

Computational Studies of Protonated Cyclic Ethers and Benzylic Organolithium Compounds

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ABSTRACT

Protonated epoxides feature prominently in organic chemistry as reactive intermediates. Gas-phase calculations studying the structure and ring-opening energetics of protonated ethylene oxide, propylene oxide and 2-methyl-1,2-epoxypropane were performed at the B3LYP and MP2 levels (both with the 6-311++G** basis set). Structural analyses were performed for 10 protonated epoxides using B3LYP, MP2, and CCSD/6-311++G** calculations. Protonated 2-methyl-1,2-epoxypropane was the most problematic species studied, where relative to CCSD, B3LYP consistently overestimates the C2-O bond length. The difficulty for DFT methods in modeling the protonated isobutylene oxide is due to the weakness of this C2-O bond. Protonated epoxides featuring more symmetrical charge distribution and cyclic homologues featuring less ring strain are treated with greater accuracy by B3LYP.

Ion-pair separation (IPS) of THF-solvated fluorenyl, diphenylmethyl, and trityl lithium was studied computationally. Minimum-energy equilibrium geometries of explicit mono, bis and tris-solvated contact ion pairs (CIPs) and tetrakis-solvated solvent separated ion pair (SSIPs) were modeled at B3LYP/6-31G*. Associative transition structures linking the tris-solvated CIPs and tetrakis-solvated SIPs were also located. In vacuum, B3LYP/6-31G* ΔH_{IPS} values are 6-8 kcal/mol less exothermic than the experimentally determined values in THF solution. Incorporation of secondary solvation in the form of Onsager and PCM single-point calculations showed an increase in exothermicity of IPS. Application of a continuum solvation model (Onsager) during optimization at the B3LYP/6-31G* level of theory produced significant changes in the C_{α} -Li contact distances in the SSIPs. An increase in exothermicity of ion pair

separation was observed upon using both PCM and Onsager solvation models, highlighting the importance of both explicit and implicit solvation in modeling of ion pair separation.

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Dedication

*To my parents,
who made me the person I am*

&

*To Binoy,
who loves me for all I am*

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Chapter 1: Electronic-Structure Theory

This is an introductory chapter covering the basic concepts of quantum chemistry, and briefly describes the principles behind the different methods and basis sets used in this study. A full detailed introduction is beyond the scope of this work; however the references below have been useful for this work, and would provide helpful sources for more detailed reading:

- 1) A. Szabo and N. S. Ostlund *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*; McGraw-Hill: New York, 1989.
- 2) Cramer, C. J. *Essentials of Computational Chemistry, Theories and Models*; John Wiley & Sons, Ltd.: New York, 2002.
- 3) Jensen, F. *Introduction to Computational Chemistry*; John Wiley & Sons, Ltd.: New York, 2002.
- 4) Koch, W. Holthausen, M.C. *A Chemist's Guide to Density Functional Theory* 2nd ed.; Wiley-VCH Verlag GmbH: Weinheim, **2001**
- 5) Lewars, E. *Computational chemistry: Introduction to the theory and applications of molecular and quantum mechanics* Kluwer Academic Publishers: Norwell, Massachusetts, 2003.
- 6) Ratner, M. A.; Schatz, G. C. *Introduction to Quantum Mechanics in Chemistry*; Prentice Hall: New Jersey, 2000.

Useful online resources covering the following topics:

- 1) Sherrill, C. D. Introduction to Electronic Correlation; **2002**,
<http://vergil.chemistry.gatech.edu/courses/chem6485/pdf/intro-e-correlation.pdf>
- 2) Sherrill, C. D. Introduction to Electronic Structure Theory; **2002**,
http://vergil.chemistry.gatech.edu/notes/intro_estruc/intro_estruc.html
- 3) Sherrill, C. D. An Introduction to Hartree-Fock Molecular Orbital Theory; **2000**,
<http://vergil.chemistry.gatech.edu/notes/hf-intro/hf-intro.html>

1.1 Introduction

The Schrödinger equation, the most fundamental equation in quantum chemistry can be written as:¹

$$\hat{H}\psi(r, R) = E\psi(r, R) \quad (1.1)$$

where $\hat{H}$ is the Hamiltonian operator acting on the wavefunction $\psi(r, R)$ which comprises of electronic coordinates 'r' and the nuclear coordinates 'R', to give energy 'E' as an eigenvalue of the wavefunction, i.e. $E\psi(r, R)$. The integral of the product of this wavefunction ψ with its complex conjugate ψ^* (i.e. $|\psi^*\psi|$) over a certain space defines the probability of finding a chemical system within that space.² The Hamiltonian $\hat{H}$ is a sum of the following components:

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{ne} + \hat{V}_{nn} + \hat{V}_{ee} \quad (1.2)$$

where $\hat{T}_n$ and $\hat{T}_e$ are the kinetic energy operators for the nuclei and the electrons respectively. The terms $\hat{V}_{nn}$ and $\hat{V}_{ee}$ are the nuclear-nuclear Coulombic repulsion and electron-electron Coulombic repulsion energy operators respectively, and $\hat{V}_{ne}$ is the nuclear-electron attraction energy operator. Due to a large number of complexities associated with solving this equation explicitly, a number of approximations have been put forth.

1.2 Born-Oppenheimer Approximation

In 1927, Born and Oppenheimer postulated that, since the nuclei are much more massive than electrons, they move much more slowly, and can thus be considered stationary.³ Incorporation of the Born-Oppenheimer approximation eliminates the nuclear kinetic energy term ($\hat{T}_n$). Thus, the nuclear-nuclear repulsion term ($\hat{V}_{nn}$) also becomes constant, and this energy is known as the nuclear repulsion energy. Since the nuclei are considered stationary, the internuclear distance can be modified stepwise, and energy can be calculated for a specific

internuclear distance at a time. After the application of the Born-Oppenheimer approximation, the resulting Hamiltonian involves the kinetic energy terms for all electrons, the nuclear-electron attraction term ($\hat{V}_{ne}$) and the electron-electron repulsion term ($\hat{V}_{ee}$), and is referred to as the electronic Hamiltonian ($\hat{H}_{elec}$).

$$\hat{H}_{elec} = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} \quad (1.3)$$

So the electronic Schrödinger equation for the electronic wavefunction ψ can be written as:

$$\hat{H}_{elec}\psi = E_{elec}\psi \quad (1.4)$$

The total energy is the sum of the electronic energy (E_{elec}) and the nuclear repulsion energy (E_{nn}):

$$E_{tot} = E_{elec} + E_{nn} \quad (1.5)$$

Within the Born-Oppenheimer approximation it is possible to solve the electronic Schrödinger equation for single-electron systems explicitly (e.g. H, H_2^+ , He^+), however for systems with more than one electron, it is not possible to solve this equation exactly.

1.3 Hartree Product

Within the Born-Oppenheimer approximation, the Schrödinger equation can be solved explicitly only for hydrogenic atoms. For atoms with more than 1 electron, the evaluation of the electron-electron repulsion term ($\hat{V}_{ee}$) makes it impossible to solve the Schrödinger equation explicitly. As a first approach in dealing with the problem associated with this term, it is ignored, and a ‘guess’ wavefunction involving one electron functions also known as molecular orbitals (MO), which are orthonormal is considered.^{4,5} If the Hamiltonian includes only terms associated with nuclear electron attraction and one electron kinetic energy, the total wavefunction can be taken to be a product of single electron hydrogenic wave functions (φ). So for an ‘ N -electron’ system, the total wavefunction can be written as:

$$\psi_{HP}(r_1, r_2, \dots, r_N) = \varphi(r_1)\varphi(r_2) \dots \varphi(r_N) \quad (1.6)$$

where r_N denotes the coordinates of the ' N^{th} ' electron and the total wave function ψ_{HP} is known as the 'Hartree product'.

1.4 Pauli's Antisymmetry Principle

In 1925, Pauli introduced the "antisymmetry principle", which states that whenever the coordinates of any two electrons are switched, the wavefunction changes sign.⁶ This is due to an intrinsic spin coordinate associated with each electron, and any wavefunction used in quantum chemistry has to be antisymmetric with respect to the spin of the electron. The energy requirement associated with this exchange of electronic coordinates is termed as '*exchange energy*'. A direct result of Pauli's antisymmetry principle is observed in Pauli's exclusion principle, which states that no two electrons can have the same set of quantum numbers.

Since a single spatial orbital can have a maximum of 2 electrons (one with α spin ($\uparrow$) and one with β spin ($\downarrow$)), no orbital can have two electrons corresponding to the same spin state, as this would violate Pauli's exclusion principle. Hence, the wavefunction for an electron should incorporate both spatial and the spin components and can be written as:⁷

$$\chi_1(x_1) = \varphi_1(r_1)(\alpha) \text{ or } \chi_2(x_2) = \varphi_1(r_1)(\beta) \quad (1.7)$$

where χ is known as the spin orbital since it includes both spatial and spin components and $\varphi_1(r_1)$ corresponds to the spatial components (i.e. the x, y and z coordinates). Antisymmetry can be incorporated into a two-electron Hartree product by taking a linear combination of the two Hartree products. Thus an antisymmetric two-electron wavefunction Φ can be written as:⁷

$$\Phi = \frac{1}{\sqrt{2}} [\chi_1(x_1)\chi_2(x_2) - \chi_1(x_2)\chi_2(x_1)] \quad (1.8)$$

It was found that the property of antisymmetry could also easily be incorporated into a Hartree product using a matrix format, i.e. ‘Slater determinants’.⁸ The Slater determinant for an N -electron function can be written as:⁷

$$\Phi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \cdots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \cdots & \chi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(x_N) & \chi_2(x_N) & \cdots & \chi_N(x_N) \end{vmatrix} \quad (1.9)$$

where Φ_{SD} is the Slater determinant, $1/\sqrt{N!}$ is the normalization constant, and χ_N is the spin orbital for the electron with spin and spatial coordinates x . Expansion of this determinant would give a linear combination of all the spin orbitals χ_N with different x_N values. Switching of any two rows in the determinant would lead to a change in the sign due to properties of determinants, and hence Pauli’s exclusion principle would be satisfied.⁹

1.5 Variational Principle

Once the ‘guess’ antisymmetric wavefunction is constructed, its accuracy has to be determined. This assessment is governed by the variational principle, which states that for any normalized wavefunction ‘ ψ ’, the expectation value is always greater than or equal to the true energy.¹⁰⁻¹²

$$E_{true} \leq \langle \psi | \hat{H} | \psi \rangle \quad (1.10)$$

Thus, the lower the energy obtained from the expectation value of a trial wavefunction, the closer it is to the true energy, and the quality of different trial wavefunctions can thus be compared.

