504654390	-1.064897979157				
C	-3.549007444382	0.215247487975	-0.691462413944				
H	-3.226915940818	1.109263739063	-0.133967060753				
C	-4.051724966761	-0.827760659123	0.334724421230				
H	-4.978322271473	-0.427746115285	0.768454328991				
C	-4.325655311327	-2.173172416347	-0.352720647744				
H	-5.051860484655	-2.072747429068	-1.167236011524				
H	-4.750452741389	-2.887161408773	0.365271315403				
C	-2.438545346960	-1.662418532516	-1.912321649132				
H	-1.440470661004	-1.949373600763	-2.260026206731				
H	-3.107276784491	-1.710652069254	-2.788345524369				
C	-3.090661268517	-1.070962826125	1.516030389649				
H	-2.835485785539	-0.121494116796	2.002744630499				
H	-3.627973042683	-1.685983786900	2.263057306494				
C	-2.972611725561	-2.672400756680	-0.875909656950				
H	-3.103185794966	-3.626584099804	-1.404226818300				
C	-2.052941875346	-2.964641693714	0.331502142393				
H	-2.608000495693	-3.690562288694	0.962464719729				
C	-0.718214560823	-3.622609167666	-0.047205997341				
H	-0.131153135557	-2.949424835564	-0.682276886161				
H	-0.931693077559	-4.526187394709	-0.633974231316				
C	0.100424463375	-3.978296121104	1.201642770221				
H	1.078800548622	-4.380544311941	0.913318206065				
H	-0.414691488360	-4.767385939979	1.770185154226				
C	0.272711434170	-2.737087944101	2.086449520979				
H	0.923496839376	-2.016278379880	1.576363813811				
H	0.758291182026	-2.996952837789	3.035755543657				
C	-1.080661859874	-2.087220345547	2.384456942983				
H	-1.694908217802	-2.773896313642	2.999695206189				
H	-0.950158762667	-1.168431372161	2.967712697109				
Li	-0.756835523901	-0.296679414626	0.011680310235				
O	-0.451459680095	1.383726410034	1.139858702032				
C	0.513731962509	1.313774683828	2.231578376704				
H	1.113265064638	0.408433488151	2.104455403025				

5.4.2 DEVJUI (Benzylcyano-N)-(1,4,7,10-tetraoxacyclododecane-O,O',O'',O''')-lithium

Reported below are the raw bond length data for each of the test functional/basis set combinations for DEVJUI. For reference, Figure 5.14 defines all atomic labels for the DEVJUI structures.

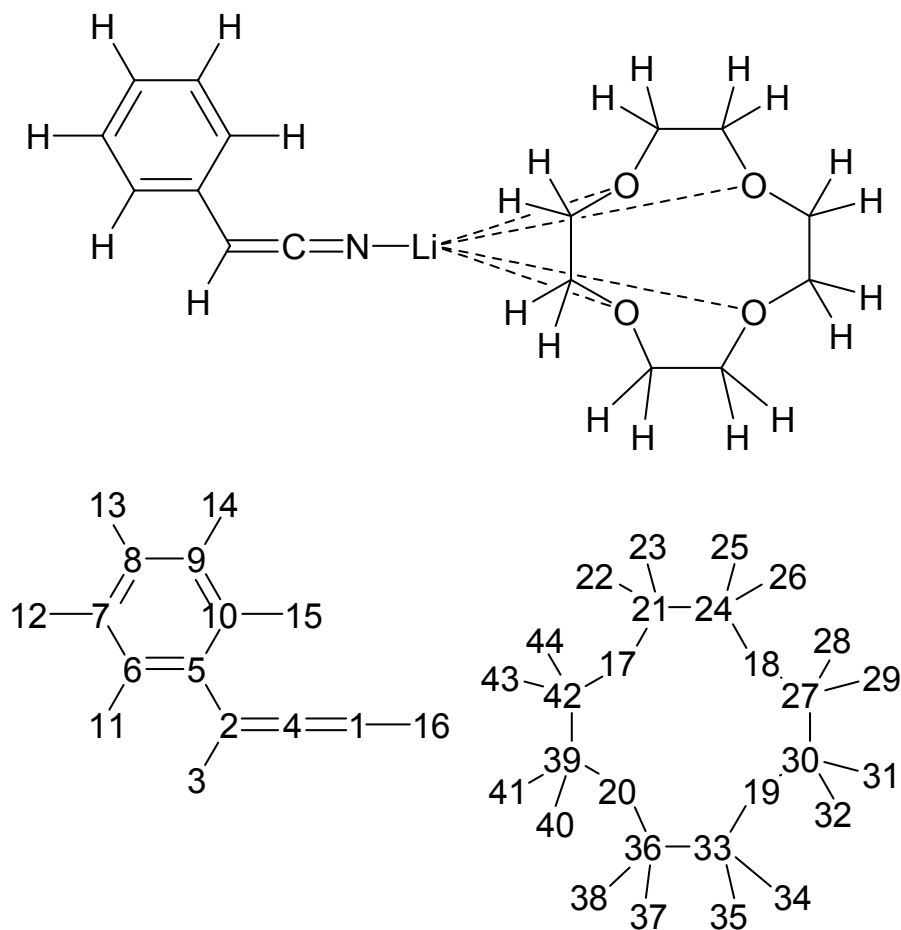


Figure 5.14 Atomic labels for DEVJUI

<i>Bond list</i>	<i>PM3</i>	<i>B3LYP/ 3-21G</i>	<i>MPWLYP/ 3-21G</i>	<i>B3LYP/ M6d/1+</i>	<i>B3LYP/ M6d/1+</i>	<i>MPW1PW91/ M6d/1+</i>	<i>B3LYP/ 6-31G(d)</i>	<i>HF/6- 31G(d)</i>	<i>B3LYP/6- 31(+1X)G(d)</i>	<i>B3LYP/6- 31++G(d)</i>	<i>B3LYP/ 6- 31+G(d)</i>
<i>long</i>	R(16,19)	2.1871	2.1283	2.0988	2.2066	2.2095	2.2043	2.1871	2.2205	2.2091	2.2092
	R(16,17)	2.1864	2.1421	2.0280	2.1462	2.1351	2.2013	2.1864	2.2164	2.2053	2.2065
	R(16,20)	2.1842	2.0945	2.1062	2.1819	2.1831	2.1882	2.1842	2.2041	2.1974	2.1994
	R(16,18)	2.1820	2.0869	2.0325	2.0999	2.0679	2.1901	2.1820	2.2002	2.1949	2.1968
	R(1,16)	1.8300	1.9208	1.9266	1.9804	1.9705	1.8695	1.8300	1.8947	1.8615	1.8601
	R(33,36)	1.5239	1.5360	1.5309	1.5307	1.5237	1.5237	1.5366	1.5232	1.5232	1.5239
	R(39,42)	1.5239	1.5357	1.5314	1.5309	1.5237	1.5235	1.5385	1.5232	1.5232	1.5239
	R(21,24)	1.5238	1.5372	1.5326	1.5313	1.5248	1.5234	1.5385	1.5232	1.5232	1.5238
	R(27,30)	1.5237	1.5355	1.5297	1.5300	1.5228	1.5233	1.5385	1.5231	1.5231	1.5237
	R(2,5)	1.4430	1.4365	1.4446	1.4360	1.4357	1.4418	1.4256	1.4430	1.4427	1.4430
<i>intermediate</i>	R(20,39)	1.4290	1.4961	1.4961	1.4492	1.4437	1.4279	1.4217	1.4239	1.4293	1.4290
	R(18,27)	1.4282	1.4676	1.4881	1.4426	1.4340	1.4273	1.4213	1.4283	1.4285	1.4282
	R(17,21)	1.4281	1.4747	1.4958	1.4308	1.4459	1.4289	1.4213	1.4279	1.4284	1.4281
	R(19,33)	1.4272	1.4699	1.4907	1.4439	1.4375	1.4261	1.4212	1.4271	1.4274	1.4272
	R(20,36)	1.4247	1.4678	1.4885	1.4419	1.4374	1.4231	1.4329	1.4243	1.4247	1.4247
	R(19,30)	1.4242	1.4701	1.4912	1.4443	1.4402	1.4229	1.4327	1.4240	1.4243	1.4242
	R(18,24)	1.4240	1.4698	1.4912	1.4462	1.4372	1.4228	1.4328	1.4238	1.4240	1.4240
	R(17,42)	1.4231	1.4628	1.4835	1.4336	1.4313	1.4218	1.4324	1.4229	1.4232	1.4231
	R(5,10)	1.4212	1.4279	1.4396	1.4244	1.4191	1.4193	1.4073	1.4190	1.4214	1.4212
	R(5,6)	1.4204	1.4245	1.4355	1.4216	1.4184	1.4184	1.4104	1.4179	1.4206	1.4204
	R(7,8)	1.4017	1.4023	1.4127	1.4003	1.3990	1.3988	1.3930	1.3967	1.4018	1.4017
	R(8,9)	1.4014	1.3994	1.4098	1.3992	1.3995	1.3994	1.3904	1.3993	1.4015	1.4014
	R(9,10)	1.3931	1.3929	1.4027	1.3908	1.3901	1.3904	1.3866	1.3905	1.3927	1.3931
	R(6,7)	1.3924	1.3890	1.3984	1.3890	1.3902	1.3908	1.3841	1.3909	1.3921	1.3924
	R(2,4)	1.3685	1.3663	1.3729	1.3781	1.3760	1.3644	1.3531	1.3639	1.3689	1.3685
	R(1,4)	1.1893	1.1915	1.2043	1.1842	1.1875	1.1906	1.1950	1.1919	1.1892	1.1893
<i>short</i>	R(24,25)	1.1007	1.0988	1.1063	1.1043	1.1033	1.1006	1.1101	1.1003	1.1003	1.1007
	R(42,43)	1.1007	1.0991	1.1067	1.1044	1.1022	1.1007	1.1102	1.1004	1.1004	1.1007
	R(42,44)	1.1006	1.0965	1.1042	1.1028	1.1023	1.1002	1.1071	1.1001	1.1000	1.1006
	R(24,26)	1.1005	1.0952	1.1031	1.1014	1.1002	1.1000	1.1071	1.1000	1.0999	1.1005
	R(30,31)	1.1005	1.0984	1.1061	1.1035	1.1015	1.1005	1.1101	1.1002	1.1002	1.1005
	R(30,32)	1.1005	1.0962	1.1038	1.1025	1.1016	1.1001	1.1071	1.1000	1.0999	1.1005
	R(36,37)	1.1005	1.0980	1.1038	1.1028	1.1013	1.1004	1.1101	1.1001	1.1001	1.1005

Table 5.12 Raw bond length data for DEVJUI

	Bond list (cont.)	PM3	E3LYP/ 3-21G	MPWLYP/ 3-21G	E3LYP/ M6d/1+	E3LYP/ M6d/1+	MPW1PW91/ M6d/1+	E3LYP/ 6-31G(d)	HF/6- 31G(d)	E3LYP/6- 31(+LiX)G(d)	E3LYP/6- 31+G(d)	E3LYP/ 6- 31+G(d)
<i>short (cont.)</i>	R(36,38)	1.1005	1.0963	1.1039	1.1026	1.1029	1.1020	1.1001	1.1071	1.1000	1.0999	1.1005
	R(33,35)	1.0990	1.0963	1.1036	1.1011	1.1016	1.1008	1.0985	1.1073	1.0985	1.0984	1.0990
	R(21,23)	1.0988	1.0961	1.1034	1.1005	1.1013	1.1005	1.0984	1.1072	1.0984	1.0982	1.0988
	R(27,29)	1.0988	1.0957	1.1030	1.0996	1.1005	1.0993	1.0983	1.1073	1.0983	1.0982	1.0988
	R(39,41)	1.0988	1.0960	1.1032	1.1004	1.1011	1.1002	1.0983	1.1073	1.0983	1.0982	1.0988
	R(33,34)	1.0936	1.0907	1.0980	1.0961	1.0964	1.0957	1.0932	1.1080	1.0932	1.0932	1.0936
	R(21,22)	1.0934	1.0913	1.0992	1.0955	1.0972	1.0981	1.0930	1.1092	1.0930	1.0931	1.0934
	R(27,28)	1.0934	1.0907	1.0981	1.0961	1.0968	1.0962	1.0930	1.1093	1.0930	1.0931	1.0934
	R(39,40)	1.0934	1.0902	1.0975	1.0938	1.0961	1.0954	1.0930	1.1093	1.0930	1.0930	1.0934
	R(9,14)	1.0895	1.0878	1.0951	1.0913	1.0913	1.0905	1.0894	1.0940	1.0894	1.0893	1.0895
	R(7,12)	1.0891	1.0862	1.0932	1.0903	1.0907	1.0899	1.0890	1.0946	1.0899	1.0890	1.0891
	R(6,11)	1.0890	1.0838	1.0930	1.0903	1.0911	1.0903	1.0887	1.0947	1.0888	1.0891	1.0890
	R(10,15)	1.0883	1.0853	1.0924	1.0881	1.0884	1.0889	1.0883	1.0946	1.0884	1.0882	1.0883
	R(8,13)	1.0872	1.0838	1.0908	1.0881	1.0887	1.0880	1.0869	1.0930	1.0869	1.0872	1.0872
	R(2,3)	1.0867	1.0840	1.0915	1.0894	1.0897	1.0887	1.0863	1.0934	1.0863	1.0867	1.0867

Table 5.12 (cont.) Raw bond length data for DEVJUI

5.4.2.1 X-ray⁶¹

N	-0.346775000000	-0.210050000000	-0.579125000000
C	-1.922775000000	0.139950000000	-2.556125000000
H	-1.941775000000	1.005950000000	-3.021125000000
C	-1.056775000000	-0.064050000000	-1.496125000000
C	-2.832775000000	-0.848050000000	-3.037125000000
C	-3.793775000000	-0.517050000000	-4.017125000000
C	-4.737775000000	-1.422050000000	-4.442125000000
C	-4.784775000000	-2.703050000000	-3.936125000000
C	-3.831775000000	-3.056050000000	-2.997125000000
C	-2.873775000000	-2.176050000000	-2.556125000000
H	-3.794775000000	0.493950000000	-4.395125000000
H	-5.244775000000	-1.219050000000	-4.990125000000
H	-5.437775000000	-3.300050000000	-4.220125000000
H	-3.828775000000	-3.816050000000	-2.630125000000
H	-2.201775000000	-2.357050000000	-1.903125000000
Li	0.921225000000	0.252950000000	0.828875000000
O	0.165225000000	1.787950000000	2.128875000000
O	0.925225000000	-0.765050000000	2.684875000000
O	2.823225000000	-0.593050000000	0.781875000000
O	2.056225000000	1.924950000000	0.175875000000
C	-0.079775000000	1.124950000000	3.457875000000
H	-0.934775000000	0.691950000000	3.452875000000
H	-0.084775000000	1.785950000000	4.150875000000
C	0.972225000000	0.136950000000	3.741875000000
H	1.831225000000	0.561950000000	3.776875000000
H	0.818225000000	-0.314050000000	4.573875000000
C	2.109225000000	-1.698050000000	2.644875000000
H	1.892225000000	-2.478050000000	2.134875000000
H	2.326225000000	-1.969050000000	3.539875000000
C	3.264225000000	-1.028050000000	2.042875000000
H	3.530225000000	-0.281050000000	2.577875000000
H	4.010225000000	-1.620050000000	1.948875000000
C	3.726225000000	0.399950000000	0.136875000000
H	3.633225000000	0.313950000000	-0.815125000000
H	4.636225000000	0.201950000000	0.369875000000
C	3.397225000000	1.766950000000	0.510875000000
H	3.513225000000	1.875950000000	1.456875000000
H	3.947225000000	2.401950000000	0.052875000000
C	1.408225000000	3.137950000000	0.805875000000
H	0.608225000000	3.353950000000	0.320875000000
H	2.004225000000	3.884950000000	0.754875000000
C	1.057225000000	2.871950000000	2.190875000000
H	1.842225000000	2.623950000000	2.685875000000
H	0.657225000000	3.633950000000	2.608875000000

5.4.2.2 PM3

N	-0.100833229905	0.224590803275	-0.962321400674
C	-1.564605511174	-0.173918655290	-3.009441888589
H	-1.267311568319	0.327888112728	-3.934226047053
C	-0.794434003287	0.028539177641	-1.915452737123
C	-2.727287217008	-0.998863918734	-3.012843077042
C	-3.465290576438	-1.148315177715	-4.205439089095
C	-4.598544177058	-1.942269668513	-4.240018730335
C	-5.031324764832	-2.609128803496	-3.096084865451
C	-4.313813717780	-2.471215533733	-1.913113601478
C	-3.176903625833	-1.678812661196	-1.865633738956
H	-3.133734271808	-0.628729196418	-5.110185067523
H	-5.160523948882	-2.048225916276	-5.173325614715
H	-5.927034081122	-3.234611471841	-3.129075924432
H	-4.648915822823	-2.992918310880	-1.011857550267
H	-2.621235216631	-1.578984763784	-0.927811120576
Li	0.972174238770	0.531546345134	0.513123994631
O	0.055360132108	1.688705462048	2.125864488699
O	0.826035388948	-0.974776192077	2.085010995839
O	2.980544884885	-0.331453839739	0.442063548457
O	2.205686748040	2.333623101356	0.473155618504
C	-0.357621542057	0.795755659202	3.151657144194
H	-1.328013154610	0.437645724447	2.751075812840
H	-0.545537587547	1.322465994212	4.107289297013
C	0.641813044298	-0.354633796624	3.363427231052
H	1.602772567929	0.002993633360	3.788966003372
H	0.227182013736	-1.107185695242	4.061560896621
C	1.960564903344	-1.825997173942	1.993311008468
H	1.652191958459	-2.512038560784	1.177909023542
H	2.104527332112	-2.420303194095	2.916487310003
C	3.247638730071	-1.056920154769	1.648279048439
H	3.562302874332	-0.382644942033	2.472140569298
H	4.080691276118	-1.760327873686	1.456423774683
C	3.911844705596	0.701553784557	0.150034344352
H	3.821088225354	0.772217090670	-0.952999508009
H	4.949537196228	0.405257914582	0.397921884005
C	3.554407862909	2.026033666655	0.846625556385
H	3.671038024094	1.959555858442	1.948600666867
H	4.211074258387	2.843047927194	0.490387586114
C	1.574499473645	3.318425928820	1.281203326994
H	0.808489088860	3.713558983758	0.582941857267
H	2.268601881162	4.140524656158	1.542885734472
C	0.946842716139	2.724838485276	2.554262768526
H	1.715888995972	2.341215642150	3.257048542104
H	0.358494816956	3.493608527476	3.091326281159

Table 5.13 Signed and Unsigned differences in bond length for the PM3 structure of DEVJUI relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(16,19)	2.2092	2.1871	-0.0221	0.0221
R(16,17)	2.2065	2.1864	-0.0201	0.0201
R(16,20)	2.1994	2.1842	-0.0152	0.0152
R(16,18)	2.1968	2.1820	-0.0148	0.0148
R(1,16)	1.8601	1.8500	-0.0101	0.0101
R(33,36)	1.5239	1.5386	0.0147	0.0147
R(39,42)	1.5239	1.5385	0.0146	0.0146
R(21,24)	1.5238	1.5385	0.0147	0.0147
R(27,30)	1.5237	1.5385	0.0148	0.0148
R(2,5)	1.4430	1.4256	-0.0174	0.0174
R(20,39)	1.4290	1.4217	-0.0073	0.0073
R(18,27)	1.4282	1.4213	-0.0069	0.0069
R(17,21)	1.4281	1.4213	-0.0068	0.0068
R(19,33)	1.4272	1.4212	-0.0060	0.0060
R(20,36)	1.4247	1.4329	0.0082	0.0082
R(19,30)	1.4242	1.4327	0.0085	0.0085
R(18,24)	1.4240	1.4328	0.0088	0.0088
R(17,42)	1.4231	1.4324	0.0093	0.0093
R(5,10)	1.4212	1.4073	-0.0139	0.0139
R(5,6)	1.4204	1.4104	-0.0100	0.0100
R(7,8)	1.4017	1.3930	-0.0087	0.0087
R(8,9)	1.4014	1.3904	-0.0110	0.0110
R(9,10)	1.3931	1.3866	-0.0065	0.0065
R(6,7)	1.3924	1.3841	-0.0083	0.0083
R(2,4)	1.3685	1.3531	-0.0154	0.0154
R(1,4)	1.1893	1.1950	0.0057	0.0057
R(24,25)	1.1007	1.1101	0.0094	0.0094
R(42,43)	1.1007	1.1102	0.0095	0.0095
R(42,44)	1.1006	1.1071	0.0065	0.0065
R(24,26)	1.1005	1.1071	0.0066	0.0066
R(30,31)	1.1005	1.1101	0.0096	0.0096
R(30,32)	1.1005	1.1071	0.0066	0.0066
R(36,37)	1.1005	1.1101	0.0096	0.0096
R(36,38)	1.1005	1.1071	0.0066	0.0066
R(33,35)	1.0990	1.1073	0.0083	0.0083
R(21,23)	1.0988	1.1072	0.0084	0.0084
R(27,29)	1.0988	1.1073	0.0085	0.0085
R(39,41)	1.0988	1.1073	0.0085	0.0085
R(33,34)	1.0936	1.1090	0.0154	0.0154
R(21,22)	1.0934	1.1092	0.0158	0.0158
R(27,28)	1.0934	1.1093	0.0159	0.0159
R(39,40)	1.0934	1.1093	0.0159	0.0159
R(9,14)	1.0895	1.0940	0.0045	0.0045
R(7,12)	1.0891	1.0946	0.0055	0.0055
R(6,11)	1.0890	1.0947	0.0057	0.0057
R(10,15)	1.0883	1.0946	0.0063	0.0063
R(8,13)	1.0872	1.0930	0.0058	0.0058
R(2,3)	1.0867	1.0934	0.0067	0.0067

5.4.2.3 B3LYP/3-21G

N	0.037910438084	0.580333600899	-1.194199387831
C	-1.553929022782	-0.042392987936	-3.089186060487
H	-1.406640264691	0.406922927594	-4.065192388333
C	-0.696607698135	0.300187272494	-2.087809292736
C	-2.640500735870	-0.969442432124	-2.914084154208
C	-3.504157132465	-1.289397538930	-3.997892762956
C	-4.558554615144	-2.183544289124	-3.850672272416
C	-4.810798876679	-2.806396626508	-2.621749114864
C	-3.973254572085	-2.506559360962	-1.539903851905
C	-2.916142500821	-1.614101331426	-1.675365813231
H	-3.326147828814	-0.817657342455	-4.959653900317
H	-5.194264532701	-2.400020232503	-4.704487552097
H	-5.633712380309	-3.503250148665	-2.511084793839
H	-4.150122500835	-2.978432136748	-0.577021016286
H	-2.277465521993	-1.395606403656	-0.824223874040
Li	1.025655703179	0.711243111780	0.388073771129
O	0.072336865950	1.744252383917	1.950920400802
O	0.603393762452	-0.885077682671	1.696167361469
O	2.883441054687	-0.283093813979	0.382474727065
O	2.343288270299	2.357180237411	0.616941062080
C	-0.606390243112	0.787274363472	2.837778826976
H	-1.497924875369	0.480768937721	2.289851401941
H	-0.887726927859	1.254678386605	3.788497048965
C	0.302687332633	-0.419050761863	3.053638849493
H	1.218261433476	-0.126898264516	3.586066311942
H	-0.213133555113	-1.196610807907	3.629024056228
C	1.664481747573	-1.897714337381	1.596726850295
H	1.472097859703	-2.415822802547	0.656836847769
H	1.622989356162	-2.603755417722	2.434193299450
C	3.015384898910	-1.192146291270	1.526046719455
H	3.214023846243	-0.636960589150	2.453091747092
H	3.823524027490	-1.914123820177	1.360148865934
C	3.971703085833	0.690975997985	0.222551582162
H	3.953775927808	0.964167938654	-0.833025236446
H	4.942746005490	0.253734739417	0.482880215064
C	3.666794218153	1.918408873364	1.075116553446
H	3.648502943553	1.654230230347	2.141038782315
H	4.415682661881	2.702607293411	0.913064425108
C	1.699963343267	3.376735521954	1.460375037965
H	0.970763230563	3.859951549206	0.809517509153
H	2.428989322249	4.110378812877	1.823816424960
C	0.975010904527	2.689132967157	2.613523242378
H	1.687502323725	2.168687525527	3.267943088734
H	0.412118843296	3.419041852223	3.207298690592

Table 5.14 Signed and Unsigned differences in bond length for the B3LYP/3-21G structure of DEVJUI relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(16,19)	2.2092	2.1127	-0.0965	0.0965
R(16,17)	2.2065	2.0981	-0.1084	0.1084
R(16,20)	2.1994	2.0953	-0.1041	0.1041
R(16,18)	2.1968	2.0703	-0.1265	0.1265
R(1,16)	1.8601	1.9166	0.0565	0.0565
R(33,36)	1.5239	1.5253	0.0014	0.0014
R(39,42)	1.5239	1.5258	0.0019	0.0019
R(21,24)	1.5238	1.5270	0.0032	0.0032
R(27,30)	1.5237	1.5252	0.0015	0.0015
R(2,5)	1.4430	1.4365	-0.0065	0.0065
R(20,39)	1.4290	1.4748	0.0458	0.0458
R(18,27)	1.4282	1.4676	0.0394	0.0394
R(17,21)	1.4281	1.4747	0.0466	0.0466
R(19,33)	1.4272	1.4699	0.0427	0.0427
R(20,36)	1.4247	1.4678	0.0431	0.0431
R(19,30)	1.4242	1.4701	0.0459	0.0459
R(18,24)	1.4240	1.4698	0.0458	0.0458
R(17,42)	1.4231	1.4628	0.0397	0.0397
R(5,10)	1.4212	1.4279	0.0067	0.0067
R(5,6)	1.4204	1.4245	0.0041	0.0041
R(7,8)	1.4017	1.4023	0.0006	0.0006
R(8,9)	1.4014	1.3994	-0.0020	0.0020
R(9,10)	1.3931	1.3929	-0.0002	0.0002
R(6,7)	1.3924	1.3890	-0.0034	0.0034
R(2,4)	1.3685	1.3663	-0.0022	0.0022
R(1,4)	1.1893	1.1915	0.0022	0.0022
R(24,25)	1.1007	1.0988	-0.0019	0.0019
R(42,43)	1.1007	1.0991	-0.0016	0.0016
R(42,44)	1.1006	1.0965	-0.0041	0.0041
R(24,26)	1.1005	1.0952	-0.0053	0.0053
R(30,31)	1.1005	1.0984	-0.0021	0.0021
R(30,32)	1.1005	1.0962	-0.0043	0.0043
R(36,37)	1.1005	1.0980	-0.0025	0.0025
R(36,38)	1.1005	1.0963	-0.0042	0.0042
R(33,35)	1.0990	1.0963	-0.0027	0.0027
R(21,23)	1.0988	1.0961	-0.0027	0.0027
R(27,29)	1.0988	1.0957	-0.0031	0.0031
R(39,41)	1.0988	1.0960	-0.0028	0.0028
R(33,34)	1.0936	1.0907	-0.0029	0.0029
R(21,22)	1.0934	1.0913	-0.0021	0.0021
R(27,28)	1.0934	1.0907	-0.0027	0.0027
R(39,40)	1.0934	1.0902	-0.0032	0.0032
R(9,14)	1.0895	1.0878	-0.0017	0.0017
R(7,12)	1.0891	1.0862	-0.0029	0.0029
R(6,11)	1.0890	1.0858	-0.0032	0.0032
R(10,15)	1.0883	1.0853	-0.0030	0.0030
R(8,13)	1.0872	1.0838	-0.0034	0.0034
R(2,3)	1.0867	1.0840	-0.0027	0.0027

5.4.2.4 MPWLYP/3-21G

N	0.215564866789	-1.870007560858	-1.206199306866
C	2.482309100554	-2.129900249155	-0.009851244346
H	2.833597508295	-3.120330893017	0.285147644793
C	1.276240624611	-2.026067348329	-0.657515576748
C	3.279163463097	-0.977342228718	0.341429586482
C	4.485777839278	-1.122515239746	1.105328029381
C	5.251725890833	-0.016600431069	1.487099453714
C	4.868824215837	1.295831468561	1.131100902738
C	3.696837628841	1.464803742433	0.365925985865
C	2.917750738894	0.366554643165	-0.027178596209
H	4.800509180256	-2.128392349584	1.394648499584
H	6.162278021580	-0.173809693937	2.071307688483
H	5.471624806505	2.154191555362	1.430611455595
H	3.393932160420	2.471082903356	0.057861562658
H	2.017407525745	0.525051045648	-0.625144160785
Li	-1.180312048455	-0.673143288191	-0.650709636964
O	-0.963371171103	-0.282030756968	1.444204373309
O	-0.344296279665	1.237887736431	-0.716151405368
O	-2.397327770353	0.193688472560	-2.166280652864
O	-3.053198905889	-1.336101982967	0.012536260646
C	-0.091506541032	0.918154250011	1.636465823055
H	0.932266321530	0.558326170785	1.461635459195
H	-0.193569764432	1.322970103387	2.657848049317
C	-0.444965447622	1.974112142380	0.576750441712
H	-1.466135050214	2.373821489632	0.723111382955
H	0.284203005829	2.801345894102	0.605659830184
C	-0.838494141772	1.982602540014	-1.906004924691
H	-0.270723260659	1.570810313131	-2.750870426996
H	-0.653733050552	3.065787617059	-1.810473498905
C	-2.333561196095	1.681253057847	-2.084308356504
H	-2.910818961264	2.056709899847	-1.218670094957
H	-2.723728325689	2.137482926705	-3.010636699162
C	-3.774712196409	-0.363950730347	-2.047354401688
H	-3.710111304450	-1.359075440908	-2.506767098040
H	-4.508789612255	0.258972600403	-2.586798714408
C	-4.142223196368	-0.499856330940	-0.562169776300
H	-4.178178309031	0.492673870575	-0.076080742243
H	-5.120503827014	-0.997638817937	-0.444545614845
C	-3.061348906323	-1.394690608348	1.507488634097
H	-2.511013794298	-2.312867890579	1.749681450256
H	-4.093107150066	-1.449435843123	1.894159976680
C	-2.305848791437	-0.180441866141	2.067202084177
H	-2.815379050775	0.760652709473	1.785064260719
H	-2.238306484851	-0.238074001961	3.167856854677

Table 5.15 Signed and Unsigned differences in bond length for the MPWLYP/3-21G structure of DEVJUI relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(16,19)	2.2092	2.1283	-0.0809	0.0809
R(16,17)	2.2065	2.1421	-0.0644	0.0644
R(16,20)	2.1994	2.0945	-0.1049	0.1049
R(16,18)	2.1968	2.0869	-0.1099	0.1099
R(1,16)	1.8601	1.9208	0.0607	0.0607
R(33,36)	1.5239	1.5360	0.0121	0.0121
R(39,42)	1.5239	1.5357	0.0118	0.0118
R(21,24)	1.5238	1.5372	0.0134	0.0134
R(27,30)	1.5237	1.5355	0.0118	0.0118
R(2,5)	1.4430	1.4446	0.0016	0.0016
R(20,39)	1.4290	1.4961	0.0671	0.0671
R(18,27)	1.4282	1.4881	0.0599	0.0599
R(17,21)	1.4281	1.4958	0.0677	0.0677
R(19,33)	1.4272	1.4907	0.0635	0.0635
R(20,36)	1.4247	1.4885	0.0638	0.0638
R(19,30)	1.4242	1.4912	0.0670	0.0670
R(18,24)	1.4240	1.4912	0.0672	0.0672
R(17,42)	1.4231	1.4835	0.0604	0.0604
R(5,10)	1.4212	1.4396	0.0184	0.0184
R(5,6)	1.4204	1.4355	0.0151	0.0151
R(7,8)	1.4017	1.4127	0.0110	0.0110
R(8,9)	1.4014	1.4098	0.0084	0.0084
R(9,10)	1.3931	1.4027	0.0096	0.0096
R(6,7)	1.3924	1.3984	0.0060	0.0060
R(2,4)	1.3685	1.3729	0.0044	0.0044
R(1,4)	1.1893	1.2043	0.0150	0.0150
R(24,25)	1.1007	1.1063	0.0056	0.0056
R(42,43)	1.1007	1.1067	0.0060	0.0060
R(42,44)	1.1006	1.1042	0.0036	0.0036
R(24,26)	1.1005	1.1031	0.0026	0.0026
R(30,31)	1.1005	1.1061	0.0056	0.0056
R(30,32)	1.1005	1.1038	0.0033	0.0033
R(36,37)	1.1005	1.1058	0.0053	0.0053
R(36,38)	1.1005	1.1039	0.0034	0.0034
R(33,35)	1.0990	1.1036	0.0046	0.0046
R(21,23)	1.0988	1.1034	0.0046	0.0046
R(27,29)	1.0988	1.1030	0.0042	0.0042
R(39,41)	1.0988	1.1032	0.0044	0.0044
R(33,34)	1.0936	1.0980	0.0044	0.0044
R(21,22)	1.0934	1.0992	0.0058	0.0058
R(27,28)	1.0934	1.0981	0.0047	0.0047
R(39,40)	1.0934	1.0975	0.0041	0.0041
R(9,14)	1.0895	1.0951	0.0056	0.0056
R(7,12)	1.0891	1.0932	0.0041	0.0041
R(6,11)	1.0890	1.0930	0.0040	0.0040
R(10,15)	1.0883	1.0924	0.0041	0.0041
R(8,13)	1.0872	1.0908	0.0036	0.0036
R(2,3)	1.0867	1.0915	0.0048	0.0048

5.4.2.5 B3LYP/Midi!

N	0.920419209004	0.499795064492	-2.030026840540
C	-1.612398238222	0.492238745341	-2.417180108835
H	-2.056855009236	1.357915599686	-2.906820049402
C	-0.248780040384	0.500627425150	-2.217895233017
C	-2.465184177168	-0.609938585353	-2.070575084635
C	-3.855516662177	-0.576786932069	-2.365180054180
C	-4.702918685293	-1.621890482030	-2.020182574522
C	-4.217605951315	-2.759791333051	-1.364089963882
C	-2.852116402505	-2.819009997198	-1.064593882328
C	-1.995107343013	-1.777242523770	-1.403199492446
H	-4.256022837419	0.295735660670	-2.881963889543
H	-5.761850145447	-1.553485352947	-2.270762793728
H	-4.883790078316	-3.578991679451	-1.101287449770
H	-2.447786757713	-3.700297479702	-0.563745181215
H	-0.940189022642	-1.832630293800	-1.142525063925
Li	1.363106969833	0.655498614902	-0.161445789598
O	-0.156040486012	1.587335558238	0.806381399448
O	0.500027322710	-0.977261255215	0.687316938083
O	3.072601754208	-0.337992780074	0.542638590826
O	2.423867828027	2.277811969042	0.667686959541
C	-1.171069291291	0.614563023911	1.164451193388
H	-1.689475478597	0.397774034944	0.224019837623
H	-1.878810332256	1.027033192629	1.899386313157
C	-0.490902130075	-0.654350938110	1.689896772066
H	-0.015867382147	-0.483983424511	2.672183437271
H	-1.225794714186	-1.468077880306	1.779730958199
C	1.470252894526	-1.967528744187	1.086383079466
H	1.736139529907	-2.512997427438	0.173577218540
H	1.061958693736	-2.669655312039	1.827691976228
C	2.701142096945	-1.229793735745	1.616236995878
H	2.447566128055	-0.675850644303	2.536279333336
H	3.522988458221	-1.928603906193	1.843762591394
C	4.087498146150	0.623141858614	0.904804010140
H	4.530821011014	0.947126534835	-0.043787872737
H	4.867686996579	0.171210631208	1.536893678240
C	3.430616852612	1.822029644617	1.593789027918
H	2.986022618959	1.520826529646	2.556989684642
H	4.170798108136	2.615525079911	1.789446583853
C	1.471925065368	3.195361647029	1.260985101796
H	1.071924709307	3.780797741179	0.425521118330
H	1.957609389286	3.867124032690	1.984636553055
C	0.332764050514	2.389545578134	1.891952128926
H	0.704805243312	1.773543980293	2.729699437492
H	-0.453386960575	3.058703243214	2.279796233953

Table 5.16 Signed and Unsigned differences in bond length for the B3LYP/Midi! structure of DEVJUI relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(16,19)	2.2092	2.0988	-0.1104	0.1104
R(16,17)	2.2065	2.0280	-0.1785	0.1785
R(16,20)	2.1994	2.1082	-0.0912	0.0912
R(16,18)	2.1968	2.0325	-0.1643	0.1643
R(1,16)	1.8601	1.9266	0.0665	0.0665
R(33,36)	1.5239	1.5309	0.0070	0.0070
R(39,42)	1.5239	1.5314	0.0075	0.0075
R(21,24)	1.5238	1.5326	0.0088	0.0088
R(27,30)	1.5237	1.5297	0.0060	0.0060
R(2,5)	1.4430	1.4360	-0.0070	0.0070
R(20,39)	1.4290	1.4492	0.0202	0.0202
R(18,27)	1.4282	1.4426	0.0144	0.0144
R(17,21)	1.4281	1.4508	0.0227	0.0227
R(19,33)	1.4272	1.4439	0.0167	0.0167
R(20,36)	1.4247	1.4419	0.0172	0.0172
R(19,30)	1.4242	1.4443	0.0201	0.0201
R(18,24)	1.4240	1.4462	0.0222	0.0222
R(17,42)	1.4231	1.4356	0.0125	0.0125
R(5,10)	1.4212	1.4244	0.0032	0.0032
R(5,6)	1.4204	1.4216	0.0012	0.0012
R(7,8)	1.4017	1.4003	-0.0014	0.0014
R(8,9)	1.4014	1.3992	-0.0022	0.0022
R(9,10)	1.3931	1.3908	-0.0023	0.0023
R(6,7)	1.3924	1.3890	-0.0034	0.0034
R(2,4)	1.3685	1.3781	0.0096	0.0096
R(1,4)	1.1893	1.1842	-0.0051	0.0051
R(24,25)	1.1007	1.1043	0.0036	0.0036
R(42,43)	1.1007	1.1044	0.0037	0.0037
R(42,44)	1.1006	1.1028	0.0022	0.0022
R(24,26)	1.1005	1.1001	-0.0004	0.0004
R(30,31)	1.1005	1.1035	0.0030	0.0030
R(30,32)	1.1005	1.1025	0.0020	0.0020
R(36,37)	1.1005	1.1028	0.0023	0.0023
R(36,38)	1.1005	1.1026	0.0021	0.0021
R(33,35)	1.0990	1.1011	0.0021	0.0021
R(21,23)	1.0988	1.1005	0.0017	0.0017
R(27,29)	1.0988	1.0996	0.0008	0.0008
R(39,41)	1.0988	1.1004	0.0016	0.0016
R(33,34)	1.0936	1.0961	0.0025	0.0025
R(21,22)	1.0934	1.0955	0.0021	0.0021
R(27,28)	1.0934	1.0961	0.0027	0.0027
R(39,40)	1.0934	1.0958	0.0024	0.0024
R(9,14)	1.0895	1.0913	0.0018	0.0018
R(7,12)	1.0891	1.0903	0.0012	0.0012
R(6,11)	1.0890	1.0903	0.0013	0.0013
R(10,15)	1.0883	1.0881	-0.0002	0.0002
R(8,13)	1.0872	1.0881	0.0009	0.0009
R(2,3)	1.0867	1.0894	0.0027	0.0027

5.4.2.6 B3LYP/Midi!+

N	0.861734905910	0.612957747656	-2.179331267278
C	-1.692815953645	0.482983276858	-2.404712911357
H	-2.229864294251	1.382060246227	-2.705876635786
C	-0.319124073057	0.554281524084	-2.318239427291
C	-2.443783449751	-0.703078717601	-2.080010252104
C	-3.863907532627	-0.663236198014	-1.997354963812
C	-4.610770382798	-1.789464798946	-1.656739046383
C	-3.984211807106	-3.013559253675	-1.377822179566
C	-2.585285887550	-3.080338922226	-1.466814258642
C	-1.831465408984	-1.961297614810	-1.816453653919
H	-4.374215418217	0.276725819517	-2.212948462480
H	-5.697939099536	-1.714669558419	-1.610751217274
H	-4.569928431454	-3.893273630162	-1.116288600871
H	-2.078204915296	-4.028819425683	-1.281878904063
H	-0.748716686956	-2.043899764444	-1.904235000576
Li	1.347040882393	0.728671156548	-0.283475486758
O	-0.160986349490	1.813059833386	0.791844591640
O	0.350345590742	-0.827848929484	0.713297161851
O	3.010894502655	-0.433458626383	0.582721624268
O	2.522252230601	2.265675779947	0.725039809019
C	-1.219565825821	0.881312292508	1.157322569633
H	-1.739282612189	0.678294439105	0.212556950528
H	-1.915687503134	1.339674283627	1.877164047503
C	-0.610856612190	-0.409667675288	1.712043152665
H	-0.113198310481	-0.251684103020	2.684993823314
H	-1.393142341224	-1.175272575684	1.834053770778
C	1.227745244983	-1.911329022444	1.093079145746
H	1.414090440139	-2.480741209301	0.174339102159
H	0.754220112573	-2.574659997679	1.832529834376
C	2.536429618091	-1.324119618932	1.625347692524
H	2.365041748588	-0.772299914790	2.564047059544
H	3.280092359243	-2.116314390596	1.812538307391
C	4.060915855706	0.474700597916	0.997310704432
H	4.569253607054	0.766421396390	0.070704564224
H	4.784585742990	-0.028309004841	1.658304223532
C	3.461765595527	1.709036923560	1.675974772709
H	2.954511193206	1.442789546606	2.617531236173
H	4.252134676584	2.444008070400	1.903091073153
C	1.626947006072	3.267960912078	1.280992014757
H	1.336673777289	3.895235519031	0.430272114907
H	2.147182272089	3.889857189827	2.025985327554
C	0.387569305353	2.592723790271	1.874043553712
H	0.650382107032	1.956278804547	2.735974862417
H	-0.338817361896	3.351011124346	2.212610881875