1.6 Basis Sets

A wavefunction can be written as a Slater determinant of molecular orbitals χ_i , which are a linear combination of atomic wavefunctions ϕ_i .¹¹

$$\chi_i = \sum_i^n c_i \phi_i \quad (1.11)$$

In this case, the set of n functions ϕ_i is the basis set and each function ϕ_i has associated with it a coefficient c_i . This coefficient is the variational parameter, and can be optimized to get lower and lower energies. The value of this coefficient is calculated using the Hartree-Fock approach for certain basis sets, which is discussed in detail in Section 1.7.1. A detailed description of different types of basis sets used will be presented in Section 1.8.

1.7 Methods

This section will cover the different methods that will be used in this study including Hartree-Fock, post Hartree-Fock methods, and density functional theory.

1.7.1 Hartree-Fock¹³

The Hartree-Fock method is an *ab initio* method (i.e. from first principles) that is used to calculate the ground state for a many body system.¹³ Hartree-Fock uses a single Slater determinant to calculate the ground state of the system and has the following general formula:

$$f\chi_i = \varepsilon_i \chi_i \quad (1.12)$$

where ' f ' is known as the Fock operator and is made up of three components: 1) the Hamiltonian $\hat{h}$ known as the core operator, which involves the movement of a single electron under the influence of the nucleus with no interactions with the other electrons. It is a single-electron operator, and represents the kinetic energy of the electron and the nuclear-electron Coulombic

attraction. 2) $\hat{J}_j$ is the Coulomb operator and defines the average repulsive force at position x_i . 3) $\hat{K}_{ij}$ is the exchange operator corresponding to the energy required to switch the spin and/or spatial coordinates of electron i and j . Summation of multiple $\hat{J}$ and $\hat{K}$ terms is taken to account for every electron in the system.

$$f(x_i) = \hat{h}(x_i) + \sum_j \hat{J}_j(x_i) - \sum_j \hat{K}_j(x_i) \quad (1.13)$$

The exchange and Coulomb operators can also be summed together to get the Hartree-Fock potential ' $\hat{V}_{HF}$ '.

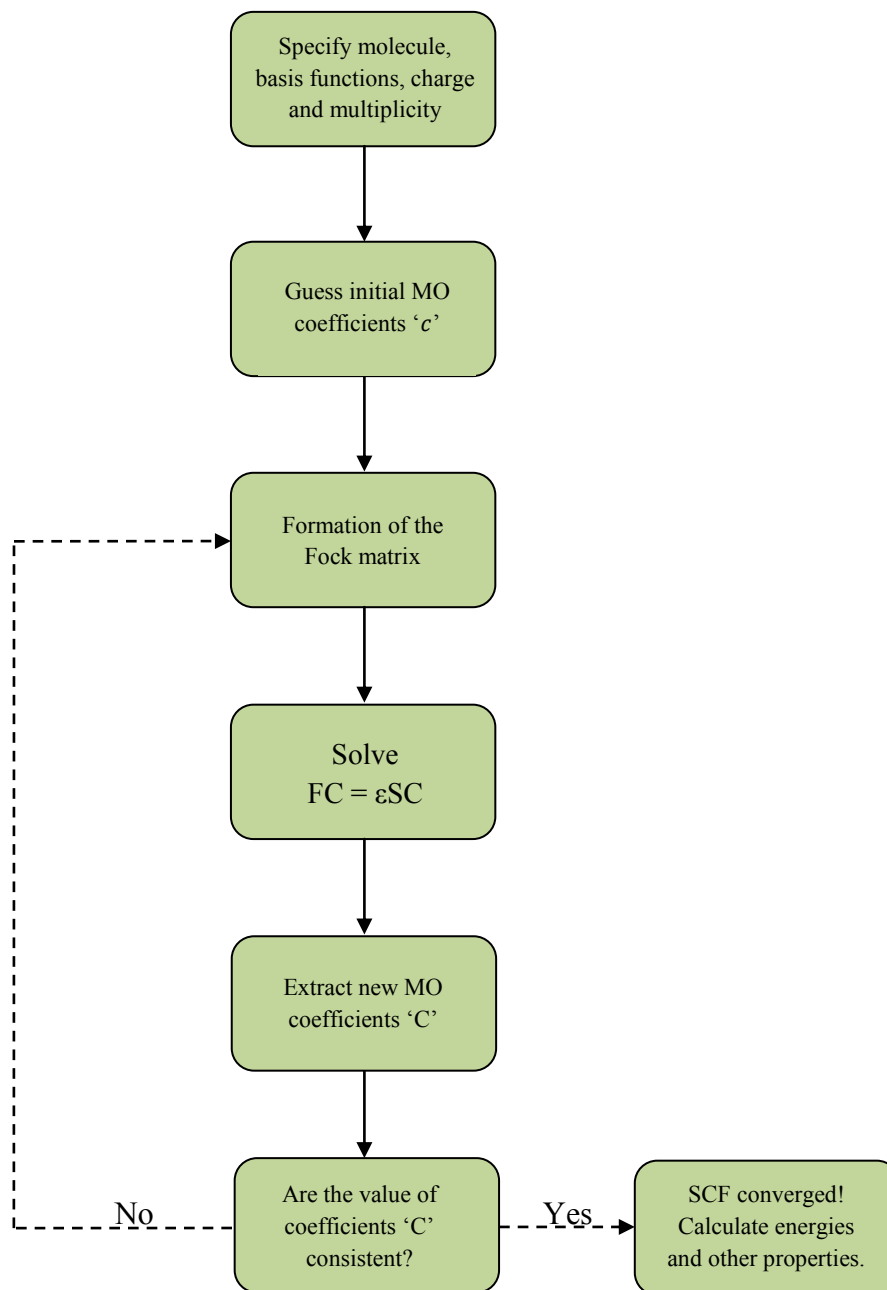
$$\hat{V}_{HF} = \sum_j \hat{J}_j(x_i) - \sum_j \hat{K}_j(x_i) \quad (1.14)$$

The variational parameter for the Hartree-Fock equation are the coefficients of the molecular orbitals ' χ ', which are optimized until lower and lower energies are obtained. Computational difficulties associated with the solving these equations directly led to modifications by Roothaan in 1951.¹⁴ This method, also referred as the Hartree-Fock Roothaan method, uses atomic orbitals to define molecular orbitals as defined in Section 1.6. (See equation 1.11) The HF equations can then be rewritten as the following:

$$FC = \epsilon SC \quad (1.15)$$

The term S is known as the overlap integral, and arises due to the absence of orthonormality between the atomic orbitals, F is a matrix representation of the Fock operator ' f '. and ' ϵ ' is a diagonal matrix of the orbital energies ϵ_i . A single Slater determinant is used to describe all the spin orbitals associated with the Hartree-Fock approximation. Both the Coulomb operator ($\hat{J}$) and the exchange operator ($\hat{K}$) require the MO coefficients ' c ' as their input, and since these have no known values, the initial ' c_i ' values have to be guessed. The coefficients are

then calculated iteratively until self consistency is achieved. Hence, Hartree-Fock is also known as self consistent field method (SCF method). A useful electronic reference for this chapter has been written by Sherrill.¹⁵ The different steps involved in a Hartree Fock calculation can be put in a flowchart as follows in Scheme 1.1.



Scheme 1.1: Schematic of a Hartree-Fock calculation adapted from Sherrill⁷

Hartree-Fock theory uses average electron repulsion to define the interaction of one electron with the rest of the electrons, however in reality electrons avoid each other, and the total energy of the system should be less than the energy calculated by Hartree-Fock. A number of methods known as post Hartree-Fock methods have been developed to calculate this difference in the Hartree-Fock energy and the true energy of the system.

1.7.2 Post Hartree-Fock Methods

The instantaneous electron-electron repulsion that occurs when any two electrons are in close proximity of each other is termed as electron correlation, and the energy arising from this interaction is termed as the '*correlation energy*'. The true correlation energy would be the difference between the true ground state energy for a system, and the energy calculated using the Hartree-Fock method with an infinite basis set to get the energy at 'Hartree-Fock limit'.

$$E_{corr} = E_{true} - E_{HF}^{\infty} \quad (1.16)$$

Since the fundamental assumption in Hartree-Fock is that an electron feels an average repulsion of the other electrons, it fails to take the total electron correlation into account. This leads to considerable errors in calculations of molecular properties. However, it is possible to obtain the exchange energy using the Hartree-Fock approach. A variety of methods known as post Hartree-Fock methods build upon this exchange energy and calculate the electron correlation energy explicitly. Examples of these methods include Configuration Interaction (CI), Møller Plesset (MP n), and Coupled Cluster theories (CC) and together these are termed as post Hartree-Fock methods.

1.7.2.1 Configuration Interaction (CI)

In Hartree-Fock theory only a single Slater determinant is used to describe the lowest energy or ground state of the system.¹⁶ However, since this is only one of the many Slater determinants associated with a particular system, there still exist a large number of determinants that could be written with electrons in other orbitals including determinants corresponding to systems with unoccupied orbitals in the ground state. In CI, the Hartree-Fock determinant is taken as the ground or reference state, while the other Slater determinants are termed as excited or substituted states. Depending on the number of electrons transferred from occupied to the unoccupied or virtual orbitals, the substitutions can be defined as single, doubles, triples, etc. excitation (Figure 1.1).

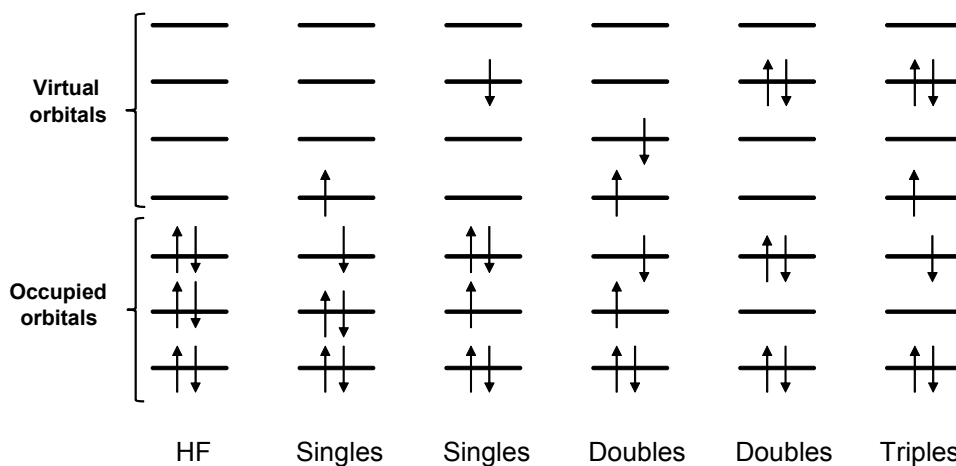


Figure 1.1: Electron transfer to get singles, doubles or triples excitation.

Mathematically, this can be explained as follows: For a complete set of functions of a single variable, any arbitrary function of that variable can be expanded as the weighted sum of this complete set of single-variable functions. Similarly, an arbitrary function of two variables can be written as a linear combination of products of pairs of single-variable functions, chosen from a complete set. Thus, any N -electron wavefunction (i.e. an N -variable function) can be

written exactly as a linear combination of all unique N -electron Slater determinants, formed from a complete set of spin orbitals χ_N . Use of infinite virtual orbitals for excitations would thus give the true energy of the system.⁴

The first term in the CI method calculation is the ground or reference state, which comes directly from Hartree-Fock. Coefficients are then evaluated by transfer of electrons from the occupied orbitals to ‘virtual’ orbitals, followed by calculation of energy.^{4,15} A general CI equation can be written as:

$$|\psi_{CI}\rangle = \sum_i c_i |\Phi_i\rangle \quad (1.17)$$

where Φ_i are the determinants that include Hartree-Fock ground state and all excited states. With the Hartree-Fock ground state function as ‘ Φ_0 ’ the CI wavefunction can be expanded as:^{4,15}

$$|\psi_{CI}\rangle = c_0 |\Phi_0\rangle + \sum_i^a c_i^a |\Phi_i^a\rangle + \sum_{ij}^{ab} c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \sum_{ijk}^{abc} c_{ijk}^{abc} |\Phi_{ijk}^{abc}\rangle + \dots \quad (1.18)$$

where the term $c_i^a \Phi_i^a$ describes the substitution of a single electron (singles excitation) from the occupied orbital ‘ i ’ to a virtual orbital ‘ a ’. The summation signifies all possible combinations of this substitution, and the CI method with only a single substitution is called Configuration Interaction Singles (CIS). Doubles excitation is written as $c_{ij}^{ab} \Phi_{ij}^{ab}$, showing the excitation of two electrons from occupied orbitals (i & j) to virtual orbitals (a & b). The method that incorporates the ground state, singles and doubles excitation, is called Configuration Interaction Singles and Doubles (CISD). Further excitations can be added to give triples (CISDT) and so on until the excitation of all the N -electrons to give full CI which would give the true energy for a system at infinite basis set. However, owing to the large computational expense associated with these calculations, the more popular method which is considered a good compromise between computational cost and accuracy is CISD.

1.7.2.2 Coupled Cluster (CC) Theory

The coupled cluster theory was developed in the 1960s by Čížek and Paldus.¹⁷ The governing principle behind CC theory is similar to CI, where the electron is excited or substituted from an occupied orbital to an unoccupied or virtual orbital. However, unlike in the case of CI, which involves the linear combination of the determinants corresponding to these excited states, the coupled cluster method uses an exponential calculation to improve cost efficiency. A useful review article on coupled cluster theory has been written by Crawford and Schaefer.⁹ A generalized coupled cluster equation can be written as:¹⁵

$$|\psi_{cc}\rangle = e^{\hat{T}}|\Phi_0\rangle \quad (1.19)$$

where Φ is the wavefunction and operator $\hat{T}$ is defined as:⁵

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots + \hat{T}_N \quad (1.20)$$

where N is the number of electrons, and the various $\hat{T}_i$ operators correspond to the determinants having ' i ' excitations from the ground state, so $\hat{T}_1$ corresponds to single excitation and $\hat{T}_2$ corresponds to double excitations. Expansion of $e^{\hat{T}}$ using the Taylor series expansion gives:⁹

$$e^{\hat{T}} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \frac{\hat{T}^4}{4!} \dots \quad (1.21)$$

For coupled-cluster method, the commuter expansion has been shown to naturally truncate after the $\hat{T}^4$ term since the Hamiltonian is at most a two-electron operator (i.e. two-electron repulsion (V_{ee}) is the maximum inter-electron interaction calculated). For multiple excitations, $\hat{T} = (\hat{T}_1 + \hat{T}_2 + \dots)$, equation 1.21 can be written as:⁵

$$e^{\hat{T}} = 1 + (\hat{T}_1 + \hat{T}_2 + \dots) + \frac{1}{2!}(\hat{T}_1 + \hat{T}_2 + \dots)^2 \quad (1.22)$$

Operators $\hat{T}_1$ and $\hat{T}_2$ act on the wavefunction ' Φ_0 ' to give the single and double excited determinants respectively.¹⁵

$$\hat{T}_1|\Phi_0\rangle = \sum_i^a t_i^a |\Phi_i^a\rangle \quad \text{and} \quad \hat{T}_2|\Phi_0\rangle = \sum_{jk}^{bc} t_{jk}^{bc} |\Phi_{jk}^{bc}\rangle \quad (1.23)$$

where t_i^a and t_{jk}^{bc} are coefficients to be determined. So if both the singles and the doubles excitations are performed, the determinants of the product of $\hat{T}_1\hat{T}_2$ would also be determined, which would give the following product:

$$\hat{T}_1\hat{T}_2|\Phi_0\rangle = \sum_i^a t_i^a \sum_{jk}^{bc} t_{jk}^{bc} |\Phi_{ijk}^{abc}\rangle \quad (1.24)$$

The advantage of the coupled cluster theory lies in its ability to estimate the coefficients of a triples excitation to some extent from the coefficients of a singles and doubles excitation. The product term $t_i^a t_{jk}^{bc}$ has been found to be a good estimate for the coefficient of a coupled cluster triples excitation t_{ijk}^{abc} . Coupled-cluster method including both singles and doubles excitation is termed as CCSD¹⁵

$$|\psi_{\text{CCSD}}\rangle = e^{(\hat{T}_1+\hat{T}_2)}|\Phi_0\rangle \quad (1.25)$$

where $e^{(\hat{T}_1+\hat{T}_2)}$ is the operator acting on the wavefunction Φ_0 . Substituting for $e^{(\hat{T}_1+\hat{T}_2)}$ from equation 1.22:¹⁵

$$e^{(\hat{T}_1+\hat{T}_2)}|\Phi_0\rangle = (1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2!}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2!}\hat{T}_2^2 + \dots) |\Phi_0\rangle \quad (1.26)$$

Thus the wavefunction becomes:¹⁵

$$\begin{aligned}
e^{(\hat{T}_1 + \hat{T}_2)}|\Phi_0\rangle = & |\Phi_0\rangle + \sum_i^a t_i^a |\Phi_i^a\rangle + \sum_{ij}^{ab} t_{ij}^{ab} |\Phi_{ij}^{ab}\rangle \\
& + \frac{1}{2} \sum_i^a t_i^a \sum_j^b t_j^b |\Phi_{ij}^{ab}\rangle + \sum_i^a t_i^a \sum_{jk}^{bc} t_{jk}^{bc} |\Phi_{ijk}^{abc}\rangle + \frac{1}{2} \sum_{ij}^{ab} t_{ij}^{ab} \sum_{kl}^{cd} t_{kl}^{cd} |\Phi_{ijkl}^{abcd}\rangle
\end{aligned} \tag{1.27}$$

Thus CCSD methods have proven very useful to recover the contributions from a triples excitation to a significant extent. Another method known as the CCSD(T) method involves the evaluation of coupled cluster singles and doubles along with the evaluation of contributions of triples excitation via use of perturbation theory.^{9,18} CCSD(T) method has been found to work very well for a large number of systems, and is termed as the ‘gold standard’.¹¹