Table 5.17 Signed and Unsigned differences in bond length for the B3LYP/Midi!+ structure of DEVJUI relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(16,19)	2.2092	2.2066	-0.0026	0.0026
R(16,17)	2.2065	2.1462	-0.0603	0.0603
R(16,20)	2.1994	2.1819	-0.0175	0.0175
R(16,18)	2.1968	2.0999	-0.0969	0.0969
R(1,16)	1.8601	1.9604	0.1003	0.1003
R(33,36)	1.5239	1.5307	0.0068	0.0068
R(39,42)	1.5239	1.5309	0.0070	0.0070
R(21,24)	1.5238	1.5313	0.0075	0.0075
R(27,30)	1.5237	1.5300	0.0063	0.0063
R(2,5)	1.4430	1.4409	-0.0021	0.0021
R(20,39)	1.4290	1.4544	0.0254	0.0254
R(18,27)	1.4282	1.4450	0.0168	0.0168
R(17,21)	1.4281	1.4568	0.0287	0.0287
R(19,33)	1.4272	1.4489	0.0217	0.0217
R(20,36)	1.4247	1.4480	0.0233	0.0233
R(19,30)	1.4242	1.4510	0.0268	0.0268
R(18,24)	1.4240	1.4479	0.0239	0.0239
R(17,42)	1.4231	1.4422	0.0191	0.0191
R(5,10)	1.4212	1.4239	0.0027	0.0027
R(5,6)	1.4204	1.4231	0.0027	0.0027
R(7,8)	1.4017	1.4031	0.0014	0.0014
R(8,9)	1.4014	1.4033	0.0019	0.0019
R(9,10)	1.3931	1.3938	0.0007	0.0007
R(6,7)	1.3924	1.3936	0.0012	0.0012
R(2,4)	1.3685	1.3783	0.0098	0.0098
R(1,4)	1.1893	1.1904	0.0011	0.0011
R(24,25)	1.1007	1.1042	0.0035	0.0035
R(42,43)	1.1007	1.1032	0.0025	0.0025
R(42,44)	1.1006	1.1033	0.0027	0.0027
R(24,26)	1.1005	1.1014	0.0009	0.0009
R(30,31)	1.1005	1.1023	0.0018	0.0018
R(30,32)	1.1005	1.1026	0.0021	0.0021
R(36,37)	1.1005	1.1021	0.0016	0.0016
R(36,38)	1.1005	1.1029	0.0024	0.0024
R(33,35)	1.0990	1.1016	0.0026	0.0026
R(21,23)	1.0988	1.1013	0.0025	0.0025
R(27,29)	1.0988	1.1005	0.0017	0.0017
R(39,41)	1.0988	1.1011	0.0023	0.0023
R(33,34)	1.0936	1.0964	0.0028	0.0028
R(21,22)	1.0934	1.0972	0.0038	0.0038
R(27,28)	1.0934	1.0968	0.0034	0.0034
R(39,40)	1.0934	1.0961	0.0027	0.0027
R(9,14)	1.0895	1.0913	0.0018	0.0018
R(7,12)	1.0891	1.0907	0.0016	0.0016
R(6,11)	1.0890	1.0911	0.0021	0.0021
R(10,15)	1.0883	1.0894	0.0011	0.0011
R(8,13)	1.0872	1.0887	0.0015	0.0015
R(2,3)	1.0867	1.0897	0.0030	0.0030

5.4.2.7 MPW1PW91/Midi!+

N	0.873719081029	0.615542029183	-2.232797903444
C	-1.679851052902	0.482669927523	-2.400872851885
H	-2.223207402592	1.378328185258	-2.697239881278
C	-0.306816114411	0.553537979498	-2.345062060218
C	-2.414425428040	-0.696515319840	-2.038718535435
C	-3.825567727821	-0.657857712578	-1.900607985754
C	-4.552534601479	-1.777321441301	-1.512028183547
C	-3.913508442486	-2.991692192985	-1.239511589992
C	-2.523263358486	-3.057051890622	-1.386583927192
C	-1.789800765680	-1.944948461843	-1.783719950236
H	-4.346570491742	0.276583805562	-2.110729254216
H	-5.636371213308	-1.704055428846	-1.423492571555
H	-4.485077901620	-3.867698360144	-0.940219487103
H	-2.006810198004	-4.001300384905	-1.210794963815
H	-0.712846450001	-2.026748611655	-1.921900559558
Li	1.353497251959	0.743049917213	-0.325853297883
O	-0.158622689883	1.817899982955	0.731021296509
O	0.354762995037	-0.789152645247	0.639041989827
O	2.991642218636	-0.433781648433	0.576035846271
O	2.511232723227	2.247863585024	0.751639500792
C	-1.231399219319	0.896348247617	1.031873315942
H	-1.714112868420	0.717246699844	0.061998042857
H	-1.953766256871	1.345624534593	1.730014058311
C	-0.662204945696	-0.407597238194	1.580156650732
H	-0.229922633993	-0.289171208180	2.588351540707
H	-1.452370355861	-1.172113220565	1.620414823663
C	1.193276150994	-1.883088625907	1.034820221521
H	1.396828098778	-2.458535989786	0.124239883628
H	0.690211507322	-2.538922401641	1.759554463934
C	2.489104567110	-1.315268556402	1.598087024419
H	2.299500579000	-0.765744252084	2.533651009233
H	3.219350816938	-2.114306305186	1.802305644911
C	4.028084920901	0.455650871906	1.024505036165
H	4.560318579174	0.760562805399	0.116561246707
H	4.736121238141	-0.059546903940	1.691655451360
C	3.422068007539	1.676536269754	1.705573264112
H	2.896293207764	1.400193954203	2.632970865714
H	4.210435024606	2.402907266339	1.960916174518
C	1.614109035849	3.227278911187	1.317377842240
H	1.343013859605	3.887715652004	0.486546559110
H	2.118172755400	3.821206634990	2.094278431167
C	0.365592297968	2.536735207774	1.852255045813
H	0.607786093419	1.861034173260	2.688664812430
H	-0.362803231200	3.281665351645	2.212229959716

Table 5.18 Signed and Unsigned differences in bond length for the MPW1PW91/Midi!+ structure of DEVJUI relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(16,19)	2.2092	2.2095	0.0003	0.0003
R(16,17)	2.2065	2.1351	-0.0714	0.0714
R(16,20)	2.1994	2.1831	-0.0163	0.0163
R(16,18)	2.1968	2.0679	-0.1289	0.1289
R(1,16)	1.8601	1.9705	0.1104	0.1104
R(33,36)	1.5239	1.5237	-0.0002	0.0002
R(39,42)	1.5239	1.5237	-0.0002	0.0002
R(21,24)	1.5238	1.5248	0.0010	0.0010
R(27,30)	1.5237	1.5228	-0.0009	0.0009
R(2,5)	1.4430	1.4357	-0.0073	0.0073
R(20,39)	1.4290	1.4437	0.0147	0.0147
R(18,27)	1.4282	1.4340	0.0058	0.0058
R(17,21)	1.4281	1.4459	0.0178	0.0178
R(19,33)	1.4272	1.4375	0.0103	0.0103
R(20,36)	1.4247	1.4374	0.0127	0.0127
R(19,30)	1.4242	1.4402	0.0160	0.0160
R(18,24)	1.4240	1.4372	0.0132	0.0132
R(17,42)	1.4231	1.4313	0.0082	0.0082
R(5,10)	1.4212	1.4191	-0.0021	0.0021
R(5,6)	1.4204	1.4184	-0.0020	0.0020
R(7,8)	1.4017	1.3990	-0.0027	0.0027
R(8,9)	1.4014	1.3995	-0.0019	0.0019
R(9,10)	1.3931	1.3901	-0.0030	0.0030
R(6,7)	1.3924	1.3902	-0.0022	0.0022
R(2,4)	1.3685	1.3760	0.0075	0.0075
R(1,4)	1.1893	1.1875	-0.0018	0.0018
R(24,25)	1.1007	1.1033	0.0026	0.0026
R(42,43)	1.1007	1.1022	0.0015	0.0015
R(42,44)	1.1006	1.1023	0.0017	0.0017
R(24,26)	1.1005	1.1002	-0.0003	0.0003
R(30,31)	1.1005	1.1015	0.0010	0.0010
R(30,32)	1.1005	1.1016	0.0011	0.0011
R(36,37)	1.1005	1.1013	0.0008	0.0008
R(36,38)	1.1005	1.1020	0.0015	0.0015
R(33,35)	1.0990	1.1008	0.0018	0.0018
R(21,23)	1.0988	1.1005	0.0017	0.0017
R(27,29)	1.0988	1.0993	0.0005	0.0005
R(39,41)	1.0988	1.1002	0.0014	0.0014
R(33,34)	1.0936	1.0957	0.0021	0.0021
R(21,22)	1.0934	1.0981	0.0047	0.0047
R(27,28)	1.0934	1.0962	0.0028	0.0028
R(39,40)	1.0934	1.0954	0.0020	0.0020
R(9,14)	1.0895	1.0905	0.0010	0.0010
R(7,12)	1.0891	1.0899	0.0008	0.0008
R(6,11)	1.0890	1.0903	0.0013	0.0013
R(10,15)	1.0883	1.0889	0.0006	0.0006
R(8,13)	1.0872	1.0880	0.0008	0.0008
R(2,3)	1.0867	1.0887	0.0020	0.0020

5.4.2.8 B3LYP/6-31G(d)

N	-0.090252403751	0.479393067998	-1.134986219223
C	-1.751569686752	0.072668483071	-3.032987155980
H	-1.675961736972	0.708607473232	-3.910393837147
C	-0.862659430368	0.293725349800	-2.021822543091
C	-2.773464019076	-0.943835163387	-2.995992496580
C	-3.664316694043	-1.109379588519	-4.087186229398
C	-4.660133261856	-2.080267087574	-4.079509863617
C	-4.821503968716	-2.937149773937	-2.985708602279
C	-3.953476303896	-2.792337989626	-1.897648563122
C	-2.955462920080	-1.824227109028	-1.897668353516
H	-3.558813010954	-0.454223460052	-4.950311675178
H	-5.320813353729	-2.169776280386	-4.940531778684
H	-5.600224644364	-3.695439210990	-2.981334123664
H	-4.056806804224	-3.446896187368	-1.033009586968
H	-2.293584296387	-1.733637823547	-1.038519621084
Li	0.955335454344	0.646954594321	0.405673794054
O	0.131201865205	1.809132826567	2.083791100582
O	0.683501942753	-0.865420758748	1.966290170276
O	2.915159107787	-0.360153621154	0.466008163050
O	2.357878370990	2.317654483783	0.578276843564
C	-0.441501808898	0.912008561665	3.034154947385
H	-1.387740155688	0.586058098870	2.594760401395
H	-0.647935721286	1.419776132557	3.986001567264
C	0.464006443361	-0.293782280713	3.250539520242
H	1.415223605143	0.008157893730	3.714509517132
H	-0.022328285738	-1.019196609682	3.919382063660
C	1.730699179886	-1.831147173271	1.877506585255
H	1.481058825438	-2.458154100506	1.017727898881
H	1.767404977030	-2.460366308610	2.776925995742
C	3.071420133479	-1.148049062757	1.640453624243
H	3.348173433954	-0.521385105229	2.501711619180
H	3.862907074682	-1.899239455480	1.500746851579
C	3.936748313442	0.601237878503	0.209537182478
H	3.900052499988	0.787525216846	-0.867028316477
H	4.928959327904	0.206152405009	0.466788235717
C	3.662012433033	1.897070164058	0.962508161417
H	3.719741980776	1.738089776910	2.049833094018
H	4.409096090748	2.658513566131	0.693465660777
C	1.769707987332	3.346424100018	1.374954967980
H	1.034877974328	3.833772736703	0.729027537360
H	2.520162688175	4.087549543285	1.681359973915
C	1.066087350696	2.753569098420	2.589201388881
H	1.788896053148	2.272995787455	3.266006471490
H	0.551921162117	3.545626768246	3.153838561939

Table 5.19 Signed and Unsigned differences in bond length for the B3LYP/6-31G(d) structure of DEVJUI relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(16,19)	2.2092	2.2043	-0.0049	0.0049
R(16,17)	2.2065	2.2013	-0.0052	0.0052
R(16,20)	2.1994	2.1882	-0.0112	0.0112
R(16,18)	2.1968	2.1901	-0.0067	0.0067
R(1,16)	1.8601	1.8695	0.0094	0.0094
R(33,36)	1.5239	1.5237	-0.0002	0.0002
R(39,42)	1.5239	1.5235	-0.0004	0.0004
R(21,24)	1.5238	1.5234	-0.0004	0.0004
R(27,30)	1.5237	1.5233	-0.0004	0.0004
R(2,5)	1.4430	1.4418	-0.0012	0.0012
R(20,39)	1.4290	1.4279	-0.0011	0.0011
R(18,27)	1.4282	1.4273	-0.0009	0.0009
R(17,21)	1.4281	1.4269	-0.0012	0.0012
R(19,33)	1.4272	1.4261	-0.0011	0.0011
R(20,36)	1.4247	1.4231	-0.0016	0.0016
R(19,30)	1.4242	1.4229	-0.0013	0.0013
R(18,24)	1.4240	1.4228	-0.0012	0.0012
R(17,42)	1.4231	1.4218	-0.0013	0.0013
R(5,10)	1.4212	1.4193	-0.0019	0.0019
R(5,6)	1.4204	1.4184	-0.0020	0.0020
R(7,8)	1.4017	1.3988	-0.0029	0.0029
R(8,9)	1.4014	1.3994	-0.0020	0.0020
R(9,10)	1.3931	1.3904	-0.0027	0.0027
R(6,7)	1.3924	1.3908	-0.0016	0.0016
R(2,4)	1.3685	1.3644	-0.0041	0.0041
R(1,4)	1.1893	1.1906	0.0013	0.0013
R(24,25)	1.1007	1.1006	-0.0001	0.0001
R(42,43)	1.1007	1.1007	0.0000	0.0000
R(42,44)	1.1006	1.1002	-0.0004	0.0004
R(24,26)	1.1005	1.1000	-0.0005	0.0005
R(30,31)	1.1005	1.1005	0.0000	0.0000
R(30,32)	1.1005	1.1001	-0.0004	0.0004
R(36,37)	1.1005	1.1004	-0.0001	0.0001
R(36,38)	1.1005	1.1001	-0.0004	0.0004
R(33,35)	1.0990	1.0985	-0.0005	0.0005
R(21,23)	1.0988	1.0984	-0.0004	0.0004
R(27,29)	1.0988	1.0983	-0.0005	0.0005
R(39,41)	1.0988	1.0983	-0.0005	0.0005
R(33,34)	1.0936	1.0932	-0.0004	0.0004
R(21,22)	1.0934	1.0930	-0.0004	0.0004
R(27,28)	1.0934	1.0930	-0.0004	0.0004
R(39,40)	1.0934	1.0930	-0.0004	0.0004
R(9,14)	1.0895	1.0894	-0.0001	0.0001
R(7,12)	1.0891	1.0890	-0.0001	0.0001
R(6,11)	1.0890	1.0887	-0.0003	0.0003
R(10,15)	1.0883	1.0883	0.0000	0.0000
R(8,13)	1.0872	1.0869	-0.0003	0.0003
R(2,3)	1.0867	1.0863	-0.0004	0.0004

5.4.2.9 HF/6-31G(d)

N	-0.134365232031	0.524185121482	-1.152548085504
C	-1.741386733408	0.059167372981	-3.047921818453
H	-1.651208716139	0.662872880195	-3.931137903756
C	-0.872844716897	0.312769626635	-2.027482493175
C	-2.754191145717	-0.967052826106	-2.985400029215
C	-3.619969423907	-1.176798870731	-4.074089284465
C	-4.599295166593	-2.149521781363	-4.046955509732
C	-4.770385595188	-2.965086948485	-2.937345833521
C	-3.926212697451	-2.773964126073	-1.853043104023
C	-2.943282674723	-1.803924172666	-1.869606706775
H	-3.511917155249	-0.559429111346	-4.949869028972
H	-5.238986971250	-2.272881009226	-4.905442895883
H	-5.534187627761	-3.722393099154	-2.918540698374
H	-4.035055472269	-3.392513568470	-0.976772459749
H	-2.306431610530	-1.684358359674	-1.009929161168
Li	0.941975199626	0.690825844889	0.391715803245
O	0.174072008332	1.812553550490	2.096952773034
O	0.669221716364	-0.825857110907	1.925131997571
O	2.876908360390	-0.317696600392	0.472980638795
O	2.376490678737	2.325158509700	0.633150945345
C	-0.438220239974	0.929966797413	3.002655519851
H	-1.379283442426	0.644740248176	2.555670927960
H	-0.635371188655	1.418874266663	3.952142364850
C	0.423773998867	-0.303198370335	3.200992281643
H	1.355337586438	-0.048582577939	3.700429705524
H	-0.098133810862	-1.030445730844	3.816837104319
C	1.662102986598	-1.811838874845	1.800834334886
H	1.395449240381	-2.401578429497	0.936036766682
H	1.682283019139	-2.458592651974	2.672965500285
C	3.018006147094	-1.167911266303	1.577196023329
H	3.332200950765	-0.610844821649	2.456390289077
H	3.766988806010	-1.929511081135	1.378136864127
C	3.906604555645	0.601858295556	0.218135958445
H	3.879839442503	0.799293470336	-0.843719546532
H	4.876681001006	0.184057999395	0.470928313764
C	3.662673306581	1.891066740728	0.980318850662
H	3.738140076172	1.726005809950	2.052008594906
H	4.403208157588	2.636705561114	0.703819430934
C	1.802416902820	3.343628601634	1.413045025471
H	1.091346631243	3.847795128419	0.774995307377
H	2.553512093602	4.059461293080	1.733843308705
C	1.077843609365	2.751289440887	2.607716613766
H	1.779135109614	2.281819525115	3.293036754502
H	0.551744116752	3.531766248727	3.150829840087

Table 5.20 Signed and Unsigned differences in bond length for the HF/6-31G(d) structure of DEVJUI relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(16,19)	2.2092	2.1871	-0.0221	0.0221
R(16,17)	2.2065	2.1864	-0.0201	0.0201
R(16,20)	2.1994	2.1842	-0.0152	0.0152
R(16,18)	2.1968	2.1820	-0.0148	0.0148
R(1,16)	1.8601	1.8500	-0.0101	0.0101
R(33,36)	1.5239	1.5386	0.0147	0.0147
R(39,42)	1.5239	1.5385	0.0146	0.0146
R(21,24)	1.5238	1.5385	0.0147	0.0147
R(27,30)	1.5237	1.5385	0.0148	0.0148
R(2,5)	1.4430	1.4256	-0.0174	0.0174
R(20,39)	1.4290	1.4217	-0.0073	0.0073
R(18,27)	1.4282	1.4213	-0.0069	0.0069
R(17,21)	1.4281	1.4213	-0.0068	0.0068
R(19,33)	1.4272	1.4212	-0.0060	0.0060
R(20,36)	1.4247	1.4329	0.0082	0.0082
R(19,30)	1.4242	1.4327	0.0085	0.0085
R(18,24)	1.4240	1.4328	0.0088	0.0088
R(17,42)	1.4231	1.4324	0.0093	0.0093
R(5,10)	1.4212	1.4073	-0.0139	0.0139
R(5,6)	1.4204	1.4104	-0.0100	0.0100
R(7,8)	1.4017	1.3930	-0.0087	0.0087
R(8,9)	1.4014	1.3904	-0.0110	0.0110
R(9,10)	1.3931	1.3866	-0.0065	0.0065
R(6,7)	1.3924	1.3841	-0.0083	0.0083
R(2,4)	1.3685	1.3531	-0.0154	0.0154
R(1,4)	1.1893	1.1950	0.0057	0.0057
R(24,25)	1.1007	1.1101	0.0094	0.0094
R(42,43)	1.1007	1.1102	0.0095	0.0095
R(42,44)	1.1006	1.1071	0.0065	0.0065
R(24,26)	1.1005	1.1071	0.0066	0.0066
R(30,31)	1.1005	1.1101	0.0096	0.0096
R(30,32)	1.1005	1.1071	0.0066	0.0066
R(36,37)	1.1005	1.1101	0.0096	0.0096
R(36,38)	1.1005	1.1071	0.0066	0.0066
R(33,35)	1.0990	1.1073	0.0083	0.0083
R(21,23)	1.0988	1.1072	0.0084	0.0084
R(27,29)	1.0988	1.1073	0.0085	0.0085
R(39,41)	1.0988	1.1073	0.0085	0.0085
R(33,34)	1.0936	1.1090	0.0154	0.0154
R(21,22)	1.0934	1.1092	0.0158	0.0158
R(27,28)	1.0934	1.1093	0.0159	0.0159
R(39,40)	1.0934	1.1093	0.0159	0.0159
R(9,14)	1.0895	1.0940	0.0045	0.0045
R(7,12)	1.0891	1.0946	0.0055	0.0055
R(6,11)	1.0890	1.0947	0.0057	0.0057
R(10,15)	1.0883	1.0946	0.0063	0.0063
R(8,13)	1.0872	1.0930	0.0058	0.0058
R(2,3)	1.0867	1.0934	0.0067	0.0067

5.4.2.10 B3LYP/6-31(+LiX)G(d)

N	-0.087544194057	0.445654579478	-1.133374649730
C	-1.727921599065	0.032915659933	-3.049317180939
H	-1.622432797514	0.646158402907	-3.939763338067
C	-0.849991905509	0.256438005288	-2.029769323722
C	-2.776803675215	-0.957095089036	-3.006495065990
C	-3.655031010128	-1.120932295066	-4.107526234675
C	-4.675879354125	-2.065504726837	-4.096270152756
C	-4.875267045615	-2.895853615629	-2.988482623919
C	-4.019977055033	-2.752072908235	-1.890387491608
C	-2.997140926839	-1.810079502259	-1.894092908714
H	-3.519721203075	-0.485849703105	-4.981458721710
H	-5.325888607343	-2.155109953164	-4.965284657761
H	-5.673323766265	-3.633725812256	-2.981120005450
H	-4.152925858289	-3.386725382269	-1.014960067849
H	-2.345699649800	-1.720798188509	-1.026743966900
Li	0.953615925368	0.631750324729	0.390205509816
O	0.126551147602	1.793713136210	2.086797962005
O	0.711736902142	-0.875886085254	1.974352978670
O	2.943884018333	-0.349183651237	0.474684368921
O	2.352230717371	2.324725498907	0.579321867104
C	-0.435915149178	0.889812464562	3.038427797687
H	-1.377496750367	0.553540660277	2.596811641480
H	-0.649086753842	1.397214311378	3.988948024150
C	0.483821014692	-0.304273318835	3.258352028723
H	1.431886100478	0.008075403140	3.721297061722
H	0.003490889859	-1.035303213841	3.925268941868
C	1.769323436087	-1.831643646668	1.883823308835
H	1.523957203755	-2.457590946665	1.022018268832
H	1.810199322671	-2.462371087928	2.781985061879
C	3.104099805019	-1.136014050020	1.650659450547
H	3.372978485563	-0.504535100576	2.510589988110
H	3.902080172470	-1.879990927629	1.510348433117
C	3.953662651049	0.626460885343	0.219453755505
H	3.916063578373	0.808952141513	-0.857715047306
H	4.949950790127	0.244144585217	0.480275416538
C	3.660139004086	1.918632369457	0.970720672092
H	3.711070831998	1.760632796128	2.058194932724
H	4.398008530634	2.689466561586	0.703512442474
C	1.746051951967	3.348767324434	1.370533681286
H	1.005716345274	3.819931250000	0.718968566648
H	2.485331893411	4.102496326271	1.673401424288
C	1.051341410710	2.752102248111	2.587746543039
H	1.779475546154	2.280205817416	3.264475562759
H	0.526035677013	3.539439013312	3.148441111176

Table 5.21 Signed and Unsigned differences in bond length for the B3LYP/6-31(+LiX)G(d) structure of DEVJUI relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(16,19)	2.2092	2.2205	0.0113	0.0113
R(16,17)	2.2065	2.2164	0.0099	0.0099
R(16,20)	2.1994	2.2041	0.0047	0.0047
R(16,18)	2.1968	2.2002	0.0034	0.0034
R(1,16)	1.8601	1.8547	-0.0054	0.0054
R(33,36)	1.5239	1.5232	-0.0007	0.0007
R(39,42)	1.5239	1.5232	-0.0007	0.0007
R(21,24)	1.5238	1.5232	-0.0006	0.0006
R(27,30)	1.5237	1.5231	-0.0006	0.0006
R(2,5)	1.4430	1.4430	0.0000	0.0000
R(20,39)	1.4290	1.4290	0.0000	0.0000
R(18,27)	1.4282	1.4283	0.0001	0.0001
R(17,21)	1.4281	1.4279	-0.0002	0.0002
R(19,33)	1.4272	1.4271	-0.0001	0.0001
R(20,36)	1.4247	1.4243	-0.0004	0.0004
R(19,30)	1.4242	1.4240	-0.0002	0.0002
R(18,24)	1.4240	1.4238	-0.0002	0.0002
R(17,42)	1.4231	1.4229	-0.0002	0.0002
R(5,10)	1.4212	1.4190	-0.0022	0.0022
R(5,6)	1.4204	1.4179	-0.0025	0.0025
R(7,8)	1.4017	1.3987	-0.0030	0.0030
R(8,9)	1.4014	1.3993	-0.0021	0.0021
R(9,10)	1.3931	1.3905	-0.0026	0.0026
R(6,7)	1.3924	1.3909	-0.0015	0.0015
R(2,4)	1.3685	1.3639	-0.0046	0.0046
R(1,4)	1.1893	1.1919	0.0026	0.0026
R(24,25)	1.1007	1.1003	-0.0004	0.0004
R(42,43)	1.1007	1.1004	-0.0003	0.0003
R(42,44)	1.1006	1.1001	-0.0005	0.0005
R(24,26)	1.1005	1.1000	-0.0005	0.0005
R(30,31)	1.1005	1.1002	-0.0003	0.0003
R(30,32)	1.1005	1.1000	-0.0005	0.0005
R(36,37)	1.1005	1.1001	-0.0004	0.0004
R(36,38)	1.1005	1.1000	-0.0005	0.0005
R(33,35)	1.0990	1.0985	-0.0005	0.0005
R(21,23)	1.0988	1.0984	-0.0004	0.0004
R(27,29)	1.0988	1.0983	-0.0005	0.0005
R(39,41)	1.0988	1.0983	-0.0005	0.0005
R(33,34)	1.0936	1.0932	-0.0004	0.0004
R(21,22)	1.0934	1.0930	-0.0004	0.0004
R(27,28)	1.0934	1.0930	-0.0004	0.0004
R(39,40)	1.0934	1.0930	-0.0004	0.0004
R(9,14)	1.0895	1.0894	-0.0001	0.0001
R(7,12)	1.0891	1.0889	-0.0002	0.0002
R(6,11)	1.0890	1.0888	-0.0002	0.0002
R(10,15)	1.0883	1.0884	0.0001	0.0001
R(8,13)	1.0872	1.0869	-0.0003	0.0003
R(2,3)	1.0867	1.0863	-0.0004	0.0004

5.4.2.11 B3LYP/6-31'+G(d)

N	-0.106425328412	0.443567547954	-1.111259162330
C	-1.727245146055	0.039741642852	-3.048558150280
H	-1.614581646967	0.653529358969	-3.938185643532
C	-0.855650515935	0.262203433437	-2.016737712595
C	-2.772707480673	-0.953734907862	-3.009920358402
C	-3.644640262905	-1.126391810243	-4.118072505786
C	-4.662305102309	-2.076305420921	-4.110137526134
C	-4.866710021361	-2.905517595820	-2.998528784727
C	-4.018171728831	-2.752792573908	-1.893658273667
C	-2.997939363936	-1.804760213313	-1.894005295820
H	-3.506849218359	-0.494433596180	-4.994247884904
H	-5.305872378787	-2.171933469589	-4.983363265467
H	-5.661817710248	-3.647041176314	-2.994041777583
H	-4.154115454840	-3.384329449780	-1.016562308781
H	-2.354019687911	-1.709641655509	-1.021881958155
Li	0.952874808142	0.636896261272	0.407249935561
O	0.134201176279	1.795385969284	2.095767494318
O	0.708559346116	-0.873691155863	1.980840020488
O	2.929524652342	-0.347428210042	0.470226379391
O	2.348550765202	2.325648488213	0.576951985685
C	-0.427892033323	0.894548178812	3.051157214051
H	-1.373001920923	0.561796532609	2.614344361878
H	-0.634291086653	1.403821897317	4.002020745307
C	0.488547472592	-0.302841539484	3.266742755908
H	1.439893202090	0.005728480972	3.725538505063
H	0.008514080473	-1.032828798310	3.934912583176
C	1.762358977290	-1.833073917004	1.882407206780
H	1.508895106198	-2.457271807236	1.021629397780
H	1.807273084555	-2.464865466385	2.779518528354
C	3.097498882480	-1.141022576322	1.640986333649
H	3.376452388706	-0.514350295106	2.501208482588
H	3.891450518505	-1.886961203271	1.489614735406
C	3.942910157477	0.623085311932	0.208089325924
H	3.900449358419	0.804732969846	-0.869102851048
H	4.938599201449	0.236255091343	0.463835445161
C	3.658588136742	1.916990691882	0.959867836836
H	3.716414179543	1.760511851188	2.047246378060
H	4.396152890836	2.685736664649	0.686178219018
C	1.749180432671	3.351356358202	1.371709911264
H	1.006471026906	3.824475331744	0.724187942049
H	2.491906939225	4.103195166533	1.670452059626
C	1.059982193871	2.755458870661	2.592410912559
H	1.790948535920	2.284505967136	3.266776340146
H	0.535966360031	3.542721655740	3.154181919075

Table 5.22 Signed and Unsigned differences in bond length for the B3LYP/6-31+'G(d) structure of DEVJUI relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(16,19)	2.2092	2.2091	-0.0001	0.0001
R(16,17)	2.2065	2.2053	-0.0012	0.0012
R(16,20)	2.1994	2.1974	-0.0020	0.0020
R(16,18)	2.1968	2.1949	-0.0019	0.0019
R(1,16)	1.8601	1.8615	0.0014	0.0014
R(33,36)	1.5239	1.5232	-0.0007	0.0007
R(39,42)	1.5239	1.5232	-0.0007	0.0007
R(21,24)	1.5238	1.5232	-0.0006	0.0006
R(27,30)	1.5237	1.5231	-0.0006	0.0006
R(2,5)	1.4430	1.4427	-0.0003	0.0003
R(20,39)	1.4290	1.4293	0.0003	0.0003
R(18,27)	1.4282	1.4285	0.0003	0.0003
R(17,21)	1.4281	1.4284	0.0003	0.0003
R(19,33)	1.4272	1.4274	0.0002	0.0002
R(20,36)	1.4247	1.4247	0.0000	0.0000
R(19,30)	1.4242	1.4243	0.0001	0.0001
R(18,24)	1.4240	1.4240	0.0000	0.0000
R(17,42)	1.4231	1.4232	0.0001	0.0001
R(5,10)	1.4212	1.4214	0.0002	0.0002
R(5,6)	1.4204	1.4206	0.0002	0.0002
R(7,8)	1.4017	1.4018	0.0001	0.0001
R(8,9)	1.4014	1.4015	0.0001	0.0001
R(9,10)	1.3931	1.3927	-0.0004	0.0004
R(6,7)	1.3924	1.3921	-0.0003	0.0003
R(2,4)	1.3685	1.3689	0.0004	0.0004
R(1,4)	1.1893	1.1892	-0.0001	0.0001
R(24,25)	1.1007	1.1003	-0.0004	0.0004
R(42,43)	1.1007	1.1004	-0.0003	0.0003
R(42,44)	1.1006	1.1000	-0.0006	0.0006
R(24,26)	1.1005	1.0999	-0.0006	0.0006
R(30,31)	1.1005	1.1002	-0.0003	0.0003
R(30,32)	1.1005	1.0999	-0.0006	0.0006
R(36,37)	1.1005	1.1001	-0.0004	0.0004
R(36,38)	1.1005	1.0999	-0.0006	0.0006
R(33,35)	1.0990	1.0984	-0.0006	0.0006
R(21,23)	1.0988	1.0982	-0.0006	0.0006
R(27,29)	1.0988	1.0982	-0.0006	0.0006
R(39,41)	1.0988	1.0982	-0.0006	0.0006
R(33,34)	1.0936	1.0932	-0.0004	0.0004
R(21,22)	1.0934	1.0931	-0.0003	0.0003
R(27,28)	1.0934	1.0931	-0.0003	0.0003
R(39,40)	1.0934	1.0930	-0.0004	0.0004
R(9,14)	1.0895	1.0893	-0.0002	0.0002
R(7,12)	1.0891	1.0890	-0.0001	0.0001
R(6,11)	1.0890	1.0891	0.0001	0.0001
R(10,15)	1.0883	1.0882	-0.0001	0.0001
R(8,13)	1.0872	1.0872	0.0000	0.0000
R(2,3)	1.0867	1.0867	0.0000	0.0000

5.4.2.12 B3LYP/6-31+G(d)

N	-0.117229060317	0.446381264187	-1.103165632999
C	-1.736136972732	0.046804606527	-3.042604818433
H	-1.627508374489	0.668223607114	-3.927419924735
C	-0.865780867902	0.266986595601	-2.009709551233
C	-2.775843947204	-0.953335472486	-3.011760601242
C	-3.646819707045	-1.121953985205	-4.121078210589
C	-4.659509359164	-2.077653981346	-4.121001922992
C	-4.859091568775	-2.916957947880	-3.016194702766
C	-4.011202098307	-2.768726209566	-1.910275197293
C	-2.995952880782	-1.814828197247	-1.903053132460
H	-3.512897612325	-0.482180420007	-4.992103047694
H	-5.302840127471	-2.169822954219	-4.994926598831
H	-5.650106302540	-3.662782638517	-3.017638995121
H	-4.143670553247	-3.408376315445	-1.038319460075
H	-2.352634432063	-1.723515107484	-1.030074067175
Li	0.946606262187	0.637499754925	0.410675287910
O	0.140327515389	1.799896097371	2.104006376336
O	0.708488857172	-0.869622641253	1.991186419941
O	2.922396212828	-0.348922668677	0.471530475624
O	2.348348433654	2.324282753515	0.576007581217
C	-0.421448521508	0.903493751697	3.063284967550
H	-1.370970021350	0.574342717696	2.632414073977
H	-0.620997225552	1.415693725849	4.014713508100
C	0.490827187127	-0.298169697561	3.277174030187
H	1.443901572964	0.005396770850	3.736522369322
H	0.007575749943	-1.027083568661	3.945181601509
C	1.758802355936	-1.832195035463	1.891154097574
H	1.499330730925	-2.460527081653	1.034706004635
H	1.806804205688	-2.460543990311	2.791242085670
C	3.095346412111	-1.144997599608	1.639756022245
H	3.385358493983	-0.520953828312	2.498633199758
H	3.884800216769	-1.895015874784	1.480603549920
C	3.937870447628	0.616871877075	0.201617521571
H	3.893067715690	0.794324888625	-0.876561722019
H	4.933637144817	0.227366795832	0.455532153505
C	3.661027520804	1.915498007866	0.949430152866
H	3.728732131445	1.766058880701	2.037603271640
H	4.397415818519	2.682177342425	0.664582922781
C	1.755639578337	3.353273812661	1.370931686635
H	1.013157174734	3.829924475275	0.725095940410
H	2.502802413685	4.102612051450	1.667014604387
C	1.066997537280	2.761909400149	2.594960373202
H	1.797879520615	2.293971307808	3.272048141731
H	0.543107547760	3.552353222746	3.153652841697

5.4.3 JAYFIY (μ 2-Di-isopropylamide)-(μ 2-phenylacetonitrile) bis (tetramethylene-diamine) -di-lithium

Reported below are the raw bond length data for each of the test functional/basis set combinations for JAYFIY. For reference, Figure 5.15 defines all atomic labels for the JAYFIY structures.

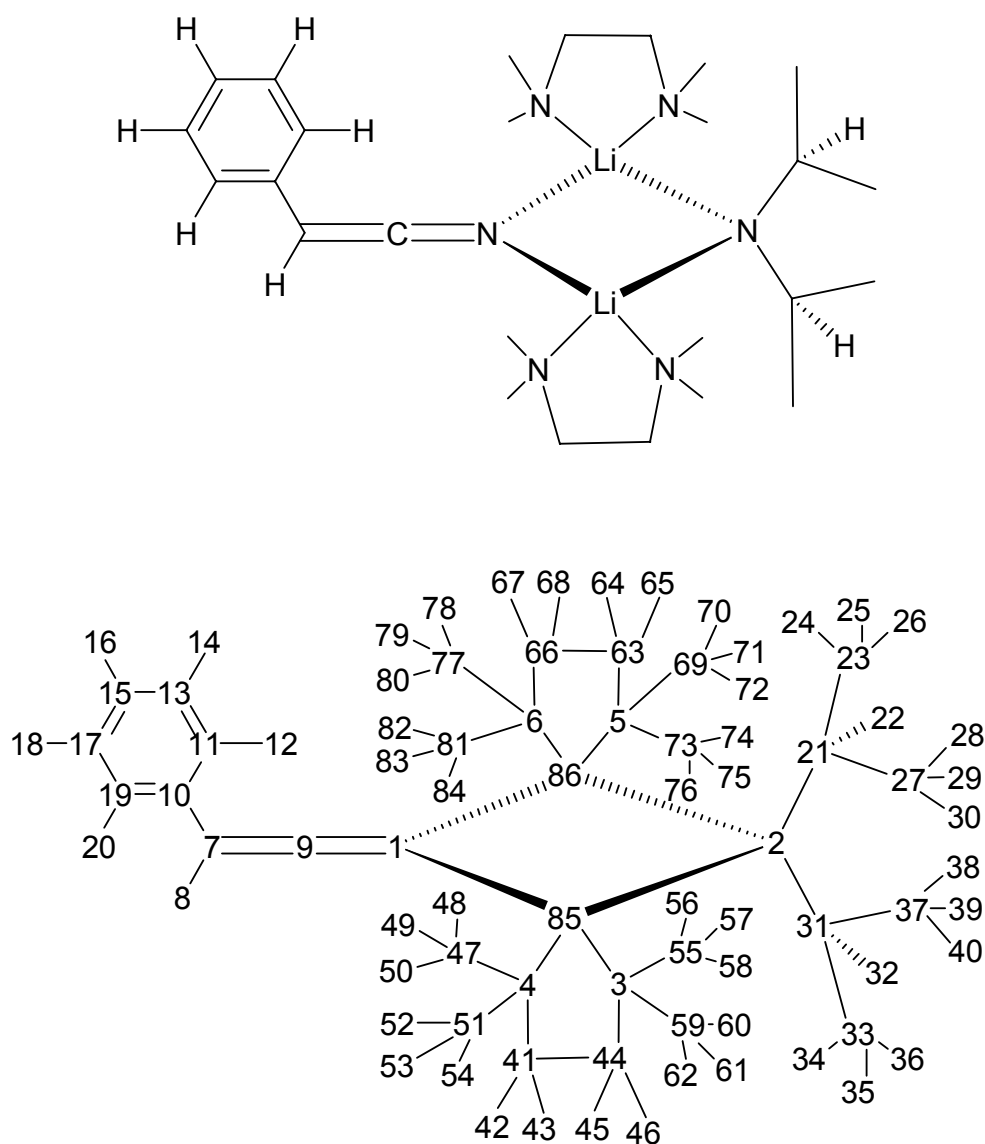


Figure 5.15 Atomic labels for JAYFIY

<i>Bond list</i>	<i>PM3</i>	<i>B3LYP/ 3-21G</i>	<i>MPWLYP/ 3-21G</i>	<i>B3LYP/ Midt!</i>	<i>B3LYP/ Midt!</i>	<i>MPW1PW91/ Midt!</i>	<i>B3LYP/ 6-31G(d)</i>	<i>HF/6- 31G(d)</i>	<i>B3LYP/6- 31(+LX)G(d)</i>	<i>B3LYP/6- 31+G(d)</i>	<i>B3LYP/ 6- 31+G(d)</i>
<i>long</i>	R(8,86)	2.9314	2.7051	2.6882	2.6882	2.7265	2.7053	2.7249	2.6892	2.6870	2.6910
	R(3,85)	2.2901	2.3004	2.2940	2.2943	2.3344	2.3796	2.4266	2.3886	2.4263	2.4109
	R(6,86)	2.2391	2.2687	2.2883	2.2886	2.2947	2.3621	2.4099	2.3644	2.3805	2.3950
	R(5,86)	2.2362	2.2127	2.1981	2.1979	2.3142	2.3575	2.3912	2.3586	2.3608	2.3548
	R(4,85)	2.2326	2.2149	2.2459	2.2457	2.2562	2.3309	2.3496	2.3260	2.3202	2.3431
	R(1,86)	2.0641	2.0924	2.0745	2.0746	2.1139	2.0817	2.0991	2.0686	2.0779	2.0718
	R(1,85)	2.0708	2.0791	2.0431	2.0431	2.0595	2.0658	2.0880	2.0583	2.0690	2.0708
	R(2,86)	2.1126	2.0532	2.0197	2.0197	2.0599	2.0691	2.0819	2.0625	2.0577	2.0635
<i>intermediate</i>	R(2,85)	2.1305	2.0578	2.0335	2.0335	2.0571	2.0753	2.0821	2.0671	2.0581	2.0623
	R(31,37)	1.5348	1.5563	1.5622	1.5622	1.5499	1.5475	1.5414	1.5477	1.5475	1.5488
	R(21,27)	1.5342	1.5562	1.5627	1.5627	1.5495	1.5472	1.5414	1.5474	1.5474	1.5487
	R(21,23)	1.5292	1.5415	1.5433	1.5433	1.5361	1.5343	1.5295	1.5343	1.5348	1.5354
	R(31,33)	1.5299	1.5420	1.5448	1.5448	1.5357	1.5342	1.5293	1.5342	1.5344	1.5352
	R(41,44)	1.5313	1.5288	1.5323	1.5323	1.5268	1.5267	1.5223	1.5269	1.5272	1.5272
	R(63,66)	1.5341	1.5298	1.5344	1.5344	1.5251	1.5267	1.5220	1.5269	1.5266	1.5267
	R(4,41)	1.5078	1.5005	1.4900	1.4900	1.4802	1.4762	1.4635	1.4762	1.4767	1.4770
	R(5,63)	1.5091	1.5010	1.4897	1.4897	1.4810	1.4765	1.4630	1.4764	1.4761	1.4764
	R(6,66)	1.5077	1.5004	1.4907	1.4907	1.4792	1.4750	1.4614	1.4748	1.4749	1.4752
	R(3,44)	1.5092	1.4987	1.4880	1.4880	1.4786	1.4742	1.4605	1.4742	1.4743	1.4749
	R(4,47)	1.4942	1.4984	1.4877	1.4877	1.4767	1.4717	1.4602	1.4716	1.4722	1.4726
	R(5,69)	1.4927	1.4987	1.4871	1.4871	1.4775	1.4719	1.4600	1.4716	1.4718	1.4722
	R(6,81)	1.4926	1.4984	1.4867	1.4867	1.4774	1.4709	1.4596	1.4706	1.4713	1.4714
	R(3,55)	1.4937	1.4995	1.4882	1.4882	1.4761	1.4712	1.4590	1.4706	1.4704	1.4710
	R(4,51)	1.4947	1.4981	1.4867	1.4867	1.4753	1.4703	1.4587	1.4701	1.4705	1.4708
	R(5,73)	1.4944	1.4973	1.4855	1.4855	1.4756	1.4701	1.4583	1.4698	1.4704	1.4708
	R(3,59)	1.4952	1.4965	1.4857	1.4857	1.4751	1.4694	1.4574	1.4692	1.4694	1.4700
	R(6,77)	1.4962	1.4975	1.4867	1.4867	1.4757	1.4694	1.4579	1.4695	1.4695	1.4699
	R(2,21)	1.5051	1.5000	1.4733	1.4733	1.4690	1.4673	1.4561	1.4675	1.4671	1.4671
	R(2,31)	1.5051	1.5005	1.4735	1.4735	1.4685	1.4674	1.4561	1.4676	1.4674	1.4671
	R(7,10)	1.4241	1.4504	1.4454	1.4454	1.4440	1.4518	1.4545	1.4531	1.4520	1.4523
	R(10,11)	1.4042	1.4184	1.4165	1.4165	1.4144	1.4157	1.4032	1.4156	1.4167	1.4170
	R(10,19)	1.4076	1.4172	1.4154	1.4154	1.4133	1.4143	1.4025	1.4139	1.4160	1.4163
	R(15,17)	1.3930	1.3994	1.3985	1.3985	1.3979	1.3980	1.3871	1.3981	1.3999	1.4003

Table 5.23 Raw bond length data for JAYFIY

<i>Bond list</i> (<i>cont.</i>)	<i>PM3</i>	<i>B3LYP/ 3-21G</i>	<i>MPWLYP/ 3-21G</i>	<i>B3LYP/ Midi+</i>	<i>B3LYP/ Midi+</i>	<i>MPW1PW91/ Midi+</i>	<i>B3LYP/ 6-31G(d)</i>	<i>HF/6- 31G(d)</i>	<i>B3LYP/6- 31(+LX)G(d)</i>	<i>B3LYP/6- 31+G(d)</i>	<i>B3LYP/ 6- 31+G(d)</i>
<i>int. (cont.)</i>	R(13,15)	1.3896	1.3988	1.3977	1.3977	1.3969	1.3978	1.3859	1.3978	1.3992	1.3998
	R(11,13)	1.3884	1.3920	1.3911	1.3911	1.3909	1.3920	1.3830	1.3922	1.3941	1.3941
	R(17,19)	1.3852	1.3912	1.3903	1.3903	1.3902	1.3916	1.3815	1.3917	1.3916	1.3934
	R(7,9)	1.3464	1.3583	1.3681	1.3681	1.3648	1.3612	1.3568	1.3612	1.3631	1.3631
	R(1,9)	1.2091	1.1971	1.1897	1.1897	1.1904	1.1957	1.1704	1.1962	1.1953	1.1955
	R(31,32)	1.1304	1.1059	1.1130	1.1130	1.1122	1.1099	1.0959	1.1102	1.1107	1.1114
	R(21,22)	1.1309	1.1060	1.1116	1.1116	1.1128	1.1105	1.0959	1.1109	1.1107	1.1112
	R(44,45)	1.1130	1.1051	1.1096	1.1096	1.1089	1.1067	1.0935	1.1070	1.1074	1.1074
	R(66,67)	1.1125	1.1046	1.1088	1.1088	1.1091	1.1067	1.0934	1.1070	1.1068	1.1073
	R(59,62)	1.1019	1.1036	1.1088	1.1088	1.1078	1.1055	1.0924	1.1059	1.1064	1.1062
<i>short</i>	R(77,80)	1.1012	1.1032	1.1084	1.1084	1.1077	1.1053	1.0922	1.1057	1.1056	1.1061
	R(55,58)	1.1022	1.1033	1.1086	1.1086	1.1074	1.1050	1.0924	1.1054	1.1059	1.1058
	R(69,72)	1.1017	1.1034	1.1085	1.1085	1.1076	1.1051	1.0921	1.1055	1.1058	1.1058
	R(63,64)	1.1108	1.1025	1.1069	1.1069	1.1069	1.1045	1.0916	1.1047	1.1056	1.1056
	R(73,75)	1.1011	1.1030	1.1082	1.1082	1.1073	1.1047	1.0920	1.1053	1.1057	1.1056
	R(47,50)	1.1017	1.1030	1.1080	1.1080	1.1073	1.1049	1.0918	1.1052	1.1050	1.1054
	R(51,53)	1.1010	1.1030	1.1083	1.1083	1.1074	1.1048	1.0919	1.1052	1.1050	1.1054
	R(41,42)	1.1112	1.1031	1.1075	1.1075	1.1068	1.1047	1.0915	1.1049	1.1048	1.1053
	R(81,83)	1.1017	1.1028	1.1079	1.1079	1.1069	1.1046	1.0919	1.1050	1.1049	1.1053
	R(37,40)	1.1039	1.0977	1.1021	1.1021	1.1019	1.0992	1.0884	1.0995	1.0998	1.0997
	R(27,30)	1.1058	1.0981	1.1023	1.1023	1.1016	1.0995	1.0883	1.0997	1.0996	1.0996
	R(27,29)	1.0977	1.0979	1.1019	1.1019	1.1014	1.0982	1.0880	1.0982	1.0983	1.0991
	R(37,39)	1.0976	1.0979	1.1020	1.1020	1.1015	1.0983	1.0880	1.0983	1.0982	1.0990
	R(33,34)	1.0997	1.0975	1.1006	1.1006	1.1003	1.0975	1.0876	1.0977	1.0977	1.0981
	R(23,24)	1.0996	1.0975	1.1006	1.1006	1.1004	1.0976	1.0875	1.0977	1.0977	1.0980
	R(23,26)	1.1087	1.0923	1.1011	1.0969	1.0976	1.0952	1.0835	1.0931	1.0958	1.0959
	R(27,28)	1.1037	1.0944	1.1019	1.0985	1.0979	1.0949	1.0840	1.0949	1.0950	1.0956
	R(37,38)	1.1039	1.0945	1.1017	1.0983	1.0979	1.0950	1.0840	1.0950	1.0950	1.0955
	R(33,36)	1.1062	1.0932	1.1012	1.0964	1.0977	1.0959	1.0836	1.0958	1.0953	1.0952
	R(66,68)	1.1141	1.0935	1.1006	1.0981	1.0981	1.0949	1.0821	1.0950	1.0951	1.0950
	R(44,46)	1.1141	1.0930	1.0969	1.0969	1.0976	1.0944	1.0821	1.0945	1.0947	1.0947
	R(23,25)	1.1095	1.0923	1.0946	1.0946	1.0963	1.0945	1.0828	1.0945	1.0944	1.0945
	R(33,35)	1.1109	1.0922	1.1003	1.0965	1.0957	1.0940	1.0824	1.0939	1.0942	1.0944

Table 5.23 (cont.) Raw bond length data for JAYFIY

Bond list (cont.)	PM3	B3LYP/ 3-21G	MPWLYP/ 3-21G	B3LYP/ Midi!	B3LYP/ Midi!+	MPW1PW91/ Midi!+	B3LYP/ 6-31G(d)	HF/6- 31G(d)	B3LYP/6- 31(+LX)G(d)	B3LYP/6- 31++G(d)	B3LYP/ 6- 31+G(d)
R(41,43)	1.1170	1.0930	1.1001	1.0968	1.0968	1.0967	1.0941	1.0814	1.0942	1.0941	1.0943
R(51,52)	1.1022	1.0930	1.0999	1.0980	1.0980	1.0969	1.0941	1.0828	1.0941	1.0941	1.0943
R(73,74)	1.1016	1.0929	1.0996	1.0977	1.0977	1.0970	1.0943	1.0829	1.0942	1.0942	1.0943
R(55,56)	1.1004	1.0922	1.0994	1.0966	1.0966	1.0968	1.0938	1.0824	1.0938	1.0941	1.0942
R(63,65)	1.1170	1.0928	1.1001	1.0968	1.0968	1.0968	1.0940	1.0814	1.0941	1.0941	1.0942
R(81,84)	1.1064	1.0925	1.1000	1.0977	1.0977	1.0962	1.0938	1.0822	1.0937	1.0938	1.0941
R(47,49)	1.1075	1.0917	1.0992	1.0966	1.0966	1.0958	1.0933	1.0816	1.0932	1.0933	1.0935
R(69,71)	1.1076	1.0914	1.0990	1.0962	1.0962	1.0959	1.0933	1.0816	1.0931	1.0933	1.0935
R(59,60)	1.1049	1.0913	1.0981	1.0965	1.0965	1.0954	1.0928	1.0811	1.0927	1.0929	1.0930
R(77,79)	1.1059	1.0914	1.0984	1.0961	1.0961	1.0961	1.0927	1.0811	1.0926	1.0927	1.0930
R(59,61)	1.1007	1.0917	1.0987	1.0967	1.0967	1.0959	1.0928	1.0812	1.0927	1.0927	1.0929
R(77,78)	1.1050	1.0913	1.0980	1.0962	1.0962	1.0957	1.0928	1.0811	1.0927	1.0927	1.0929
R(51,54)	1.1069	1.0901	1.0966	1.0950	1.0950	1.0951	1.0920	1.0803	1.0919	1.0921	1.0924
R(69,70)	1.1007	1.0911	1.0979	1.0962	1.0962	1.0951	1.0922	1.0800	1.0921	1.0921	1.0923
R(73,76)	1.1071	1.0908	1.0978	1.0958	1.0958	1.0949	1.0924	1.0803	1.0923	1.0920	1.0922
R(55,57)	1.1032	1.0910	1.0975	1.0958	1.0958	1.0949	1.0921	1.0796	1.0920	1.0919	1.0920
R(47,48)	1.1023	1.0899	1.0968	1.0946	1.0946	1.0942	1.0916	1.0797	1.0915	1.0916	1.0916
R(81,82)	1.1033	1.0892	1.0956	1.0935	1.0935	1.0941	1.0912	1.0790	1.0913	1.0912	1.0913
R(13,14)	1.0945	1.0856	1.0926	1.0898	1.0898	1.0897	1.0884	1.0771	1.0884	1.0885	1.0887
R(19,20)	1.0951	1.0855	1.0926	1.0900	1.0900	1.0898	1.0883	1.0766	1.0883	1.0887	1.0887
R(17,18)	1.0946	1.0854	1.0923	1.0896	1.0896	1.0893	1.0882	1.0769	1.0881	1.0879	1.0884
R(11,12)	1.0967	1.0859	1.0932	1.0899	1.0899	1.0890	1.0881	1.0762	1.0881	1.0878	1.0880
R(7,8)	1.0946	1.0861	1.0937	1.0898	1.0898	1.0895	1.0869	1.0744	1.0871	1.0877	1.0877
R(15,16)	1.0936	1.0835	1.0905	1.0878	1.0878	1.0877	1.0865	1.0753	1.0864	1.0868	1.0868

short (cont.)

Table 5.23 (cont.) Raw bond length data for JAYFIY

5.4.3.1 X-ray⁵⁹

N	0.492732031250	0.225403515625	0.231532421875	C	3.019932031250	-2.641496484375	-1.008367578125
N	-1.326767968750	-0.843996484375	-2.080067578125	H	3.810332031250	-2.196296484375	-0.694367578125
N	-0.803867968750	3.057803515625	-1.116167578125	H	3.270132031250	-3.398596484375	-1.543167578125
N	-2.785567968750	1.518003515625	0.503932421875	C	2.491032031250	-3.108696484375	-0.012167578125
N	2.387132031250	-1.705596484375	-1.935667578125	H	2.761932031250	-4.029496484375	0.006632421875
N	1.063232031250	-3.126596484375	0.282132421875	H	2.891732031250	-2.641996484375	0.724932421875
C	2.103932031250	1.298903515625	1.901232421875	C	3.145832031250	-0.459496484375	-1.948967578125
H	2.936532031250	1.780303515625	1.537432421875	H	3.135732031250	-0.068596484375	-1.072167578125
C	1.236132031250	0.716803515625	0.994732421875	H	2.748132031250	0.149503515625	-2.575467578125
C	1.925632031250	1.235303515625	3.320732421875	H	4.052432031250	-0.639196484375	-2.208667578125
C	0.892832031250	0.495703515625	3.906632421875	C	2.440032031250	-2.245996484375	-3.289667578125
H	0.286932031250	-0.001596484375	3.352432421875	H	1.950432031250	-3.071096484375	-3.323167578125
C	0.743432031250	0.478203515625	5.286032421875	H	3.354232031250	-2.406096484375	-3.534867578125
H	0.010832031250	-0.006496484375	5.673332421875	H	2.049932031250	-1.617396484375	-3.901567578125
C	1.625932031250	1.145403515625	6.113332421875	C	0.505932031250	-4.462596484375	0.003832421875
H	1.529332031250	1.102603515625	7.067532421875	H	0.657132031250	-4.687396484375	-0.917067578125
C	2.644332031250	1.869703515625	5.544932421875	H	-0.437467968750	-4.457796484375	0.181232421875
H	3.246432031250	2.362203515625	6.107832421875	H	0.934032031250	-5.112196484375	0.566332421875
C	2.812332031250	1.898903515625	4.178332421875	C	0.812532031250	-2.823296484375	1.693932421875
H	3.552332031250	2.383703515625	3.805432421875	H	1.167632031250	-1.956096484375	1.903032421875
C	-2.425067968750	-1.778396484375	-1.860667578125	H	1.238532031250	-3.484596484375	2.244132421875
H	-3.233167968750	-1.335796484375	-2.130267578125	H	-0.133067968750	-2.830196484375	1.859232421875
C	-2.449467968750	-2.156396484375	-0.379367578125	Li	-1.204267968750	0.762103515625	-0.835767578125
H	-3.168667968750	-2.770996484375	-0.217167578125	Li	0.371032031250	-1.400996484375	-1.105867578125
H	-2.577967968750	-1.366496484375	0.150932421875				
H	-1.615867968750	-2.569196484375	-0.141667578125				
C	-2.328567968750	-3.040096484375	-2.698167578125				
H	-2.314067968750	-2.807196484375	-3.629367578125				
H	-3.087067968750	-3.601096484375	-2.520567578125				
H	-1.522667968750	-3.510796484375	-2.473367578125				
C	-1.297867968750	-0.386896484375	-3.479567578125				
H	-1.232567968750	-1.176696484375	-4.021367578125				
C	-0.100467968750	0.526803515625	-3.671967578125				
H	-0.072167968750	0.830803515625	-4.582067578125				
H	0.705032031250	0.044903515625	-3.470467578125				
H	-0.176767968750	1.282303515625	-3.084467578125				
C	-2.551767968750	0.310203515625	-3.943167578125				
H	-3.305567968750	-0.271296484375	-3.819967578125				
H	-2.468867968750	0.533803515625	-4.873167578125				
H	-2.679367968750	1.112303515625	-3.431467578125				
C	-2.680967968750	2.990403515625	0.466632421875				
H	-2.936767968750	3.328803515625	1.327832421875				
H	-3.292167968750	3.314703515625	-0.198967578125				
C	-1.369267968750	3.504003515625	0.155232421875				
H	-1.422467968750	4.462303515625	0.135432421875				
H	-0.772667968750	3.231003515625	0.856032421875				
C	-2.502867968750	1.040503515625	1.862232421875				
H	-1.613967968750	1.300403515625	2.114532421875				
H	-2.575367968750	0.083503515625	1.886432421875				
H	-3.134667968750	1.424703515625	2.474432421875				
C	-4.124967968750	1.116903515625	0.145132421875				
H	-4.324067968750	1.423203515625	-0.742667578125				
H	-4.750367968750	1.500903515625	0.763932421875				
H	-4.191267968750	0.159703515625	0.175832421875				
C	0.594632031250	3.392703515625	-1.120867578125				
H	0.989332031250	3.109103515625	-1.948667578125				
H	1.031632031250	2.950003515625	-0.389667578125				
H	0.696432031250	4.342603515625	-1.026667578125				
C	-1.467167968750	3.764503515625	-2.228167578125				
H	-2.402067968750	3.546803515625	-2.233667578125				
H	-1.070967968750	3.494903515625	-3.060067578125				
H	-1.359767968750	4.711603515625	-2.114667578125				

5.4.3.2 PM3

N	0.587883817973	0.343026628860	0.149842989277	H	4.272465581286	-2.796411266501	-1.238734997700
N	-1.239477506801	-0.793087175679	-1.927613917612	H	3.009898819543	-3.984623032409	-1.651804635360
N	-0.868108620550	3.254208962443	-0.987008234285	C	2.663008899455	-2.939089527248	0.216426438639
N	-2.899754009388	1.652156686141	0.452471860478	H	3.178896807044	-3.732979133772	0.800510412197
N	2.451906916407	-1.944228481975	-2.076066121199	H	2.921979254468	-1.974494090092	0.710028481958
N	1.166126871935	-3.114213894035	0.258994850799	C	3.235619091475	-0.683436176182	-2.231643977750
C	2.073693711691	1.4317111110629	1.920932590015	H	3.498970977719	-0.274509375078	-1.244230463306
H	2.887685989310	2.070672692406	1.564170827880	H	2.604227144385	0.055885963673	-2.762317012115
C	1.284688331372	0.849185625685	0.998540728336	H	4.165954652715	-0.821074912145	-2.805506842107
C	1.905774182694	1.256546147526	3.334363155650	C	2.081964084553	-2.500986472298	-3.412575044522
C	0.856379518355	0.498794803580	3.878734498203	H	1.422554830589	-3.375140439419	-3.291725710812
H	0.129985951119	0.020155196998	3.210853430951	H	2.954847389387	-2.804504757197	-4.011231466416
C	0.728954449893	0.354978069230	5.253751741053	H	1.521089390546	-1.731637981961	-3.977535594739
H	-0.093877367041	-0.239417188942	5.663125031993	C	0.756889500652	-4.455047173738	-0.263896855920
C	1.637804348879	0.960675940765	6.112928265257	H	1.383355033999	-4.738379445823	-1.128934144497
H	1.534762829712	0.845072810782	7.195478600044	H	-0.292204344321	-4.402355539397	-0.609635223740
C	2.681778162899	1.717376154397	5.585754624007	H	0.840084572561	-5.257087818738	0.486128612352
H	3.398799750215	2.196387706479	6.259934456604	C	0.620602912130	-2.904770018346	1.632476620955
C	2.818369821624	1.866691178671	4.215416322710	H	0.963915587730	-1.944833588709	2.054226362333
H	3.642481861029	2.463053044590	3.809895152897	H	0.902958727083	-3.703883470547	2.336345893749
C	-2.322946942592	-1.812426378984	-1.698846984003	H	-0.483121083203	-2.869825152184	1.564268003233
H	-3.279441100308	-1.405565080559	-2.144345807507	Li	-1.150961344251	0.992219481886	-0.768435373273
C	-2.562107919880	-2.069990246660	-0.210601852283	Li	0.574264611649	-1.365627411661	-1.008152175807
H	-3.300272054446	-2.873935486729	-0.076967754154				
H	-2.964822073569	-1.177545382593	0.311360840559				
H	-1.648254503315	-2.379709969993	0.335446309600				
C	-2.024835599885	-3.144526824728	-2.399199945767				
H	-1.737118895938	-2.984257407888	-3.452663355909				
H	-2.904640968435	-3.800973776864	-2.391704381283				
H	-1.200861038836	-3.697712418500	-1.911450016948				
C	-1.211296385001	-0.406657761276	-3.382003571471				
H	-1.148883902885	-1.353221264808	-3.996755363469				
C	0.006346805773	0.461875677768	-3.703733921274				
H	-0.026565012114	0.794163983980	-4.751547329156				
H	0.965684439672	-0.082916443075	-3.573166543041				
H	0.061711405768	1.373392764977	-3.079385133238				
C	-2.488037302751	0.334805802879	-3.801353988029				
H	-3.387137983623	-0.252055257820	-3.544792965239				
H	-2.505813845071	0.514511747698	-4.883982377048				
H	-2.586153985245	1.314327655564	-3.301929616929				
C	-2.877314685453	3.158559875469	0.514051396289				
H	-3.296715537161	3.532871577731	1.472603640267				
H	-3.527914288330	3.569654943988	-0.295506980508				
C	-1.455812059414	3.697418014884	0.330503093196				
H	-1.475264730235	4.807757883670	0.404854261409				
H	-0.789401723697	3.345130937828	1.150910876326				
C	-2.731480372936	1.037078345812	1.803759158776				
H	-1.790010521625	1.374712258442	2.267237468492				
H	-2.683949392958	-0.063479319049	1.689224268528				
H	-3.557903159174	1.277144333727	2.491617185528				
C	-4.152777735774	1.161126053414	-0.197921374967				
H	-4.194736519043	1.505447314698	-1.244148278792				
H	-5.066241301254	1.496639017968	0.317105618043				
H	-4.145711925156	0.054314398296	-0.208729565884				
C	0.569820119549	3.648996731028	-1.074119633529				
H	0.996937368024	3.276169967802	-2.017206875824				
H	1.142651768148	3.206900452091	-0.241346638681				
H	0.713445136822	4.741384574483	-1.043393910993				
C	-1.631766960827	3.830555440441	-2.136030512614				
H	-2.711722866673	3.641475788638	-1.999425807546				
H	-1.311652573637	3.347197011810	-3.071640039697				
H	-1.491120318966	4.918118790890	-2.243842808822				
C	3.174384633211	-2.963582577617	-1.229765210699				

Table 5.24 Signed and Unsigned differences in bond length for the PM3 structure of JAYFIY relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(85,86)	2.6910	2.9314	0.2404	0.2404
R(3,85)	2.4109	2.2901	-0.1208	0.1208
R(6,86)	2.3950	2.2391	-0.1559	0.1559
R(5,86)	2.3548	2.2362	-0.1186	0.1186
R(4,85)	2.3431	2.2326	-0.1105	0.1105
R(1,86)	2.0718	2.0641	-0.0077	0.0077
R(1,85)	2.0708	2.0708	0.0000	0.0000
R(2,86)	2.0635	2.1126	0.0491	0.0491
R(2,85)	2.0623	2.1305	0.0682	0.0682
R(31,37)	1.5488	1.5348	-0.014	0.014
R(21,27)	1.5487	1.5342	-0.0145	0.0145
R(21,23)	1.5354	1.5292	-0.0062	0.0062
R(31,33)	1.5352	1.5299	-0.0053	0.0053
R(41,44)	1.5272	1.5313	0.0041	0.0041
R(63,66)	1.5267	1.5341	0.0074	0.0074
R(4,41)	1.4770	1.5078	0.0308	0.0308
R(5,63)	1.4764	1.5091	0.0327	0.0327
R(6,66)	1.4752	1.5077	0.0325	0.0325
R(3,44)	1.4749	1.5092	0.0343	0.0343
R(4,47)	1.4726	1.4942	0.0216	0.0216
R(5,69)	1.4722	1.4927	0.0205	0.0205
R(6,81)	1.4714	1.4926	0.0212	0.0212
R(3,55)	1.4710	1.4937	0.0227	0.0227
R(4,51)	1.4708	1.4947	0.0239	0.0239
R(5,73)	1.4708	1.4944	0.0236	0.0236
R(3,59)	1.4700	1.4952	0.0252	0.0252
R(6,77)	1.4699	1.4962	0.0263	0.0263
R(2,21)	1.4671	1.5051	0.0380	0.0380
R(2,31)	1.4671	1.5051	0.0380	0.0380
R(7,10)	1.4523	1.4341	-0.0182	0.0182
R(10,11)	1.4170	1.4042	-0.0128	0.0128
R(10,19)	1.4163	1.4076	-0.0087	0.0087
R(15,17)	1.4003	1.3930	-0.0073	0.0073
R(13,15)	1.3998	1.3896	-0.0102	0.0102
R(11,13)	1.3941	1.3884	-0.0057	0.0057
R(17,19)	1.3934	1.3852	-0.0082	0.0082
R(7,9)	1.3631	1.3464	-0.0167	0.0167
R(1,9)	1.1955	1.2091	0.0136	0.0136
R(31,32)	1.1114	1.1304	0.0190	0.0190
R(21,22)	1.1112	1.1309	0.0197	0.0197
R(44,45)	1.1074	1.1130	0.0056	0.0056
R(66,67)	1.1073	1.1125	0.0052	0.0052
R(59,62)	1.1062	1.1019	-0.0043	0.0043
R(77,80)	1.1061	1.1012	-0.0049	0.0049
R(55,58)	1.1058	1.1022	-0.0036	0.0036
R(69,72)	1.1058	1.1017	-0.0041	0.0041
R(63,64)	1.1056	1.1108	0.0052	0.0052
R(73,75)	1.1056	1.1011	-0.0045	0.0045

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(47,50)	1.1054	1.1017	-0.0037	0.0037
R(51,53)	1.1054	1.1010	-0.0044	0.0044
R(41,42)	1.1053	1.1112	0.0059	0.0059
R(81,83)	1.1053	1.1017	-0.0036	0.0036
R(37,40)	1.0997	1.1039	0.0042	0.0042
R(27,30)	1.0996	1.1058	0.0062	0.0062
R(27,29)	1.0991	1.0977	-0.0014	0.0014
R(37,39)	1.0990	1.0976	-0.0014	0.0014
R(33,34)	1.0981	1.0997	0.0016	0.0016
R(23,24)	1.0980	1.0996	0.0016	0.0016
R(23,26)	1.0959	1.1087	0.0128	0.0128
R(27,28)	1.0956	1.1037	0.0081	0.0081
R(37,38)	1.0955	1.1039	0.0084	0.0084
R(33,36)	1.0952	1.1062	0.0110	0.0110
R(66,68)	1.0950	1.1141	0.0191	0.0191
R(44,46)	1.0947	1.1141	0.0194	0.0194
R(23,25)	1.0945	1.1095	0.0150	0.0150
R(33,35)	1.0944	1.1109	0.0165	0.0165
R(41,43)	1.0943	1.1170	0.0227	0.0227
R(51,52)	1.0943	1.1022	0.0079	0.0079
R(73,74)	1.0943	1.1016	0.0073	0.0073
R(55,56)	1.0942	1.1004	0.0062	0.0062
R(63,65)	1.0942	1.1170	0.0228	0.0228
R(81,84)	1.0941	1.1064	0.0123	0.0123
R(47,49)	1.0935	1.1075	0.0140	0.0140
R(69,71)	1.0935	1.1076	0.0141	0.0141
R(59,60)	1.0930	1.1049	0.0119	0.0119
R(77,79)	1.0930	1.1059	0.0129	0.0129
R(59,61)	1.0929	1.1007	0.0078	0.0078
R(77,78)	1.0929	1.1050	0.0121	0.0121
R(51,54)	1.0924	1.1069	0.0145	0.0145
R(69,70)	1.0923	1.1007	0.0084	0.0084
R(73,76)	1.0922	1.1071	0.0149	0.0149
R(55,57)	1.0920	1.1032	0.0112	0.0112
R(47,48)	1.0916	1.1023	0.0107	0.0107
R(81,82)	1.0913	1.1033	0.0120	0.0120
R(13,14)	1.0887	1.0945	0.0058	0.0058
R(19,20)	1.0887	1.0951	0.0064	0.0064
R(17,18)	1.0884	1.0946	0.0062	0.0062
R(11,12)	1.0880	1.0967	0.0087	0.0087
R(7,8)	1.0877	1.0946	0.0069	0.0069
R(15,16)	1.0868	1.0936	0.0068	0.0068

5.4.3.3 B3LYP/3-21G

N	0.410749286428	0.265712118146	0.244858039303	C	2.838045649652	-2.942021510852	-0.934681090211
N	-1.292063635437	-0.792828460974	-2.162040773446	H	3.938208672703	-2.938055174938	-0.862658207860
N	-0.995437385884	3.048534498148	-0.951652359785	H	2.545191156502	-3.870673947680	-1.430640245383
N	-2.967458202882	1.308188052682	0.528197704749	C	2.228324847353	-2.886759682446	0.467299794294
N	2.360576630452	-1.799390512432	-1.782940581085	H	2.694445914846	-3.662055085981	1.101242617966
N	0.740092716029	-3.072075981877	0.422529915256	H	2.423960356364	-1.912109996982	0.922903831545
C	2.211988181868	1.362128603056	1.688356014334	C	3.223590701964	-0.598856424931	-1.538143182734
H	3.008372878768	1.894543669152	1.176673176172	H	3.204598343388	-0.337836662677	-0.478915148393
C	1.251403629332	0.777154999127	0.926680963796	H	2.826065531491	0.243989847605	-2.106179380928
C	2.226872009509	1.342324907544	3.138561693099	H	4.264784595306	-0.790726349769	-1.848900959673
C	1.225784852421	0.700913634110	3.912075562763	C	2.425299324122	-2.174807603287	-3.230993665895
H	0.410651786385	0.196468180894	3.401930885782	H	1.762822205229	-3.025713510946	-3.408504292882
C	1.271439548055	0.704577142095	5.303357223949	H	3.450619322222	-2.437090466075	-3.541618448912
H	0.488797184480	0.202024353809	5.863246374851	H	2.074946118616	-1.334286581060	-3.831545805213
C	2.310628640383	1.346497156964	5.984936820639	C	0.399572081002	-4.486012592219	0.065826464780
H	2.342963073694	1.348024410181	7.067997758487	H	0.738868749888	-4.713414900954	-0.946129040335
C	3.307473393779	1.986749954710	5.240176673936	H	-0.685139481745	-4.604172292312	0.091922244526
H	4.122071226214	2.490767237639	5.750479769142	H	0.856300501909	-5.199729548103	0.772280265464
C	3.269852680778	1.986772112267	3.849486135221	C	0.167711101275	-2.769019789678	1.773721075956
H	4.051764379786	2.488447997228	3.287988823263	H	0.403944121728	-1.737292394690	2.030860561885
C	-2.427096705985	-1.773179506530	-2.138332165738	H	0.571094113629	-3.445426538861	2.545665628288
H	-3.381798595824	-1.297351403319	-2.430487744813	H	-0.917866407128	-2.882954561258	1.728107088884
C	-2.609375981052	-2.303103976553	-0.702287701208	Li	-1.298382950279	0.771712092693	-0.825367946944
H	-3.529567331124	-2.894374022325	-0.611779646530	Li	0.319146705150	-1.386255707131	-1.036139197591
H	-2.643723296851	-1.470656368920	0.004119088112				
H	-1.758461948813	-2.933606181438	-0.434922855632				
C	-2.240576544554	-3.001669969869	-3.075237403197				
H	-2.204889938330	-2.711082233246	-4.129723016424				
H	-3.064080667108	-3.716266573976	-2.946818884549				
H	-1.295761519943	-3.502028238567	-2.824745489282				
C	-1.053498279231	-0.318603923855	-3.565471783713				
H	-0.731518028962	-1.145217140206	-4.225827722406				
C	0.084141573074	0.722300771914	-3.561877546817				
H	0.348672436567	1.022786093499	-4.583734072269				
H	0.968758701681	0.315712933965	-3.066921513369				
H	-0.232282868084	1.607272282836	-3.003570747658				
C	-2.293262141687	0.331546946956	-4.245527949622				
H	-3.115256952273	-0.381630821539	-4.361914737118				
H	-2.032365755466	0.715783247964	-5.240304297481				
H	-2.648346400492	1.165392830646	-3.626286207616				
C	-2.970930192830	2.807841333501	0.577397221948				
H	-3.390941191120	3.162831146323	1.533589796002				
H	-3.627483186236	3.162189776144	-0.221309540078				
C	-1.569533934971	3.389378744426	0.390164456516				
H	-1.615487490499	4.485352629355	0.524282229846				
H	-0.888563323130	2.984817059701	1.143377719722				
C	-2.580912244696	0.754751651946	1.865885224612				
H	-1.579551235861	1.095422091613	2.128928975941				
H	-2.563375480923	-0.334892258837	1.801680936580				
H	-3.295261053122	1.064780933867	2.647049007133				
C	-4.336369636835	0.820618411009	0.163927473877				
H	-4.595041107944	1.196389993091	-0.829281784874				
H	-5.095368631766	1.155125802270	0.890934038177				
H	-4.330192196596	-0.268918706835	0.130278828571				
C	0.433285649334	3.502301946559	-0.987780888818				
H	0.885210537167	3.176072030348	-1.927057095713				
H	0.972440194532	3.050363416589	-0.153948034425				
H	0.504605061940	4.600840799018	-0.914601086074				
C	-1.745164947745	3.741086548336	-2.046147769252				
H	-2.768589823747	3.366339205877	-2.101225955988				
H	-1.255399192626	3.520818066457	-2.996645112627				
H	-1.763510710768	4.834199467088	-1.895714668259				

Table 5.25 Signed and Unsigned differences in bond length for the B3LYP/3-21G structure of JAYFIY relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(85,86)	2.6910	2.7051	0.0141	0.0141
R(3,85)	2.4109	2.3004	-0.1105	0.1105
R(6,86)	2.3950	2.2687	-0.1263	0.1263
R(5,86)	2.3548	2.2127	-0.1421	0.1421
R(4,85)	2.3431	2.2149	-0.1282	0.1282
R(1,86)	2.0718	2.0924	0.0206	0.0206
R(1,85)	2.0708	2.0791	0.0083	0.0083
R(2,86)	2.0635	2.0532	-0.0103	0.0103
R(2,85)	2.0623	2.0578	-0.0045	0.0045
R(31,37)	1.5488	1.5693	0.0205	0.0205
R(21,27)	1.5487	1.5706	0.0219	0.0219
R(21,23)	1.5354	1.5525	0.0171	0.0171
R(31,33)	1.5352	1.5535	0.0183	0.0183
R(41,44)	1.5272	1.5392	0.0120	0.0120
R(63,66)	1.5267	1.5413	0.0146	0.0146
R(4,41)	1.4770	1.5174	0.0404	0.0404
R(5,63)	1.4764	1.5181	0.0417	0.0417
R(6,66)	1.4752	1.5184	0.0432	0.0432
R(3,44)	1.4749	1.5158	0.0409	0.0409
R(4,47)	1.4726	1.5150	0.0424	0.0424
R(5,69)	1.4722	1.5148	0.0426	0.0426
R(6,81)	1.4714	1.5150	0.0436	0.0436
R(3,55)	1.4710	1.5162	0.0452	0.0452
R(4,51)	1.4708	1.5140	0.0432	0.0432
R(5,73)	1.4708	1.5134	0.0426	0.0426
R(3,59)	1.4700	1.5131	0.0431	0.0431
R(6,77)	1.4699	1.5141	0.0442	0.0442
R(2,21)	1.4671	1.5170	0.0499	0.0499
R(2,31)	1.4671	1.5169	0.0498	0.0498
R(7,10)	1.4523	1.4583	0.0060	0.0060
R(10,11)	1.4170	1.4299	0.0129	0.0129
R(10,19)	1.4163	1.4283	0.0120	0.0120
R(15,17)	1.4003	1.4096	0.0093	0.0093
R(13,15)	1.3998	1.4092	0.0094	0.0094
R(11,13)	1.3941	1.4013	0.0072	0.0072
R(17,19)	1.3934	1.4005	0.0071	0.0071
R(7,9)	1.3631	1.3668	0.0037	0.0037
R(1,9)	1.1955	1.2092	0.0137	0.0137
R(31,32)	1.1114	1.1133	0.0019	0.0019
R(21,22)	1.1112	1.1126	0.0014	0.0014
R(44,45)	1.1074	1.1128	0.0054	0.0054
R(66,67)	1.1073	1.1121	0.0048	0.0048
R(59,62)	1.1062	1.1112	0.0050	0.0050
R(77,80)	1.1061	1.1105	0.0044	0.0044
R(55,58)	1.1058	1.1106	0.0048	0.0048
R(69,72)	1.1058	1.1108	0.0050	0.0050
R(63,64)	1.1056	1.1099	0.0043	0.0043
R(73,75)	1.1056	1.1103	0.0047	0.0047

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(47,50)	1.1054	1.1105	0.0051	0.0051
R(51,53)	1.1054	1.1103	0.0049	0.0049
R(41,42)	1.1053	1.1103	0.0050	0.0050
R(81,83)	1.1053	1.1100	0.0047	0.0047
R(37,40)	1.0997	1.1038	0.0041	0.0041
R(27,30)	1.0996	1.1042	0.0046	0.0046
R(27,29)	1.0991	1.1059	0.0068	0.0068
R(37,39)	1.0990	1.1058	0.0068	0.0068
R(33,34)	1.0981	1.1044	0.0063	0.0063
R(23,24)	1.0980	1.1045	0.0065	0.0065
R(23,26)	1.0959	1.1011	0.0052	0.0052
R(27,28)	1.0956	1.1019	0.0063	0.0063
R(37,38)	1.0955	1.1017	0.0062	0.0062
R(33,36)	1.0952	1.1012	0.0060	0.0060
R(66,68)	1.0950	1.1006	0.0056	0.0056
R(44,46)	1.0947	1.0998	0.0051	0.0051
R(23,25)	1.0945	1.0990	0.0045	0.0045
R(33,35)	1.0944	1.1003	0.0059	0.0059
R(41,43)	1.0943	1.1001	0.0058	0.0058
R(51,52)	1.0943	1.0999	0.0056	0.0056
R(73,74)	1.0943	1.0996	0.0053	0.0053
R(55,56)	1.0942	1.0994	0.0052	0.0052
R(63,65)	1.0942	1.1001	0.0059	0.0059
R(81,84)	1.0941	1.1000	0.0059	0.0059
R(47,49)	1.0935	1.0992	0.0057	0.0057
R(69,71)	1.0935	1.0990	0.0055	0.0055
R(59,60)	1.0930	1.0981	0.0051	0.0051
R(77,79)	1.0930	1.0984	0.0054	0.0054
R(59,61)	1.0929	1.0987	0.0058	0.0058
R(77,78)	1.0929	1.0980	0.0051	0.0051
R(51,54)	1.0924	1.0966	0.0042	0.0042
R(69,70)	1.0923	1.0979	0.0056	0.0056
R(73,76)	1.0922	1.0978	0.0056	0.0056
R(55,57)	1.0920	1.0975	0.0055	0.0055
R(47,48)	1.0916	1.0968	0.0052	0.0052
R(81,82)	1.0913	1.0956	0.0043	0.0043
R(13,14)	1.0887	1.0926	0.0039	0.0039
R(19,20)	1.0887	1.0926	0.0039	0.0039
R(17,18)	1.0884	1.0923	0.0039	0.0039
R(11,12)	1.0880	1.0932	0.0052	0.0052
R(7,8)	1.0877	1.0937	0.0060	0.0060
R(15,16)	1.0868	1.0905	0.0037	0.0037