1.7.2.3 Møller-Plesset Theory (MP n)

MP n , which stands for Møller-Plesset theory, is a type of many-body perturbation theory which was first applied by Møller and Plesset in 1934.¹⁹ In MP n theory, the Hamiltonian is divided into two parts, a known part that can be calculated explicitly, and a second part that has to be estimated. The Hartree-Fock wavefunction is taken as the zeroth order Hamiltonian operator ($\hat{H}_0$) and a perturbation (via the perturbation operator ($\hat{V}$)) is applied to the wavefunction in an attempt to estimate electron correlation.¹¹ I.e.:

$$\hat{H} = \hat{H}_0 + \lambda \hat{V} \tag{1.28}$$

The term λ serves as a bookkeeping tool. From equations 1.13 and 1.14, $\hat{H}_0$ is the sum of the one electron Hamiltonian ($\hat{h}$), and Hartree-Fock potential $\hat{V}_{HF}$, and can be written as:⁴

$$\hat{H}_0 = \sum \hat{f}(x_i) = \sum \hat{h}(x_i) + \hat{V}_{HF}(x_i) \tag{1.29}$$

The perturbation term is the difference between inter-electronic interaction $\hat{V}$ and the Hartree-Fock potential $\hat{V}_{HF}$

$$\hat{V} = \sum_{i < j} r_{ij}^{-1} - \sum \hat{V}_{HF}(x_i) \quad (1.30)$$

The first order correction (MP1) is zero, thus Hartree-Fock is the sum of zero and first order energy. The first correction that is actually applied to the Hartree-Fock energy is the second order correction at MP2. It is possible to go to higher orders to get methods like MP3 (third order perturbation), MP4 (fourth order perturbation) etc. However, unlike full CI where going to higher excitations gives better results, increasing the order of perturbation does not guarantee convergence and has also been shown to give more divergent results for some systems.²⁰ Thus, today MP2 represents the most popular implementation of the Møller-Plesset theory.

1.7.2.4 Quantum Composite Methods

Another category of *ab initio* post Hartree-Fock methods include the thermodynamic methods Gaussian-2 (G2), Gaussian-3 (G3) and Complete Basis Set (CBS) methods. These methods are a composite of a number of methods with variable basis sets in an attempt to achieve maximum compromise between cost and accuracy.¹²

The first of these methods are Gaussian-X methods. Gaussian-1 was introduced by Pople and coworkers in 1989²¹ and further modifications led to the Gaussian-2²² and Gaussian-3²³ methods, which have been used in this study. These methods are comprised of a series of high-level calculations with a variety of basis sets, and correction factors which have been optimized based on empirical data for a large number of systems. These methods have been optimized to accurately provide thermochemical data for processes such as atomization energies, ionization potentials, electron affinities, etc.

1.7.2.4.1 Gaussian-2 (G2) Calculations

Gaussian-2 (G2) method was introduced in 1991 by Pople and coworkers.²² This method was introduced as an improvement over Gaussian-1 (G1) method,²¹ and is a composite of the following steps:

- 1) The first geometry optimization is performed at HF/6-31G(*d*), and the geometry obtained is used to calculate zero-point vibrational energy (ZPVE). A scaling factor of 0.8929 is applied to this ZPVE.
- 2) The geometry from step 1 is reoptimized at MP2(full)/6-31G*. This is the reference geometry for all higher-order single-point calculations.
- 3) The first single-point calculation is performed at MP4(fc)/6-311G(*d,p*) and this energy is further modified using a series of single-point calculations.
- 4) The next calculation is performed at MP4(fc)/6-311+G(*d,p*) to compute the correction for the addition of diffuse functions.
- 5) A correction factor is then obtained for addition of higher polarization *2df*-functions on non-hydrogen atoms and *p*-functions on hydrogen using single-point calculations at MP4(fc)/6-311G(*2df, p*).
- 6) The next correction is computed to incorporate the effects of electron correlation beyond MP4 using a quadratic configuration interaction [QCISD(T)] at 6-311G(*d,p*)
- 7) A correction for larger basis set is incorporated by use of a larger basis set at 6-311(*3df,2p*) at the MP2 level of theory.
- 8) The next correction added is termed as higher-level correction (HLC), and is determined from data fitting to experimental atomization energies of 55 molecules whose energies are

well known. A correction of -0.00614 hartree is added for each valence electron pair and -0.00019 hartree is added for each unpaired electron.

1.7.2.4.2 Gaussian-3 (G3) Calculations

Significant deviations of the Gaussian-2 values from experimental values especially for non-hydrogen systems (e.g. SiF₄ and CF₄) led to the development of the Gaussian-3 (G3) method. This method, which is a modification of the Gaussian-2 method was introduced in 1998²³ and involves the following calculations:

- 1) The first geometry optimization is performed at HF/6-31G(*d*) and the geometry obtained is used to calculate the zero-point vibrational energy (ZPVE). A scaling factor of 0.8929 is applied to this ZPVE.
- 2) The next step involves reoptimization at MP2(full)/6-31G(*d*). This is the reference geometry for all higher-order single-point calculations.
- 3) The first single-point calculation is done at MP4(fc)/6-31G(*d*) and this energy is then modified using a series of higher-level calculations.
- 4) The first three steps are the same for G2 and G3 methods. Differences in the two methods arise by different single-point calculations at higher levels of theory.
- 5) The next calculation is performed at MP2(full)/6-31+G(*d*) to compute the correction for the addition of diffuse functions.
- 6) A correction factor is then obtained for addition of higher polarization functions on non-hydrogen atoms (*2df*) and *p*-functions on hydrogen using single-point calculations at MP4(fc)/6-31G(*2df,p*).
- 7) Next correction is obtained to incorporate the effects of electron correlation beyond MP4 using a quadratic configuration interaction QCISD(T)/6-31G(*d*).

- 9) A correction for larger basis set is incorporated by use of a modified basis set termed as G3large which includes $3d2f$ functions for the second-row atoms and $2df$ on the first-row atoms.
- 10) All the single-point energy corrections obtained thus far are combined in an additive manner to the MP4(fc)/6-31G(d) energy. To this is added an energy termed as spin-orbit correction $\Delta E(\text{SO})$ for atomic species, which is derived from experiment or high-level theoretical data.
- 11) A correction for higher-level correlation E(HLC) is added as the final energy correction (derived from fitting experimental data). G3 method uses different values for atoms and molecules unlike in the case of G2, where the same values are applied for both.
- 12) Finally as the last step, the corrected zero-point vibrational energy from step 1 is added the energy obtained in step 10 to get the final energy.

1.7.2.4.3 Complete Basis Set (CBS-Q) Calculations

The Complete Basis Set (CBS) methods are different from Gaussian-2 and -3 methods in the use of smaller basis sets.^{12,24} In CBS-Q the following calculations are performed:

- 1) First, geometry optimization is performed at HF/6-31G(d^+) method and basis (d^+ signifies that the exponents (α) for the d -functions are taken directly from the 6-311G(d) basis set). The geometry obtained is used to calculate the zero-point vibrational energy (ZPVE), and a scaling factor of 0.918 is applied to this ZPVE.
- 2) The next step is reoptimization at MP2(full)/6-31G(d^+). This is the reference geometry for all higher-order single-point calculations.
- 3) The first single-point calculation is performed at MP4(fc)/6-311G($2df,2p$). This result is then extrapolated to the basis-set limit.

- 4) The next calculation involves single-point calculations at MP4/6-31G(*d,p*) and QCISD(T) /6-31G(*d,p*) to incorporate the effects of higher-order electron correlation.
- 5) An empirical correction due to two-electron parameter obtained by minimization of the RMS error for the dissociation energy of the 55 test molecules used in the G2 model is added to the energy.
- 6) Similarly, a spin correction term also obtained from empirical data is added to the total energy.

The ability of the CBS-Q methods to extrapolate the effects of bigger basis sets considerably improves their cost efficiency, and hence they should be better suited for larger molecules compared to Gaussian-X methods.

1.7.3 Density Functional Theory (DFT)²⁵

In *ab initio* methods, the wavefunction for an *N*-electron system can only be described by the incorporation of 3 spatial and 1 spin coordinate for each electron in the system. In DFT, the energy of the system is written as a function of the density, and the *N*-electron system can now be defined by only 3 spatial coordinates defining the electron density.²⁵ The fundamentals of the density functional theory come from the Hohenberg-Kohn theorem, which states that the ground state electronic energy of a system can be expressed as a functional of the density, which in turn is a function of the electron coordinates.²⁶ The density $[\rho(x_1)]$ of a single electron can be obtained by integrating over the spin and spatial coordinates of all but one electron (Equation 1.31).

$$\rho(x_1) = N \int \psi^*(x_1, x_2, \dots, x_N) \psi(x_1, x_2, \dots, x_N) dx_2, \dots, dx_N \quad (1.31)$$

The total ground state energy of a system can be written as a sum of kinetic energy of the electrons (T), electron-electron repulsion energy (V_{ee}), and nuclear electron attraction energy (V_{ne}), also known as the external potential.^{25,28}

$$E(\rho) = T(\rho) + V_{ee}(\rho) + V_{ne}(\rho) \quad (1.32)$$

The energy in equation 1.32 can be split into two types of components: Nuclear independent components (T and V_{ee}) and nuclear dependent component (V_{ne}). Coupling the nuclear independent components together gives the Hohenberg-Kohn functional ($F_{HK}(\rho)$)

$$F_{HK}(\rho) = T(\rho) + V_{ee}(\rho) \quad (1.33)$$

If it were possible to solve for $F_{HK}(\rho)$ exactly, then the exact solution to the Schrödinger equation could be achieved, and as this functional is independent of the system studied, it would apply equally to all systems. However, there are a number of complexities associated with the determination of this functional, and even the authors acknowledged the same in their paper:

“If $F_{HK}(\rho)$ were a known and sufficiently simple function of ρ , the problem of determining the ground-state energy and density in a given external potential would be rather easy since it requires merely the minimization of a functional of the three-dimensional density function. The major part of the complexities of the many-electron problems are associated with the determination of the universal functional $F_{HK}(\rho)$.”²⁶

The second component of the Hohenberg-Kohn functional, the electron-electron repulsion term can also be split into two components, the classical Coulomb interaction (J) and

the non-classical correlation and exchange component (E_{XC}) which also includes the kinetic energy of the interacting system.

$$V_{ee}(\rho) = J(\rho) + E_{XC}(\rho) \quad (1.34)$$

Thus, the functional $F(\rho)$ can now be written as:

$$F_{HK}(\rho) = T(\rho) + J(\rho) + E_{XC}(\rho) \quad (1.35)$$

The total energy of the system becomes:

$$E(\rho) = V_{ne}(\rho) + T(\rho) + J(\rho) + E_{XC}(\rho) \quad (1.36)$$

The problem associated with calculating the exact energy using the density functional theory lies in evaluating the exchange-correlation term (E_{XC}) exactly as all the other terms can be calculated explicitly. The quality of a particular DFT method thus depends solely on the accuracy by which this functional is evaluated.