5.4.3.4 MPWLYP/3-21G

N	0.376943722863	0.284365631157	0.207385208953	H	3.905917255782	-2.970843157088	-0.816030309987
N	-1.320647012146	-0.810599851056	-2.213940086514	H	2.494863972930	-3.921929057190	-1.355713252415
N	-0.972720360118	3.084185339280	-0.938343553853	C	2.187235909549	-2.870341987553	0.524271075660
N	-3.000390615816	1.333904485227	0.499905391554	H	2.643731465789	-3.644121508793	1.179772375891
N	2.314478740902	-1.848516327538	-1.783352934145	H	2.399337710318	-1.881117261253	0.957513757574
N	0.677675585415	-3.028859801039	0.485204864791	C	3.193707460298	-0.631037987046	-1.584768726432
C	2.231286543397	1.338190943645	1.651768089747	H	3.177627993237	-0.334129776803	-0.527933367256
H	3.042475066165	1.855613907019	1.131691163291	H	2.787764300749	0.194621410610	-2.185864352301
C	1.243765675236	0.778402588575	0.890484431165	H	4.239394795549	-0.838934037052	-1.896380102472
C	2.259098549017	1.323180036731	3.109741781235	C	2.395631427320	-2.282936470116	-3.230783983182
C	1.229598500600	0.726500184912	3.902631149244	H	1.731102236051	-3.146142199202	-3.380296172516
H	0.380526199940	0.256433081913	3.399478495541	H	3.431853892670	-2.552405636801	-3.524676723486
C	1.290499576227	0.733934564838	5.302548854305	H	2.042817597322	-1.457363341424	-3.862549543569
H	0.486542957821	0.267346303905	5.876766235409	C	0.311713462585	-4.465993082502	0.180040042876
C	2.372497792627	1.336365694810	5.974916482574	H	0.666322148875	-4.739425836298	-0.822520654546
H	2.416083505941	1.341251784766	7.064520230038	H	-0.782959692253	-4.555449883237	0.190956625835
C	3.396467169914	1.933562431081	5.212191195914	H	0.746445539930	-5.161870229719	0.928335942728
H	4.242725856059	2.406372901100	5.715665582449	C	0.119676497725	-2.686703729614	1.851554185056
C	3.344855162025	1.929120486954	3.812619600610	H	0.380776589318	-1.648942044223	2.086592996042
H	4.147490590612	2.395548580900	3.236335384788	H	0.518189128624	-3.362042334404	2.637236118577
C	-2.274714865938	-1.987741351645	-2.288208473857	H	-0.975523620038	-2.781744812006	1.812069695981
H	-3.200455257250	-1.728067792346	-2.848011248754	Li	-1.355713609150	0.756341465394	-0.849561179362
C	-2.714916252378	-2.411573412591	-0.861033832406	Li	0.306624828157	-1.374357617426	-1.066702166218
H	-3.341315015111	-3.320784168179	-0.890615657510				
H	-3.284855819898	-1.603293504009	-0.381799921040				
H	-1.822786495621	-2.612659712274	-0.247749126360				
C	-1.655260904261	-3.239053810435	-3.007446703463				
H	-1.296784232359	-2.974714278283	-4.015321773467				
H	-2.398343103927	-4.052065970668	-3.106356891868				
H	-0.797841921627	-3.610905149020	-2.419413098763				
C	-1.204671365214	-0.204006611044	-3.599410649573				
H	-1.025179451365	-0.984986317461	-4.372233348372				
C	0.001916669941	0.772798371130	-3.658286663987				
H	0.078011823498	1.247640806422	-4.652533690444				
H	0.939864535062	0.238972883643	-3.443758396997				
H	-0.122674598305	1.559550650545	-2.897930610538				
C	-2.492901449294	0.573117323454	-4.045786922934				
H	-3.381154705234	-0.076185068807	-3.989800258060				
H	-2.397806817654	0.941116463395	-5.084225042761				
H	-2.650908861251	1.435183596501	-3.374718277035				
C	-2.952154624086	2.845490142323	0.623982117174				
H	-3.347200789858	3.169043729935	1.609909935178				
H	-3.613612982099	3.257210519167	-0.152655067276				
C	-1.527490020904	3.397230354267	0.437060768314				
H	-1.543511952236	4.496059733687	0.611862514725				
H	-0.843170536033	2.942382104838	1.168053944249				
C	-2.623016614786	0.699303856315	1.822857129164				
H	-1.597808823721	0.987650632633	2.085133178261				
H	-2.654481194475	-0.393065543057	1.704499716517				
H	-3.319976145651	1.007586805590	2.630570588123				
C	-4.413099340748	0.921073958060	0.144722214188				
H	-4.673515462095	1.353757505299	-0.832344258683				
H	-5.145897814916	1.255116630863	0.909025384069				
H	-4.447634284463	-0.171928660715	0.063170853250				
C	0.474916905680	3.533556484894	-0.972423484789				
H	0.911272459789	3.237211562376	-1.937074866594				
H	1.019693565553	3.039134957544	-0.157982519630				
H	0.556542198542	4.635099659331	-0.856393389545				
C	-1.723645335902	3.853522098530	-2.003033835307				
H	-2.766148688241	3.512021731317	-2.051573156446				
H	-1.250963586667	3.647033998506	-2.973158567051				
H	-1.700441397603	4.947691694197	-1.810706136440				
C	2.798247767885	-2.974101783273	-0.886883030479				

Table 5.26 Signed and Unsigned differences in bond length for the MPWLYP/3-21G structure of JAYFIY relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(85,86)	2.6910	2.7112	0.0202	0.0202
R(3,85)	2.4109	2.3608	-0.0501	0.0501
R(6,86)	2.3950	2.2986	-0.0964	0.0964
R(5,86)	2.3548	2.1840	-0.1708	0.1708
R(4,85)	2.3431	2.2045	-0.1386	0.1386
R(1,86)	2.0718	2.0928	0.0210	0.0210
R(1,85)	2.0708	2.0837	0.0129	0.0129
R(2,86)	2.0635	2.0693	0.0058	0.0058
R(2,85)	2.0623	2.0780	0.0157	0.0157
R(31,37)	1.5488	1.5693	0.0205	0.0205
R(21,27)	1.5487	1.5706	0.0219	0.0219
R(21,23)	1.5354	1.5525	0.0171	0.0171
R(31,33)	1.5352	1.5535	0.0183	0.0183
R(41,44)	1.5272	1.5392	0.0120	0.0120
R(63,66)	1.5267	1.5413	0.0146	0.0146
R(4,41)	1.4770	1.5174	0.0404	0.0404
R(5,63)	1.4764	1.5181	0.0417	0.0417
R(6,66)	1.4752	1.5184	0.0432	0.0432
R(3,44)	1.4749	1.5158	0.0409	0.0409
R(4,47)	1.4726	1.5150	0.0424	0.0424
R(5,69)	1.4722	1.5148	0.0426	0.0426
R(6,81)	1.4714	1.5150	0.0436	0.0436
R(3,55)	1.4710	1.5162	0.0452	0.0452
R(4,51)	1.4708	1.5140	0.0432	0.0432
R(5,73)	1.4708	1.5134	0.0426	0.0426
R(3,59)	1.4700	1.5131	0.0431	0.0431
R(6,77)	1.4699	1.5141	0.0442	0.0442
R(2,21)	1.4671	1.5170	0.0499	0.0499
R(2,31)	1.4671	1.5169	0.0498	0.0498
R(7,10)	1.4523	1.4583	0.0060	0.0060
R(10,11)	1.4170	1.4299	0.0129	0.0129
R(10,19)	1.4163	1.4283	0.0120	0.0120
R(15,17)	1.4003	1.4096	0.0093	0.0093
R(13,15)	1.3998	1.4092	0.0094	0.0094
R(11,13)	1.3941	1.4013	0.0072	0.0072
R(17,19)	1.3934	1.4005	0.0071	0.0071
R(7,9)	1.3631	1.3668	0.0037	0.0037
R(1,9)	1.1955	1.2092	0.0137	0.0137
R(31,32)	1.1114	1.1133	0.0019	0.0019
R(21,22)	1.1112	1.1126	0.0014	0.0014
R(44,45)	1.1074	1.1128	0.0054	0.0054
R(66,67)	1.1073	1.1121	0.0048	0.0048
R(59,62)	1.1062	1.1112	0.0050	0.0050
R(77,80)	1.1061	1.1105	0.0044	0.0044
R(55,58)	1.1058	1.1106	0.0048	0.0048
R(69,72)	1.1058	1.1108	0.0050	0.0050
R(63,64)	1.1056	1.1099	0.0043	0.0043
R(73,75)	1.1056	1.1103	0.0047	0.0047

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(47,50)	1.1054	1.1105	0.0051	0.0051
R(51,53)	1.1054	1.1103	0.0049	0.0049
R(41,42)	1.1053	1.1103	0.0050	0.0050
R(81,83)	1.1053	1.1100	0.0047	0.0047
R(37,40)	1.0997	1.1038	0.0041	0.0041
R(27,30)	1.0996	1.1042	0.0046	0.0046
R(27,29)	1.0991	1.1059	0.0068	0.0068
R(37,39)	1.0990	1.1058	0.0068	0.0068
R(33,34)	1.0981	1.1044	0.0063	0.0063
R(23,24)	1.0980	1.1045	0.0065	0.0065
R(23,26)	1.0959	1.1011	0.0052	0.0052
R(27,28)	1.0956	1.1019	0.0063	0.0063
R(37,38)	1.0955	1.1017	0.0062	0.0062
R(33,36)	1.0952	1.1012	0.0060	0.0060
R(66,68)	1.0950	1.1006	0.0056	0.0056
R(44,46)	1.0947	1.0998	0.0051	0.0051
R(23,25)	1.0945	1.0990	0.0045	0.0045
R(33,35)	1.0944	1.1003	0.0059	0.0059
R(41,43)	1.0943	1.1001	0.0058	0.0058
R(51,52)	1.0943	1.0999	0.0056	0.0056
R(73,74)	1.0943	1.0996	0.0053	0.0053
R(55,56)	1.0942	1.0994	0.0052	0.0052
R(63,65)	1.0942	1.1001	0.0059	0.0059
R(81,84)	1.0941	1.1000	0.0059	0.0059
R(47,49)	1.0935	1.0992	0.0057	0.0057
R(69,71)	1.0935	1.0990	0.0055	0.0055
R(59,60)	1.0930	1.0981	0.0051	0.0051
R(77,79)	1.0930	1.0984	0.0054	0.0054
R(59,61)	1.0929	1.0987	0.0058	0.0058
R(77,78)	1.0929	1.0980	0.0051	0.0051
R(51,54)	1.0924	1.0966	0.0042	0.0042
R(69,70)	1.0923	1.0979	0.0056	0.0056
R(73,76)	1.0922	1.0978	0.0056	0.0056
R(55,57)	1.0920	1.0975	0.0055	0.0055
R(47,48)	1.0916	1.0968	0.0052	0.0052
R(81,82)	1.0913	1.0956	0.0043	0.0043
R(13,14)	1.0887	1.0926	0.0039	0.0039
R(19,20)	1.0887	1.0926	0.0039	0.0039
R(17,18)	1.0884	1.0923	0.0039	0.0039
R(11,12)	1.0880	1.0932	0.0052	0.0052
R(7,8)	1.0877	1.0937	0.0060	0.0060
R(15,16)	1.0868	1.0905	0.0037	0.0037

5.4.3.5 B3LYP/Midi!

N	0.290836136249	0.333790538939	0.237550017617			
N	-1.266681026517	-0.759407994375	-2.173790805524	C	2.731963191457	-2.967080285452
N	-1.087154602671	3.058554243677	-0.918634456371	H	3.835389767332	-3.043928694398
N	-3.087627340887	1.315234604414	0.500171384074	H	2.367098433023	-3.873124161155
N	2.307272481438	-1.793218792488	-1.738642119580	C	2.161403041503	-2.892847958254
N	0.674827036936	-3.003256790814	0.490852856073	H	2.614498633513	-3.692264761536
C	2.238635503586	1.281678351302	1.597641018229	H	2.422713647511	-1.931276477461
H	3.058036924033	1.743440971943	1.047243079814	C	3.239724532475	-0.662168950899
C	1.194130070588	0.777357008832	0.872068549547	H	3.235293756717	-0.393799938524
C	2.303895504834	1.267435164274	3.041456977532	H	2.904329898237	0.210579493459
C	1.254938969538	0.773849332294	3.855370412808	H	4.274433330108	-0.915854245796
H	0.349965138503	0.399152148907	3.377314862308	C	2.356144324848	-2.148864533737
C	1.351068474431	0.767479928164	5.243124364157	H	1.639999815538	-2.956737564356
H	0.522582292269	0.378627446163	5.834881646573	H	3.367280686740	-2.474829167022
C	2.492356555421	1.258141087446	5.883747970940	H	2.063232965938	-1.277576610517
H	2.565199245965	1.253986900282	6.969081842431	C	0.274143992510	-4.403298925472
C	3.536804131162	1.758422682781	5.099700691562	H	0.559370741633	-4.676879256355
H	4.434213480494	2.148969958949	5.578568146910	H	-0.816398596947	-4.485601726423
C	3.447218377450	1.763630446493	3.712338581644	H	0.735445521152	-5.121419046547
H	4.273173986983	2.155157295148	3.118589215748	C	0.174214569741	-2.663155490761
C	-2.289064268696	-1.819027221562	-2.224579421468	H	0.465733279086	-1.637898638514
H	-3.241191426671	-1.482805950085	-2.689507256894	H	0.572693055017	-3.349770099183
C	-2.629646112869	-2.241211328401	-0.779710617899	H	-0.921643315933	-2.727213165970
H	-3.416150855431	-3.010596592143	-0.752233465334	Li	-1.376549133996	0.783773466704
H	-2.965915275665	-1.366990190471	-0.213331878563	Li	0.286925212821	-1.321969058761
H	-1.729485928247	-2.632560976892	-0.289991182352			
C	-1.850896308494	-3.093219504757	-3.016060026441			
H	-1.696738369152	-2.874411033893	-4.081458189722			
H	-2.606703873297	-3.891632154813	-2.941325510647			
H	-0.897623479106	-3.461719151613	-2.603201815203			
C	-0.951697645193	-0.281062974270	-3.531455682337			
H	-0.535083007763	-1.078090443811	-4.187213912984			
C	0.128138448481	0.818891488205	-3.429463925172			
H	0.464595553957	1.152197188308	-4.422969227060			
H	0.992519963355	0.452848736955	-2.862796033505			
H	-0.278614298701	1.679460308596	-2.885256631770			
C	-2.170174077988	0.313824009474	-4.307283821527			
H	-2.927585200820	-0.451515776638	-4.523778044903			
H	-1.854419645636	0.756456479594	-5.265787531295			
H	-2.641510681215	1.094038988673	-3.687870950232			
C	-3.061348856716	2.800928751813	0.609858865524			
H	-3.462918677971	3.132263599638	1.587407024347			
H	-3.727763343544	3.204667915921	-0.162100810360			
C	-1.651162947698	3.370235527632	0.422580534076			
H	-1.686525204645	4.466293054496	0.591841375537			
H	-0.967911500487	2.944407540363	1.167627239837			
C	-2.683897466975	0.715715986834	1.800539086805			
H	-1.6533602111152	1.000288929784	2.036335622909			
H	-2.716006890436	-0.376856468901	1.712559474140			
H	-3.354001912814	1.032352835742	2.624173448121			
C	-4.479996621687	0.895962100202	0.190425746969			
H	-4.770170944056	1.300306578402	-0.788279181204			
H	-5.200242973061	1.249801491845	0.954914941551			
H	-4.530498046705	-0.196704409264	0.139807517539			
C	0.311463442976	3.566398086352	-0.942609790638			
H	0.775842836748	3.301485960734	-1.900095157597			
H	0.884123834385	3.104442019887	-0.130618435257			
H	0.345002018807	4.668119883238	-0.823617404482			
C	-1.852070213151	3.760247418937	-1.981579172015			
H	-2.862671865661	3.343620506394	-2.068184786218			
H	-1.345634436263	3.601774401596	-2.941299648950			
H	-1.924925643167	4.850470993160	-1.793007235113			

Table 5.27 Signed and Unsigned differences in bond length for the B3LYP/Midi! structure of JAYFIY relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(85,86)	2.6910	2.6882	-0.0028	0.0028
R(3,85)	2.4109	2.2940	-0.1169	0.1169
R(6,86)	2.3950	2.2883	-0.1067	0.1067
R(5,86)	2.3548	2.1981	-0.1567	0.1567
R(4,85)	2.3431	2.2459	-0.0972	0.0972
R(1,86)	2.0718	2.0745	0.0027	0.0027
R(1,85)	2.0708	2.0431	-0.0277	0.0277
R(2,86)	2.0635	2.0197	-0.0438	0.0438
R(2,85)	2.0623	2.0335	-0.0288	0.0288
R(31,37)	1.5488	1.5622	0.0134	0.0134
R(21,27)	1.5487	1.5627	0.0140	0.0140
R(21,23)	1.5354	1.5433	0.0079	0.0079
R(31,33)	1.5352	1.5448	0.0096	0.0096
R(41,44)	1.5272	1.5323	0.0051	0.0051
R(63,66)	1.5267	1.5344	0.0077	0.0077
R(4,41)	1.4770	1.4900	0.0130	0.0130
R(5,63)	1.4764	1.4897	0.0133	0.0133
R(6,66)	1.4752	1.4907	0.0155	0.0155
R(3,44)	1.4749	1.488	0.0131	0.0131
R(4,47)	1.4726	1.4877	0.0151	0.0151
R(5,69)	1.4722	1.4871	0.0149	0.0149
R(6,81)	1.4714	1.4867	0.0153	0.0153
R(3,55)	1.4710	1.4882	0.0172	0.0172
R(4,51)	1.4708	1.4867	0.0159	0.0159
R(5,73)	1.4708	1.4855	0.0147	0.0147
R(3,59)	1.4700	1.4857	0.0157	0.0157
R(6,77)	1.4699	1.4867	0.0168	0.0168
R(2,21)	1.4671	1.4733	0.0062	0.0062
R(2,31)	1.4671	1.4735	0.0064	0.0064
R(7,10)	1.4523	1.4454	-0.0069	0.0069
R(10,11)	1.4170	1.4165	-0.0005	0.0005
R(10,19)	1.4163	1.4154	-0.0009	0.0009
R(15,17)	1.4003	1.3985	-0.0018	0.0018
R(13,15)	1.3998	1.3977	-0.0021	0.0021
R(11,13)	1.3941	1.3911	-0.0030	0.0030
R(17,19)	1.3934	1.3903	-0.0031	0.0031
R(7,9)	1.3631	1.3681	0.0050	0.0050
R(1,9)	1.1955	1.1897	-0.0058	0.0058
R(31,32)	1.1114	1.1130	0.0016	0.0016
R(21,22)	1.1112	1.1116	0.0004	0.0004
R(44,45)	1.1074	1.1096	0.0022	0.0022
R(66,67)	1.1073	1.1088	0.0015	0.0015
R(59,62)	1.1062	1.1088	0.0026	0.0026
R(77,80)	1.1061	1.1084	0.0023	0.0023
R(55,58)	1.1058	1.1086	0.0028	0.0028
R(69,72)	1.1058	1.1085	0.0027	0.0027
R(63,64)	1.1056	1.1069	0.0013	0.0013
R(73,75)	1.1056	1.1082	0.0026	0.0026

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(47,50)	1.1054	1.1080	0.0026	0.0026
R(51,53)	1.1054	1.1083	0.0029	0.0029
R(41,42)	1.1053	1.1075	0.0022	0.0022
R(81,83)	1.1053	1.1079	0.0026	0.0026
R(37,40)	1.0997	1.1021	0.0024	0.0024
R(27,30)	1.0996	1.1023	0.0027	0.0027
R(27,29)	1.0991	1.1019	0.0028	0.0028
R(37,39)	1.0990	1.1020	0.0030	0.0030
R(33,34)	1.0981	1.1006	0.0025	0.0025
R(23,24)	1.0980	1.1006	0.0026	0.0026
R(23,26)	1.0959	1.0969	0.0010	0.0010
R(27,28)	1.0956	1.0985	0.0029	0.0029
R(37,38)	1.0955	1.0983	0.0028	0.0028
R(33,36)	1.0952	1.0964	0.0012	0.0012
R(66,68)	1.0950	1.0981	0.0031	0.0031
R(44,46)	1.0947	1.0969	0.0022	0.0022
R(23,25)	1.0945	1.0946	1E-04	1E-04
R(33,35)	1.0944	1.0965	0.0021	0.0021
R(41,43)	1.0943	1.0968	0.0025	0.0025
R(51,52)	1.0943	1.0980	0.0037	0.0037
R(73,74)	1.0943	1.0977	0.0034	0.0034
R(55,56)	1.0942	1.0966	0.0024	0.0024
R(63,65)	1.0942	1.0968	0.0026	0.0026
R(81,84)	1.0941	1.0977	0.0036	0.0036
R(47,49)	1.0935	1.0966	0.0031	0.0031
R(69,71)	1.0935	1.0962	0.0027	0.0027
R(59,60)	1.0930	1.0965	0.0035	0.0035
R(77,79)	1.0930	1.0961	0.0031	0.0031
R(59,61)	1.0929	1.0967	0.0038	0.0038
R(77,78)	1.0929	1.0962	0.0033	0.0033
R(51,54)	1.0924	1.0950	0.0026	0.0026
R(69,70)	1.0923	1.0962	0.0039	0.0039
R(73,76)	1.0922	1.0958	0.0036	0.0036
R(55,57)	1.0920	1.0958	0.0038	0.0038
R(47,48)	1.0916	1.0946	0.0030	0.0030
R(81,82)	1.0913	1.0935	0.0022	0.0022
R(13,14)	1.0887	1.0898	0.0011	0.0011
R(19,20)	1.0887	1.0900	0.0013	0.0013
R(17,18)	1.0884	1.0896	0.0012	0.0012
R(11,12)	1.0880	1.0899	0.0019	0.0019
R(7,8)	1.0877	1.0898	0.0021	0.0021
R(15,16)	1.0868	1.0878	0.0010	0.0010

5.4.3.6 B3LYP/Midi!+

N	0.290645188496	0.333688661232	0.237716494222	H	2.364195708349	-3.876696565336	-1.419474559200
N	-1.264890761256	-0.758925397800	-2.175194106474	C	2.157332631125	-2.895076393740	0.501083610279
N	-1.082299394863	3.059582821621	-0.921254993202	H	2.608693481112	-3.694735864337	1.122570560731
N	-3.086714565362	1.319091846594	0.495462126991	H	2.419284441560	-1.933591433877	0.962308509825
N	2.307164495160	-1.796915279260	-1.734839817930	C	3.240649057794	-0.666810775980	-1.484017904680
N	0.670635183413	-3.003640571098	0.493390182113	H	3.235277461348	-0.397849151187	-0.421338051824
C	2.238127382026	1.279554350281	1.599671120726	H	2.906953977697	0.206005403298	-2.057252846904
H	3.058771868312	1.740026315097	1.050044740069	H	4.275419803248	-0.921890377348	-1.788924283205
C	1.193807009282	0.776303537853	0.873079655472	C	2.357365735388	-2.153498917558	-3.176031188683
C	2.301632836814	1.265899779095	3.043570568613	H	1.640513196909	-2.960651840670	-3.375134886861
C	1.251040883171	0.774096871130	3.856454363522	H	3.368501391547	-2.480841656540	-3.490088133393
H	0.346134052062	0.400405816052	3.377487243709	H	2.066206683348	-1.282233331796	-3.773462392736
C	1.345494225553	0.768241930695	5.244326533718	C	0.268567837322	-4.403346065915	0.194377562064
H	0.5157729843061	0.380772990239	5.835265554839	H	0.554689725957	-4.677857693126	-0.827589792992
C	2.486663310623	1.257680215084	5.886093121842	H	-0.822162138684	-4.484249002743	0.266401413490
H	2.558199535668	1.253936347024	6.971515538937	H	0.728119050792	-5.121647921083	0.902453322726
C	3.532716428397	1.756210365542	5.103068093372	C	0.168773534863	-2.662182672965	1.850562013563
H	4.430064206626	2.145792422130	5.582836495247	H	0.461392489519	-1.637215853924	2.094805168131
C	3.444806868608	1.760891634691	3.715598052166	H	0.565321604765	-3.348964051399	2.624160011516
H	4.271993919154	2.151044449363	3.122659399013	H	-0.927174287438	-2.724736161129	1.850778903497
C	-2.288016477736	-1.817791449946	-2.227001657528	Li	-1.374805308049	0.784920024939	-0.856242611075
H	-3.239140900783	-1.481119798130	-2.693637280533	Li	0.286624890657	-1.322674658339	-1.011475843785
C	-2.631235621967	-2.238918920408	-0.782444306005				
H	-3.417896274101	-3.008176884653	-0.755838314042				
H	-2.968394731025	-1.364281854455	-0.217234462692				
H	-1.731988603574	-2.630069859161	-0.290882333610				
C	-1.849517659783	-3.092722055129	-3.017102102793				
H	-1.693264734496	-2.874510305622	-4.082317163616				
H	-2.606127874228	-3.890469115990	-2.943369942842				
H	-0.897296021612	-3.461859802706	-2.602401222866				
C	-0.948060945879	-0.280999449304	-3.532585172380				
H	-0.531945937475	-1.078578258945	-4.187987519268				
C	0.133169965857	0.817488163633	-3.429615646151				
H	0.470456819369	1.150859987116	-4.422817281575				
H	0.996860293143	0.450022321737	-2.862823004881				
H	-0.272673490810	1.678295424503	-2.885104257011				
C	-2.165087710404	0.315523428238	-4.309419236712				
H	-2.923415512888	-0.448777781111	-4.526357441558				
H	-1.847993031891	0.757561126646	-5.267755832368				
H	-2.635795588028	1.096495059700	-3.690485449678				
C	-3.058711603153	2.804771861702	0.604882939548				
H	-3.461033115023	3.136810444972	1.581883113666				
H	-3.723695244686	3.209180859824	-0.167960439603				
C	-1.647591296016	3.372276801385	0.419183865194				
H	-1.681816205304	4.468421017790	0.588130638368				
H	-0.965778128851	2.945794151558	1.165168888984				
C	-2.685322937387	0.719317227461	1.796437641789				
H	-1.654995674839	1.002725312585	2.033481773725				
H	-2.718597979368	-0.373229372843	1.708593433457				
H	-3.356100390951	1.036882065260	2.619165975042				
C	-4.479224328673	0.901489182014	0.184096976387				
H	-4.767745139055	1.306093886507	-0.794989608048				
H	-5.199945522348	1.256280869680	0.947696901546				
H	-4.530992561782	-0.191119384266	0.133528436777				
C	0.316906437221	3.565876694613	-0.943639796095				
H	0.782158603590	3.300261612099	-1.900509407978				
H	0.888069334972	3.103460672333	-0.130855731443				
H	0.351517296071	4.667585483458	-0.824835528234				
C	-1.845115205565	3.761799001424	-1.985355046912				
H	-2.856050295358	3.346225601927	-2.073116794770				
H	-1.337638158582	3.602492778981	-2.944389877085				
H	-1.917038058828	4.852156464835	-1.797199722372				
C	2.729510863891	-2.970785634388	-0.920627695289				
H	3.832796718652	-3.048878488207	-0.876484485734				

Table 5.28 Signed and Unsigned differences in bond length for the B3LYP/Midi!+ structure of JAYFIY relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(85,86)	2.6910	2.6882	-0.0028	0.0028
R(3,85)	2.4109	2.2943	-0.1166	0.1166
R(6,86)	2.3950	2.2886	-0.1064	0.1064
R(5,86)	2.3548	2.1979	-0.1569	0.1569
R(4,85)	2.3431	2.2457	-0.0974	0.0974
R(1,86)	2.0718	2.0746	0.0028	0.0028
R(1,85)	2.0708	2.0431	-0.0277	0.0277
R(2,86)	2.0635	2.0197	-0.0438	0.0438
R(2,85)	2.0623	2.0335	-0.0288	0.0288
R(31,37)	1.5488	1.5622	0.0134	0.0134
R(21,27)	1.5487	1.5627	0.0104	0.0140
R(21,23)	1.5354	1.5433	0.0079	0.0079
R(31,33)	1.5352	1.5448	0.0096	0.0096
R(41,44)	1.5272	1.5323	0.0051	0.0051
R(63,66)	1.5267	1.5344	0.0077	0.0077
R(4,41)	1.4770	1.4900	0.0130	0.0130
R(5,63)	1.4764	1.4897	0.0133	0.0133
R(6,66)	1.4752	1.4907	0.0155	0.0155
R(3,44)	1.4749	1.4880	0.0131	0.0131
R(4,47)	1.4726	1.4877	0.0151	0.0151
R(5,69)	1.4722	1.4871	0.0149	0.0149
R(6,81)	1.4714	1.4867	0.0153	0.0153
R(3,55)	1.4710	1.4882	0.0172	0.0172
R(4,51)	1.4708	1.4867	0.0159	0.0159
R(5,73)	1.4708	1.4855	0.0147	0.0147
R(3,59)	1.4700	1.4857	0.0157	0.0157
R(6,77)	1.4699	1.4867	0.0168	0.0168
R(2,21)	1.4671	1.4733	0.0062	0.0062
R(2,31)	1.4671	1.4735	0.0064	0.0064
R(7,10)	1.4523	1.4454	-0.0069	0.0069
R(10,11)	1.4170	1.4165	-0.0005	0.0005
R(10,19)	1.4163	1.4154	-0.0009	0.0009
R(15,17)	1.4003	1.3985	-0.0018	0.0018
R(13,15)	1.3998	1.3977	-0.0021	0.0021
R(11,13)	1.3941	1.3911	-0.0030	0.0030
R(17,19)	1.3934	1.3903	-0.0031	0.0031
R(7,9)	1.3631	1.3681	0.0050	0.0050
R(1,9)	1.1955	1.1897	-0.0058	0.0058
R(31,32)	1.1114	1.1130	0.0016	0.0016
R(21,22)	1.1112	1.1116	0.0004	0.0004
R(44,45)	1.1074	1.1096	0.0022	0.0022
R(66,67)	1.1073	1.1088	0.0015	0.0015
R(59,62)	1.1062	1.1088	0.0026	0.0026
R(77,80)	1.1061	1.1084	0.0023	0.0023
R(55,58)	1.1058	1.1086	0.0028	0.0028
R(69,72)	1.1058	1.1085	0.0027	0.0027
R(63,64)	1.1056	1.1069	0.0013	0.0013
R(73,75)	1.1056	1.1082	0.0026	0.0026

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(47,50)	1.1054	1.1080	0.0026	0.0026
R(51,53)	1.1054	1.1083	0.0029	0.0029
R(41,42)	1.1053	1.1075	0.0022	0.0022
R(81,83)	1.1053	1.1079	0.0026	0.0026
R(37,40)	1.0997	1.1021	0.0024	0.0024
R(27,30)	1.0996	1.1023	0.0027	0.0027
R(27,29)	1.0991	1.1020	0.0029	0.0029
R(37,39)	1.0990	1.1020	0.0030	0.0030
R(33,34)	1.0981	1.1006	0.0025	0.0025
R(23,24)	1.0980	1.1006	0.0026	0.0026
R(23,26)	1.0959	1.0969	0.0010	0.0010
R(27,28)	1.0956	1.0985	0.0029	0.0029
R(37,38)	1.0955	1.0983	0.0028	0.0028
R(33,36)	1.0952	1.0964	0.0012	0.0012
R(66,68)	1.0950	1.0981	0.0031	0.0031
R(44,46)	1.0947	1.0969	0.0022	0.0022
R(23,25)	1.0945	1.0946	1E-04	1E-04
R(33,35)	1.0944	1.0965	0.0021	0.0021
R(41,43)	1.0943	1.0968	0.0025	0.0025
R(51,52)	1.0943	1.0980	0.0037	0.0037
R(73,74)	1.0943	1.0977	0.0034	0.0034
R(55,56)	1.0942	1.0966	0.0024	0.0024
R(63,65)	1.0942	1.0968	0.0026	0.0026
R(81,84)	1.0941	1.0977	0.0036	0.0036
R(47,49)	1.0935	1.0966	0.0031	0.0031
R(69,71)	1.0935	1.0962	0.0027	0.0027
R(59,60)	1.0930	1.0965	0.0035	0.0035
R(77,79)	1.0930	1.0961	0.0031	0.0031
R(59,61)	1.0929	1.0967	0.0038	0.0038
R(77,78)	1.0929	1.0962	0.0033	0.0033
R(51,54)	1.0924	1.0950	0.0026	0.0026
R(69,70)	1.0923	1.0962	0.0039	0.0039
R(73,76)	1.0922	1.0958	0.0036	0.0036
R(55,57)	1.0920	1.0958	0.0038	0.0038
R(47,48)	1.0916	1.0946	0.0030	0.0030
R(81,82)	1.0913	1.0935	0.0022	0.0022
R(13,14)	1.0887	1.0898	0.0011	0.0011
R(19,20)	1.0887	1.0900	0.0013	0.0013
R(17,18)	1.0884	1.0896	0.0012	0.0012
R(11,12)	1.0880	1.0899	0.0019	0.0019
R(7,8)	1.0877	1.0898	0.0021	0.0021
R(15,16)	1.0868	1.0878	0.0010	0.0010

5.4.3.7 MPW1PW91/Midi!+

N	0.451529661915	0.436414800148	0.173467662064	H	4.206172738705	-2.604044184450	-1.147193466080
N	-1.350727209841	-0.815665777552	-2.047035610992	H	2.880315177250	-3.666908772111	-1.615264116533
N	-0.961850115620	3.163257557463	-1.221224470133	C	2.590982069264	-2.683610666429	0.289038054512
N	-2.898063690746	1.624587274662	0.486499230273	H	3.144539330903	-3.443116385307	0.877874644431
N	2.484638211846	-1.635370733716	-1.969583112105	H	2.784301780681	-1.710114981727	0.758997382116
N	1.134333222343	-2.928490410713	0.368205746892	C	3.231766369040	-0.375836445438	-1.773898280835
C	2.154945047259	1.202159602456	1.917194922249	H	3.236423264139	-0.098035348746	-0.714619829173
H	3.043055119470	1.723549048853	1.561679304783	H	2.743126586353	0.430394955996	-2.332703912842
C	1.238516120070	0.801105900302	0.988737253278	H	4.278339740667	-0.470655124488	-2.123892537757
C	1.994060642821	0.998189791837	3.337685066113	C	2.568342592300	-2.024328698779	-3.390582164894
C	0.841029122916	0.405763598448	3.903394993482	H	1.966797141884	-2.925889473439	-3.560386694413
H	0.027213660330	0.096186929139	3.249396730991	H	3.611562454184	-2.226278052188	-3.702132584937
C	0.719809261146	0.222294265167	5.276841657257	H	2.166824114818	-1.223432624255	-4.020010886145
H	-0.184123969222	-0.236285490036	5.676954323016	C	0.814688675976	-4.300988641394	-0.069625992621
C	1.737422254470	0.621270047394	6.146700566613	H	0.973359927584	-4.416480828454	-1.147590078120
H	1.639388827827	0.477256251130	7.220323576726	H	-0.243053385163	-4.504761655267	0.133146070685
C	2.882554453895	1.214252100164	5.606995704598	H	1.423627636536	-5.055190240780	0.466512654646
H	3.688038662119	1.536299179335	6.265848864736	C	0.737241082378	-2.791305561564	1.784606908651
C	3.009830920328	1.398650770273	4.234969452884	H	1.019826035685	-1.800177240263	2.151885555999
H	3.911451575100	1.862148120591	3.835141149931	H	1.226797595375	-3.554555177102	2.419479606428
C	-2.439891697457	-1.761414787039	-1.768986827035	H	-0.349293322941	-2.904379657393	1.875982137823
H	-3.437007821653	-1.314946898692	-1.980375006272	Li	-1.264824008111	0.874274341305	-0.877298755227
C	-2.424477491971	-2.115074211125	-0.274194502146	Li	0.389686076156	-1.285963649042	-1.050607854812
H	-3.290093504998	-2.735868693970	0.001713245776				
H	-2.435372917089	-1.207549938934	0.340836966281				
H	-1.511916691910	-2.671856491211	-0.025372880385				
C	-2.371868281376	-3.083968865035	-2.573375381742				
H	-2.492901938047	-2.921177253076	-3.652352434553				
H	-3.162436355322	-3.780975960097	-2.253554283698				
H	-1.395439260299	-3.567460648405	-2.410861610440				
C	-1.274601390993	-0.507283298996	-3.480753899258				
H	-1.006281687820	-1.404060750809	-4.081421593367				
C	-0.159302593243	0.523852194359	-3.707407068048				
H	0.000357260468	0.718075845510	-4.778575103022				
H	0.782117433812	0.170504910793	-3.272292176882				
H	-0.415222622088	1.473367517170	-3.219657114526				
C	-2.581532884049	0.057946242066	-4.092848058723				
H	-3.406754955248	-0.664977913099	-4.051117926691				
H	-2.435996825524	0.333099426261	-5.149429386703				
H	-2.891638727914	0.958918179916	-3.539529359024				
C	-2.898894401534	3.097632417920	0.341338805269				
H	-3.317988580037	3.581154926394	1.244472707252				
H	-3.567773375800	3.358826820857	-0.487551087922				
C	-1.496060646188	3.637534973548	0.073327280355				
H	-1.515482790882	4.745703566722	0.108164614519				
H	-0.803820414261	3.303099856853	0.856725048487				
C	-2.538444846656	1.274180626319	1.875229247227				
H	-1.551702567534	1.675334967332	2.125415040272				
H	-2.494900295845	0.184144666214	1.978761584981				
H	-3.279641817594	1.670112161277	2.596352279379				
C	-4.249364535409	1.108584660251	0.196277899137				
H	-4.505036966218	1.318642582532	-0.849545233924				
H	-5.015813856194	1.564275399490	0.853003409068				
H	-4.267045763413	0.023044646893	0.339410612950				
C	0.464065038136	3.536449175643	-1.301513877367				
H	0.889634353792	3.147314988317	-2.234464524799				
H	1.005820382713	3.092616931738	-0.459938760741				
H	0.602549017855	4.634956414203	-1.280968316623				
C	-1.672381257527	3.813885185063	-2.338280689090				
H	-2.718811539368	3.492430742151	-2.377161326944				
H	-1.201302168778	3.524113283166	-3.284389202499				
H	-1.639879851571	4.918179893978	-2.255794130888				
C	3.103480941585	-2.700379288302	-1.147290776072				

Table 5.29 Signed and Unsigned differences in bond length for the MPW1PW91/Midi!+ structure of JAYFIY relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(85,86)	2.6910	2.7265	0.0355	0.0355
R(3,85)	2.4109	2.3344	-0.0765	0.0765
R(6,86)	2.3950	2.2947	-0.1003	0.1003
R(5,86)	2.3548	2.3142	-0.0406	0.0406
R(4,85)	2.3431	2.2562	-0.0869	0.0869
R(1,86)	2.0718	2.1139	0.0421	0.0421
R(1,85)	2.0708	2.0595	-0.0113	0.0113
R(2,86)	2.0635	2.0599	-0.0036	0.0036
R(2,85)	2.0623	2.0571	-0.0052	0.0052
R(31,37)	1.5488	1.5499	0.0011	0.0011
R(21,27)	1.5487	1.5495	0.0008	0.0008
R(21,23)	1.5354	1.5361	0.0007	0.0007
R(31,33)	1.5352	1.5357	0.0005	0.0005
R(41,44)	1.5272	1.5268	-0.0004	0.0004
R(63,66)	1.5267	1.5251	-0.0016	0.0016
R(4,41)	1.4770	1.4802	0.0032	0.0032
R(5,63)	1.4764	1.4810	0.0046	0.0046
R(6,66)	1.4752	1.4792	0.0040	0.0040
R(3,44)	1.4749	1.4786	0.0037	0.0037
R(4,47)	1.4726	1.4767	0.0041	0.0041
R(5,69)	1.4722	1.4775	0.0053	0.0053
R(6,81)	1.4714	1.4774	0.0060	0.0060
R(3,55)	1.4710	1.4761	0.0051	0.0051
R(4,51)	1.4708	1.4753	0.0045	0.0045
R(5,73)	1.4708	1.4756	0.0048	0.0048
R(3,59)	1.4700	1.4751	0.0051	0.0051
R(6,77)	1.4699	1.4757	0.0058	0.0058
R(2,21)	1.4671	1.4690	0.0019	0.0019
R(2,31)	1.4671	1.4685	0.0014	0.0014
R(7,10)	1.4523	1.4440	-0.0083	0.0083
R(10,11)	1.4170	1.4144	-0.0026	0.0026
R(10,19)	1.4163	1.4133	-0.0030	0.0030
R(15,17)	1.4003	1.3979	-0.0024	0.0024
R(13,15)	1.3998	1.3969	-0.0029	0.0029
R(11,13)	1.3941	1.3909	-0.0032	0.0032
R(17,19)	1.3934	1.3902	-0.0032	0.0032
R(7,9)	1.3631	1.3648	0.0017	0.0017
R(1,9)	1.1955	1.1904	-0.0051	0.0051
R(31,32)	1.1114	1.1122	0.0008	0.0008
R(21,22)	1.1112	1.1128	0.0016	0.0016
R(44,45)	1.1074	1.1089	0.0015	0.0015
R(66,67)	1.1073	1.1091	0.0018	0.0018
R(59,62)	1.1062	1.1078	0.0016	0.0016
R(77,80)	1.1061	1.1077	0.0016	0.0016
R(55,58)	1.1058	1.1074	0.0016	0.0016
R(69,72)	1.1058	1.1076	0.0018	0.0018
R(63,64)	1.1056	1.1069	0.0013	0.0013
R(73,75)	1.1056	1.1073	0.0017	0.0017

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(47,50)	1.1054	1.1073	0.0019	0.0019
R(51,53)	1.1054	1.1074	0.0020	0.0020
R(41,42)	1.1053	1.1068	0.0015	0.0015
R(81,83)	1.1053	1.1069	0.0016	0.0016
R(37,40)	1.0997	1.1019	0.0022	0.0022
R(27,30)	1.0996	1.1016	0.0020	0.0020
R(27,29)	1.0991	1.1014	0.0023	0.0023
R(37,39)	1.0990	1.1015	0.0025	0.0025
R(33,34)	1.0981	1.1003	0.0022	0.0022
R(23,24)	1.0980	1.1004	0.0024	0.0024
R(23,26)	1.0959	1.0976	0.0017	0.0017
R(27,28)	1.0956	1.0979	0.0023	0.0023
R(37,38)	1.0955	1.0979	0.0024	0.0024
R(33,36)	1.0952	1.0977	0.0025	0.0025
R(66,68)	1.0950	1.0981	0.0031	0.0031
R(44,46)	1.0947	1.0976	0.0029	0.0029
R(23,25)	1.0945	1.0963	0.0018	0.0018
R(33,35)	1.0944	1.0957	0.0013	0.0013
R(41,43)	1.0943	1.0967	0.0024	0.0024
R(51,52)	1.0943	1.0969	0.0026	0.0026
R(73,74)	1.0943	1.0970	0.0027	0.0027
R(55,56)	1.0942	1.0968	0.0026	0.0026
R(63,65)	1.0942	1.0968	0.0026	0.0026
R(81,84)	1.0941	1.0962	0.0021	0.0021
R(47,49)	1.0935	1.0958	0.0023	0.0023
R(69,71)	1.0935	1.0959	0.0024	0.0024
R(59,60)	1.0930	1.0954	0.0024	0.0024
R(77,79)	1.0930	1.0961	0.0031	0.0031
R(59,61)	1.0929	1.0959	0.0030	0.0030
R(77,78)	1.0929	1.0957	0.0028	0.0028
R(51,54)	1.0924	1.0951	0.0027	0.0027
R(69,70)	1.0923	1.0951	0.0028	0.0028
R(73,76)	1.0922	1.0949	0.0027	0.0027
R(55,57)	1.0920	1.0949	0.0029	0.0029
R(47,48)	1.0916	1.0942	0.0026	0.0026
R(81,82)	1.0913	1.0941	0.0028	0.0028
R(13,14)	1.0887	1.0897	0.0010	0.0010
R(19,20)	1.0887	1.0898	0.0011	0.0011
R(17,18)	1.0884	1.0893	0.0009	0.0009
R(11,12)	1.0880	1.0890	0.0010	0.0010
R(7,8)	1.0877	1.0895	0.0018	0.0018
R(15,16)	1.0868	1.0877	0.0009	0.0009

5.4.3.8 B3LYP/6-31G(d)

N	0.409479214496	0.275592265767	0.226016733376	H	4.059842595181	-2.968123074993	-0.966414033381
N	-1.331654265295	-0.803897228010	-2.155265318620	H	2.673675420548	-3.881889429544	-1.542299792853
N	-1.016856552540	3.155785546378	-1.010900611573	C	2.374927012529	-2.939322374839	0.375466443855
N	-3.031511565435	1.472366033595	0.550229971222	H	2.878181657448	-3.723573819000	0.972461208415
N	2.499624364679	-1.822021587619	-1.864522166391	H	2.593544024195	-1.981789363560	0.859337472385
N	0.911795830423	-3.124425329915	0.401002849227	C	3.320350575728	-0.630417747388	-1.594536833160
C	2.179619910502	1.308409082217	1.754908337067	H	3.271114530750	-0.364062600194	-0.536461135287
H	2.992981915840	1.842856755809	1.271097184770	H	2.940595004931	0.217245968028	-2.171134510301
C	1.233366293894	0.758326425950	0.945672110574	H	4.377761733409	-0.795819010704	-1.869865294804
C	2.155940027746	1.248789594245	3.205296003334	C	2.591500549985	-2.174512365951	-3.288780914092
C	1.121997513892	0.616993773000	3.937357772892	H	1.927143283100	-3.016501511689	-3.505776080878
H	0.299301412040	0.152572618128	3.397487026575	H	3.619514733562	-2.450681834213	-3.584393339747
C	1.134814218727	0.579385918889	5.328763180104	H	2.275733110931	-1.326699289580	-3.900993046492
H	0.321480832139	0.082559705390	5.854287319609	C	0.537299522888	-4.484346460244	-0.010714645419
C	2.173649102552	1.171083415485	6.053089373457	H	0.789414822278	-4.659674886721	-1.059473920816
H	2.180755307491	1.141224441061	7.139135804341	H	-0.542989619073	-4.611866994606	0.093224722351
C	3.202580696450	1.803294835425	5.348896331344	H	1.037000256234	-5.254256318455	0.605075100913
H	4.022010895004	2.272268902321	5.889921309788	C	0.419229090141	-2.880009864660	1.765242328722
C	3.195973971575	1.842159248451	3.957872303371	H	0.682436720793	-1.867242650001	2.074672004058
H	4.007631513380	2.338896591365	3.429774521306	H	0.844718270534	-3.595648546486	2.491152312751
C	-2.454889637701	-1.738425822125	-2.021592836114	H	-0.670046849511	-2.977070506195	-1.784419751524
H	-3.422097636142	-1.253189579116	-2.271141657136	Li	-1.283565869257	0.797636032379	-0.836312799003
C	-2.575966559029	-2.201239855810	-0.563818735192	Li	0.332623468966	-1.360304892114	-1.059054219683
H	-3.497899706422	-2.773007379019	-0.397104389565				
H	-2.570063679041	-1.350629045882	0.124915882183				
H	-1.731767758234	-2.844444808655	-0.293523270266				
C	-2.374900321363	-2.997401307834	-2.917332712547				
H	-2.400248790427	-2.752533492113	-3.984189585222				
H	-3.214518686905	-3.676746663899	-2.718227661738				
H	-1.440383313148	-3.543545904844	-2.724056493114				
C	-1.134387322849	-0.379405921636	-3.545969557165				
H	-0.860247829393	-1.233345783615	-4.199829591756				
C	0.037469624712	0.607295081807	-3.628407566502				
H	0.280969362589	0.857338694768	-4.668958005543				
H	0.934036764708	0.194414750245	-3.156564489877				
H	-0.202430417392	1.541172825776	-3.107622682831				
C	-2.368677202311	0.274929037521	-4.211607674195				
H	-3.218035912606	-0.413067077181	-4.276470244819				
H	-2.138057048217	0.606647221436	-5.232870734901				
H	-2.696157753660	1.151214106220	-3.634393152062				
C	-3.029818372499	2.946247169254	0.467028875008				
H	-3.480512705346	3.389652299197	1.372931579467				
H	-3.674218466528	3.236818153921	-0.368050058581				
C	-1.636457946339	3.538600347896	0.270867219383				
H	-1.708038417225	4.639363991376	0.359751715006				
H	-0.971449930327	3.199237691501	1.071008625679				
C	-2.660353109537	1.033179822214	1.904974687120				
H	-1.663645009750	1.394959225560	2.164306363193				
H	-2.637206900310	-0.059162131058	1.943171428447				
H	-3.378361573231	1.395546915064	2.662584216763				
C	-4.366750284569	0.958617888180	0.211240244583				
H	-4.613591781782	1.223207952325	-0.821280047296				
H	-5.149820109147	1.363783570948	0.876942469393				
H	-4.376574842991	-0.130185505834	0.293835768758				
C	0.394665274752	3.570472139934	-1.009349979254				
H	0.878477917434	3.226971876839	-1.928255100051				
H	0.910966249640	3.124986661041	-0.156327646705				
H	0.498042541412	4.669152965155	-0.952753896698				
C	-1.701793065970	3.789369240265	-2.146011122972				
H	-2.728731222030	3.427017774249	-2.237487024833				
H	-1.180200873858	3.535978959329	-3.072224710587				
H	-1.725397865706	4.890507582009	-2.051040236525				
C	2.957619075992	-2.954843352591	-1.035576150474				

Table 5.30 Signed and Unsigned differences in bond length for the B3LYP/6-31G(d) structure of JAYFIY relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(85,86)	2.6910	2.7053	0.0143	0.0143
R(3,85)	2.4109	2.3796	-0.0313	0.0313
R(6,86)	2.3950	2.3621	-0.0329	0.0329
R(5,86)	2.3548	2.3575	0.0027	0.0027
R(4,85)	2.3431	2.3309	-0.0122	0.0122
R(1,86)	2.0718	2.0817	0.0099	0.0099
R(1,85)	2.0708	2.0658	-0.0050	0.0050
R(2,86)	2.0635	2.0691	0.0056	0.0056
R(2,85)	2.0623	2.0753	0.0130	0.0130
R(31,37)	1.5488	1.5475	-0.0013	0.0013
R(21,27)	1.5487	1.5472	-0.0015	0.0015
R(21,23)	1.5354	1.5343	-0.0011	0.0011
R(31,33)	1.5352	1.5342	-0.0010	0.0010
R(41,44)	1.5272	1.5267	-0.0005	0.0005
R(63,66)	1.5267	1.5267	0.0000	0.0000
R(4,41)	1.4770	1.4762	-0.0008	0.0008
R(5,63)	1.4764	1.4765	1E-04	1E-04
R(6,66)	1.4752	1.4750	-0.0002	0.0002
R(3,44)	1.4749	1.4742	-0.0007	0.0007
R(4,47)	1.4726	1.4717	-0.0009	0.0009
R(5,69)	1.4722	1.4719	-0.0003	0.0003
R(6,81)	1.4714	1.4709	-0.0005	0.0005
R(3,55)	1.4710	1.4712	0.0002	0.0002
R(4,51)	1.4708	1.4703	-0.0005	0.0005
R(5,73)	1.4708	1.4701	-0.0007	0.0007
R(3,59)	1.4700	1.4694	-0.0006	0.0006
R(6,77)	1.4699	1.4694	-0.0005	0.0005
R(2,21)	1.4671	1.4673	0.0002	0.0002
R(2,31)	1.4671	1.4674	0.0003	0.0003
R(7,10)	1.4523	1.4518	-0.0005	0.0005
R(10,11)	1.4170	1.4157	-0.0013	0.0013
R(10,19)	1.4163	1.4143	-0.0020	0.0020
R(15,17)	1.4003	1.3980	-0.0023	0.0023
R(13,15)	1.3998	1.3978	-0.0020	0.0020
R(11,13)	1.3941	1.3920	-0.0021	0.0021
R(17,19)	1.3934	1.3916	-0.0018	0.0018
R(7,9)	1.3631	1.3612	-0.0019	0.0019
R(1,9)	1.1955	1.1957	0.0002	0.0002
R(31,32)	1.1114	1.1099	-0.0015	0.0015
R(21,22)	1.1112	1.1105	-0.0007	0.0007
R(44,45)	1.1074	1.1067	-0.0007	0.0007
R(66,67)	1.1073	1.1067	-0.0006	0.0006
R(59,62)	1.1062	1.1055	-0.0007	0.0007
R(77,80)	1.1061	1.1053	-0.0008	0.0008
R(55,58)	1.1058	1.1050	-0.0008	0.0008
R(69,72)	1.1058	1.1051	-0.0007	0.0007
R(63,64)	1.1056	1.1045	-0.0011	0.0011
R(73,75)	1.1056	1.1047	-0.0009	0.0009
R(47,50)	1.1054	1.1049	-0.0005	0.0005
R(51,53)	1.1054	1.1048	-0.0006	0.0006
R(41,42)	1.1053	1.1047	-0.0006	0.0006
R(81,83)	1.1053	1.1046	-0.0007	0.0007
R(37,40)	1.0997	1.0992	-0.0005	0.0005
R(27,30)	1.0996	1.0995	-1E-04	1E-04
R(27,29)	1.0991	1.0982	-0.0009	0.0009
R(37,39)	1.0990	1.0983	-0.0007	0.0007
R(33,34)	1.0981	1.0975	-0.0006	0.0006
R(23,24)	1.0980	1.0976	-0.0004	0.0004
R(23,26)	1.0959	1.0952	-0.0007	0.0007
R(27,28)	1.0956	1.0949	-0.0007	0.0007
R(37,38)	1.0955	1.0950	-0.0005	0.0005
R(33,36)	1.0952	1.0959	0.0007	0.0007
R(66,68)	1.0950	1.0949	-1E-04	1E-04
R(44,46)	1.0947	1.0944	-0.0003	0.0003
R(23,25)	1.0945	1.0945	0.0000	0.0000
R(33,35)	1.0944	1.0940	-0.0004	0.0004
R(41,43)	1.0943	1.0941	-0.0002	0.0002
R(51,52)	1.0943	1.0941	-0.0002	0.0002
R(73,74)	1.0943	1.0943	0.0000	0.0000
R(55,56)	1.0942	1.0938	-0.0004	0.0004
R(63,65)	1.0942	1.0940	-0.0002	0.0002
R(81,84)	1.0941	1.0938	-0.0003	0.0003
R(47,49)	1.0935	1.0933	-0.0002	0.0002
R(69,71)	1.0935	1.0933	-0.0002	0.0002
R(59,60)	1.0930	1.0928	-0.0002	0.0002
R(77,79)	1.0930	1.0927	-0.0003	0.0003
R(59,61)	1.0929	1.0928	-1E-04	1E-04
R(77,78)	1.0929	1.0928	-1E-04	1E-04
R(51,54)	1.0924	1.0920	-0.0004	0.0004
R(69,70)	1.0923	1.0922	-1E-04	1E-04
R(73,76)	1.0922	1.0924	0.0002	0.0002
R(55,57)	1.0920	1.0921	1E-04	1E-04
R(47,48)	1.0916	1.0916	0.0000	0.0000
R(81,82)	1.0913	1.0912	-1E-04	1E-04
R(13,14)	1.0887	1.0884	-0.0003	0.0003
R(19,20)	1.0887	1.0883	-0.0004	0.0004
R(17,18)	1.0884	1.0882	-0.0002	0.0002
R(11,12)	1.0880	1.0881	1E-04	1E-04
R(7,8)	1.0877	1.0869	-0.0008	0.0008
R(15,16)	1.0868	1.0865	-0.0003	0.0003

5.4.3.9 HF/6-31G(d)

N	0.452477926452	0.308313799593	0.241712013367	H	4.087323069965	-3.032566430183	-1.176235606200
N	-1.341929253548	-0.816176420931	-2.108897235884	H	2.675440917639	-3.901184357803	-1.693796542493
N	-0.997607649459	3.257374895615	-1.078055433346	C	2.499642561112	-3.024380891154	0.253497655806
N	-2.998215356576	1.621393876316	0.545513192493	H	3.014802490902	-3.831062043845	0.782070883657
N	2.520742320051	-1.847376126872	-1.946659530332	H	2.772731422305	-2.102242628288	0.749547166689
N	1.051051373497	-3.180233668374	0.368040818325	C	3.354054691058	-0.677810175474	-1.683520441840
C	2.141195633008	1.291892561640	1.844013766845	H	3.365095474905	-0.445832506330	-0.628763379788
H	2.962809830655	1.826081176023	1.403568733637	H	2.957987592915	0.182466537939	-2.205932269685
C	1.228553187861	0.761326064539	0.991644768784	H	4.382327988919	-0.837441250569	-2.014830406296
C	2.056339214713	1.194735175294	3.292801690278	C	2.527713020855	-2.152360927635	-3.372677455033
C	1.002210575295	0.556405001254	3.963904770520	H	1.831455045566	-2.954719696152	-3.582752205017
H	0.205296908157	0.110282329140	3.394610173862	H	3.518241516423	-2.452530057289	-3.720781066025
C	0.963328015728	0.488351561195	5.344651234575	H	2.219943120575	-1.285845660342	-3.939646820614
H	0.137007822231	-0.011441058045	5.821726224797	C	0.615981391441	-4.505581176925	-0.055824476417
C	1.966161845705	1.052492834609	6.117136943323	H	0.767940182065	-4.647485237217	-1.116769087701
H	1.932023452952	0.998227056751	7.190520269497	H	-0.441330665877	-4.621210906231	0.137724940170
C	3.014599766872	1.689662544169	5.470006377260	H	1.146119510234	-5.297143423059	0.478346537722
H	3.806915056094	2.137157338730	6.045945421156	C	0.649289585567	-2.958863579202	1.753671510556
C	3.061275507547	1.760231992054	4.091075271597	H	0.962975744949	-1.978534874560	2.077438815621
H	3.887337307653	2.259949074080	3.614626114549	H	1.085632455586	-3.701877703455	2.424402107827
C	-2.437865801582	-1.756838072677	-1.923898263142	H	-0.427974879777	-3.017798621098	1.838239899073
H	-3.404645463545	-1.302880911996	-2.169465417950	Li	-1.266298119900	0.822473026186	-0.826611352850
C	-2.522262012030	-2.165529776008	-0.452419199908	Li	0.363871797572	-1.350451296531	-1.041671447474
H	-3.422119429659	-2.741111609950	-0.248295330057				
H	-2.522428940757	-1.299722266366	0.197803417075				
H	-1.672303652572	-2.777386494746	-0.174514062990				
C	-2.347162493050	-3.043032095251	-2.768567357491				
H	-2.422065023332	-2.848581994529	-3.832348602576				
H	-3.147464029216	-3.733893868851	-2.511568245654				
H	-1.398990676149	-3.547705766592	-2.593218940688				
C	-1.166249820832	-0.434572936796	-3.503093214122				
H	-0.856312379509	-1.286545806650	-4.118755999699				
C	-0.045187825762	0.599675464060	-3.614368268292				
H	0.214410368267	0.798134177702	-4.651712564808				
H	0.848107800572	0.266203977484	-3.102108733812				
H	-0.343264313452	1.539540025476	-3.165013898868				
C	-2.419601212189	0.148146465904	-4.185446659447				
H	-3.222495973325	-0.575333878139	-4.269050551385				
H	-2.190216831254	0.490714191423	-5.192343150337				
H	-2.800469282944	0.997228210979	-3.620993501402				
C	-2.986299858340	3.079166898628	0.416728904439				
H	-3.417270054951	3.544500846429	1.305010378589				
H	-3.629910773420	3.352736750750	-0.408110235602				
C	-1.595603482727	3.656560149797	0.193203108608				
H	-1.661080423652	4.745925720510	0.262819610802				
H	-0.933950865108	3.332995350602	0.985917448716				
C	-2.650053956266	1.221784193847	1.906183339084				
H	-1.678286335721	1.604695043831	2.179545101646				
H	-2.610176177063	0.143159770425	1.975039860943				
H	-3.382402970258	1.585493789188	2.629596943790				
C	-4.315213893086	1.100590440051	0.196122252071				
H	-4.532226007866	1.311195077716	-0.843611656306				
H	-5.103225629545	1.539716764668	0.811236765237				
H	-4.338851751380	0.029190397749	0.332122932348				
C	0.409823893130	3.641245497516	-1.098915839130				
H	0.873681043698	3.285004712467	-2.009714639564				
H	0.926756722405	3.202654822634	-0.258690078900				
H	0.533406595836	4.725766592584	-1.054979705533				
C	-1.681329262782	3.867391649787	-2.211415529373				
H	-2.689900480060	3.490874317910	-2.310278527452				
H	-1.155971290100	3.628339162820	-3.125614893199				
H	-1.725940254489	4.955182472001	-2.121598258579				
C	2.996185488352	-3.002434915244	-1.185010512817				

Table 5.31 Signed and Unsigned differences in bond length for the HF/6-31G(d) structure of JAYF relative to B3LYP/6-31+G(d)

					Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
					R(47,50)	1.1054	1.0918	-0.0136	0.0136
					R(51,53)	1.1054	1.0919	-0.0135	0.0135
					R(41,42)	1.1053	1.0915	-0.0138	0.0138
					R(81,83)	1.1053	1.0919	-0.0134	0.0134
					R(37,40)	1.0997	1.0884	-0.0113	0.0113
Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)	R(27,30)	1.0996	1.0883	-0.0113	0.0113
R(85,86)	2.6910	2.7249	0.0339	0.0339	R(27,29)	1.0991	1.0880	-0.0111	0.0111
R(3,85)	2.4109	2.4266	0.0157	0.0157	R(37,39)	1.0990	1.0880	-0.0110	0.0110
R(6,86)	2.3950	2.4099	0.0149	0.0149	R(33,34)	1.0981	1.0876	-0.0105	0.0105
R(5,86)	2.3548	2.3912	0.0364	0.0364	R(23,24)	1.0980	1.0875	-0.0105	0.0105
R(4,85)	2.3431	2.3496	0.0065	0.0065	R(23,26)	1.0959	1.0835	-0.0124	0.0124
R(1,86)	2.0718	2.0991	0.0273	0.0273	R(27,28)	1.0956	1.0840	-0.0116	0.0116
R(1,85)	2.0708	2.0880	0.0172	0.0172	R(37,38)	1.0955	1.0840	-0.0115	0.0115
R(2,86)	2.0635	2.0819	0.0184	0.0184	R(33,36)	1.0952	1.0836	-0.0116	0.0116
R(2,85)	2.0623	2.0821	0.0198	0.0198	R(66,68)	1.0950	1.0821	-0.0129	0.0129
R(31,37)	1.5488	1.5414	-0.0074	0.0074	R(44,46)	1.0947	1.0821	-0.0126	0.0126
R(21,27)	1.5487	1.5414	-0.0073	0.0073	R(23,25)	1.0945	1.0828	-0.0117	0.0117
R(21,23)	1.5354	1.5295	-0.0059	0.0059	R(33,35)	1.0944	1.0824	-0.0120	0.0120
R(31,33)	1.5352	1.5293	-0.0059	0.0059	R(41,43)	1.0943	1.0814	-0.0129	0.0129
R(41,44)	1.5272	1.5223	-0.0049	0.0049	R(51,52)	1.0943	1.0828	-0.0115	0.0115
R(63,66)	1.5267	1.5220	-0.0047	0.0047	R(73,74)	1.0943	1.0829	-0.0114	0.0114
R(4,41)	1.4770	1.4635	-0.0135	0.0135	R(55,56)	1.0942	1.0824	-0.0118	0.0118
R(5,63)	1.4764	1.4630	-0.0134	0.0134	R(63,65)	1.0942	1.0814	-0.0128	0.0128
R(6,66)	1.4752	1.4614	-0.0138	0.0138	R(81,84)	1.0941	1.0822	-0.0119	0.0119
R(3,44)	1.4749	1.4605	-0.0144	0.0144	R(47,49)	1.0935	1.0816	-0.0119	0.0119
R(4,47)	1.4726	1.4602	-0.0124	0.0124	R(69,71)	1.0935	1.0816	-0.0119	0.0119
R(5,69)	1.4722	1.4600	-0.0122	0.0122	R(59,60)	1.0930	1.0811	-0.0119	0.0119
R(6,81)	1.4714	1.4596	-0.0118	0.0118	R(77,79)	1.0930	1.0811	-0.0119	0.0119
R(3,55)	1.4710	1.4590	-0.0120	0.0120	R(59,61)	1.0929	1.0812	-0.0117	0.0117
R(4,51)	1.4708	1.4587	-0.0121	0.0121	R(77,78)	1.0929	1.0811	-0.0118	0.0118
R(5,73)	1.4708	1.4583	-0.0125	0.0125	R(51,54)	1.0924	1.0803	-0.0121	0.0121
R(3,59)	1.4700	1.4574	-0.0126	0.0126	R(69,70)	1.0923	1.0800	-0.0123	0.0123
R(6,77)	1.4699	1.4579	-0.0120	0.0120	R(73,76)	1.0922	1.0803	-0.0119	0.0119
R(2,21)	1.4671	1.4561	-0.0110	0.0110	R(55,57)	1.0920	1.0796	-0.0124	0.0124
R(2,31)	1.4671	1.4561	-0.0110	0.0110	R(47,48)	1.0916	1.0797	-0.0119	0.0119
R(7,10)	1.4523	1.4545	0.0022	0.0022	R(81,82)	1.0913	1.0790	-0.0123	0.0123
R(10,11)	1.4170	1.4032	-0.0138	0.0138	R(13,14)	1.0887	1.0771	-0.0116	0.0116
R(10,19)	1.4163	1.4025	-0.0138	0.0138	R(19,20)	1.0887	1.0766	-0.0121	0.0121
R(15,17)	1.4003	1.3871	-0.0132	0.0132	R(17,18)	1.0884	1.0769	-0.0115	0.0115
R(13,15)	1.3998	1.3859	-0.0139	0.0139	R(11,12)	1.0880	1.0762	-0.0118	0.0118
R(11,13)	1.3941	1.3830	-0.0111	0.0111	R(7,8)	1.0877	1.0744	-0.0133	0.0133
R(17,19)	1.3934	1.3815	-0.0119	0.0119	R(15,16)	1.0868	1.0753	-0.0115	0.0115
R(7,9)	1.3631	1.3568	-0.0063	0.0063					
R(1,9)	1.1955	1.1704	-0.0251	0.0251					
R(31,32)	1.1114	1.0959	-0.0155	0.0155					
R(21,22)	1.1112	1.0959	-0.0153	0.0153					
R(44,45)	1.1074	1.0935	-0.0139	0.0139					
R(66,67)	1.1073	1.0934	-0.0139	0.0139					
R(59,62)	1.1062	1.0924	-0.0138	0.0138					
R(77,80)	1.1061	1.0922	-0.0139	0.0139					
R(55,58)	1.1058	1.0924	-0.0134	0.0134					
R(69,72)	1.1058	1.0921	-0.0137	0.0137					
R(63,64)	1.1056	1.0916	-0.0140	0.0140					
R(73,75)	1.1056	1.0920	-0.0136	0.0136					

5.4.3.10 B3LYP/6-31(+LiX)G(d)

N	0.426583905576	0.281419331756	0.208077989728				
N	-1.332087358497	-0.806643394035	-2.143609601617	C	2.959398466503	-2.950397266385	-1.056365192749
N	-0.997652679380	3.159935683709	-1.033619068472	H	4.062307545679	-2.960684679869	-0.993575571344
N	-3.003207063176	1.484640242546	0.551032794510	H	2.674810699005	-3.877443150084	-1.562936707843
N	2.494943075145	-1.817139987567	-1.880816981286	C	2.385669245417	-2.938127517517	0.358614406003
N	0.922977616200	-3.122942953519	0.394513813323	H	2.892286361683	-3.724698669795	0.950209595984
C	2.154580993770	1.332401258507	1.773097879774	H	2.608384947464	-1.982229348925	0.844074211010
H	2.960483712684	1.890372798261	1.303124107611	C	3.314099342932	-0.624347783347	-1.613011033203
C	1.230071121435	0.770656337145	0.946953930345	H	3.272805854206	-0.362618336818	-0.553531847995
C	2.122728601815	1.251675353095	3.223645693736	H	2.928044009257	0.224869091337	-2.182879988022
C	1.099283417704	0.586110157896	3.940262487194	H	4.370135951159	-0.786779522860	-1.896716179635
H	0.290703643919	0.109843265897	3.389579373954	C	2.581329092456	-2.167719479599	-3.305626495289
C	1.104611877701	0.529402539112	5.331294691209	H	1.915424711396	-3.008465828898	-3.522604182483
H	0.299979389164	0.006538111435	5.844909516627	H	3.608917182940	-2.444970454718	-3.603593904989
C	2.125227584157	1.134882885072	6.069903481015	H	2.265757394325	-1.318726481061	-3.916165634809
H	2.126763624519	1.090012576883	7.155409041965	C	0.544785755976	-4.479584619331	-0.024900296879
C	3.143437256977	1.800449164230	5.380814097546	H	0.774259938182	-4.643086450865	-1.080661645993
H	3.948664072071	2.280487984853	5.933200309054	H	-0.532109973863	-4.613383367418	0.102302796502
C	3.144122433941	1.858386645506	3.990339943647	H	1.061870751525	-5.253589587689	0.571793045375
H	3.947233634193	2.380950075720	3.474176859977	C	0.443401785945	-2.890540541439	1.765128916768
C	-2.453867347415	-1.741511447859	-1.998143876938	H	0.713946912935	-1.882610006534	2.084169662353
H	-3.422384851666	-1.257332597931	-2.246220346082	H	0.874353326766	-3.615659157335	2.478954281195
C	-2.564718475424	-2.195411019099	-0.536681969034	H	-0.645841862583	-2.984208090077	1.794217376876
H	-3.485700214485	-2.765867491504	-0.359612390018	Li	-1.269926181216	0.794939304763	-0.838270366373
H	-2.553512616657	-1.340930043795	0.147173139287	Li	0.334188498099	-1.352299901998	-1.057517844526
H	-1.718376448843	-2.836692618708	-0.268805574728				
C	-2.376655753826	-3.006195547048	-2.886347436549				
H	-2.414827876695	-2.769878471707	-3.954745952112				
H	-3.209873627551	-3.688992122971	-2.672610553236				
H	-1.436094267919	-3.544210808615	-2.698461928456				
C	-1.142874983101	-0.389621305032	-3.537912991628				
H	-0.870325238518	-1.248039942969	-4.187077294087				
C	0.026397345224	0.599347169515	-3.630315378464				
H	0.264803152805	0.844694796218	-4.673321644400				
H	0.925844753191	0.190629054107	-3.160658475758				
H	-0.212917669012	1.534876313156	-3.112411328296				
C	-2.382175532513	0.258905623960	-4.200351408823				
H	-3.228140632009	-0.433255468658	-4.264951096296				
H	-2.154757003424	0.594353754936	-5.221115304656				
H	-2.712558619451	1.131792972883	-3.619172106073				
C	-3.000497637794	2.958038002278	0.459460200419				
H	-3.444454924261	3.405992399360	1.366697737490				
H	-3.650537690514	3.245227900091	-0.372498440025				
C	-1.607789924959	3.548248516183	0.250957006568				
H	-1.678088193278	4.649814818607	0.334671709797				
H	-0.937343305971	3.212821391289	1.048413964056				
C	-2.626210680648	1.053119318209	1.906468331737				
H	-1.629928611902	1.419149207413	2.161191408333				
H	-2.600529821376	-0.038839769014	1.951147403238				
H	-3.343140387668	1.418708076032	2.664019224471				
C	-4.340846072927	0.971086347634	0.222201859479				
H	-4.593773443410	1.229166713732	-0.810468149087				
H	-5.118789587287	1.383238242002	0.890407712455				
H	-4.352830135854	-0.117002523592	0.312405054056				
C	0.413680683808	3.573137327546	-1.043536257664				
H	0.892125233159	3.225332411554	-1.963552214352				
H	0.934889530550	3.132310639162	-0.191185771783				
H	0.517345918994	4.672495744486	-0.991789024903				
C	-1.689790308882	3.789425071245	-2.166443589893				
H	-2.716049585922	3.424313549719	-2.253416390048				
H	-1.171065869813	3.537599629283	-3.094563528355				
H	-1.716268943197	4.890911662605	-2.071674336358				

Table 5.32 Signed and Unsigned differences in bond length for the B3LYP/6-31(+LiX)G(d) structure of JAYFIY relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(85,86)	2.6910	2.6892	-0.0018	0.0018
R(3,85)	2.4109	2.3886	-0.0223	0.0223
R(6,86)	2.3950	2.3644	-0.0306	0.0306
R(5,86)	2.3548	2.3586	0.0038	0.0038
R(4,85)	2.3431	2.3260	-0.0171	0.0171
R(1,86)	2.0718	2.0686	-0.0032	0.0032
R(1,85)	2.0708	2.0583	-0.0125	0.0125
R(2,86)	2.0635	2.0625	-0.001	0.001
R(2,85)	2.0623	2.0671	0.0048	0.0048
R(31,37)	1.5488	1.5477	-0.0011	0.0011
R(21,27)	1.5487	1.5474	-0.0013	0.0013
R(21,23)	1.5354	1.5343	-0.0011	0.0011
R(31,33)	1.5352	1.5342	-0.0010	0.0010
R(41,44)	1.5272	1.5269	-0.0003	0.0003
R(63,66)	1.5267	1.5269	0.0002	0.0002
R(4,41)	1.4770	1.4762	-0.0008	0.0008
R(5,63)	1.4764	1.4764	0.0000	0.0000
R(6,66)	1.4752	1.4748	-0.0004	0.0004
R(3,44)	1.4749	1.4742	-0.0007	0.0007
R(4,47)	1.4726	1.4716	-0.0010	0.0010
R(5,69)	1.4722	1.4716	-0.0006	0.0006
R(6,81)	1.4714	1.4706	-0.0008	0.0008
R(3,55)	1.4710	1.4706	-0.0004	0.0004
R(4,51)	1.4708	1.4701	-0.0007	0.0007
R(5,73)	1.4708	1.4698	-0.0010	0.0010
R(3,59)	1.4700	1.4692	-0.0008	0.0008
R(6,77)	1.4699	1.4695	-0.0004	0.0004
R(2,21)	1.4671	1.4675	0.0004	0.0004
R(2,31)	1.4671	1.4676	0.0005	0.0005
R(7,10)	1.4523	1.4531	0.0008	0.0008
R(10,11)	1.4170	1.4156	-0.0014	0.0014
R(10,19)	1.4163	1.4139	-0.0024	0.0024
R(15,17)	1.4003	1.3981	-0.0022	0.0022
R(13,15)	1.3998	1.3978	-0.0020	0.0020
R(11,13)	1.3941	1.3922	-0.0019	0.0019
R(17,19)	1.3934	1.3917	-0.0017	0.0017
R(7,9)	1.3631	1.3612	-0.0019	0.0019
R(1,9)	1.1955	1.1962	0.0007	0.0007
R(31,32)	1.1114	1.1102	-0.0012	0.0012
R(21,22)	1.1112	1.1109	-0.0003	0.0003
R(44,45)	1.1074	1.1070	-0.0004	0.0004
R(66,67)	1.1073	1.1070	-0.0003	0.0003
R(59,62)	1.1062	1.1059	-0.0003	0.0003
R(77,80)	1.1061	1.1057	-0.0004	0.0004
R(55,58)	1.1058	1.1054	-0.0004	0.0004
R(69,72)	1.1058	1.1055	-0.0003	0.0003
R(63,64)	1.1056	1.1047	-0.0009	0.0009
R(73,75)	1.1056	1.1053	-0.0003	0.0003

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(47,50)	1.1054	1.1052	-0.0002	0.0002
R(51,53)	1.1054	1.1052	-0.0002	0.0002
R(41,42)	1.1053	1.1049	-0.0004	0.0004
R(81,83)	1.1053	1.1050	-0.0003	0.0003
R(37,40)	1.0997	1.0995	-0.0002	0.0002
R(27,30)	1.0996	1.0997	1E-04	1E-04
R(27,29)	1.0991	1.0982	-0.0009	0.0009
R(37,39)	1.0990	1.0983	-0.0007	0.0007
R(33,34)	1.0981	1.0977	-0.0004	0.0004
R(23,24)	1.0980	1.0977	-0.0003	0.0003
R(23,26)	1.0959	1.0951	-0.0008	0.0008
R(27,28)	1.0956	1.0949	-0.0007	0.0007
R(37,38)	1.0955	1.0950	-0.0005	0.0005
R(33,36)	1.0952	1.0958	0.0006	0.0006
R(66,68)	1.0950	1.0950	0.0000	0.0000
R(44,46)	1.0947	1.0945	-0.0002	0.0002
R(23,25)	1.0945	1.0945	0.0000	0.0000
R(33,35)	1.0944	1.0939	-0.0005	0.0005
R(41,43)	1.0943	1.0942	-1E-04	1E-04
R(51,52)	1.0943	1.0941	-0.0002	0.0002
R(73,74)	1.0943	1.0942	-1E-04	1E-04
R(55,56)	1.0942	1.0938	-0.0004	0.0004
R(63,65)	1.0942	1.0941	-1E-04	1E-04
R(81,84)	1.0941	1.0937	-0.0004	0.0004
R(47,49)	1.0935	1.0932	-0.0003	0.0003
R(69,71)	1.0935	1.0931	-0.0004	0.0004
R(59,60)	1.0930	1.0927	-0.0003	0.0003
R(77,79)	1.0930	1.0926	-0.0004	0.0004
R(59,61)	1.0929	1.0927	-0.0002	0.0002
R(77,78)	1.0929	1.0927	-0.0002	0.0002
R(51,54)	1.0924	1.0919	-0.0005	0.0005
R(69,70)	1.0923	1.0921	-0.0002	0.0002
R(73,76)	1.0922	1.0923	1E-04	1E-04
R(55,57)	1.0920	1.0920	0.0000	0.0000
R(47,48)	1.0916	1.0915	-1E-04	1E-04
R(81,82)	1.0913	1.0913	0.0000	0.0000
R(13,14)	1.0887	1.0884	-0.0003	0.0003
R(19,20)	1.0887	1.0883	-0.0004	0.0004
R(17,18)	1.0884	1.0881	-0.0003	0.0003
R(11,12)	1.0880	1.0881	1E-04	1E-04
R(7,8)	1.0877	1.0871	-0.0006	0.0006
R(15,16)	1.0868	1.0864	-0.0004	0.0004

5.4.3.11 B3LYP/6-31'+G(d)

N	0.453395582616	0.326532232109	0.202011529069	H	-1.630071815532	4.951118064658	-2.156075360805
N	-1.342174565028	-0.821032235889	-2.101679417121	C	2.979963311109	-2.925712976700	-1.223900384131
N	-0.946333972742	3.202550507075	-1.126525288314	H	4.084998588346	-2.953670366931	-1.242952987987
N	-2.947276020309	1.589035506453	0.537465976454	H	2.642464677854	-3.835300203919	-1.729766646147
N	2.479122415735	-1.767229962387	-1.989280019490	C	2.511607163750	-2.938231762523	0.229052882238
N	1.052390141654	-3.101624897869	0.368017520066	H	3.048140214676	-3.745735308579	0.762937832704
C	2.133547134244	1.265971569764	1.887143436709	H	2.786192911841	-1.998315426896	0.719325844874
H	2.986360547720	1.800274840110	1.474411737771	C	3.305400135174	-0.579414260851	-1.719708381820
C	1.233354995718	0.763489896556	0.995464078176	H	3.301229054854	-0.345696330064	-0.652923951024
C	2.019516742197	1.161361940464	3.330895460355	H	2.897709403971	0.283417728382	-2.253167902379
C	0.936388581879	0.522484164764	3.983346809410	H	4.351127925291	-0.732588822888	-2.045109762667
H	0.139471244787	0.084585888679	3.386226590334	C	2.506613591841	-2.075272818845	-3.426756437118
C	0.869096304401	0.444952449088	5.373701258333	H	1.829152336464	-2.907551366247	-3.640547742135
H	0.020495444631	-0.055258674245	5.836791308883	H	3.521992103201	-2.346711418136	-3.770215223584
C	1.872540229567	1.000742578746	6.174966181895	H	2.171760482514	-1.208008447939	-3.999711930916
H	1.815455721032	0.938748694261	7.258479711531	C	0.625704740192	-4.451402862546	-0.026272329538
C	2.949628714230	1.638927202404	5.548586010362	H	0.798379705866	-4.623403820811	-1.091475732800
H	3.742227068551	2.080112758522	6.149127285031	H	-0.446088623675	-4.562050345880	0.155666969682
C	3.022666594620	1.717659956370	4.161089094167	H	1.156518633202	-5.233609732473	0.547148529491
H	3.869424536027	2.217645214022	3.693884190417	C	0.671856807556	-2.866602376592	1.769712723032
C	-2.430990199635	-1.782496948797	-1.895826064261	H	0.980265990671	-1.865243608899	2.074403570550
H	-3.416334134954	-1.345556012453	-2.163797239654	H	1.139381634024	-3.601464079548	2.449544796621
C	-2.519428164845	-2.154408119344	-0.409440012351	H	-0.414415804643	-2.942292402835	1.873380986771
H	-3.405457428050	-2.767596018515	-0.199907520766	Li	-1.259453966070	0.812199593756	-0.852098598608
H	-2.564779415171	-1.261280491232	0.221460937133	Li	0.356477455472	-1.324939885990	-1.055316661399
H	-1.637336738587	-2.725240799546	-0.098341198513				
C	-2.315580866525	-3.090414286472	-2.714671335105				
H	-2.354651061259	-2.910602272951	-3.794140460002				
H	-3.131188384181	-3.783644217955	-2.468752066445				
H	-1.362177071081	-3.592863793699	-2.496415766078				
C	-1.185965851755	-0.455905762579	-3.514265833694				
H	-0.87171716132904	-1.326513027670	-4.128163540995				
C	-0.074132403731	0.591724829270	-3.658278032049				
H	0.162210391004	0.786322546909	-4.712443792371				
H	0.842530722036	0.268628444901	-3.155778802044				
H	-0.376038911639	1.540668302309	-3.202235517830				
C	-2.460959930416	0.099026069928	-4.193379118308				
H	-3.268541425538	-0.639465741526	-4.230445257158				
H	-2.254527436033	0.410160257625	-5.226206271946				
H	-2.835769069224	0.973082442447	-3.640971250045				
C	-2.920613322862	3.059910295115	0.409122274065				
H	-3.343237189141	3.537389974285	1.311275115507				
H	-3.577317423602	3.339064484130	-0.420312210179				
C	-1.519665770431	3.617478427645	0.166749063028				
H	-1.562694612051	4.721835714844	0.236888318620				
H	-0.840724540740	3.276785720578	0.954929354723				
C	-2.572213755392	1.189383067844	1.903840046516				
H	-1.578346830802	1.565879256653	2.152867905046				
H	-2.542569927867	0.098856287795	1.975279271870				
H	-3.291816213982	1.571487137808	2.650256232364				
C	-4.293911298976	1.087156914407	0.226052518083				
H	-4.545742844458	1.321048846896	-0.812708234999				
H	-5.062750073031	1.529201981250	0.885189542825				
H	-4.322463529553	0.001995106184	0.345814660265				
C	0.478850682261	3.561853301131	-1.168824360157				
H	0.919193292326	3.205603104800	-2.104899884395				
H	1.003151172499	3.089303371910	-0.335738171002				
H	0.626048497072	4.656200981521	-1.108050595052				
C	-1.640829754735	3.848649439725	-2.248712688562				
H	-2.679807866903	3.515899011723	-2.313387997115				
H	-1.148919794176	3.579489831071	-3.186595156246				