1.7.3.1 Kohn-Sham DFT

In 1965, Kohn and Sham presented an approximate method to deal with a system of interacting electrons in an inhomogeneous system.²⁷ They split a system into two parts: a non-interacting reference system made up of one electron functions and a second part which is composed of an interacting system. Part of the kinetic energy (i.e., the part for the non interacting system) can be computed exactly, and the remainder of the kinetic energy (i.e., of the interacting system) would be included in the non-classical contributions to the energy (E_{XC}). For the non-interacting system, a Hartree-Fock type approach is used, wherein for a given choice of E_{XC} , the energy could be computed using a single Slater determinant for a set of orthonormal one-electron functions (orbitals). Thus, the energy expression could be written as the following:

$$\hat{h}_{KS} \chi_i = \epsilon_i \chi_i \quad (1.37)$$

where Φ_i is an eigenfunction of the operator $\hat{h}_{KS}$, and gives the energy ' ϵ_i ' as an eigenvalue. The accuracy of a particular DFT method lies in the ability to evaluate the term E_{XC} . Over the years, a number of approximations have been made to estimate this term, some of which are described below.

1.7.3.2 Local Density Approximation (LDA)²⁵

One of the earliest ways to estimate the exchange-correlation functional was by the use of the Local Density Approximation (LDA), which is based on the assumption that the density of a system acts as a homogenous electron gas.

$$E_{XC}^{LDA}[\rho] = \int \rho(x) \epsilon_{XC} \rho(x) dx \quad (1.38)$$

where ϵ_{XC} is the exchange-correlation energy for each particle in the uniform electron gas of electron density ρ . The exchange-correlation functional (E_{XC}) can be split linearly into the exchange and correlation components.

$$E_{XC} = E_X + E_C \quad (1.39)$$

where E_X is the exchange functional and E_C is the correlation functional. The LDA exchange functional E_X has the same form as that put forth by Slater for Hartree-Fock exchange.

$$E_X[\rho] = -C_X \int \rho^{4/3}(x) dx \quad (1.40)$$

The most popular local correlation functional (E_C) is the Vosko-Wilk-Nusair (VWN), which uses the uniform gas model that was developed in 1980 from Monte Carlo interpolation data.²⁹ Another popular local correlation functional (E_C) currently in use is the Perdew, Burke

and Ernzerhof (PBE) functional introduced in 1996.³⁰ LDA has been shown to be successful in determining molecular features such as equilibrium geometries and harmonic frequencies.

While the LDA method has been shown to be better than Hartree-Fock in predicting the energetic properties such as atomization energies, it was still found to deviate considerably from experimental values.²⁵ LDA is based on the assumption that the density remains constant through the entire system, however in reality this is never the case, and the density of the system is constantly varying. Limited applications of LDA in most systems led to modifications in LDA to give the Generalized Gradient Approximation (GGA).

1.7.3.3 Generalized Gradient Approximation (GGA)²⁵

The GGA method includes the features of the LDA, i.e. the uniform density at a given point. Additionally, it also incorporates the derivative of the density to take into account the gradient of density with distance. As in the case of LDA, the E_{XC} functional in the GGA can also be split linearly into an exchange functional and a correlation functional.

$$E_{XC}^{GGA} = E_X^{GGA} + E_C^{GGA} \quad (1.41)$$

Two main classes of GGA exchange functionals are currently in use. The first class has been derived from parameters based on empirical data obtained by least squares fit to exact exchange energies of rare gas atoms helium to radon. Functionals based on this approach include the popular Becke88 (B88)³¹ and Perdew Wang 91 (PW91) exchange functionals.³²⁻³⁴ The second class of GGA exchange functionals are based on a reduced density gradient, and unlike the previous group of GGA functionals, are not derived from any empirical parameters. Examples of this category of exchange functionals include Perdew 86 (P86)³⁵ and Perdew Burke Ernzerhof, 1996 (PBE).³⁰ A very popular correlation functional that is widely used is the Lee

Yang Parr (LYP) functional introduced in 1988, which uses four parameters fitted to helium atom instead of using a uniform electron gas.³⁶

1.7.3.4 Meta-GGA Functionals

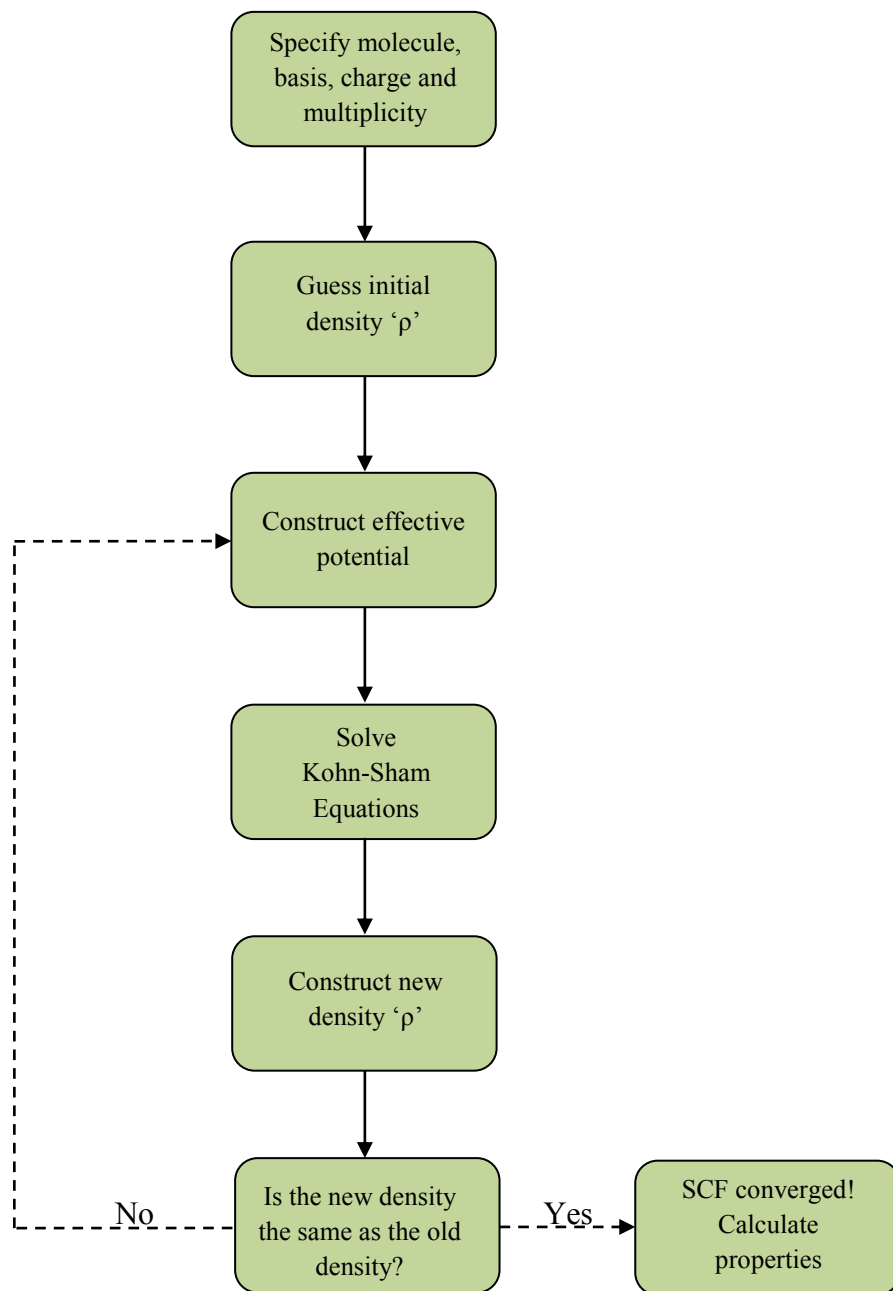
Meta-GGA functionals add further modifications to the GGA functional, and include the second-order gradients of the density along with the non-interacting kinetic energy density. Examples of this type include M06-L, which was recently introduced by Truhlar and coworkers.³⁷

1.7.3.5 Hybrid Functionals²⁵

Further improvement was done by the introduction of hybrid functionals which add some percentage of the Hartree-Fock exchange to the GGA exchange functional. Interestingly, the addition of 100% exchange from Hartree-Fock calculation to replace the DFT exchange functional was found to be greatly inferior to a variety of GGAs and methods that included a small percentage (~20%) of exact exchange. A very popular hybrid DFT exchange functional is the Becke3 (B3) functional, and the combination of B3 and LYP functionals gives the widely used B3LYP method. This popular hybrid functional was first suggested by Stephens et al. in 1994, and includes components from B88, LYP and VWN exchange and correlation functionals.^{36,38}

$$E_{XC}^{B3LYP} = (1 - a) E_X^{LSDA} + a E_X^{HF} + b E_X^{B88} + c E_C^{LYP} + (1 - c) E_C^{VWN} \quad (1.42)$$

where the coefficients a, b and c are derived semiempirically and have the values a = 0.20, b = 0.72 and c = 0.81 were taken from the B3PW91 hybrid method.³⁹ Scheme 1.2 highlights the key steps in a density functional calculation.