Table 5.33 Signed and Unsigned differences in bond length for the B3LYP/6-31'+G(d) structure of JAYFIY relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(85,86)	2.6910	2.6870	-0.0040	0.0040
R(3,85)	2.4109	2.4263	0.0154	0.0154
R(6,86)	2.3950	2.3805	-0.0145	0.0145
R(5,86)	2.3548	2.3608	0.0060	0.0060
R(4,85)	2.3431	2.3202	-0.0229	0.0229
R(1,86)	2.0718	2.0779	0.0061	0.0061
R(1,85)	2.0708	2.0690	-0.0018	0.0018
R(2,86)	2.0635	2.0577	-0.0058	0.0058
R(2,85)	2.0623	2.0581	-0.0042	0.0042
R(31,37)	1.5488	1.5475	-0.0013	0.0013
R(21,27)	1.5487	1.5474	-0.0013	0.0013
R(21,23)	1.5354	1.5348	-0.0006	0.0006
R(31,33)	1.5352	1.5344	-0.0008	0.0008
R(41,44)	1.5272	1.5272	0.0000	0.0000
R(63,66)	1.5267	1.5266	-1E-04	1E-04
R(4,41)	1.4770	1.4767	-0.0003	0.0003
R(5,63)	1.4764	1.4761	-0.0003	0.0003
R(6,66)	1.4752	1.4749	-0.0003	0.0003
R(3,44)	1.4749	1.4743	-0.0006	0.0006
R(4,47)	1.4726	1.4722	-0.0004	0.0004
R(5,69)	1.4722	1.4718	-0.0004	0.0004
R(6,81)	1.4714	1.4713	-1E-04	1E-04
R(3,55)	1.4710	1.4704	-0.0006	0.0006
R(4,51)	1.4708	1.4705	-0.0003	0.0003
R(5,73)	1.4708	1.4704	-0.0004	0.0004
R(3,59)	1.4700	1.4694	-0.0006	0.0006
R(6,77)	1.4699	1.4695	-0.0004	0.0004
R(2,21)	1.4671	1.4671	0.0000	0.0000
R(2,31)	1.4671	1.4674	0.0003	0.0003
R(7,10)	1.4523	1.4520	-0.0003	0.0003
R(10,11)	1.4170	1.4167	-0.0003	0.0003
R(10,19)	1.4163	1.4160	-0.0003	0.0003
R(15,17)	1.4003	1.3999	-0.0004	0.0004
R(13,15)	1.3998	1.3992	-0.0006	0.0006
R(11,13)	1.3941	1.3941	0.0000	0.0000
R(17,19)	1.3934	1.3916	-0.0018	0.0018
R(7,9)	1.3631	1.3631	0.0000	0.0000
R(1,9)	1.1955	1.1953	-0.0002	0.0002
R(31,32)	1.1114	1.1107	-0.0007	0.0007
R(21,22)	1.1112	1.1107	-0.0005	0.0005
R(44,45)	1.1074	1.1074	0.0000	0.0000
R(66,67)	1.1073	1.1068	-0.0005	0.0005
R(59,62)	1.1062	1.1064	0.0002	0.0002
R(77,80)	1.1061	1.1056	-0.0005	0.0005
R(55,58)	1.1058	1.1059	0.0001	0.0001
R(69,72)	1.1058	1.1058	0.0000	0.0000
R(63,64)	1.1056	1.1056	0.0000	0.0000
R(73,75)	1.1056	1.1057	1E-04	1E-04

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(47,50)	1.1054	1.1050	-0.0004	0.0004
R(51,53)	1.1054	1.1050	-0.0004	0.0004
R(41,42)	1.1053	1.1048	-0.0005	0.0005
R(81,83)	1.1053	1.1049	-0.0004	0.0004
R(37,40)	1.0997	1.0998	0.0001	0.0001
R(27,30)	1.0996	1.0996	0.0000	0.0000
R(27,29)	1.0991	1.0983	-0.0008	0.0008
R(37,39)	1.0990	1.0982	-0.0008	0.0008
R(33,34)	1.0981	1.0977	-0.0004	0.0004
R(23,24)	1.0980	1.0977	-0.0003	0.0003
R(23,26)	1.0959	1.0958	-1E-04	1E-04
R(27,28)	1.0956	1.0950	-0.0006	0.0006
R(37,38)	1.0955	1.0950	-0.0005	0.0005
R(33,36)	1.0952	1.0953	1E-04	1E-04
R(66,68)	1.0950	1.0951	1E-04	1E-04
R(44,46)	1.0947	1.0947	0.0000	0.0000
R(23,25)	1.0945	1.0944	-1E-04	1E-04
R(33,35)	1.0944	1.0942	-0.0002	0.0002
R(41,43)	1.0943	1.0941	-0.0002	0.0002
R(51,52)	1.0943	1.0941	-0.0002	0.0002
R(73,74)	1.0943	1.0942	-1E-04	1E-04
R(55,56)	1.0942	1.0941	-1E-04	1E-04
R(63,65)	1.0942	1.0941	-1E-04	1E-04
R(81,84)	1.0941	1.0938	-0.0003	0.0003
R(47,49)	1.0935	1.0933	-0.0002	0.0002
R(69,71)	1.0935	1.0933	-0.0002	0.0002
R(59,60)	1.0930	1.0929	-1E-04	1E-04
R(77,79)	1.0930	1.0927	-0.0003	0.0003
R(59,61)	1.0929	1.0927	-0.0002	0.0002
R(77,78)	1.0929	1.0927	-0.0002	0.0002
R(51,54)	1.0924	1.0921	-0.0003	0.0003
R(69,70)	1.0923	1.0921	-0.0002	0.0002
R(73,76)	1.0922	1.0920	-0.0002	0.0002
R(55,57)	1.0920	1.0919	-1E-04	1E-04
R(47,48)	1.0916	1.0916	0.0000	0.0000
R(81,82)	1.0913	1.0912	-1E-04	1E-04
R(13,14)	1.0887	1.0885	-0.0002	0.0002
R(19,20)	1.0887	1.0887	0.0000	0.0000
R(17,18)	1.0884	1.0879	-0.0005	0.0005
R(11,12)	1.0880	1.0878	-0.0002	0.0002
R(7,8)	1.0877	1.0877	0.0000	0.0000
R(15,16)	1.0868	1.0868	0.0000	0.0000

5.4.3.12 B3LYP/6-31+G(d)

N	-0.441872773042	0.005577455602	-0.389440284131				
N	2.598993135113	0.041151035802	0.386683729785	H	2.399576051288	-4.190814433483	-1.161695081059
N	0.689188715541	-3.026018836477	-1.645000488283	H	2.512234462476	-3.278529845496	-2.666445707038
N	0.406819404919	-3.072170432140	1.405561170159	H	1.514062125069	-4.752879343463	-2.606393942721
N	1.091328714475	3.079362605826	-1.612114106773	C	0.480383795274	4.240209807749	-0.934657078930
N	-0.079789442547	3.087434692931	1.220096837471	H	0.045141371267	4.936304428037	-1.675146931398
C	-2.823613952630	0.051062015071	-1.322902316684	H	1.277596561293	4.792687942027	-0.428139756905
H	-2.918647096900	0.138282263947	-2.402888300096	C	-0.600571272425	3.852922943093	0.071556427463
C	-1.558248063455	0.026682878991	-0.816736711950	H	-1.107255394483	4.775276548328	0.415972514541
C	-4.035703443610	-0.048245612992	-0.529003129179	H	-1.363300871851	3.237793244855	-0.417105971194
C	-4.033380708679	-0.192120707027	0.880665581636	C	0.232639770057	2.617343706242	-2.715030608555
H	-3.083097751050	-0.232701722295	1.408876733468	H	-0.754747348537	2.337838243675	-2.340922837430
C	-5.220547157209	-0.283855628743	1.605765383194	H	0.675514475031	1.733195822746	-3.181721453736
H	-5.175154274242	-0.392045973302	2.688097974791	H	0.111428196986	3.398891819944	-3.487817726153
C	-6.462435219998	-0.238897151731	0.961350544138	C	2.413458698896	3.453871363640	-2.136584277810
H	-7.386280191217	-0.311019972513	1.529134165338	H	3.079048709746	3.719381640117	-1.309538815162
C	-6.486484592721	-0.099772527184	-0.431818445370	H	2.352708517328	4.310873742877	-2.832401060063
H	-7.438961998793	-0.063022262793	-0.957181857364	H	2.855214028185	2.609852376277	-2.670736937017
C	-5.302636751952	-0.006363130221	-1.160694387307	C	0.745898971127	3.932826053826	2.094239750852
H	-5.346090497033	0.101210020042	-2.243156443852	H	1.648740135972	4.269954041702	1.578808459328
C	3.093957606060	0.137920582803	1.764344064045	H	1.060891536683	3.357311451925	2.968451040963
H	3.652984042237	-0.775329096466	2.061485776031	H	0.189782261144	4.821443143194	2.447200640117
C	1.908579320781	0.247484688023	2.733974464534	C	-1.208197240537	2.549834846621	1.996463685357
H	2.237218212506	0.183628761830	3.779679776435	H	-1.830750049507	1.920526474041	1.358319540768
H	1.176067354632	-0.546212964366	2.557042621065	H	-1.835537675838	3.356717704443	2.417332779936
H	1.388605764029	1.203543991944	2.605539036383	H	-0.829476012745	1.940303356356	2.822414285649
C	4.052507823159	1.323112242634	2.038124697194	Li	1.097169799774	-1.321111274819	0.010129098829
H	4.980522067169	1.251314689229	1.460182446678	Li	1.066312466300	1.369663587701	0.007001119863
H	4.331944478406	1.364659581860	3.100253014867				
H	3.569867781863	2.275308253646	1.774591351438				
C	3.690362641679	-0.020771094283	-0.591835718100				
H	4.276480252312	0.923349004582	-0.608596249795				
C	3.112383481946	-0.190523637429	-2.003946492519				
H	3.890407013944	-0.087339640367	-2.771914271491				
H	2.331785626883	0.549515958985	-2.205704233386				
H	2.658664734392	-1.180651424503	-2.119239939988				
C	4.722924660467	-1.150814385760	-0.356293235058				
H	5.269008982289	-1.027399046795	0.585326367818				
H	5.467122344370	-1.176710401713	-1.164582313236				
H	4.219628680849	-2.128061236321	-0.323219241983				
C	0.183668539730	-4.218423561537	0.501167027345				
H	-0.544678363276	-4.923818178604	0.941123519877				
H	1.125410934458	-4.768605013212	0.412747934192				
C	-0.305586817957	-3.806543227158	-0.885625328346				
H	-0.591162116005	-4.719671386293	-1.443235995408				
H	-1.208953776653	-3.194671304667	-0.796750153447				
C	-0.866046778785	-2.640746616927	2.007470953652				
H	-1.583126541386	-2.366386010004	1.231441776118				
H	-0.699799263901	-1.760194489686	2.634159718342				
H	-1.308720422685	-3.438154125282	2.631970178096				
C	1.352518580673	-3.453055030309	2.465621581347				
H	2.322228077486	-3.704500188935	2.025162337951				
H	0.991774718780	-4.321155458744	3.047164906233				
H	1.498594721750	-2.616812448784	3.153133238564				
C	0.057179413373	-2.476005819160	-2.854032415396				
H	0.774170550554	-1.846438595464	-3.389575328613				
H	-0.802972375310	-1.863902511158	-2.574875254730				
H	-0.282836356795	-3.276227743992	-3.537203600340				
C	1.834322451302	-3.860286711126	-2.036804248061				

5.4.4 FAHBEV bis((μ 2-Benzylcyano-N)-(N,N,N',N'-tetramethyl-ethylenediamine-N,N')-lithium) benzene solvate

Reported below are the raw bond length data for each of the test functional/basis set combinations for FAHBEV. For reference, Figure 516 defines all atomic labels for the FAHBEV structures.

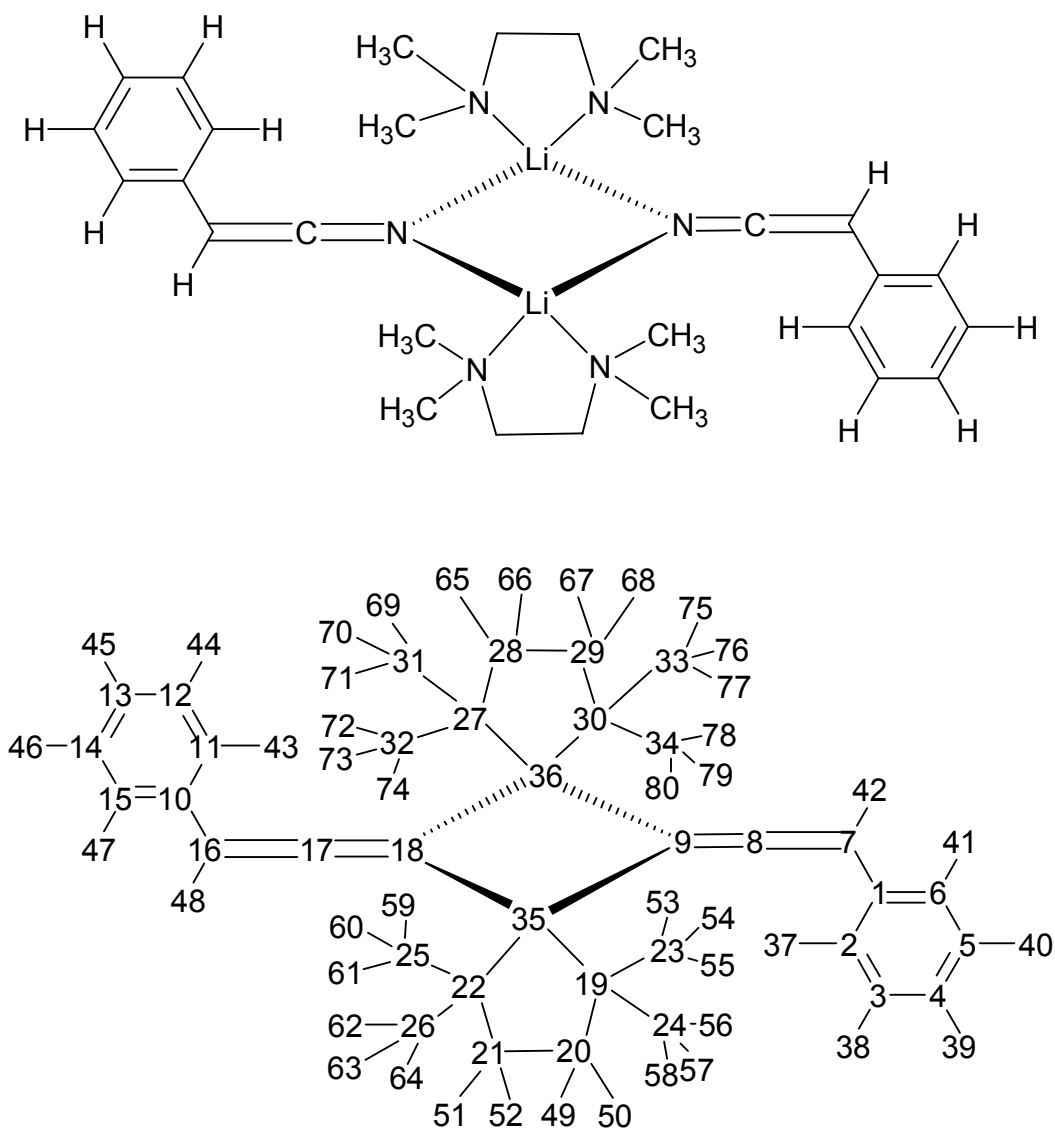


Figure 5.16 Atomic labels for FAHBEV

Bond list	PM3	B3LYP/ 3-21G	MPWLTP/ 3-21G	B3LYP/ Midi!+	MPW1PW91/ Midi!+	B3LYP/ 6-31G(d)	HF/6- 31G(d)	B3LYP/6- 31(+LX)G(d)	B3LYP/6- 31+*G(d)	B3LYP/ 6- 31+G(d)
<i>long</i>	R(35,36)	2.8083	2.6176	2.6225	2.5983	--	2.7106	2.6412	2.6507	2.6515
	R(19,35)	2.1845	2.0644	2.0742	2.0541	--	2.1608	2.1385	2.1382	2.1478
	R(30,36)	2.1845	2.0643	2.0743	2.0499	--	2.1608	2.1385	2.1382	2.1478
	R(22,35)	2.1845	2.0653	2.0755	2.0431	--	2.1449	2.1362	2.1340	2.1459
	R(27,36)	2.1845	2.0653	2.0755	2.0489	--	2.1448	2.1362	2.1340	2.1459
	R(9,36)	2.0380	1.9901	2.0424	2.0321	--	2.0379	2.0240	2.0333	2.0272
	R(18,35)	2.0381	1.9902	2.0422	2.0384	--	2.0376	2.0240	2.0333	2.0271
	R(9,35)	2.0381	2.0356	1.9946	1.9664	--	2.0057	1.9989	2.0044	2.0065
	R(18,36)	2.0381	2.0355	1.9946	1.9689	--	2.0058	1.9989	2.0044	2.0065
	R(20,21)	1.5340	1.5362	1.5474	1.5422	--	1.5312	1.5314	1.5311	1.5313
	R(28,29)	1.5340	1.5362	1.5474	1.5421	--	1.5312	1.5314	1.5311	1.5313
	R(19,20)	1.5112	1.4981	1.5145	1.4887	--	1.4755	1.4758	1.4764	1.4766
	R(21,22)	1.5112	1.4977	1.5150	1.4877	--	1.4759	1.4758	1.4765	1.4766
	R(27,28)	1.5112	1.4977	1.5150	1.4882	--	1.4759	1.4758	1.4765	1.4766
	R(29,30)	1.5112	1.4981	1.5145	1.4874	--	1.4755	1.4758	1.4764	1.4766
	R(19,24)	1.4962	1.4951	1.5109	1.4838	--	1.4709	1.4709	1.4715	1.4719
<i>intermediate</i>	R(30,34)	1.4962	1.4951	1.5109	1.4832	--	1.4709	1.4709	1.4715	1.4719
	R(22,25)	1.4962	1.4950	1.5110	1.4833	--	1.4707	1.4709	1.4714	1.4718
	R(27,31)	1.4962	1.4950	1.5110	1.4839	--	1.4707	1.4709	1.4714	1.4718
	R(22,26)	1.4967	1.4943	1.5110	1.4825	--	1.4704	1.4699	1.4706	1.4710
	R(27,32)	1.4967	1.4943	1.5110	1.4841	--	1.4704	1.4699	1.4706	1.4710
	R(19,23)	1.4967	1.4950	1.5102	1.4830	--	1.4696	1.4695	1.4701	1.4706
	R(30,33)	1.4967	1.4951	1.5102	1.4814	--	1.4696	1.4695	1.4701	1.4706
	R(1,7)	1.4369	1.4521	1.4597	1.4470	--	1.4525	1.4537	1.4524	1.4529
	R(10,16)	1.4369	1.4521	1.4597	1.4459	--	1.4525	1.4537	1.4524	1.4529
	R(1,2)	1.4033	1.4185	1.4302	1.4169	--	1.4157	1.4158	1.4170	1.4169
	R(10,11)	1.4033	1.4185	1.4302	1.4168	--	1.4157	1.4158	1.4170	1.4169
	R(1,6)	1.4069	1.4163	1.4274	1.4148	--	1.4138	1.4134	1.4160	1.4159
	R(10,15)	1.4069	1.4163	1.4274	1.4151	--	1.4138	1.4134	1.4160	1.4159
	R(4,5)	1.3930	1.3992	1.4094	1.3982	--	1.3978	1.3979	1.4002	1.4002
	R(13,14)	1.3930	1.3992	1.4094	1.3984	--	1.3978	1.3979	1.4002	1.4002
	R(3,4)	1.3894	1.3989	1.4093	1.3980	--	1.3980	1.3980	1.3999	1.3999
	R(12,13)	1.3894	1.3989	1.4093	1.3977	--	1.3980	1.3980	1.3999	1.3999

Table 5.34 Raw bond length data for FAHBEV

Bond list (cont.)	PM3	B3LYP/ 3-21G	MPWLYP/ 3-21G	B3LYP/ Medi!	B3LYP/ Medi!+	MPW1PW91/ Medi!+	B3LYP/ 6-31G(d)	HF/6- 31G(d)	B3LYP/6- 31(+LX)G(d)	B3LYP/6- 31++G(d)	B3LYP/ 6- 31+G(d)
<i>int. (cont.)</i>	R(2,3)	1.3889	1.3922	1.4015	1.3910	--	1.3920	1.3827	1.3923	1.3940	1.3942
	R(11,12)	1.3889	1.3922	1.4015	1.3915	--	1.3920	1.3827	1.3923	1.3940	1.3942
	R(5,6)	1.3855	1.3917	1.4010	1.3907	--	1.3918	1.3820	1.3919	1.3933	1.3935
	R(14,15)	1.3855	1.3917	1.4010	1.3906	--	1.3919	1.3820	1.3919	1.3933	1.3935
	R(7,8)	1.3426	1.3531	1.3615	1.3629	--	1.3565	1.3517	1.3568	1.3593	1.3589
	R(16,17)	1.3426	1.3531	1.3615	1.3633	--	1.3565	1.3517	1.3568	1.3593	1.3589
	R(8,9)	1.2124	1.1996	1.2113	1.1918	--	1.1983	1.1734	1.1986	1.1974	1.1978
	R(17,18)	1.2124	1.1996	1.2113	1.1917	--	1.1983	1.1734	1.1986	1.1974	1.1978
	R(21,52)	1.1130	1.1031	1.1108	1.1073	--	1.1049	1.0917	1.1052	1.1050	1.1056
	R(28,65)	1.1130	1.1031	1.1108	1.1072	--	1.1049	1.0917	1.1052	1.1050	1.1056
	R(20,50)	1.1130	1.1033	1.1107	1.1067	--	1.1049	1.0917	1.1050	1.1049	1.1055
	R(29,67)	1.1025	1.1033	1.1107	1.1070	--	1.1049	1.0917	1.1050	1.1049	1.1055
	R(24,57)	1.1025	1.1026	1.1100	1.1078	--	1.1043	1.0914	1.1047	1.1046	1.1050
	R(34,79)	1.1025	1.1026	1.1100	1.1079	--	1.1043	1.0914	1.1047	1.1046	1.1050
	R(25,60)	1.1025	1.1026	1.1100	1.1078	--	1.1043	1.0914	1.1046	1.1044	1.1049
	R(31,71)	1.1018	1.1026	1.1100	1.1078	--	1.1043	1.0914	1.1046	1.1044	1.1049
<i>short</i>	R(23,55)	1.1018	1.1022	1.1096	1.1073	--	1.1039	1.0912	1.1044	1.1042	1.1046
	R(26,64)	1.1018	1.1022	1.1096	1.1076	--	1.1039	1.0912	1.1044	1.1041	1.1046
	R(32,73)	1.1018	1.1022	1.1096	1.1074	--	1.1039	1.0912	1.1044	1.1041	1.1046
	R(33,77)	1.1134	1.1022	1.1096	1.1074	--	1.1039	1.0912	1.1044	1.1042	1.1046
	R(20,49)	1.1134	1.0937	1.1009	1.0975	--	1.0948	1.0822	1.0948	1.0949	1.0949
	R(29,68)	1.1134	1.0937	1.1009	1.0977	--	1.0948	1.0822	1.0948	1.0949	1.0949
	R(21,51)	1.1134	1.0938	1.1008	1.0978	--	1.0947	1.0822	1.0948	1.0947	1.0947
	R(28,66)	1.1019	1.0938	1.1008	1.0976	--	1.0947	1.0822	1.0948	1.0947	1.0947
	R(23,54)	1.1019	1.0932	1.1002	1.0979	--	1.0939	1.0827	1.0939	1.0940	1.0942
	R(26,63)	1.1019	1.0931	1.1003	1.0985	--	1.0940	1.0827	1.0940	1.0941	1.0942
	R(32,74)	1.1019	1.0931	1.1003	1.0977	--	1.0940	1.0827	1.0940	1.0941	1.0942
	R(33,75)	1.1027	1.0932	1.1002	1.0983	--	1.0939	1.0827	1.0939	1.0940	1.0942
	R(23,53)	1.1027	1.0917	1.0991	1.0966	--	1.0933	1.0815	1.0934	1.0934	1.0934
	R(33,76)	1.1010	1.0917	1.0991	1.0967	--	1.0933	1.0815	1.0934	1.0934	1.0934
	R(24,58)	1.1010	1.0919	1.0989	1.0974	--	1.0930	1.0817	1.0930	1.0932	1.0933
	R(25,61)	1.1010	1.0919	1.0989	1.0969	--	1.0931	1.0817	1.0930	1.0932	1.0933
	R(31,70)	1.1130	1.0919	1.0989	1.0968	--	1.0931	1.0817	1.0930	1.0932	1.0933

Table 5.34 (cont.) Raw bond length data for FAHBEV

Bond list (cont.)	PM3	B3LYP/ 3-21G	MPWLYP/ 3-21G	B3LYP/ Medi!	B3LYP/ Medi!+	MPWLYP/01/ Medi!+	B3LYP/ 6-31G(d)	HF/6- 31G(d)	B3LYP/6- 31(+LX)G(d)	B3LYP/6- 31(+*)G(d)	B3LYP/ 6- 31+G(d)
R(3,4,78)	1.1010	1.0919	1.0989	1.0972	--	--	1.0930	1.0817	1.0930	1.0932	1.0933
R(26,62)	1.1027	1.0921	1.0986	1.0964	--	--	1.0930	1.0815	1.0930	1.0931	1.0932
R(32,72)	1.1027	1.0921	1.0986	1.0966	--	--	1.0930	1.0815	1.0930	1.0931	1.0932
R(24,56)	1.1013	1.0912	1.0982	1.0968	--	--	1.0925	1.0808	1.0925	1.0925	1.0926
R(25,59)	1.1013	1.0913	1.0982	1.0958	--	--	1.0925	1.0808	1.0924	1.0925	1.0926
R(31,69)	1.1013	1.0913	1.0982	1.0959	--	--	1.0926	1.0808	1.0924	1.0925	1.0926
R(34,80)	1.1013	1.0912	1.0982	1.0969	--	--	1.0925	1.0808	1.0925	1.0925	1.0926
R(3,38)	1.0945	1.0857	1.0928	1.0898	--	--	1.0885	1.0772	1.0885	1.0885	1.0887
R(12,44)	1.0945	1.0857	1.0928	1.0899	--	--	1.0885	1.0772	1.0885	1.0885	1.0887
R(6,41)	1.0953	1.0854	1.0926	1.0899	--	--	1.0883	1.0765	1.0883	1.0886	1.0886
R(15,47)	1.0953	1.0854	1.0926	1.0899	--	--	1.0883	1.0765	1.0883	1.0886	1.0886
R(2,37)	1.0974	1.0857	1.0930	1.0899	--	--	1.0882	1.0763	1.0883	1.0882	1.0883
R(5,40)	1.0946	1.0853	1.0923	1.0895	--	--	1.0881	1.0768	1.0881	1.0881	1.0883
R(11,43)	1.0974	1.0857	1.0930	1.0896	--	--	1.0882	1.0763	1.0883	1.0882	1.0883
R(14,46)	1.0946	1.0853	1.0923	1.0895	--	--	1.0881	1.0768	1.0881	1.0881	1.0883
R(7,42)	1.0948	1.0852	1.0926	1.0896	--	--	1.0864	1.0740	1.0864	1.0870	1.0871
R(16,48)	1.0948	1.0852	1.0926	1.0895	--	--	1.0864	1.0740	1.0864	1.0870	1.0871
R(4,39)	1.0937	1.0835	1.0905	1.0878	--	--	1.0865	1.0753	1.0864	1.0868	1.0868
R(13,45)	1.0937	1.0835	1.0905	1.0877	--	--	1.0865	1.0753	1.0864	1.0868	1.0868
<i>short (cont.)</i>											

Table 5.34 (cont.) Raw bond length data for FAHBEV

5.4.4.1 X-ray⁶³

C	-3.192750000000	-3.969696153846	-0.297115384615	H	3.323250000000	0.594303846154	-1.123115384615
C	-3.162750000000	-3.933696153846	1.103884615385	H	2.412250000000	0.594303846154	-2.399115384615
C	-3.898750000000	-4.782696153846	1.870884615385	H	3.837250000000	-0.057696153846	-2.451115384615
C	-4.718750000000	-5.721696153846	1.289884615385	H	-3.411750000000	3.280303846154	-0.255115384615
C	-4.767750000000	-5.793696153846	-0.076115384615	H	-4.083750000000	1.914303846154	-0.630115384615
C	-4.028750000000	-4.942696153846	-0.864115384615	H	-3.445750000000	2.244303846154	-2.293115384615
C	-2.433750000000	-3.082696153846	-1.144115384615	H	-2.430750000000	3.322303846154	-1.779115384615
C	-1.603750000000	-2.090696153846	-0.684115384615	H	-1.544750000000	3.319303846154	1.221884615385
N	-0.905750000000	-1.239696153846	-0.283115384615	H	-1.763750000000	2.214303846154	2.308884615385
C	3.051250000000	3.781303846154	1.325884615385	H	-2.908750000000	3.236303846154	1.987884615385
C	3.067250000000	4.059303846154	-0.045115384615	H	-3.814750000000	0.117303846154	0.709884615385
C	3.829250000000	5.098303846154	-0.557115384615	H	-4.344750000000	1.296303846154	1.593884615385
C	4.607250000000	5.880303846154	0.251884615385	H	-3.088750000000	0.478303846154	2.051884615385
C	4.613250000000	5.616303846154	1.610884615385	H	0.156250000000	1.832303846154	-2.909115384615
C	3.849250000000	4.575303846154	2.141884615385	H	-0.317750000000	3.071303846154	-2.072115384615
C	2.275250000000	2.715303846154	1.903884615385	H	-0.898750000000	2.826303846154	-3.508115384615
C	1.461250000000	1.889303846154	1.162884615385	H	-1.374750000000	-0.047696153846	-3.296115384615
N	0.776250000000	1.182303846154	0.520884615385	H	-2.480750000000	0.949303846154	-3.789115384615
N	2.091250000000	-2.077696153846	1.235884615385	H	-2.758750000000	0.013303846154	-2.562115384615
C	3.084250000000	-2.581696153846	0.298884615385				
C	3.283250000000	-1.986696153846	-0.847115384615				
N	2.361250000000	-1.080696153846	-1.463115384615				
C	1.294250000000	-3.198696153846	1.749884615385				
C	2.750250000000	-1.432696153846	2.367884615385				
C	1.702250000000	-1.700696153846	-2.605115384615				
C	3.065250000000	0.096303846154	-1.902115384615				
N	-2.618750000000	1.730303846154	0.638884615385				
C	-3.246750000000	2.369303846154	-0.515115384615				
C	-2.735750000000	2.418303846154	-1.670115384615				
N	-1.616750000000	1.561303846154	-2.072115384615				
C	-2.186750000000	2.724303846154	1.615884615385				
C	-3.559750000000	0.834303846154	1.294884615385				
C	-0.589750000000	2.401303846154	-2.704115384615				
C	-2.090750000000	0.529303846154	-3.020115384615				
Li	1.018250000000	-0.798696153846	0.110884615385				
Li	-1.058750000000	0.777303846154	-0.217115384615				
H	-2.603750000000	-3.284696153846	1.539884615385				
H	-3.842750000000	-4.726696153846	2.827884615385				
H	-5.246750000000	-6.311696153846	1.832884615385				
H	-5.329750000000	-6.452696153846	-0.493115384615				
H	-4.084750000000	-5.014696153846	-1.819115384615				
H	-2.521750000000	-3.173696153846	-2.105115384615				
H	2.541250000000	3.522303846154	-0.642115384615				
H	3.810250000000	5.272303846154	-1.501115384615				
H	5.135250000000	6.591303846154	-0.116115384615				
H	5.150250000000	6.156303846154	2.195884615385				
H	3.872250000000	4.406303846154	3.087884615385				
H	2.296250000000	2.671303846154	2.908884615385				
H	2.837250000000	-3.485696153846	0.095884615385				
H	3.927250000000	-2.575696153846	0.758884615385				
H	4.100250000000	-1.492696153846	-0.743115384615				
H	3.415250000000	-2.693696153846	-1.484115384615				
H	0.844250000000	-3.554696153846	0.980884615385				
H	0.645250000000	-2.895696153846	2.389884615385				
H	1.840250000000	-3.881696153846	2.146884615385				
H	3.221250000000	-0.669696153846	2.023884615385				
H	3.373250000000	-2.029696153846	2.792884615385				
H	2.096250000000	-1.145696153846	3.007884615385				
H	1.253250000000	-2.496696153846	-2.310115384615				
H	2.356250000000	-1.928696153846	-3.270115384615				
H	1.060250000000	-1.093696153846	-2.982115384615				

5.4.4.2 PM3

				H	4.552012827838	-0.321212155102	-1.959536697679
C	-3.002658911899	-3.877036788102	-0.581463481388	H	-4.490880446315	2.772109332181	0.609988825418
C	-3.029525709336	-3.711510689828	0.811828140211	H	-4.321692513239	1.463140200547	-0.574884847543
C	-3.789798182961	-4.557985129770	1.608340706104	H	-3.567666947654	3.627835468643	-1.526833186634
C	-4.535310835463	-5.581679786898	1.036765363185	H	-2.427866183633	3.893908848358	-0.194074446504
C	-4.516892568826	-5.756255004713	-0.345129702566	H	-1.966909055081	3.081817294694	1.911808447182
C	-3.761719059197	-4.917199596527	-1.148371614180	H	-1.842736422618	1.587378833117	2.871320192376
C	-2.230750605370	-3.025256163674	-1.443709665636	H	-3.381116011320	2.484669348167	2.817036396992
C	-1.475527110008	-2.007394974107	-1.000718804052	H	-3.819709904075	-0.520935895849	0.566816873624
N	-0.785791321893	-1.082574983013	-0.627964532931	H	-4.553596305832	0.323952963143	1.957297220985
C	3.001993729931	3.876247240314	0.582871553701	H	-2.966683412957	-0.469948478599	2.124597455114
C	3.027965920896	3.712451913471	-0.810637547855	H	0.098900744300	2.734050669324	-2.460139480784
C	3.788295853478	4.559459602152	-1.606523298761	H	-0.245699301356	3.742291324115	-1.038332895943
C	4.534713740177	5.582014039631	-1.034097372953	H	-1.033933982495	4.102987100657	-2.598641125456
C	4.517129404995	5.754914448127	0.348018180199	H	-1.545439870413	1.088277440792	-3.258160673584
C	3.761934528653	4.915295584958	1.150639824589	H	-2.752838054042	2.373272255853	-3.514518637925
C	2.230064904132	3.023851912615	1.444475331891	H	-3.147437208284	0.968802851431	-2.490946798146
C	1.474844774302	2.006313408553	1.000719152932				
N	0.785173678498	1.081770461949	0.627186065972				
N	1.805333434594	-2.357861699163	1.556709160603				
C	2.896835436671	-3.095856159889	0.816693810825				
C	3.737886755839	-2.161127310505	-0.062038673743				
N	2.889136809013	-1.360657070811	-1.022516869559				
C	0.698136230734	-3.291680991855	1.933774609628				
C	2.342951492964	-1.668817523152	2.771101565342				
C	2.510046294968	-2.174171732752	-2.219620146789				
C	3.601095426402	-0.113235356208	-1.443412345923				
N	-2.889048946179	1.361750459161	1.021407776549				
C	-3.736560316511	2.164503155034	0.061734426441				
C	-2.893844999753	3.097579245850	-0.817211354136				
N	-1.804420629557	2.357366171422	-1.558090441353				
C	-2.508621700914	2.173553337290	2.219246649230				
C	-3.602920825390	0.115027828660	1.441113894296				
C	-0.696235535628	3.289260595112	-1.937051594472				
C	-2.344586070866	1.668546711443	-2.771499251300				
Li	1.096257688702	-0.868614458169	0.124292456468				
Li	-1.096788536782	0.867874826005	-0.125549793306				
H	-2.445082832222	-2.906830565857	1.275591972200				
H	-3.801066111059	-4.416811573939	2.693670467345				
H	-5.133005300116	-6.246580900551	1.666740692625				
H	-5.103212616178	-6.561901774429	-0.798315388481				
H	-3.753076433908	-5.061706795400	-2.234036540179				
H	-2.256777406688	-3.212698285374	-2.522032844258				
H	2.442753129817	2.908707730881	-1.275069466972				
H	3.798866003650	4.419630897775	-2.692034958695				
H	5.132446810879	6.247346386954	-1.663579123283				
H	5.104153946479	6.559672163664	0.801871540390				
H	3.753941565250	5.058484162760	2.236484937588				
H	2.256096044855	3.210476542791	2.522937710021				
H	2.433086790871	-3.893486535938	0.193544738025				
H	3.571475623801	-3.624351437045	1.526858934780				
H	4.320950239879	-1.458124837079	0.574686386211				
H	4.493982769348	-2.767140191550	-0.609618303878				
H	0.249848782091	-3.745329130721	1.034258025569				
H	-0.098774339054	-2.737881101708	2.455666377356				
H	1.036145365265	-4.104935163589	2.595775639846				
H	3.145197258921	-0.967851177832	2.491879590888				
H	2.751213193684	-2.373288727458	3.514358013138				
H	1.542350320764	-1.089883454470	3.256960286753				
H	1.969647173015	-3.082950950091	-1.911385774902				
H	3.383066899406	-2.484578504738	-2.817011893687				
H	1.843357418046	-1.589610634392	-2.872310661201				
H	3.817082579153	0.523854754919	-0.569732345351				
H	2.963884172009	0.470166329227	-2.127330866711				

Table 5.35 Signed and Unsigned differences in bond length for the PM3 structure of FAHBEV relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(35,36)	2.6515	2.8083	0.1568	0.1568
R(19,35)	2.1478	2.1845	0.0367	0.0367
R(30,36)	2.1478	2.1845	0.0367	0.0367
R(22,35)	2.1459	2.1845	0.0386	0.0386
R(27,36)	2.1459	2.1845	0.0386	0.0386
R(9,36)	2.0272	2.0380	0.0108	0.0108
R(18,35)	2.0271	2.0381	0.0110	0.0110
R(9,35)	2.0065	2.0381	0.0316	0.0316
R(18,36)	2.0065	2.0381	0.0316	0.0316
R(20,21)	1.5313	1.5340	0.0027	0.0027
R(28,29)	1.5313	1.5340	0.0027	0.0027
R(19,20)	1.4766	1.5112	0.0346	0.0346
R(21,22)	1.4766	1.5112	0.0346	0.0346
R(27,28)	1.4766	1.5112	0.0346	0.0346
R(29,30)	1.4766	1.5112	0.0346	0.0346
R(19,24)	1.4719	1.4962	0.0243	0.0243
R(30,34)	1.4719	1.4962	0.0243	0.0243
R(22,25)	1.4718	1.4962	0.0244	0.0244
R(27,31)	1.4718	1.4962	0.0244	0.0244
R(22,26)	1.4710	1.4967	0.0257	0.0257
R(27,32)	1.4710	1.4967	0.0257	0.0257
R(19,23)	1.4706	1.4967	0.0261	0.0261
R(30,33)	1.4706	1.4967	0.0261	0.0261
R(1,7)	1.4529	1.4369	-0.0160	0.0160
R(10,16)	1.4529	1.4369	-0.0160	0.0160
R(1,2)	1.4169	1.4033	-0.0136	0.0136
R(10,11)	1.4169	1.4033	-0.0136	0.0136
R(1,6)	1.4159	1.4069	-0.0090	0.0090
R(10,15)	1.4159	1.4069	-0.0090	0.0090
R(4,5)	1.4002	1.3930	-0.0072	0.0072
R(13,14)	1.4002	1.3930	-0.0072	0.0072
R(3,4)	1.3999	1.3894	-0.0105	0.0105
R(12,13)	1.3999	1.3894	-0.0105	0.0105
R(2,3)	1.3942	1.3889	-0.0053	0.0053
R(11,12)	1.3942	1.3889	-0.0053	0.0053
R(5,6)	1.3935	1.3855	-0.0080	0.0080
R(14,15)	1.3935	1.3855	-0.0080	0.0080
R(7,8)	1.3589	1.3426	-0.0163	0.0163
R(16,17)	1.3589	1.3426	-0.0163	0.0163
R(8,9)	1.1978	1.2124	0.0146	0.0146
R(17,18)	1.1978	1.2124	0.0146	0.0146
R(21,52)	1.1056	1.1130	0.0074	0.0074
R(28,65)	1.1056	1.1130	0.0074	0.0074
R(20,50)	1.1055	1.1130	0.0075	0.0075
R(29,67)	1.1055	1.1130	0.0075	0.0075
R(24,57)	1.1050	1.1025	-0.0025	0.0025
R(34,79)	1.1050	1.1025	-0.0025	0.0025
R(25,60)	1.1049	1.1025	-0.0024	0.0024