Scheme 1.2: Calculation scheme of density functional theory adapted from Koch et al.²⁵

Calculations start with the determination of the initial density, followed by conversion to the effective potential. The next step is the calculation of the Kohn-Sham equations, followed by the calculation of the final density. If the initial and the final density are the same, the calculation

has converged and the molecular properties are calculated. Table 1.1 summarizes the dependence of each of these approximations on different parameters such as exact exchange, density and density gradient.

Table 1.1: Dependence of different DFT approximations⁴⁰

Approximation	Depends on
LDA	Density (ρ)
GGA	Density (ρ), $d\rho/dx$
Hybrid	Exact exchange, Density (ρ) and $d\rho/dx$

1.7.3.6 DFT Functionals

This study used 18 different DFT functionals comprising of combinations of exchange functionals - B3³¹, mPW⁴¹, mPW1⁴¹, G96⁴², and PBE³⁰ and correlation functionals – PW91³⁴, LYP³⁶, P86³⁵ and PBE³⁰. Six different exchange functionals have been used which include a combination of GGAs and hybrid functionals. Table 1.2 lists the different DFT functionals used, along with their type and the year in which they were introduced.

Table 1.2: Different DFT exchange functionals used

Exchange Functional	Name	Year Introduced	Type
B	Becke88	1988	GGA
B3	Becke3	1993	Hybrid
G96	Gill 96	1996	GGA
PBE	Perdew Becke Ernzerhof	1996	GGA
mPW	modified Perdew Wang	1998	GGA
mPW1	modified Perdew Wang 1	1998	Hybrid

Four different gradient corrected correlation functionals were applied in this study. Table 1.3 shows the different functionals used along with the year of their introduction.

Table 1.3: Different DFT correlation functionals used

Correlation Functional	Name	Year Introduced	Type
P86	Perdew 86	1986	GGA
LYP	Lee Yang Parr	1988	GGA
PW91	Perdew Wang 91	1991	GGA
PBE	Perdew Becke Ernzerhof	1996	GGA

1.8 Basis Sets

Basis sets are a set of one electron functions (orbitals) that add to form molecular orbitals.⁴³ They essentially provide a finite space in which a calculation is performed. An infinite basis set would thus involve entire space along all the coordinate axes, which would be ideal but unattainable for practical calculations.²

1.8.1 Hydrogenic Orbitals

Since, the electronic Schrödinger equation can be solved explicitly only for hydrogenic atoms, the wavefunction has to be guessed for systems with more than one electron. Hydrogenic wavefunctions have been solved explicitly and have a Slater type form i.e. $e^{-\zeta r}$ orbital.^{2,4} E.g.

$$|1s\rangle = 2 \left[\frac{1}{4\pi} \right]^{1/2} e^{-r} \quad \& \quad |2s\rangle = \frac{\sqrt{2}}{2} \left[\frac{1}{4\pi} \right]^{1/2} (2 - r) e^{-\frac{r}{2}} \quad (1.43)$$

The general equation for hydrogenic wavefunctions is Slater-type and can be given by:

$$\phi_i(\zeta, l, m, n, x, y, z) = L e^{-\zeta r} x^l y^m z^n \quad (1.44)$$

where l , m , n are the angular momentum components, x , y and z correspond to the cartesian coordinates, ζ is the exponent and L is the normalization constant. These orbitals have been found to be like hydrogenic orbitals especially in the region near the nucleus where the slope has to be non zero. However, while Slater-type orbitals are apt in their description of hydrogenic orbitals, they have limited applicability due to high computational costs involved.²

1.8.2 Gaussian-Type Orbitals

Cost efficiency in calculation of Gaussian-type orbitals have led to their wide applicability in construction of basis sets. Primitive Gaussian functions have the following generalized formula.

$$\phi_i(\alpha, l, m, n, x, y, z) = L e^{-\alpha r^2} x^l y^m z^n \quad (1.45)$$

where the Gaussian function ' ϕ_i ' is a function of the x, y, z coordinates. L is the normalization constant and the exponent ' α ' gives the size of the orbital. The integers l , m and n are the angular momentum components whose sum defines the type of Gaussian orbital. Example:

$l + m + n = 0$ defines a spherical s -type orbital

$l + m + n = 1$ defines a p -type orbital ($l = 1$ gives p_x , $m = 1$ gives p_y and $n = 1$ gives p_z)

$l + m + n = 2$ defines a d -type orbital.

Due to their Gaussian form, these functionals can be computed much more cost effectively than the corresponding Slater-type orbitals. However, to further optimize computational expenses, these orbitals are contracted or reduced to a preset linear combination of the primitive functions to get Contracted Gaussian Type Orbitals (CGTO).

$$\phi^{\text{CGTO}}(l, m, n, x, y, z) = \sum_i c_i \phi^{\text{GTO}}(\alpha_i, l, m, n, x, y, z) \quad (1.46)$$

A CGTO given by the function ' ϕ^{CGTO} ' is a linear combination of primitive Gaussian type orbitals (GTO) for which the exponent ' α ' and the coefficients ' c ' in CGTOs are fixed.⁴⁴ The extensive use of CGTOs is done as a compromise between gain by reduction of computational expense and a minor loss in accuracy of energy calculations.

1.8.3 Pople Basis Sets

In 1971, Pople and coworkers introduced the concept of split-valence basis sets.^{44,45} These basis sets were termed as split-valence sets due to differential treatment of the valence atomic orbitals and the core orbitals. The labels used for the Pople basis sets are descriptive in terms of the different components of the basis sets, and the degree of contraction of different orbitals can be deciphered directly from the labels of these basis sets e.g. **6-31G**. The term 'G' stands for the word 'Gaussian', indicating that all these orbitals are Gaussian-type orbitals. The single digit before the hyphen pertains to core (non-valence) orbitals of a given atom. Since the core orbitals do not take part in bonding, it is believed that they can be sufficiently described by using only one set of CGTOs. The number '6' indicates the degree of contraction or the number of primitive functions that are added to form the CGTO. So, for 6-31G, each core orbital is described as a single CGTO comprised of a linear combination of 6 primitive Gaussian functions or GTO. The second term '31' describes the valence orbitals. The presence of 2 digits (3 and 1) after the hyphen indicates that the valence orbitals are described by a linear combination of 2 CGTOs. The numbers 3 and 1 are descriptors showing that one of the CGTO comprises a linear combination of 3 primitive functions or GTOs (denoted by '3'), and other comprises one primitive function or GTO (denoted by the number '1'). This type of basis set is termed as a double-zeta basis set wherein there is 1 CGTO for the core, and 2 for the valence orbitals. Based on a double-zeta basis set:

$$\text{Total number of AOs} = 1 (\text{No. of core orbitals}) + 2 (\text{No. of valence orbitals})$$

Carbon is a second-row atom, with 1 core orbital (1s) and 4 valence orbitals (2s, 2p_x, 2p_y, 2p_z). Hydrogen is a first-row atom with 0 core orbitals, and 1 valence orbital (1s). So for 6-31G the basis functions for C and H are given by:

$$\text{C: } 1(1s) + 2(2s+2p_x+2p_y+2p_z) = 1(1) + 2(4) = 9 \text{ CGTOs}$$

$$\text{H: } 1(0) + 2(1s) = 2(1) = 2 \text{ CGTOs}$$

If a triple-zeta basis function is used (e.g. 6-311G), it signifies that a single CGTO is used for the core orbital, however unlike in the case of double-zeta, a linear combination of 3 CGTOs is taken to describe the valence orbitals, one comprising of 3 GTOs and two comprising of 1 GTO each.

While the minimum number of basis sets is a requirement for the description of atomic orbitals, they fail to provide the mathematical flexibility needed for accurate geometry descriptions, e.g., pyramidalization of ammonia.¹¹ Therefore, additional basis functions are added to gain the mathematical flexibility. This is done by the addition of a higher angular momentum function to each atom⁴⁶ and is indicated by an ‘*’ at the end of the basis set description. E.g. 6-31G* for second-row atoms or by 6-31G(d) showing the addition of *d*-type functions. These would add higher angular momentum orbitals to the second-row atoms, e.g. for carbon, a *d*-type CGTO function would be added to the already existing 9 CGTOs. *d*-type orbitals are treated differently using the Gaussian-type orbitals, and instead of using 5 pure *d*-type orbitals, there are 6 cartesian *d*-type CGTOs

$$6 \text{ cartesian } d\text{-type CGTOs: } d_{xy}, d_{xz}, d_{yz}, d_{x^2}, d_{y^2}, d_{z^2}$$

Another set of *d*-type orbitals used in defining basis sets are the ‘angular momentum *d*-type CGTOs’ that incorporate the linear combination of *d*_{x²} and *d*_{y²}. However, out of the plus

and the minus combination ($d_{x^2+y^2}$ and $d_{x^2-y^2}$ respectively) only the minus combination is used due to the considerable overlap between $d_{x^2+y^2}$ and d_{z^2} orbital.

5 angular momentum d -type CGTOs: $d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}, d_{z^2}$

As per convention, the d -type CGTOs added for the double-zeta basis functions are the cartesian d -type CGTOs. So, 6 CGTOs would be added to the already existing 9 CGTOs for carbon. 6-31G* can also be written as 6-31G(d). A second ‘*’ is added to show the incorporation of polarization functions on the first-row atoms (e.g. 6-31G** or 6-31G(d,p)). Polarization functions for the first-row atoms are added in the form of a p -type CGTO. While cartesian d -type CGTOs are used for polarization at the double-zeta basis set, convention dictates the use of angular momentum d -type CGTOs for the triple-zeta basis set.

For certain interactions in ionic species, and systems with a high degree of charge delocalization, it becomes imperative to add greater flexibility than available by the polarization functions. This is done by the addition of functions called ‘diffuse functions’.⁴⁷ Diffuse functions are added as another set of valence functions (e.g. s and p for second-row atoms, and s for the first-row atoms) in addition to the already existing functions. The exponent ‘ α ’ of diffuse functions is much smaller in order to provide for movement of more loosely held electrons. Addition of diffuse functions is done by addition of a ‘+’ sign. A single ‘+’ indicates the addition of diffuse functions only on the heavy atoms (e.g. 6-31+G*), while a second ‘+’ sign signifies the addition of diffuse functions on hydrogen by addition of an s -type CGTO (e.g. 6-31++G). Thus a double-zeta basis set with diffuse and polarization functions on first-row and second-row atoms can be shown by 6-31++G**.

1.8.4 Dunning Correlation-Consistent Basis Sets

Correlation-consistent basis sets were developed by Dunning and coworkers in 1989.⁴⁸ Computational advances led to increasing popularity of post Hartree-Fock methods and the popularly used Pople basis sets had coefficients that had been optimized using Hartree-Fock theory. While these basis sets worked well for Hartree-Fock and density functional methods, they were found to be lacking for methods explicitly calculating electron correlation. Hence, basis sets known as Dunning correlation-consistent basis sets were introduced, which are denoted by cc-pVXZ (where cc stands for correlation consistent and pVXZ denotes polarized valence X zeta basis). The major difference between these and the Pople split-valence basis set stems from the way the coefficients ‘c’ of the wavefunction are calculated. In Pople basis sets, these values are extracted by a Hartree-Fock calculation by improving the ‘c’ values iteratively until self consistency is achieved. However, in the case of Dunning correlation-consistent basis sets, while the same approach is used, the coefficients are extracted from a configuration interaction calculation instead of a Hartree-Fock calculation, thus incorporating the effects of electron correlation in the total wavefunction. Thus, these basis sets are supposed to be better suited for methods that include electron correlation explicitly, such as MP2, CI or CCSD.^{49,50} Similar to the Pople basis sets, the nomenclature used to describe the Dunning basis sets is descriptive, example: cc-pVXZ, where cc: correlation consistent; pVXZ: p stands for polarization and VXZ stands for ‘valence X zeta’, which indicates that the coefficients are calculated using the CI method only for the valence orbitals, while the core electrons are treated without any electron correlation using Hartree-Fock method. The term ‘X’ indicates the number of CGTOs and ‘Zeta’ is the exponent, corresponding to the term ‘ ζ ’ from the Slater-type orbital. Depending on the basis set chosen, X can be: ‘D’ (double), T (triple), Q (quadruple), etc. These

basis sets include polarization functions, so for second-row atoms, d -type CGTOs will be included, whereas for first-row atoms, p -type CGTOs would be included. Since they are usually a ‘valence only’ basis set, the number of basis functions involves the use of ‘X’ functions for each valence atomic orbital with the largest value of ‘ l ’. For example, in case of carbon the largest angular momentum value ‘ l ’ = 1, i.e. a p -type CGTO. So for cc-pVDZ basis set, there would be 2 p -type CGTOs for the heavy atom (2 corresponding to the ‘D’ of the double-zeta). After the number of largest angular momentum is set, an additional functional is added on going down to the lower angular momentum ‘ l ’ (i.e. $l = 0$), giving three s -type CGTOs. Increase in angular momentum is accompanied by a unity decrease in the total number of functionals added. Therefore, going up from p -type CGTOs to the higher angular momentum ($l=2$), a single d -type CGTO be added. Thus, the cc-pVDZ basis set for carbon would include $3s2p1d$ CGTOs. For hydrogen, the highest angular momentum $l = 0$ (s orbital). Therefore for the cc-pVDZ, there would be 2 s orbitals. An additional p orbital will be added on reduction of the angular momentum to give total of $2sp$ orbitals.

The addition of diffuse functions is done by term ‘aug’ (which stands for augmented) before the term cc-pVXZ. Unlike in the case of Pople basis set, the incorporation of diffuse function is done by addition of a function for all the types of orbitals present. So for carbon, aug-cc-pVDZ will have the functions $[4s3p2d]$ and for hydrogen the total number of basis functions becomes $[3s2p]$. Table 1.4 summarizes the total number of basis functions in the corresponding Pople and Dunning correlation-consistent basis set.

Table 1.4: Number of functions associated with the different Pople and Dunning basis sets

Basis Set	C		H	
	CGTOs	No. of Functions	CGTOs	No. of Functions
6-31G**	$3s2p1d$	15	$2s1p$	5
cc-pVDZ	$3s2p1d$	14	$2s1p$	5
6-311G**	$4s3p1d$	18	$3s1p$	6
cc-pVTZ	$4s3p2d1f$	30	$3s2p1d$	14
6-31++G**	$4s3p1d$	19	$3s1p$	6
aug-cc-pVDZ	$4s3p2d$	23	$3s2p$	9
6-311++G**	$5s4p1d$	22	$4s1p$	7
aug-cc-pVTZ	$5s4p3d2f$	46	$4s3p2d$	23

A point to be noted is that the total number of CGTOs for the polarized basis functions (6-31G** and cc-pVDZ) are identical (CGTOs = $3s2p1d$). Until the addition of triple-zeta or diffuse functions, the space provided by these basis functions is essentially the same (the coefficients and the exponents still vary). It is only the addition of the diffuse functions and the triple-zeta that leads to considerable difference in sizes of the two types of basis sets.

1.9 Solvation Models

One of the more difficult and highly-researched areas of quantum chemistry involves solvation modeling in aqueous and non-aqueous media.⁴³ Unless solvation effects are explicitly specified, the calculations are performed in gas phase only. Reactivities of a number of systems could be significantly affected by the presence of solvent.

There exist a number of ways to incorporate solvent effects in a theoretical model. The first is the use of explicit solvation, wherein solvent molecules are explicitly placed around the molecule. The second solvation model incorporates solvent effects in the form of a dielectric and is known as the continuum solvent model.⁵¹ Two popular implicit-solvation models that will be used in this study are the Onsager and PCM solvation models.

1.9.1 Onsager Solvation Model

This method was introduced in 1936 by Onsager.⁵² It is considered one of the simplest models to describe solvation, and consists of placing a solute molecule in a spherical cavity of a solvent with a constant dielectric.

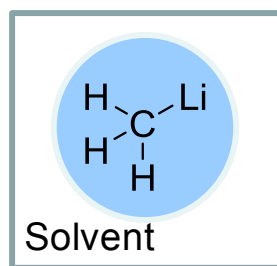


Figure 1.2: Spherical cavity for Onsager calculation with methyllithium as solute

For the Onsager model, the energy of solvation is calculated using the following formula:

$$E = \frac{(\epsilon - 1)}{(2\epsilon + 1)} \frac{\mu^2}{a_0^3} \left[1 - \frac{(\epsilon - 1)}{(2\epsilon + 1)} \frac{2\alpha}{a_0^3} \right]^{-1} \quad (1.47)$$

where ϵ is the dielectric constant of the solvent of study, μ is the molecular dipole moment of the solute that is embedded in a spherical cavity of radius a_0 and α is the polarizability at the center of the solute.⁵¹ The Onsager solvation model has applicability in geometry optimizations, transition structure optimizations,⁵³⁻⁵⁵ and has also been applied successfully towards the studies of conformational equilibria and rotational barriers.⁵⁶

1.9.2 Polarized Continuum Model

This popular method was introduced by Tomasi and coworkers in 1981⁵⁷ and has seen a number of variations over the years.⁵⁸ Polarized Continuum Model (PCM) calculates solvation energy as a sum of three steps: cavitation, i.e., cavity formation, dispersion-repulsion, and electrostatics. Cavity formation in PCM is considerably more realistic in comparison to Onsager

model with interlocking spheres each of which are centered at atomic positions and a number of predefined radii models are available.⁵⁹

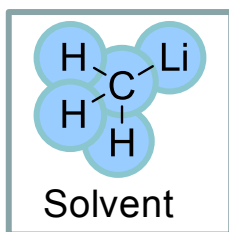


Figure 1.3: Interlocking spheres cavity for PCM calculation with methyllithium as solute

Predefined cavity models like United Atom Topological Model (UA0) include cavities where the hydrogens are enclosed in the spheres of the heavy atoms they are attached to. Two popular radii models available include Bondi and Pauling, both of which have individual spheres for all atoms including hydrogens. Both these models have been found to work well with ionic systems. The PCM solvation model has wide applicability in modeling of solvent effects, and has been shown to be particularly useful in modeling of optical rotations,⁶⁰ electronic excitations of molecules in solution, charge transfer reactions, and geometry optimizations.⁶¹

In chapter three, we will show that implicit solvation models are important for the modeling of ion pair separation of organolithiums. We now turn to the study of protonated heterocycles in vacuo. This study will involve calculations using all the methods described above except configuration interaction.