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(31,71)	1.1049	1.1025	-0.0024	0.0024
R(23,55)	1.1046	1.1018	-0.0028	0.0028
R(26,64)	1.1046	1.1018	-0.0028	0.0028
R(32,73)	1.1046	1.1018	-0.0028	0.0028
R(33,77)	1.1046	1.1018	-0.0028	0.0028
R(20,49)	1.0949	1.1134	0.0185	0.0185
R(29,68)	1.0949	1.1134	0.0185	0.0185
R(21,51)	1.0947	1.1134	0.0187	0.0187
R(28,66)	1.0947	1.1134	0.0187	0.0187
R(23,54)	1.0942	1.1019	0.0077	0.0077
R(26,63)	1.0942	1.1019	0.0077	0.0077
R(32,74)	1.0942	1.1019	0.0077	0.0077
R(33,75)	1.0942	1.1019	0.0077	0.0077
R(23,53)	1.0934	1.1027	0.0093	0.0093
R(33,76)	1.0934	1.1027	0.0093	0.0093
R(24,58)	1.0933	1.1010	0.0077	0.0077
R(25,61)	1.0933	1.1010	0.0077	0.0077
R(31,70)	1.0933	1.1010	0.0077	0.0077
R(34,78)	1.0933	1.1010	0.0077	0.0077
R(26,62)	1.0932	1.1027	0.0095	0.0095
R(32,72)	1.0932	1.1027	0.0095	0.0095
R(24,56)	1.0926	1.1013	0.0087	0.0087
R(25,59)	1.0926	1.1013	0.0087	0.0087
R(31,69)	1.0926	1.1013	0.0087	0.0087
R(34,80)	1.0926	1.1013	0.0087	0.0087
R(3,38)	1.0887	1.0945	0.0058	0.0058
R(12,44)	1.0887	1.0945	0.0058	0.0058
R(6,41)	1.0886	1.0953	0.0067	0.0067
R(15,47)	1.0886	1.0953	0.0067	0.0067
R(2,37)	1.0883	1.0974	0.0091	0.0091
R(5,40)	1.0883	1.0946	0.0063	0.0063
R(11,43)	1.0883	1.0974	0.0091	0.0091
R(14,46)	1.0883	1.0946	0.0063	0.0063
R(7,42)	1.0871	1.0948	0.0077	0.0077
R(16,48)	1.0871	1.0948	0.0077	0.0077
R(4,39)	1.0868	1.0937	0.0069	0.0069
R(13,45)	1.0868	1.0937	0.0069	0.0069

5.4.4.3 B3LYP/3-21G

C	-2.838480783791	-4.018567467021	-0.760175687164	H	4.128215555411	-0.724473764773	-2.321787899762
C	-3.046590189312	-3.796781240074	0.625287403110	H	-4.027924752911	2.957448365917	0.746056519967
C	-3.777068772641	-4.693684712028	1.400064170978	H	-3.962894644528	1.583177333513	-0.376025259948
C	-4.334670879589	-5.843761388243	0.831480543140	H	-3.137889835912	3.701195186133	-1.443776525486
C	-4.146780237811	-6.075904256695	-0.535464378194	H	-1.868827454631	3.820490307615	-0.206808317712
C	-3.415611067483	-5.186088025174	-1.316714042377	H	-1.280113163327	3.117969369711	1.773754037726
C	-2.074002027073	-3.108894610407	-1.594896314175	H	-1.289098779566	1.719204444191	2.844276907705
C	-1.453387387264	-2.004197168265	-1.120205866140	H	-2.707480182862	2.812372276923	2.814256683450
N	-0.894733397644	-1.039383052795	-0.677450049132	H	-3.633266677397	-0.293513483876	0.930288708739
C	2.840532782018	4.017521557219	0.760058070974	H	-4.128504153384	0.723569937403	2.322157571478
C	3.047242342874	3.796687060262	-0.625764338091	H	-2.608797006911	-0.213969594587	2.374098390401
C	3.778246617668	4.693333037091	-1.400336863308	H	0.232462856289	2.365038923571	-2.675484322641
C	4.337744846747	5.842220088545	-0.831200314441	H	0.114208015397	3.542736401260	-1.356321098048
C	4.151203501268	6.073427243091	0.536083604801	H	-0.820866050926	3.794657863152	-2.864041905777
C	3.419547911025	5.183842174554	1.317143877125	H	-1.565840640808	0.843777757469	-3.140888064672
C	2.075605915765	3.108074175503	1.594609380489	H	-2.735433401172	2.183781965907	-3.358385427637
C	1.453442655552	2.004424443614	1.119533790662	H	-3.050710414197	0.860088589981	-2.192485023603
N	0.893375375368	1.040558442086	0.676489609907				
N	1.552765924847	-2.238178322423	1.553466553313				
C	2.483412750412	-3.115774240071	0.773770146139				
C	3.347137320477	-2.288288838191	-0.190092941515				
N	2.494760915549	-1.487193078865	-1.125399680873				
C	0.442491868808	-3.041948825846	2.150472462906				
C	2.275501338237	-1.492717324760	2.629188721128				
C	1.916036678616	-2.344125004932	-2.205115952103				
C	3.273894511415	-0.362770071348	-1.726652008947				
N	-2.495814347785	1.487289854384	1.125372870318				
C	-3.348685377416	2.288695017696	0.190802408182				
C	-2.485438832944	3.116718176068	-0.773038946243				
N	-1.554956953687	2.239581332679	-1.553447363777				
C	-1.916726239489	2.343741367319	2.205256775606				
C	-3.274415947507	0.362390316562	1.726367033518				
C	-0.444787943798	3.043657208949	-2.150245303257				
C	-2.277918662332	1.494647507604	-2.629362726358				
Li	0.969385806947	-0.869439832116	0.122370673959				
Li	-0.970681742158	0.870510140547	-0.123168026301				
H	-2.632814246913	-2.901776745650	1.079820788516				
H	-3.918720535094	-4.492367865395	2.457505931183				
H	-4.903887981174	-6.539183989953	1.436816421132				
H	-4.574517989682	-6.960750682507	-0.995930101992				
H	-3.278478967965	-5.383363295011	-2.375221238581				
H	-2.005737715255	-3.318995766041	-2.657332684618				
H	2.631919838364	2.902633942908	-1.080766108320				
H	3.918784228020	4.492769267338	-2.458070160119				
H	4.907353121701	6.537450408704	-1.436389243866				
H	4.580387764057	6.957350599169	0.996976032101				
H	3.283503688452	5.380375275480	2.375929793761				
H	2.008142829061	3.317552225791	2.657221324110				
H	1.866901082712	-3.819697402346	0.207618484677				
H	3.135543289518	-3.700049234676	1.444996906892				
H	3.961223931311	-1.582602224398	0.376656847846				
H	4.026503277581	-2.957378975609	-0.744785812248				
H	-0.116265778190	-3.541588485893	1.356736804642				
H	-0.234946124432	-2.363045246764	2.675103977412				
H	0.818442830526	-3.792461739680	2.864850663072				
H	3.048411239744	-0.858378067897	2.192205499207				
H	2.732817439884	-2.181518573216	3.358649402189				
H	1.563310589211	-0.841588981704	3.140225158484				
H	1.278796286326	-3.117802310283	-1.773544842049				
H	2.707015173175	-2.813457178646	-2.813281466291				
H	1.289117560096	-1.719731367921	-2.844976781688				
H	3.632475830984	0.293527438999	-0.930776819208				
H	2.608725103936	0.213332738807	-2.375071510360				

Table 5.36 Signed and Unsigned differences in bond length for the B3LYP/3-21G structure of FAHBEV relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(35,36)	2.6515	2.6176	-0.0339	0.0339
R(19,35)	2.1478	2.0644	-0.0834	0.0834
R(30,36)	2.1478	2.0643	-0.0835	0.0835
R(22,35)	2.1459	2.0653	-0.0806	0.0806
R(27,36)	2.1459	2.0653	-0.0806	0.0806
R(9,36)	2.0272	1.9901	-0.0371	0.0371
R(18,35)	2.0271	1.9902	-0.0369	0.0369
R(9,35)	2.0065	2.0356	0.0291	0.0291
R(18,36)	2.0065	2.0355	0.0290	0.0290
R(20,21)	1.5313	1.5362	0.0049	0.0049
R(28,29)	1.5313	1.5362	0.0049	0.0049
R(19,20)	1.4766	1.4981	0.0215	0.0215
R(21,22)	1.4766	1.4977	0.0211	0.0211
R(27,28)	1.4766	1.4977	0.0211	0.0211
R(29,30)	1.4766	1.4981	0.0215	0.0215
R(19,24)	1.4719	1.4951	0.0232	0.0232
R(30,34)	1.4719	1.4951	0.0232	0.0232
R(22,25)	1.4718	1.4950	0.0232	0.0232
R(27,31)	1.4718	1.4950	0.0232	0.0232
R(22,26)	1.4710	1.4943	0.0233	0.0233
R(27,32)	1.4710	1.4943	0.0233	0.0233
R(19,23)	1.4706	1.4950	0.0244	0.0244
R(30,33)	1.4706	1.4951	0.0245	0.0245
R(1,7)	1.4529	1.4521	-0.0008	0.0008
R(10,16)	1.4529	1.4521	-0.0008	0.0008
R(1,2)	1.4169	1.4185	0.0016	0.0016
R(10,11)	1.4169	1.4185	0.0016	0.0016
R(1,6)	1.4159	1.4163	0.0004	0.0004
R(10,15)	1.4159	1.4163	0.0004	0.0004
R(4,5)	1.4002	1.3992	-0.0010	0.0010
R(13,14)	1.4002	1.3992	-0.0010	0.0010
R(3,4)	1.3999	1.3989	-0.0010	0.0010
R(12,13)	1.3999	1.3989	-0.0010	0.0010
R(2,3)	1.3942	1.3922	-0.0020	0.0020
R(11,12)	1.3942	1.3922	-0.0020	0.0020
R(5,6)	1.3935	1.3917	-0.0018	0.0018
R(14,15)	1.3935	1.3917	-0.0018	0.0018
R(7,8)	1.3589	1.3531	-0.0058	0.0058
R(16,17)	1.3589	1.3531	-0.0058	0.0058
R(8,9)	1.1978	1.1996	0.0018	0.0018
R(17,18)	1.1978	1.1996	0.0018	0.0018
R(21,52)	1.1056	1.1031	-0.0025	0.0025
R(28,65)	1.1056	1.1031	-0.0025	0.0025
R(20,50)	1.1055	1.1033	-0.0022	0.0022
R(29,67)	1.1055	1.1033	-0.0022	0.0022
R(24,57)	1.1050	1.1026	-0.0024	0.0024
R(34,79)	1.1050	1.1026	-0.0024	0.0024
R(25,60)	1.1049	1.1026	-0.0023	0.0023

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(31,71)	1.1049	1.1026	-0.0023	0.0023
R(23,55)	1.1046	1.1022	-0.0024	0.0024
R(26,64)	1.1046	1.1022	-0.0024	0.0024
R(32,73)	1.1046	1.1022	-0.0024	0.0024
R(33,77)	1.1046	1.1022	-0.0024	0.0024
R(20,49)	1.0949	1.0937	-0.0012	0.0012
R(29,68)	1.0949	1.0937	-0.0012	0.0012
R(21,51)	1.0947	1.0938	-0.0009	0.0009
R(28,66)	1.0947	1.0938	-0.0009	0.0009
R(23,54)	1.0942	1.0932	-0.0010	0.0010
R(26,63)	1.0942	1.0931	-0.0011	0.0011
R(32,74)	1.0942	1.0931	-0.0011	0.0011
R(33,75)	1.0942	1.0932	-0.0010	0.0010
R(23,53)	1.0934	1.0917	-0.0017	0.0017
R(33,76)	1.0934	1.0917	-0.0017	0.0017
R(24,58)	1.0933	1.0919	-0.0014	0.0014
R(25,61)	1.0933	1.0919	-0.0014	0.0014
R(31,70)	1.0933	1.0919	-0.0014	0.0014
R(34,78)	1.0933	1.0919	-0.0014	0.0014
R(26,62)	1.0932	1.0921	-0.0011	0.0011
R(32,72)	1.0932	1.0921	-0.0011	0.0011
R(24,56)	1.0926	1.0912	-0.0014	0.0014
R(25,59)	1.0926	1.0913	-0.0013	0.0013
R(31,69)	1.0926	1.0913	-0.0013	0.0013
R(34,80)	1.0926	1.0912	-0.0014	0.0014
R(3,38)	1.0887	1.0857	-0.0030	0.0030
R(12,44)	1.0887	1.0857	-0.0030	0.0030
R(6,41)	1.0886	1.0854	-0.0032	0.0032
R(15,47)	1.0886	1.0854	-0.0032	0.0032
R(2,37)	1.0883	1.0857	-0.0026	0.0026
R(5,40)	1.0883	1.0853	-0.0030	0.0030
R(11,43)	1.0883	1.0857	-0.0026	0.0026
R(14,46)	1.0883	1.0853	-0.0030	0.0030
R(7,42)	1.0871	1.0852	-0.0019	0.0019
R(16,48)	1.0871	1.0852	-0.0019	0.0019
R(4,39)	1.0868	1.0835	-0.0033	0.0033
R(13,45)	1.0868	1.0835	-0.0033	0.0033

5.4.4.4 MPWLYP/3-21G

C	-3.168553663395	-3.777125319498	-0.804321664432	H	4.288358009588	-0.199790276500	-2.296974103041
C	-3.090373852481	-3.769947173388	0.623704311783	H	-4.498486076049	2.310601084787	0.583713820791
C	-3.909246514925	-4.599467194587	1.401889283825	H	-4.150467636007	0.915491722614	-0.484151693813
C	-4.834806395355	-5.473445391806	0.797150263805	H	-3.661644755632	3.123684633044	-1.622262734391
C	-4.920557716018	-5.501636838889	-0.609383279876	H	-2.469387688320	3.504652463254	-0.342574139618
C	-4.108423343986	-4.674016473354	-1.395756738799	H	-1.835651398810	2.986631085551	1.667000020100
C	-2.338662655000	-2.918644956080	-1.643973592338	H	-1.617508143502	1.647913377377	2.811628323953
C	-1.461304501841	-2.003666351698	-1.147260886147	H	-3.216937547005	2.480203435589	2.713508760781
N	-0.702467763017	-1.183567113052	-0.679373042473	H	-3.616708805019	-0.823732222686	0.968995007492
C	3.167555045762	3.778270791736	0.804031561998	H	-4.287081562324	0.198925831848	2.297667009120
C	3.090122106102	3.770353621201	-0.624032601589	H	-2.640410736035	-0.512858006405	2.430265214213
C	3.908693451463	4.600197014618	-1.402178672276	H	-0.033978460734	2.341105285292	-2.691315585402
C	4.833221484892	5.475228301033	-0.797368752296	H	-0.389097948769	3.502343392177	-1.383240666707
C	4.918240927212	5.504129722373	0.609188535605	H	-1.297564818235	3.597660780483	-2.942792346480
C	4.106382366782	4.676201599842	1.395530474462	H	-1.551232620255	0.544596093945	-3.202565255374
C	2.337927679362	2.919512312036	1.643657968050	H	-2.930639124810	1.674453328361	-3.481933638282
C	1.461509563261	2.003636061287	1.146957260719	H	-3.061665709147	0.314460134640	-2.300495031666
N	0.703513585526	1.182718165713	0.679136072232				
N	1.831567964444	-1.942752755404	1.621872927345				
C	2.940342188943	-2.682993866729	0.903264490457				
C	3.690541845082	-1.746108062359	-0.073400226461				
N	2.736598573335	-1.128691082325	-1.075373355176				
C	0.833158498481	-2.916968377512	2.200361061516				
C	2.388620458758	-1.072332926581	2.724023275643				
C	2.338520987864	-2.130023415455	-2.134648020357				
C	3.372270335384	0.073632488886	-1.733657111738				
N	-2.735557191802	1.127618411060	1.075625563513				
C	-3.689735390116	1.745002941887	0.073849283407				
C	-2.939822180015	2.682043858141	-0.902876974456				
N	-1.831080725183	1.941989680205	-1.621749517050				
C	-2.337228820951	2.128992947814	2.134787303300				
C	-3.371164340506	-0.074618590590	1.734130855211				
C	-0.832923963533	2.916423079515	-2.200346345802				
C	-2.388278571533	1.071659843255	-2.723908029912				
Li	1.076077125199	-0.742415217037	0.108339032291				
Li	-1.075205286055	0.741621761176	-0.108358332750				
H	-2.366023179592	-3.109790397650	1.107619935804				
H	-3.822252854483	-4.570361150658	2.490803049235				
H	-5.469522664107	-6.118518906406	1.405554770552				
H	-5.629046809710	-6.175528813412	-1.096332472498				
H	-4.189461760837	-4.707130633302	-2.484815782216				
H	-2.418117317140	-3.024937594191	-2.728484134052				
H	2.366598096674	3.109334352376	-1.108011341379				
H	3.822298030591	4.570508133407	-2.491124233931				
H	5.467709839265	6.120543544878	-1.405754755246				
H	5.625934496896	6.178816388352	1.096194287463				
H	4.186841691273	4.709889206771	2.484614950215				
H	2.416878472371	3.026252008740	2.728162884575				
H	2.469903374413	-3.505574530707	0.342921058336				
H	3.661986775987	-3.124682817598	1.622800547157				
H	4.151275735382	-0.916614380666	0.484624307089				
H	4.499321473055	-2.311830484754	-0.583079801100				
H	0.389434076852	-3.502913900143	1.383216929216				
H	0.034181194774	-2.341482540046	2.691084803040				
H	1.297531621997	-3.598190345028	2.942991147970				
H	3.062318847418	-0.315392980882	2.300649448587				
H	2.930625772093	-1.675082923892	3.482338970673				
H	1.551562552996	-0.544959503504	3.202314375221				
H	1.836950305904	-2.987724728345	-1.666965428522				
H	3.218339748034	-2.481137525258	-2.713262489989				
H	1.618854223698	-1.648970154303	-2.811566061735				
H	3.617541958673	0.822725412732	-0.968410298221				
H	2.641654519888	0.511848473718	-2.429948465098				

Table 5.37 Signed and Unsigned differences in bond length for the MPWLYP/3-21G structure of FAHBEV relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(35,36)	2.6515	2.6225	-0.0290	0.0290
R(19,35)	2.1478	2.0742	-0.0736	0.0736
R(30,36)	2.1478	2.0743	-0.0735	0.0735
R(22,35)	2.1459	2.0755	-0.0704	0.0704
R(27,36)	2.1459	2.0755	-0.0704	0.0704
R(9,36)	2.0272	2.0424	0.0152	0.0152
R(18,35)	2.0271	2.0422	0.0151	0.0151
R(9,35)	2.0065	1.9946	-0.0119	0.0119
R(18,36)	2.0065	1.9946	-0.0119	0.0119
R(20,21)	1.5313	1.5474	0.0161	0.0161
R(28,29)	1.5313	1.5474	0.0161	0.0161
R(19,20)	1.4766	1.5145	0.0379	0.0379
R(21,22)	1.4766	1.5150	0.0384	0.0384
R(27,28)	1.4766	1.5150	0.0384	0.0384
R(29,30)	1.4766	1.5145	0.0379	0.0379
R(19,24)	1.4719	1.5109	0.0390	0.0390
R(30,34)	1.4719	1.5109	0.0390	0.0390
R(22,25)	1.4718	1.5110	0.0392	0.0392
R(27,31)	1.4718	1.5110	0.0392	0.0392
R(22,26)	1.4710	1.5110	0.0400	0.0400
R(27,32)	1.4710	1.5110	0.0400	0.0400
R(19,23)	1.4706	1.5102	0.0396	0.0396
R(30,33)	1.4706	1.5102	0.0396	0.0396
R(1,7)	1.4529	1.4597	0.0068	0.0068
R(10,16)	1.4529	1.4597	0.0068	0.0068
R(1,2)	1.4169	1.4302	0.0133	0.0133
R(10,11)	1.4169	1.4302	0.0133	0.0133
R(1,6)	1.4159	1.4274	0.0115	0.0115
R(10,15)	1.4159	1.4274	0.0115	0.0115
R(4,5)	1.4002	1.4094	0.0092	0.0092
R(13,14)	1.4002	1.4094	0.0092	0.0092
R(3,4)	1.3999	1.4093	0.0094	0.0094
R(12,13)	1.3999	1.4093	0.0094	0.0094
R(2,3)	1.3942	1.4015	0.0073	0.0073
R(11,12)	1.3942	1.4015	0.0073	0.0073
R(5,6)	1.3935	1.4010	0.0075	0.0075
R(14,15)	1.3935	1.4010	0.0075	0.0075
R(7,8)	1.3589	1.3615	0.0026	0.0026
R(16,17)	1.3589	1.3615	0.0026	0.0026
R(8,9)	1.1978	1.2113	0.0135	0.0135
R(17,18)	1.1978	1.2113	0.0135	0.0135
R(21,52)	1.1056	1.1108	0.0052	0.0052
R(28,65)	1.1056	1.1108	0.0052	0.0052
R(20,50)	1.1055	1.1107	0.0052	0.0052
R(29,67)	1.1055	1.1107	0.0052	0.0052
R(24,57)	1.1050	1.1100	0.0050	0.0050
R(34,79)	1.1050	1.1100	0.0050	0.0050
R(25,60)	1.1049	1.1100	0.0051	0.0051

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(31,71)	1.1049	1.1100	0.0051	0.0051
R(23,55)	1.1046	1.1096	0.0050	0.0050
R(26,64)	1.1046	1.1096	0.0050	0.0050
R(32,73)	1.1046	1.1096	0.0050	0.0050
R(33,77)	1.1046	1.1096	0.0050	0.0050
R(20,49)	1.0949	1.1009	0.0060	0.0060
R(29,68)	1.0949	1.1009	0.0060	0.0060
R(21,51)	1.0947	1.1008	0.0061	0.0061
R(28,66)	1.0947	1.1008	0.0061	0.0061
R(23,54)	1.0942	1.1002	0.0060	0.0060
R(26,63)	1.0942	1.1003	0.0061	0.0061
R(32,74)	1.0942	1.1003	0.0061	0.0061
R(33,75)	1.0942	1.1002	0.0060	0.0060
R(23,53)	1.0934	1.0991	0.0057	0.0057
R(33,76)	1.0934	1.0991	0.0057	0.0057
R(24,58)	1.0933	1.0989	0.0056	0.0056
R(25,61)	1.0933	1.0989	0.0056	0.0056
R(31,70)	1.0933	1.0989	0.0056	0.0056
R(34,78)	1.0933	1.0989	0.0056	0.0056
R(26,62)	1.0932	1.0986	0.0054	0.0054
R(32,72)	1.0932	1.0986	0.0054	0.0054
R(24,56)	1.0926	1.0982	0.0056	0.0056
R(25,59)	1.0926	1.0982	0.0056	0.0056
R(31,69)	1.0926	1.0982	0.0056	0.0056
R(34,80)	1.0926	1.0982	0.0056	0.0056
R(3,38)	1.0887	1.0928	0.0041	0.0041
R(12,44)	1.0887	1.0928	0.0041	0.0041
R(6,41)	1.0886	1.0926	0.0040	0.0040
R(15,47)	1.0886	1.0926	0.0040	0.0040
R(2,37)	1.0883	1.093	0.0047	0.0047
R(5,40)	1.0883	1.0923	0.0040	0.0040
R(11,43)	1.0883	1.093	0.0047	0.0047
R(14,46)	1.0883	1.0923	0.0040	0.0040
R(7,42)	1.0871	1.0926	0.0055	0.0055
R(16,48)	1.0871	1.0926	0.0055	0.0055
R(4,39)	1.0868	1.0905	0.0037	0.0037
R(13,45)	1.0868	1.0905	0.0037	0.0037

5.4.4.5 B3LYP/Midi!

C	-3.314635588040	-3.646608267085	-0.533040131070	H	4.069627259489	0.182061965945	-2.491329570004
C	-3.102470891377	-3.714975479774	0.866166836392	H	-4.546951356395	2.237600574220	0.140545621688
C	-3.900492674583	-4.507793869199	1.684467306427	H	-4.172505042917	0.783851729061	-0.811278746790
C	-4.942196597757	-5.269903315222	1.147457041094	H	-3.533936357601	2.879314491231	-2.045281370272
C	-5.164327454146	-5.222531866412	-0.232180818270	H	-2.454520562020	3.336290005096	-0.711147618634
C	-4.370947150101	-4.430042998642	-1.054761654465	H	-1.961207625741	2.895827342713	1.363654183834
C	-2.506837788829	-2.827467527018	-1.410653548621	H	-1.887581485728	1.621500314646	2.584073970942
C	-1.484828589991	-2.033381895234	-0.983618485343	H	-3.434483693786	2.493974382258	2.312125609058
N	-0.606520915675	-1.322267166472	-0.605084173675	H	-3.773862184847	-0.864638129848	0.720144288186
C	3.200545885662	3.586437828241	0.964013998021	H	-4.521593204851	0.232149522124	1.932458893652
C	3.020499252759	3.861318887111	-0.414194481983	H	-2.917168458319	-0.502975682629	2.233236796459
C	3.836955871594	4.763377243354	-1.089388657427	H	0.140912146068	1.971661056945	-2.683594346103
C	4.865135822392	5.435814228390	-0.422911865655	H	-0.314590283333	3.205740849078	-1.492702915372
C	5.053638415120	5.187147010024	0.940241076561	H	-1.046043577987	3.236240758007	-3.137653763951
C	4.242592764034	4.284493879966	1.619249788059	H	-1.348397378465	0.215068265599	-3.252495288717
C	2.375654411258	2.647902230016	1.691658782275	H	-2.666431903485	1.340581205821	-3.723707051080
C	1.395957500272	1.890182125613	1.121964030268	H	-2.935845668801	0.057342379757	-2.491839007180
N	0.557714013623	1.208661217356	0.619018561295				
N	2.047201770731	-1.856892523158	1.471595261260				
C	3.166318536347	-2.458864447647	0.696147613510				
C	3.765961854113	-1.434426987603	-0.288381033765				
N	2.715522799794	-0.886205257690	-1.187999894042				
C	1.149903217787	-2.916799094049	1.991978122218				
C	2.562675351558	-1.039453348738	2.597564365399				
C	2.329025726000	-1.869952620577	-2.228719274408				
C	3.193729864533	0.358118998607	-1.836624777881				
N	-2.869561581580	1.053491228374	0.806561151167				
C	-3.720941519860	1.626113680747	-0.271440976755				
C	-2.882252385983	2.478125504675	-1.245432825929				
N	-1.751296715134	1.686970779531	-1.799972510836				
C	-2.530715185422	2.080042215100	1.823117940691				
C	-3.570536676501	-0.080287681504	1.459018836088				
C	-0.691831641123	2.585447246787	-2.314663472280				
C	-2.211209287507	0.782548172313	-2.881816153739				
Li	1.121457563213	-0.672290989504	0.071902868659				
Li	-1.133525622675	0.593669270738	-0.179772338104				
H	-2.286145367867	-3.138932159037	1.301569767799				
H	-3.705267885874	-4.537084909720	2.756283844529				
H	-5.563600002029	-5.890809144187	1.788992184076				
H	-5.967497076588	-5.812704440905	-0.672208889439				
H	-4.559645496848	-4.406245513040	-2.127967626694				
H	-2.689061073756	-2.884642344756	-2.483348941234				
H	2.208309315205	3.366247234892	-0.945705980235				
H	3.664970216684	4.951370367171	-2.149066429923				
H	5.500903052770	6.142392054151	-0.951786205785				
H	5.844837702146	5.705434844206	1.480981397356				
H	4.406120550544	4.104199807204	2.681642393771				
H	2.512909971677	2.567125622836	2.769506040470				
H	2.761656828033	-3.313005267795	0.138373749586				
H	3.961860780162	-2.847441101080	1.360102875581				
H	4.189154521904	-0.588993371025	0.269557803151				
H	4.590298453202	-1.905135666036	-0.858561561504				
H	0.710368739730	-3.464368508856	1.149604569166				
H	0.332083599384	-2.443288980005	2.550915825319				
H	1.673676533722	-3.625340071016	2.662629931083				
H	3.157956967094	-0.198661509654	2.221236805088				
H	3.174723943833	-1.640822929782	3.298233820277				
H	1.708813433505	-0.616818714231	3.142179206385				
H	1.913151884699	-2.771003159447	-1.764099238867				
H	3.185343308120	-2.151408403067	-2.872677464699				
H	1.538752503158	-1.430768183281	-2.849802073662				
H	3.459561648655	1.098338638656	-1.072776260600				
H	2.378904650254	0.772852875064	-2.445545061016				

Table 5.38 Signed and Unsigned differences in bond length for the B3LYP/Midi! structure of FAHBEV relative to B3LYP/6-31+G(d)

					Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)					
					R(31,71)	1.1049	1.1078	0.0029	0.0029
					R(23,55)	1.1046	1.1073	0.0027	0.0027
					R(26,64)	1.1046	1.1076	0.0030	0.0030
					R(32,73)	1.1046	1.1074	0.0028	0.0028
					R(33,77)	1.1046	1.1074	0.0028	0.0028
R(35,36)	2.6515	2.5983	-0.0532	0.0532	R(20,49)	1.0949	1.0975	0.0026	0.0026
R(19,35)	2.1478	2.0541	-0.0937	0.0937	R(29,68)	1.0949	1.0977	0.0028	0.0028
R(30,36)	2.1478	2.0499	-0.0979	0.0979	R(21,51)	1.0947	1.0978	0.0031	0.0031
R(22,35)	2.1459	2.0431	-0.1028	0.1028	R(28,66)	1.0947	1.0976	0.0029	0.0029
R(27,36)	2.1459	2.0489	-0.0970	0.0970	R(23,54)	1.0942	1.0979	0.0037	0.0037
R(9,36)	2.0272	2.0321	0.0049	0.0049	R(26,63)	1.0942	1.0985	0.0043	0.0043
R(18,35)	2.0271	2.0384	0.0113	0.0113	R(32,74)	1.0942	1.0977	0.0035	0.0035
R(9,35)	2.0065	1.9664	-0.0401	0.0401	R(33,75)	1.0942	1.0983	0.0041	0.0041
R(18,36)	2.0065	1.9689	-0.0376	0.0376	R(23,53)	1.0934	1.0966	0.0032	0.0032
R(20,21)	1.5313	1.5422	0.0109	0.0109	R(33,76)	1.0934	1.0967	0.0033	0.0033
R(28,29)	1.5313	1.5421	0.0108	0.0108	R(24,58)	1.0933	1.0974	0.0041	0.0041
R(19,20)	1.4766	1.4887	0.0121	0.0121	R(25,61)	1.0933	1.0969	0.0036	0.0036
R(21,22)	1.4766	1.4877	0.0111	0.0111	R(31,70)	1.0933	1.0968	0.0035	0.0035
R(27,28)	1.4766	1.4882	0.0116	0.0116	R(34,78)	1.0933	1.0972	0.0039	0.0039
R(29,30)	1.4766	1.4874	0.0108	0.0108	R(26,62)	1.0932	1.0964	0.0032	0.0032
R(19,24)	1.4719	1.4838	0.0119	0.0119	R(32,72)	1.0932	1.0966	0.0034	0.0034
R(30,34)	1.4719	1.4832	0.0113	0.0113	R(24,56)	1.0926	1.0968	0.0042	0.0042
R(22,25)	1.4718	1.4833	0.0115	0.0115	R(25,59)	1.0926	1.0958	0.0032	0.0032
R(27,31)	1.4718	1.4839	0.0121	0.0121	R(31,69)	1.0926	1.0959	0.0033	0.0033
R(22,26)	1.4710	1.4825	0.0115	0.0115	R(34,80)	1.0926	1.0969	0.0043	0.0043
R(27,32)	1.4710	1.4841	0.0131	0.0131	R(3,38)	1.0887	1.0898	0.0011	0.0011
R(19,23)	1.4706	1.4830	0.0124	0.0124	R(12,44)	1.0887	1.0899	0.0012	0.0012
R(30,33)	1.4706	1.4814	0.0108	0.0108	R(6,41)	1.0886	1.0899	0.0013	0.0013
R(1,7)	1.4529	1.4470	-0.0059	0.0059	R(15,47)	1.0886	1.0899	0.0013	0.0013
R(10,16)	1.4529	1.4459	-0.0070	0.0070	R(2,37)	1.0883	1.0899	0.0016	0.0016
R(1,2)	1.4169	1.4169	0.0000	0.0000	R(5,40)	1.0883	1.0895	0.0012	0.0012
R(10,11)	1.4169	1.4168	-1E-04	1E-04	R(11,43)	1.0883	1.0896	0.0013	0.0013
R(1,6)	1.4159	1.4148	-0.0011	0.0011	R(14,46)	1.0883	1.0895	0.0012	0.0012
R(10,15)	1.4159	1.4151	-0.0008	0.0008	R(7,42)	1.0871	1.0896	0.0025	0.0025
R(4,5)	1.4002	1.3982	-0.0020	0.0020	R(16,48)	1.0871	1.0895	0.0024	0.0024
R(13,14)	1.4002	1.3984	-0.0018	0.0018	R(4,39)	1.0868	1.0878	0.0010	0.0010
R(3,4)	1.3999	1.3980	-0.0019	0.0019	R(13,45)	1.0868	1.0877	0.0009	0.0009
R(12,13)	1.3999	1.3977	-0.0022	0.0022					
R(2,3)	1.3942	1.3910	-0.0032	0.0032					
R(11,12)	1.3942	1.3915	-0.0027	0.0027					
R(5,6)	1.3935	1.3907	-0.0028	0.0028					
R(14,15)	1.3935	1.3906	-0.0029	0.0029					
R(7,8)	1.3589	1.3629	0.0040	0.0040					
R(16,17)	1.3589	1.3633	0.0044	0.0044					
R(8,9)	1.1978	1.1918	-0.0060	0.0060					
R(17,18)	1.1978	1.1917	-0.0061	0.0061					
R(21,52)	1.1056	1.1073	0.0017	0.0017					
R(28,65)	1.1056	1.1072	0.0016	0.0016					
R(20,50)	1.1055	1.1067	0.0012	0.0012					
R(29,67)	1.1055	1.1070	0.0015	0.0015					
R(24,57)	1.1050	1.1078	0.0028	0.0028					
R(34,79)	1.1050	1.1079	0.0029	0.0029					
R(25,60)	1.1049	1.1078	0.0029	0.0029					

5.4.4.6 B3LYP/Midi!+

Structural minima not located

5.4.4.7 MPW1PW91/Midi!+

Structural minima not located

5.4.4.8 B3LYP/6-31G(d)

C	-3.157790368983	-3.780328148884	-0.781920028772	H	2.490851708668	-3.574773509489	0.374574433507
C	-3.113407237563	-3.773922133851	0.633047457653	H	3.698451935115	-3.200144301620	1.604039605696
C	-3.918988734265	-4.620996226255	1.388827013212	H	4.205854168512	-1.034464194409	0.455478178849
C	-4.800351224478	-5.513244634676	0.771220962769	H	4.510007049497	-2.437632567089	-0.569214588479
C	-4.855010987465	-5.538268608336	-0.625287445270	H	0.470184288261	-3.551486024310	1.433997009128
C	-4.053493602308	-4.692150095928	-1.386141155237	H	0.158172619350	-2.398978879890	2.740883576658
C	-2.337494125927	-2.907363092251	-1.603381600147	H	1.409592553943	-3.649172511674	2.952249404216
C	-1.475877814069	-1.987589825629	-1.101592084330	H	3.129972139894	-0.402378596161	2.261417090689
N	-0.728678708715	-1.168757319606	-0.646506970820	H	3.031512094926	-1.737622181577	3.445151877098
C	3.153514368950	3.781825124585	0.789247544717	H	1.654024091338	-0.629243311547	3.192710341647
C	3.114828184317	3.775836635773	-0.625888954315	H	1.871236717116	-3.056659086387	-1.648344631756
C	3.922148882494	4.624394589250	-1.378135938823	H	3.257722478531	-2.597351872258	-2.676082678326
C	4.799639358415	5.517785483210	-0.756675513414	H	1.699174741892	-1.731896017290	-2.795578354142
C	4.848620378499	5.542430660596	0.640050724320	H	3.686555872111	0.675837039384	-0.964805050895
C	4.045342451481	4.694830241762	1.397392125688	H	2.744997928698	0.365448284780	-2.431573393988
C	2.331321140891	2.907223426645	1.607056652877	H	4.365091455491	-0.353686200333	-2.258473721163
C	1.473623492414	1.985961186098	1.101345369817	H	-4.507443851226	2.439282931660	0.560977499331
N	0.729909858911	1.165942198863	0.642687139282	H	-4.204450869799	1.035474565272	-0.463154755796
N	1.909844824412	-2.023666460740	1.642162788519	H	-3.693184607403	3.200195417613	-1.611847797409
C	2.967163848815	-2.747413990482	0.910501336098	H	-2.486000561441	3.573428969823	-0.381527068522
C	3.711300233158	-1.849776539122	-0.082085960325	H	-1.869820514309	3.055305135600	1.642853517658
N	2.808132789985	-1.242151368541	-1.078773369877	H	-1.699816126898	1.730183650290	2.790017808508
C	0.941414106333	-2.962598990319	2.225552989385	H	-3.257577738594	2.596848136790	2.669245133987
C	2.468937891163	-1.158215334715	2.691925486970	H	-3.687644769317	-0.675591430298	0.956995554616
C	2.395273647072	-2.212937981303	-2.103516792889	H	-4.366591319034	0.354424437816	2.250065195871
C	3.443348340863	-0.079443156731	-1.716511154331	H	-2.747350379333	-0.366228801113	2.424769496818
N	-2.807587428279	1.241606904819	1.072098848055	H	-0.153542388560	2.394041873975	-2.746381640672
C	-3.709179138614	1.850224603851	0.074588398392	H	-0.464985497519	3.547653988513	-1.440318183706
C	-2.963063189614	2.746611855805	-0.917633047405	H	-1.403527617437	3.645443347054	-2.959098240941
N	-1.906157143497	2.021251457112	-1.648307046971	H	-1.651009261585	0.625563640733	-3.197817378199
C	-2.394900184808	2.211888012538	2.097393992369	H	-3.027164826392	1.735261850813	-3.451727432723
C	-3.444541464861	0.079383291556	1.709034988033	H	-3.127714921283	0.400900448973	-2.267167215530
C	-0.936439605753	2.958798584855	-2.231766089638				
C	-2.465624992742	1.155741590036	-2.697814351341				
Li	1.085807237898	-0.767914080684	0.108324623823				
Li	-1.084452970432	0.765665063995	-0.112970274665				
H	-2.428548862210	-3.094316513064	1.136216865636				
H	-3.855020130305	-4.586596049815	2.474859245708				
H	-5.427074531607	-6.174252349546	1.363431005417				
H	-5.531273713426	-6.225538653505	-1.129639825468				
H	-4.113063722290	-4.727454092916	-2.472186731379				
H	-2.397332997099	-2.998926290744	-2.684228826597				
H	2.433014040906	3.095366253740	-1.132019147056				
H	3.862626977951	4.590255146142	-2.464429037419				
H	5.427739785837	6.179948874190	-1.346129687645				
H	5.521790194856	6.230569681067	1.147347353764				
H	4.100481136001	4.729844314001	2.483680760344				
H	2.386891155555	2.998165445067	2.688182111482				

Table 5.39 Signed and Unsigned differences in bond length for the B3LYP/6-31G(d) structure of FAHBEV relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(35,36)	2.6515	2.6666	0.0151	0.0151
R(19,35)	2.1478	2.1468	-0.0010	0.0010
R(30,36)	2.1478	2.1468	-0.0010	0.0010
R(22,35)	2.1459	2.1449	-0.0010	0.0010
R(27,36)	2.1459	2.1448	-0.0011	0.0011
R(9,36)	2.0272	2.0379	0.0107	0.0107
R(18,35)	2.0271	2.0376	0.0105	0.0105
R(9,35)	2.0065	2.0057	-0.0008	0.0008
R(18,36)	2.0065	2.0058	-0.0007	0.0007
R(20,21)	1.5313	1.5312	-0.0001	0.0001
R(28,29)	1.5313	1.5312	-0.0001	0.0001
R(19,20)	1.4766	1.4755	-0.0011	0.0011
R(21,22)	1.4766	1.4759	-0.0007	0.0007
R(27,28)	1.4766	1.4759	-0.0007	0.0007
R(29,30)	1.4766	1.4755	-0.0011	0.0011
R(19,24)	1.4719	1.4709	-0.0010	0.0010
R(30,34)	1.4719	1.4709	-0.0010	0.0010
R(22,25)	1.4718	1.4707	-0.0011	0.0011
R(27,31)	1.4718	1.4707	-0.0011	0.0011
R(22,26)	1.4710	1.4704	-0.0006	0.0006
R(27,32)	1.4710	1.4704	-0.0006	0.0006
R(19,23)	1.4706	1.4696	-0.0010	0.0010
R(30,33)	1.4706	1.4696	-0.0010	0.0010
R(1,7)	1.4529	1.4525	-0.0004	0.0004
R(10,16)	1.4529	1.4525	-0.0004	0.0004
R(1,2)	1.4169	1.4157	-0.0012	0.0012
R(10,11)	1.4169	1.4157	-0.0012	0.0012
R(1,6)	1.4159	1.4138	-0.0021	0.0021
R(10,15)	1.4159	1.4138	-0.0021	0.0021
R(4,5)	1.4002	1.3978	-0.0024	0.0024
R(13,14)	1.4002	1.3978	-0.0024	0.0024
R(3,4)	1.3999	1.3980	-0.0019	0.0019
R(12,13)	1.3999	1.3980	-0.0019	0.0019
R(2,3)	1.3942	1.3920	-0.0022	0.0022
R(11,12)	1.3942	1.3920	-0.0022	0.0022
R(5,6)	1.3935	1.3918	-0.0017	0.0017
R(14,15)	1.3935	1.3919	-0.0016	0.0016
R(7,8)	1.3589	1.3565	-0.0024	0.0024
R(16,17)	1.3589	1.3565	-0.0024	0.0024
R(8,9)	1.1978	1.1983	0.0005	0.0005
R(17,18)	1.1978	1.1983	0.0005	0.0005
R(21,52)	1.1056	1.1049	-0.0007	0.0007
R(28,65)	1.1056	1.1049	-0.0007	0.0007
R(20,50)	1.1055	1.1049	-0.0006	0.0006
R(29,67)	1.1055	1.1049	-0.0006	0.0006
R(24,57)	1.1050	1.1043	-0.0007	0.0007
R(34,79)	1.1050	1.1043	-0.0007	0.0007
R(25,60)	1.1049	1.1043	-0.0006	0.0006

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(31,71)	1.1049	1.1043	-0.0006	0.0006
R(23,55)	1.1046	1.1039	-0.0007	0.0007
R(26,64)	1.1046	1.1039	-0.0007	0.0007
R(32,73)	1.1046	1.1039	-0.0007	0.0007
R(33,77)	1.1046	1.1039	-0.0007	0.0007
R(20,49)	1.0949	1.0948	-1E-04	1E-04
R(29,68)	1.0949	1.0948	-1E-04	1E-04
R(21,51)	1.0947	1.0947	0.0000	0.0000
R(28,66)	1.0947	1.0947	0.0000	0.0000
R(23,54)	1.0942	1.0939	-0.0003	0.0003
R(26,63)	1.0942	1.0940	-0.0002	0.0002
R(32,74)	1.0942	1.0940	-0.0002	0.0002
R(33,75)	1.0942	1.0939	-0.0003	0.0003
R(23,53)	1.0934	1.0933	-1E-04	1E-04
R(33,76)	1.0934	1.0933	-1E-04	1E-04
R(24,58)	1.0933	1.0930	-0.0003	0.0003
R(25,61)	1.0933	1.0931	-0.0002	0.0002
R(31,70)	1.0933	1.0931	-0.0002	0.0002
R(34,78)	1.0933	1.0930	-0.0003	0.0003
R(26,62)	1.0932	1.0930	-0.0002	0.0002
R(32,72)	1.0932	1.0930	-0.0002	0.0002
R(24,56)	1.0926	1.0925	-1E-04	1E-04
R(25,59)	1.0926	1.0925	-1E-04	1E-04
R(31,69)	1.0926	1.0926	0.0000	0.0000
R(34,80)	1.0926	1.0925	-1E-04	1E-04
R(3,38)	1.0887	1.0885	-0.0002	0.0002
R(12,44)	1.0887	1.0885	-0.0002	0.0002
R(6,41)	1.0886	1.0883	-0.0003	0.0003
R(15,47)	1.0886	1.0883	-0.0003	0.0003
R(2,37)	1.0883	1.0882	-1E-04	1E-04
R(5,40)	1.0883	1.0881	-0.0002	0.0002
R(11,43)	1.0883	1.0882	-1E-04	1E-04
R(14,46)	1.0883	1.0881	-0.0002	0.0002
R(7,42)	1.0871	1.0864	-0.0007	0.0007
R(16,48)	1.0871	1.0864	-0.0007	0.0007
R(4,39)	1.0868	1.0865	-0.0003	0.0003
R(13,45)	1.0868	1.0865	-0.0003	0.0003

5.4.4.9 HF/6-31G(d)

C	-3.013645722036	-3.915764938064	-0.767714294077	H	3.714793372622	0.384428571582	-0.991630634505
C	-3.102671378813	-3.827443049774	0.629561696514	H	2.726145899255	0.162301090410	-2.419925539990
C	-3.882129397486	-4.707064574974	1.357978927009	H	4.284237213034	-0.651782149491	-2.303658126197
C	-4.604866310443	-5.709852295281	0.730524462427	H	-4.321921160166	2.772252172248	0.648402545551
C	-4.527862138761	-5.810987536007	-0.650276306149	H	-4.172897307583	1.367023560807	-0.371096799664
C	-3.750860305983	-4.935351914410	-1.384843947475	H	-3.535530142430	3.449863392967	-1.543643584400
C	-2.206119983997	-3.012001313905	-1.574808001314	H	-2.287507674140	3.748772951963	-0.364936418453
C	-1.467887787144	-2.005345926328	-1.056508140907	H	-1.651859832909	3.177383479516	1.671613289625
N	-0.827441407216	-1.131787681276	-0.605224986818	H	-1.554568631573	1.843580107221	2.787748596904
C	3.013828921157	3.915564210151	0.767927571178	H	-3.029503692184	2.810070260738	2.711438051902
C	3.102830326351	3.827348183701	-0.629356654011	H	-3.715045406117	-0.384204859874	0.991473984394
C	3.882433593752	4.706899781970	-1.357703083304	H	-4.284571249025	0.652074330311	2.303412257734
C	4.605343454546	5.709511566074	-0.730166947790	H	-2.726488385628	-0.162004117069	2.419818550672
C	4.528363666984	5.810541934144	0.650642920851	H	-0.105695841993	2.404675365823	-2.742395337802
C	3.751219067666	4.934974025132	1.385140196825	H	-0.306568298126	3.568748963980	-1.449579281014
C	2.206157653503	3.011866031495	1.574949002247	H	-1.249942557550	3.730539939612	-2.933927636410
C	1.467774535220	2.005362361462	1.056570040515	H	-1.734092827862	0.760618947330	-3.162388571055
N	0.827205225904	1.131929699437	0.605217718156	H	-3.001732568672	1.965884473123	-3.398571454489
N	1.852674174386	-2.167403109276	1.627255437922	H	-3.198556675681	0.663495216352	-2.224221428474
C	2.824847761071	-2.959859729330	0.874831062635				
C	3.599847895748	-2.127551464073	-0.143343419749				
N	2.725663591315	-1.457969917443	-1.106001170690				
C	0.828596905450	-3.019568527137	2.221175065751				
C	2.486697256470	-1.351458104662	2.657831969234				
C	2.219994399522	-2.375575785687	-2.121942133849				
C	3.406255233968	-0.333822628640	-1.739051926736				
N	-2.725920803365	1.458200993662	1.105811148541				
C	-3.600037366628	2.127746041542	0.143069004048				
C	-2.824949835690	2.960007319307	-0.875074755040				
N	-1.852763805008	2.167491973098	-1.627421031288				
C	-2.220300942253	2.375858853550	2.121728790602				
C	-3.406554158785	0.334085617302	1.738877104170				
C	-0.828633167724	3.019598925883	-2.221331987643				
C	-2.486767159437	1.351516799547	-2.657984371996				
Li	1.058203626048	-0.837938731197	0.120456832297				
Li	-1.058405508906	0.838081463067	-0.120503930669				
H	-2.553496309174	-3.059670607824	1.146713449557				
H	-3.924809366786	-4.607001283498	2.429627503840				
H	-5.209959155318	-6.392077986306	1.300338315790				
H	-5.079288474910	-6.580937982799	-1.162784730652				
H	-3.708717291695	-5.036003035577	-2.455846696640				
H	-2.183791762382	-3.137016095204	-2.641230037786				
H	2.553518507310	3.059716179921	-1.146571432745				
H	3.925088985733	4.606922333447	-2.429360668712				
H	5.210547637875	6.391684360031	-1.299925881856				
H	5.079922482965	6.580355751468	1.163214001676				
H	3.709100209902	5.035539727266	2.456151886341				
H	2.183823583663	3.136819759128	2.641378030657				
H	2.287402114592	-3.748632781571	0.364710353425				
H	3.535482591341	-3.449708531916	1.543347317132				
H	4.172735955512	-1.366841728934	0.370808646239				
H	4.321705818185	-2.772028163520	-0.648752307024				
H	0.306516317508	-3.568704163890	1.449422837091				
H	0.105662612442	-2.404689911801	2.742295486225				
H	1.249961334254	-3.730524808006	2.933722756479				
H	3.198438833073	-0.663383450410	2.224075920833				
H	3.001720983533	-1.965846038668	3.398361638750				
H	1.734023156220	-0.760618680036	3.162305176486				
H	1.651560049699	-3.177115596751	-1.671847921723				
H	3.029170126944	-2.809766632263	-2.711703826338				
H	1.554243545349	-1.843257410796	-2.787911860810				

Table 5.40 Signed and Unsigned differences in bond length for the HF/6-31G(d) structure of FAHBEV relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(35,36)	2.6515	2.7106	0.0591	0.0591
R(19,35)	2.1478	2.1608	0.0130	0.0130
R(30,36)	2.1478	2.1608	0.0130	0.0130
R(22,35)	2.1459	2.1608	0.0149	0.0149
R(27,36)	2.1459	2.1608	0.0149	0.0149
R(9,36)	2.0272	2.0417	0.0145	0.0145
R(18,35)	2.0271	2.0417	0.0146	0.0146
R(9,35)	2.0065	2.0417	0.0352	0.0352
R(18,36)	2.0065	2.0417	0.0352	0.0352
R(20,21)	1.5313	1.5264	-0.0049	0.0049
R(28,29)	1.5313	1.5264	-0.0049	0.0049
R(19,20)	1.4766	1.4626	-0.0140	0.0140
R(21,22)	1.4766	1.4626	-0.0140	0.0140
R(27,28)	1.4766	1.4626	-0.0140	0.0140
R(29,30)	1.4766	1.4626	-0.0140	0.0140
R(19,24)	1.4719	1.4594	-0.0125	0.0125
R(30,34)	1.4719	1.4594	-0.0125	0.0125
R(22,25)	1.4718	1.4594	-0.0124	0.0124
R(27,31)	1.4718	1.4594	-0.0124	0.0124
R(22,26)	1.4710	1.4587	-0.0123	0.0123
R(27,32)	1.4710	1.4587	-0.0123	0.0123
R(19,23)	1.4706	1.4587	-0.0119	0.0119
R(30,33)	1.4706	1.4587	-0.0119	0.0119
R(1,7)	1.4529	1.4561	0.0032	0.0032
R(10,16)	1.4529	1.4561	0.0032	0.0032
R(1,2)	1.4169	1.4029	-0.0140	0.0140
R(10,11)	1.4169	1.4029	-0.0140	0.0140
R(1,6)	1.4159	1.4014	-0.0145	0.0145
R(10,15)	1.4159	1.4014	-0.0145	0.0145
R(4,5)	1.4002	1.3866	-0.0136	0.0136
R(13,14)	1.4002	1.3866	-0.0136	0.0136
R(3,4)	1.3999	1.3862	-0.0137	0.0137
R(12,13)	1.3999	1.3862	-0.0137	0.0137
R(2,3)	1.3942	1.3827	-0.0115	0.0115
R(11,12)	1.3942	1.3827	-0.0115	0.0115
R(5,6)	1.3935	1.3820	-0.0115	0.0115
R(14,15)	1.3935	1.3820	-0.0115	0.0115
R(7,8)	1.3589	1.3517	-0.0072	0.0072
R(16,17)	1.3589	1.3517	-0.0072	0.0072
R(8,9)	1.1978	1.1734	-0.0244	0.0244
R(17,18)	1.1978	1.1734	-0.0244	0.0244
R(21,52)	1.1056	1.0917	-0.0139	0.0139
R(28,65)	1.1056	1.0917	-0.0139	0.0139
R(20,50)	1.1055	1.0917	-0.0138	0.0138
R(29,67)	1.1055	1.0917	-0.0138	0.0138
R(24,57)	1.1050	1.0914	-0.0136	0.0136
R(34,79)	1.1050	1.0914	-0.0136	0.0136
R(25,60)	1.1049	1.0914	-0.0135	0.0135

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(31,71)	1.1049	1.0914	-0.0135	0.0135
R(23,55)	1.1046	1.0912	-0.0134	0.0134
R(26,64)	1.1046	1.0912	-0.0134	0.0134
R(32,73)	1.1046	1.0912	-0.0134	0.0134
R(33,77)	1.1046	1.0912	-0.0134	0.0134
R(20,49)	1.0949	1.0822	-0.0127	0.0127
R(29,68)	1.0949	1.0822	-0.0127	0.0127
R(21,51)	1.0947	1.0822	-0.0125	0.0125
R(28,66)	1.0947	1.0822	-0.0125	0.0125
R(23,54)	1.0942	1.0827	-0.0115	0.0115
R(26,63)	1.0942	1.0827	-0.0115	0.0115
R(32,74)	1.0942	1.0827	-0.0115	0.0115
R(33,75)	1.0942	1.0827	-0.0115	0.0115
R(23,53)	1.0934	1.0815	-0.0119	0.0119
R(33,76)	1.0934	1.0815	-0.0119	0.0119
R(24,58)	1.0933	1.0817	-0.0116	0.0116
R(25,61)	1.0933	1.0817	-0.0116	0.0116
R(31,70)	1.0933	1.0817	-0.0116	0.0116
R(34,78)	1.0933	1.0817	-0.0116	0.0116
R(26,62)	1.0932	1.0815	-0.0117	0.0117
R(32,72)	1.0932	1.0815	-0.0117	0.0117
R(24,56)	1.0926	1.0808	-0.0118	0.0118
R(25,59)	1.0926	1.0808	-0.0118	0.0118
R(31,69)	1.0926	1.0808	-0.0118	0.0118
R(34,80)	1.0926	1.0808	-0.0118	0.0118
R(3,38)	1.0887	1.0772	-0.0115	0.0115
R(12,44)	1.0887	1.0772	-0.0115	0.0115
R(6,41)	1.0886	1.0765	-0.0121	0.0121
R(15,47)	1.0886	1.0765	-0.0121	0.0121
R(2,37)	1.0883	1.0763	-0.0120	0.0120
R(5,40)	1.0883	1.0768	-0.0115	0.0115
R(11,43)	1.0883	1.0763	-0.0120	0.0120
R(14,46)	1.0883	1.0768	-0.0115	0.0115
R(7,42)	1.0871	1.0740	-0.0131	0.0131
R(16,48)	1.0871	1.0740	-0.0131	0.0131
R(4,39)	1.0868	1.0753	-0.0115	0.0115
R(13,45)	1.0868	1.0753	-0.0115	0.0115

5.4.4.10 B3LYP/6-31(+LiX)G(d)

C	-3.099295509224	-3.840105130217	-0.803014276817	H	-4.156861618015	1.090812979224	-0.402657426635
C	-3.127267138551	-3.786338808464	0.611442475446	H	-3.647366804907	3.237048071470	-1.586275236439
C	-3.946179271909	-4.632570744913	1.354291893310	H	-2.416438338362	3.615443838219	-0.381342665043
C	-4.769367119587	-5.569983799204	0.723476090289	H	-1.751186215468	3.108230709851	1.631573027374
C	-4.752308918285	-5.641276688979	-0.672496087382	H	-1.589160230556	1.800184409795	2.798326179653
C	-3.936930192836	-4.796677153847	-1.420340942908	H	-3.133772745225	2.691987105285	2.683450050058
C	-2.262505777277	-2.970022314127	-1.612927255109	H	-3.639322713781	-0.602862631566	1.037195765836
C	-1.458029144115	-2.004511816260	-1.101561718473	H	-4.281540812349	0.459110428451	2.323706621136
N	-0.757953990461	-1.148228228342	-0.639694868155	H	-2.669534115713	-0.283029467030	2.484157726269
C	3.099294809038	3.840105159193	0.803015570063	H	-0.130836444312	2.389665596670	-2.766066411177
C	3.127276439637	3.786322308634	-0.611440377149	H	-0.408482513656	3.552386622688	-1.460129856593
C	3.946200014939	4.632539893452	-1.354293588020	H	-1.370284816059	3.654745468193	-2.964255295372
C	4.769389381760	5.569954858010	-0.723482618861	H	-1.660659956258	0.632332992149	-3.184829484091
C	4.752320928095	5.641264438239	0.672488603346	H	-3.016288868858	1.770304724384	-3.429689214765
C	3.936930987645	4.796679132064	1.420337252957	H	-3.131911621933	0.444178941183	-2.237645877829
C	2.262494306747	2.970036709159	1.612932554255				
C	1.458019077424	2.004521813174	1.101573232550				
N	0.757945360769	1.148233724578	0.639712492503				
N	1.871767001713	-2.042712400567	1.640220660933				
C	2.909070016187	-2.785988976271	0.898933743432				
C	3.644883806371	-1.907289410212	-0.116697620992				
N	2.730974591269	-1.302267752862	-1.105045808156				
C	0.898902172726	-2.965506342046	2.241479009351				
C	2.458361381322	-1.182353660684	2.679112904388				
C	2.285160147890	-2.282368375205	-2.107111929419				
C	3.372254456587	-0.160467624619	-1.772585530766				
N	-2.730990822989	1.302272562272	1.105040785196				
C	-3.644889388942	1.907303460236	0.116688483533				
C	-2.909062884168	2.786000911742	-0.898935401467				
N	-1.871759225564	2.042719763956	-1.640216861179				
C	-2.285181433769	2.282365179064	2.107116656314				
C	-3.372278895737	0.160468888264	1.772566679014				
C	-0.898887738125	2.965509636624	-2.241470468256				
C	-2.458351531578	1.182362619823	-2.679111501071				
Li	1.056460290621	-0.783878283962	0.115882419973				
Li	-1.056466100255	0.783884580983	-0.115872178462				
H	-2.489860045696	-3.070039448206	1.126188974649				
H	-3.939270028573	-4.560803997597	2.440408278226				
H	-5.406677894300	-6.229900753260	1.305439465800				
H	-5.382675695952	-6.363893241273	-1.186650349528				
H	-3.940232783795	-4.868443415207	-2.506229740333				
H	-2.272462936982	-3.092073089122	-2.692432056819				
H	2.489867477577	3.070022056032	-1.126183301505				
H	3.939298481573	4.560760490415	-2.440409195837				
H	5.406709048304	6.229860627041	-1.305448937511				
H	5.382688548817	6.363882937871	1.186639095061				
H	3.940225757789	4.868458236716	2.506225224406				
H	2.272445257061	3.092099337221	2.692436077662				
H	2.416447234835	-3.615436296205	0.381346489766				
H	3.647381662576	-3.237029739130	1.586269436469				
H	4.156853918592	-1.090793757321	0.402642386049				
H	4.428970646051	-2.509048396480	-0.611227882680				
H	0.408494988060	-3.552384826087	1.460140703562				
H	0.130851539018	-2.389665516069	2.766079459422				
H	1.370305811328	-3.654740809562	2.964260852682				
H	3.131916191574	-0.444166976270	2.237644309831				
H	3.016305150057	-1.770294323976	3.429686946896				
H	1.660670330927	-0.632327656551	3.184835587747				
H	1.751170046066	-3.108231945856	-1.631559242341				
H	3.133748561682	-2.691991857175	-2.683448420575				
H	1.589132887163	-1.800193864856	-2.798319667606				
H	3.639302899337	0.602870287483	-1.037222931702				
H	2.669502765105	0.283023411082	-2.484174469832				
H	4.281512554794	-0.459111079861	-2.323730818613				
H	-4.428975425395	2.509066267144	0.611215302394				

Table 5.41 Signed and Unsigned differences in bond length for the B3LYP/6-31(+LiX)G(d) structure of FAHBEV relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(35,36)	2.6515	2.6412	-0.0103	0.0103
R(19,35)	2.1478	2.1385	-0.0093	0.0093
R(30,36)	2.1478	2.1385	-0.0093	0.0093
R(22,35)	2.1459	2.1362	-0.0097	0.0097
R(27,36)	2.1459	2.1362	-0.0097	0.0097
R(9,36)	2.0272	2.0240	-0.0032	0.0032
R(18,35)	2.0271	2.0240	-0.0031	0.0031
R(9,35)	2.0065	1.9989	-0.0076	0.0076
R(18,36)	2.0065	1.9989	-0.0076	0.0076
R(20,21)	1.5313	1.5314	1E-04	1E-04
R(28,29)	1.5313	1.5314	1E-04	1E-04
R(19,20)	1.4766	1.4758	-0.0008	0.0008
R(21,22)	1.4766	1.4758	-0.0008	0.0008
R(27,28)	1.4766	1.4758	-0.0008	0.0008
R(29,30)	1.4766	1.4758	-0.0008	0.0008
R(19,24)	1.4719	1.4709	-0.0010	0.0010
R(30,34)	1.4719	1.4709	-0.0010	0.0010
R(22,25)	1.4718	1.4709	-0.0009	0.0009
R(27,31)	1.4718	1.4709	-0.0009	0.0009
R(22,26)	1.4710	1.4699	-0.0011	0.0011
R(27,32)	1.4710	1.4699	-0.0011	0.0011
R(19,23)	1.4706	1.4695	-0.0011	0.0011
R(30,33)	1.4706	1.4695	-0.0011	0.0011
R(1,7)	1.4529	1.4537	0.0008	0.0008
R(10,16)	1.4529	1.4537	0.0008	0.0008
R(1,2)	1.4169	1.4158	-0.0011	0.0011
R(10,11)	1.4169	1.4158	-0.0011	0.0011
R(1,6)	1.4159	1.4134	-0.0025	0.0025
R(10,15)	1.4159	1.4134	-0.0025	0.0025
R(4,5)	1.4002	1.3979	-0.0023	0.0023
R(13,14)	1.4002	1.3979	-0.0023	0.0023
R(3,4)	1.3999	1.3980	-0.0019	0.0019
R(12,13)	1.3999	1.3980	-0.0019	0.0019
R(2,3)	1.3942	1.3923	-0.0019	0.0019
R(11,12)	1.3942	1.3923	-0.0019	0.0019
R(5,6)	1.3935	1.3919	-0.0016	0.0016
R(14,15)	1.3935	1.3919	-0.0016	0.0016
R(7,8)	1.3589	1.3568	-0.0021	0.0021
R(16,17)	1.3589	1.3568	-0.0021	0.0021
R(8,9)	1.1978	1.1986	0.0008	0.0008
R(17,18)	1.1978	1.1986	0.0008	0.0008
R(21,52)	1.1056	1.1052	-0.0004	0.0004
R(28,65)	1.1056	1.1052	-0.0004	0.0004
R(20,50)	1.1055	1.1050	-0.0005	0.0005
R(29,67)	1.1055	1.1050	-0.0005	0.0005
R(24,57)	1.1050	1.1047	-0.0003	0.0003
R(34,79)	1.1050	1.1047	-0.0003	0.0003
R(25,60)	1.1049	1.1046	-0.0003	0.0003

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(31,71)	1.1049	1.1046	-0.0003	0.0003
R(23,55)	1.1046	1.1044	-0.0002	0.0002
R(26,64)	1.1046	1.1044	-0.0002	0.0002
R(32,73)	1.1046	1.1044	-0.0002	0.0002
R(33,77)	1.1046	1.1044	-0.0002	0.0002
R(20,49)	1.0949	1.0948	-1E-04	1E-04
R(29,68)	1.0949	1.0948	-1E-04	1E-04
R(21,51)	1.0947	1.0948	1E-04	1E-04
R(28,66)	1.0947	1.0948	1E-04	1E-04
R(23,54)	1.0942	1.0939	-0.0003	0.0003
R(26,63)	1.0942	1.0940	-0.0002	0.0002
R(32,74)	1.0942	1.0940	-0.0002	0.0002
R(33,75)	1.0942	1.0939	-0.0003	0.0003
R(23,53)	1.0934	1.0934	0.0000	0.0000
R(33,76)	1.0934	1.0934	0.0000	0.0000
R(24,58)	1.0933	1.0930	-0.0003	0.0003
R(25,61)	1.0933	1.0930	-0.0003	0.0003
R(31,70)	1.0933	1.0930	-0.0003	0.0003
R(34,78)	1.0933	1.0930	-0.0003	0.0003
R(26,62)	1.0932	1.0930	-0.0002	0.0002
R(32,72)	1.0932	1.0930	-0.0002	0.0002
R(24,56)	1.0926	1.0925	-1E-04	1E-04
R(25,59)	1.0926	1.0924	-0.0002	0.0002
R(31,69)	1.0926	1.0924	-0.0002	0.0002
R(34,80)	1.0926	1.0925	-1E-04	1E-04
R(3,38)	1.0887	1.0885	-0.0002	0.0002
R(12,44)	1.0887	1.0885	-0.0002	0.0002
R(6,41)	1.0886	1.0883	-0.0003	0.0003
R(15,47)	1.0886	1.0883	-0.0003	0.0003
R(2,37)	1.0883	1.0883	0.0000	0.0000
R(5,40)	1.0883	1.0881	-0.0002	0.0002
R(11,43)	1.0883	1.0883	0.0000	0.0000
R(14,46)	1.0883	1.0881	-0.0002	0.0002
R(7,42)	1.0871	1.0864	-0.0007	0.0007
R(16,48)	1.0871	1.0864	-0.0007	0.0007
R(4,39)	1.0868	1.0864	-0.0004	0.0004
R(13,45)	1.0868	1.0864	-0.0004	0.0004

5.4.4.11 B3LYP/6-31'+G(d)

C	-3.127864672107	-3.848870280552	-0.784423041874	H	-4.167612119860	1.099774076537	-0.417355398468
C	-3.134199700732	-3.832021705603	0.632476547272	H	-3.639946810059	3.243557733529	-1.595105307518
C	-3.946591634958	-4.694460769193	1.366962061596	H	-2.410329909421	3.612817038601	-0.385721487808
C	-4.785701693449	-5.613167296066	0.725448458342	H	-1.767053127430	3.099257816277	1.641851101165
C	-4.790077093915	-5.648721652549	-0.674330276835	H	-1.613024254735	1.781669787376	2.800416856703
C	-3.981092631401	-4.787874716784	-1.413132152878	H	-3.156212347598	2.674307471579	2.681135466524
C	-2.302073836809	-2.962703600019	-1.585860196115	H	-3.661253557000	-0.603213703310	1.006206310000
C	-1.480591265789	-2.011040160196	-1.068852974348	H	-4.300915046415	0.448888377031	2.301435577855
N	-0.768543672922	-1.166383247394	-0.607048882266	H	-2.692942700580	-0.303315727271	2.458742852618
C	3.127650886640	3.848996691859	0.784644641656	H	-0.128469366539	2.382831965022	-2.772355545435
C	3.134267316110	3.832071195981	-0.632252533474	H	-0.410161630938	3.552814080684	-1.473286943872
C	3.946708507224	4.694560395986	-1.366624662331	H	-1.370227795583	3.644612991657	-2.978550387117
C	4.785589651122	5.613395301183	-0.724995350075	H	-1.664564230865	0.627241284867	-3.190809605371
C	4.789684873215	5.649026697378	0.674782141648	H	-3.017970153665	1.767362049613	-3.434650790239
C	3.980650516696	4.788129907831	1.413471228253	H	-3.136365024935	0.442830077882	-2.241799052799
C	2.301800580534	2.962782599288	1.585968082551				
C	1.480525717472	2.011000204072	1.068851355380				
N	0.768650689648	1.166250163930	0.606950642504				
N	1.871211634540	-2.039347711918	1.646126997966				
C	2.906718736851	-2.787300508248	0.905896712547				
C	3.650795019502	-1.911088040148	-0.105504595491				
N	2.743190674475	-1.296718688097	-1.094845433403				
C	0.898474739832	-2.960344504617	2.251716409304				
C	2.461064098865	-1.178873715606	2.683896388226				
C	2.303726313940	-2.269447002093	-2.107670905279				
C	3.391823502822	-0.151185450053	-1.750357107940				
N	-2.743136970351	1.296615794889	1.094627088021				
C	-3.650693673100	1.910981218294	0.105240170290				
C	-2.906569109896	2.787199254115	-0.906120752740				
N	-1.871023926718	2.039250658885	-1.646303108855				
C	-2.303731169593	2.269346573633	2.107475994588				
C	-3.391802453657	0.151081489539	1.750107402720				
C	-0.898251591285	2.960252516154	-2.251829330464				
C	-2.460824354696	1.178791809209	-2.684114214330				
Li	1.061754231194	-0.784861839646	0.115494600329				
Li	-1.061647939764	0.784754521452	-0.115631560063				
H	-2.486421306964	-3.132645716393	1.157242272567				
H	-3.922763745831	-4.650362799337	2.454283588772				
H	-5.417556147472	-6.284824980936	1.300618332432				
H	-5.431620976560	-6.355067888739	-1.197300499868				
H	-4.001872636446	-4.833082856706	-2.500593152840				
H	-2.329786917598	-3.060528325454	-2.668131756162				
H	2.486672326717	3.132592401895	-1.157107937599				
H	3.923102563634	4.650398568047	-2.453948441983				
H	5.417483404703	6.285091310687	-1.300077329201				
H	5.431047358492	6.355472526781	1.197840298222				
H	4.001210454037	4.833399144829	2.500933868164				
H	2.329310077383	3.060651786601	2.668240776055				
H	2.410452845956	-3.612920146083	0.385525700566				
H	3.640130960009	-3.243656611809	1.594846256742				
H	4.167744658107	-1.099883348548	0.417063658979				
H	4.431399401401	-2.516825471466	-0.600199595256				
H	0.410349031958	-3.552920494835	1.473207429115				
H	0.128716127451	-2.382919156435	2.772272163532				
H	1.370490508588	-3.644691675503	2.978424357513				
H	3.136580222538	-0.442916496327	2.241536795102				
H	3.018249640386	-1.767433480365	3.434411645448				
H	1.664830095045	-0.627316386629	3.190624832805				
H	1.767071397760	-3.099355924884	-1.642015524582				
H	3.156174370603	-2.674410400424	-2.681377890374				
H	1.612981034566	-1.781768374874	-2.800572111044				
H	3.661312667326	0.603106707706	-1.006466543702				
H	2.692927797074	0.303214422882	-2.458955616266				
H	4.300908027630	-0.448991157209	-2.301732404475				
H	-4.431326516486	2.516713949190	0.599895931350				

Table 5.42 Signed and Unsigned differences in bond length for the B3LYP/6-31'+G(d) structure of FAHBEV relative to B3LYP/6-31+G(d)

Bond list	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(35,36)	2.6515	2.6507	-0.0008	0.0008
R(19,35)	2.1478	2.1382	-0.0096	0.0096
R(30,36)	2.1478	2.1382	-0.0096	0.0096
R(22,35)	2.1459	2.1340	-0.0119	0.0119
R(27,36)	2.1459	2.1340	-0.0119	0.0119
R(9,36)	2.0272	2.0333	0.0061	0.0061
R(18,35)	2.0271	2.0333	0.0062	0.0062
R(9,35)	2.0065	2.0044	-0.0021	0.0021
R(18,36)	2.0065	2.0044	-0.0021	0.0021
R(20,21)	1.5313	1.5311	-0.0002	0.0002
R(28,29)	1.5313	1.5311	-0.0002	0.0002
R(19,20)	1.4766	1.4764	-0.0002	0.0002
R(21,22)	1.4766	1.4765	-1E-04	1E-04
R(27,28)	1.4766	1.4765	-1E-04	1E-04
R(29,30)	1.4766	1.4764	-0.0002	0.0002
R(19,24)	1.4719	1.4715	-0.0004	0.0004
R(30,34)	1.4719	1.4715	-0.0004	0.0004
R(22,25)	1.4718	1.4714	-0.0004	0.0004
R(27,31)	1.4718	1.4714	-0.0004	0.0004
R(22,26)	1.4710	1.4706	-0.0004	0.0004
R(27,32)	1.4710	1.4706	-0.0004	0.0004
R(19,23)	1.4706	1.4701	-0.0005	0.0005
R(30,33)	1.4706	1.4701	-0.0005	0.0005
R(1,7)	1.4529	1.4524	-0.0005	0.0005
R(10,16)	1.4529	1.4524	-0.0005	0.0005
R(1,2)	1.4169	1.4170	1E-04	1E-04
R(10,11)	1.4169	1.4170	1E-04	1E-04
R(1,6)	1.4159	1.4160	1E-04	1E-04
R(10,15)	1.4159	1.4160	1E-04	1E-04
R(4,5)	1.4002	1.4002	0.0000	0.0000
R(13,14)	1.4002	1.4002	0.0000	0.0000
R(3,4)	1.3999	1.3999	0.0000	0.0000
R(12,13)	1.3999	1.3999	0.0000	0.0000
R(2,3)	1.3942	1.3940	-0.0002	0.0002
R(11,12)	1.3942	1.3940	-0.0002	0.0002
R(5,6)	1.3935	1.3933	-0.0002	0.0002
R(14,15)	1.3935	1.3933	-0.0002	0.0002
R(7,8)	1.3589	1.3593	0.0004	0.0004
R(16,17)	1.3589	1.3593	0.0004	0.0004
R(8,9)	1.1978	1.1974	-0.0004	0.0004
R(17,18)	1.1978	1.1974	-0.0004	0.0004
R(21,52)	1.1056	1.1050	-0.0006	0.0006
R(28,65)	1.1056	1.1050	-0.0006	0.0006
R(20,50)	1.1055	1.1049	-0.0006	0.0006
R(29,67)	1.1055	1.1049	-0.0006	0.0006
R(24,57)	1.1050	1.1046	-0.0004	0.0004
R(34,79)	1.1050	1.1046	-0.0004	0.0004
R(25,60)	1.1049	1.1044	-0.0005	0.0005

Bond list (cont.)	B3LYP/6-31+G(d) (Å)	R _i (Å)	ΔR _i (Å)	ΔR _i (Å)
R(31,71)	1.1049	1.1044	-0.0005	0.0005
R(23,55)	1.1046	1.1042	-0.0004	0.0004
R(26,64)	1.1046	1.1041	-0.0005	0.0005
R(32,73)	1.1046	1.1041	-0.0005	0.0005
R(33,77)	1.1046	1.1042	-0.0004	0.0004
R(20,49)	1.0949	1.0949	0.0000	0.0000
R(29,68)	1.0949	1.0949	0.0000	0.0000
R(21,51)	1.0947	1.0947	0.0000	0.0000
R(28,66)	1.0947	1.0947	0.0000	0.0000
R(23,54)	1.0942	1.0940	-0.0002	0.0002
R(26,63)	1.0942	1.0941	-1E-04	1E-04
R(32,74)	1.0942	1.0941	-1E-04	1E-04
R(33,75)	1.0942	1.0940	-0.0002	0.0002
R(23,53)	1.0934	1.0934	0.0000	0.0000
R(33,76)	1.0934	1.0934	0.0000	0.0000
R(24,58)	1.0933	1.0932	-1E-04	1E-04
R(25,61)	1.0933	1.0932	-1E-04	1E-04
R(31,70)	1.0933	1.0932	-1E-04	1E-04
R(34,78)	1.0933	1.0932	-1E-04	1E-04
R(26,62)	1.0932	1.0931	-1E-04	1E-04
R(32,72)	1.0932	1.0931	-1E-04	1E-04
R(24,56)	1.0926	1.0925	-1E-04	1E-04
R(25,59)	1.0926	1.0925	-1E-04	1E-04
R(31,69)	1.0926	1.0925	-1E-04	1E-04
R(34,80)	1.0926	1.0925	-1E-04	1E-04
R(3,38)	1.0887	1.0885	-0.0002	0.0002
R(12,44)	1.0887	1.0885	-0.0002	0.0002
R(6,41)	1.0886	1.0886	0.0000	0.0000
R(15,47)	1.0886	1.0886	0.0000	0.0000
R(2,37)	1.0883	1.0882	-1E-04	1E-04
R(5,40)	1.0883	1.0881	-0.0002	0.0002
R(11,43)	1.0883	1.0882	-1E-04	1E-04
R(14,46)	1.0883	1.0881	-0.0002	0.0002
R(7,42)	1.0871	1.0870	-1E-04	1E-04
R(16,48)	1.0871	1.0870	-1E-04	1E-04
R(4,39)	1.0868	1.0868	0.0000	0.0000
R(13,45)	1.0868	1.0868	0.0000	0.0000

5.4.4.12 B3LYP/6-31+G(d)

C	-3.105085305704	-3.872315595087	-0.785031786846	H	-4.415249719781	2.562986860817	0.614855726101
C	-3.144671601479	-3.832254167523	0.630727240029	H	-4.162670412947	1.141927481375	-0.400090437752
C	-3.958217769564	-4.697495486727	1.360958662918	H	-3.629387438035	3.280859763081	-1.585568274252
C	-4.766119111650	-5.641303959773	0.715700022726	H	-2.392507401144	3.647173389544	-0.382548301617
C	-4.738069875403	-5.699310062979	-0.682983053087	H	-1.743435246223	3.136342551791	1.644736541983
C	-3.927246901945	-4.836089113124	-1.417396022503	H	-1.593477533269	1.822053740192	2.808167308719
C	-2.275702936217	-2.985296553332	-1.582653086548	H	-3.132686087815	2.722101930732	2.688896801524
C	-1.480170280803	-2.013876343947	-1.063015801723	H	-3.664008798107	-0.558078374503	1.031392269286
N	-0.788125213812	-1.153146311735	-0.599505428880	H	-4.291913243671	0.506355383433	2.323147366241
C	3.104840479906	3.872386497568	0.785491523726	H	-2.689169568071	-0.257856535305	2.479891853113
C	3.144700514274	3.832410334848	-0.630262309060	H	-0.127658969495	2.402216427841	-2.778602680610
C	3.958306295203	4.697768348977	-1.360288883101	H	-0.395653041910	3.573577970506	-1.477668102737
C	4.765994680626	5.641616318644	-0.714821548874	H	-1.364090255620	3.670788461903	-2.977824405479
C	4.737669823553	5.699542410443	0.683859342604	H	-1.677176339573	0.655579378514	-3.190904242367
C	3.926787891214	4.836203024589	1.418068261673	H	-3.023409084384	1.806444707441	-3.426820567394
C	2.275390924155	2.985240133917	1.582901786277	H	-3.146376274338	0.480015251924	-2.235727347494
C	1.480071529021	2.013758433090	1.063054122072				
N	0.788205601013	1.152982888853	0.599359841894				
N	1.867519984361	-2.068303400598	1.643094369149				
C	2.895138519168	-2.822463851125	0.897754951102				
C	3.639416394969	-1.951896201832	-0.118611303613				
N	2.732051844417	-1.336138235051	-1.107551832095				
C	0.891704943735	-2.983998515141	2.253048808976				
C	2.467555263962	-1.212237540553	2.679192716415				
C	2.283139451081	-2.310557194545	-2.115086495075				
C	3.386494953722	-0.197880157028	-1.770844026296				
N	-2.732010643864	1.336186024013	1.107159233376				
C	-3.639296378458	1.951878390280	0.118106445685				
C	-2.894929757404	2.822333091755	-0.898292650387				
N	-1.867283208164	2.068076056680	-1.643495527434				
C	-2.283121167949	2.310689193069	2.114623489290				
C	-3.386536719393	0.198019268067	1.770529387184				
C	-0.891403518486	2.983690862037	-2.253467796051				
C	-2.467276099656	1.211937569810	-2.679558279889				
Li	1.052766380532	-0.797618939803	0.115152220445				
Li	-1.052671188758	0.797490338500	-0.115381714046				
H	-2.522302614780	-3.112308795017	1.158770468827				
H	-3.960520067964	-4.635221516061	2.447898760412				
H	-5.399115801838	-6.314710872314	1.287454103787				
H	-5.355524751955	-6.425285269870	-1.208516641645				
H	-3.922143314502	-4.898989315428	-2.504148554975				
H	-2.281705189233	-3.096765023932	-2.663973477045				
H	2.522499344592	3.112437077740	-1.158465545794				
H	3.960825374849	4.635554114598	-2.447231917953				
H	5.399038514356	6.315114518645	-1.286415944348				
H	5.354954443472	6.425547088966	1.209552251728				
H	3.921468434684	4.899042300024	2.504823277666				
H	2.281178765615	3.096640567215	2.664230196634				
H	2.392704090842	-3.647269783904	0.381967127616				
H	3.629652982922	-3.281035173452	1.584940217670				
H	4.162800162234	-1.141978061976	0.399626503672				
H	4.415356140966	-2.562937079663	-0.615464832984				
H	0.395918505506	-3.573828628782	1.477229177700				
H	0.127979172691	-2.402590792376	2.778284296787				
H	1.364457977798	-3.671147736834	2.977312927598				
H	3.146616929677	-0.480267051632	2.235382519183				
H	3.023742141768	-1.806794478050	3.426375099027				
H	1.677474290329	-0.655934938491	3.190628196814				
H	1.743511216412	-3.136275886234	-1.645248162638				
H	3.132685767167	-2.721882582901	-2.689450012580				
H	1.593437711333	-1.821878680317	-2.808542408800				
H	3.663977460625	0.558153155757	-1.031645138897				
H	2.689069015366	0.258039847637	-2.480120273495				
H	4.291853145598	-0.506123550126	-2.323544138256				

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