1.10 References for Chapter 1

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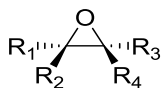
Chapter 2: Density Functional and Post Hartree-Fock Gas Phase Modeling Studies of Protonated Cyclic Ethers.

Contributions

This chapter focuses on the study of protonated cyclic ethers. Section 2.7 of this chapter represents a modified and expanded version of a published article.¹ Contributions from co-authors of the article are described as follows. The author of this dissertation (Ms. Nipa Deora) contributed significantly to the writing of the manuscript and performed the great majority of the calculations (all using Gaussian 03). Selected calculations for this paper were performed or repeated by Dr. Paul R. Carlier, who was the mentor and the principal author for the published article. Finally, Dr. T. Daniel Crawford (a member of the Thesis Committee) performed the CCSD(T) geometry optimizations and large basis set MP2 geometry optimizations and single-point calculations described in the paper; these calculations were performed using PSI3. He also provided significant intellectual direction and advice for this work.

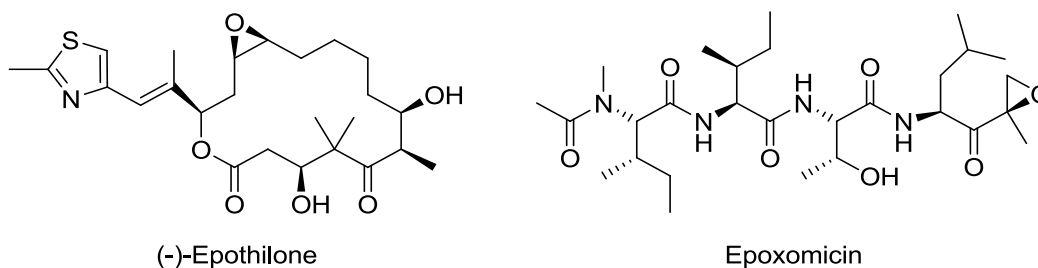
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Epoxides are strained oxygen-containing three-membered heterocycles which can undergo facile nucleophilic ring opening reactions.



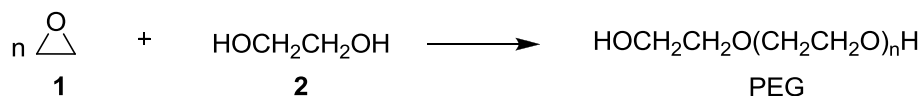
Due to their presence in the literature for a number of years, there exist a number of variations in their nomenclature. For example ethylene oxide ($R_1=R_2=R_3=R_4=H$) is also known as epoxyethane or oxirane, while 2-methyl-1,2-epoxypropane ($R_1=R_2=CH_3$ and $R_3=R_4=H$) is also known as isobutylene oxide, methylpropene oxide and 1,1-dimethyloxirane.²

Epoxides are ubiquitous in nature, and play important roles in natural product^{3,6} and medicinal chemistry.^{7,8} Figure 2.2 shows the structure of natural products (-)epothilone^{5,9} and epoxomicin,^{10,11} which are potent anticancer agents.



Epoxides also feature commonly in polymer chemistry, and have been shown to be effective monomers in addition polymerization reactions.¹²⁻¹⁵ A representative example is the polymerization of ethylene oxide to give polyethylene glycol (PEG), which is synthesized by the reaction of ethylene oxide with water, ethylene glycol or ethylene glycol oligomers. A general

reaction showing the polymerization of ethylene oxide **1**, ethylene glycol **2** to give PEG is shown in Scheme 2.1, and can occur in either acidic or basic conditions.



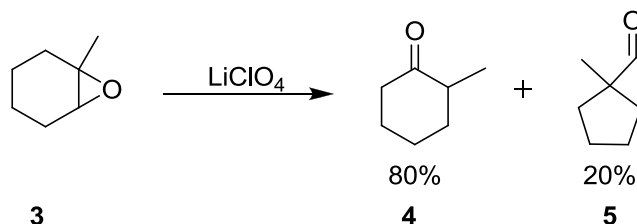
Scheme 2.1: Conversion of ethylene oxide to PEG

2.2 Synthetic Utility

Epoxides are extremely useful intermediates in organic synthesis,^{16,17} and have been used extensively due to their ability to undergo nucleophilic ring opening,¹⁸⁻²³ their Lewis acid catalyzed rearrangement to give carbonyl compounds,²⁴⁻²⁶ or their base-mediated conversion to allylic alcohols.^{27,28} Excellent review articles covering synthetic utilities of epoxides have been written by Parker and Isaacs in 1959² and by Smith in 1984.¹⁷ Epoxides can be deoxygenated to give olefins,²⁹ however their major usefulness is in: 1) Rearrangement to carbonyl compounds, 2) conversion to allylic alcohols and 3) nucleophilic ring opening.

2.2.1 Rearrangement to Carbonyl Compounds

The rearrangement of epoxides to carbonyl compounds has been extensively studied. Conversion to carbonyl compounds has been observed in the presence of protic and Lewis acids, including boron trifluoride,³⁰ lithium,³¹ magnesium³⁰ and zinc³² salts. It has been observed that mono-substituted and 1,2-disubstituted epoxides give aldehydes as products, while for other substitutions, results depend on factors such as the substituent, the stereochemistry of the epoxide as well as the Lewis acid used.³⁰ Scheme 2.2 shows the rearrangement of 1-methylcyclohexene oxide **3** with LiClO₄ to get a mixture of carbonyl compounds **4** and **5**.³¹

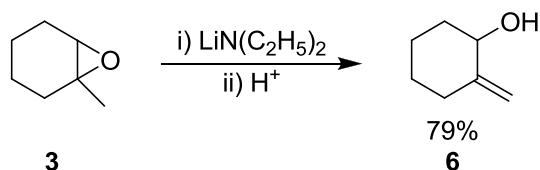


Scheme 2.2: Rearrangement of 1-methylcyclohexene oxide **3** to carbonyl compounds **4** and **5**³¹

Our computational studies will also address proton-mediated rearrangement of epoxides to carbonyl compounds.

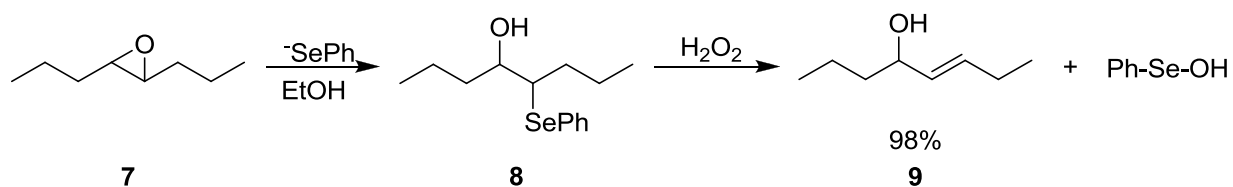
2.2.2 Conversion of Epoxides to Allylic Alcohols

One of the ways in which epoxides can be converted to allylic alcohols is in the presence of a strong base. This process occurs via proton abstraction on the β -carbon of the epoxide followed by addition of proton to give the allylic alcohol. A number of strong bases such as lithium dialkylamides^{33,34} and magnesium bromides,³⁵ can be used for this transformation.³⁶ Scheme 2.3 gives an example of conversion of 1-methylcyclohexene oxide **3** with lithium diethylamide to form the 2-methylenecyclohexanol **6**.



Scheme 2.3: Synthesis of 2-methylenecyclohexanol **6** from 1-methylcyclohexene oxide **3**³⁷

Another method used to convert epoxides to alcohols is by organoselenium²⁷ reagents which undergo an overall addition–elimination procedure following oxidative workup. Scheme 2.4 shows the ring opening of an epoxide **7** by PhSe^- to obtain the addition product **8** which upon oxidative work up gave the allylic alcohol **9**.



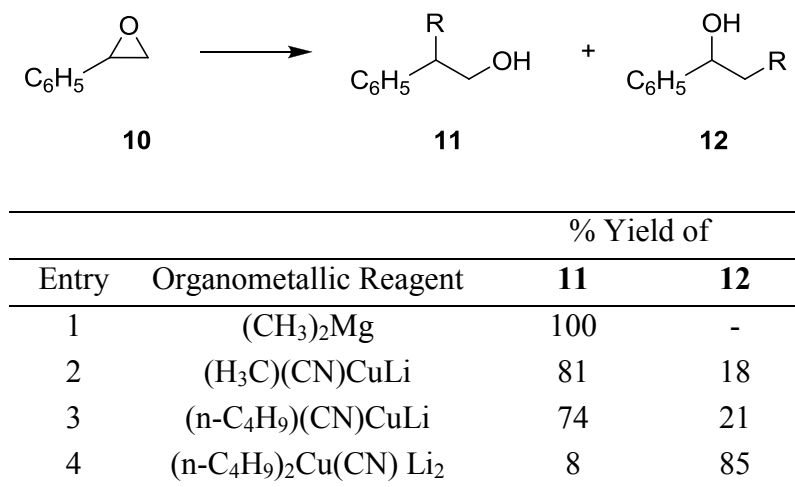
Scheme 2.4: Allylic alcohol formation with organoselenium reagents²⁷

2.3 Nucleophilic Ring Opening Reactions

Epoxides can undergo nucleophilic ring opening to give the corresponding alcohols as products. Ring opening can occur with carbon nucleophiles and heteroatomic nucleophiles as described below.

2.3.1 With Carbon Nucleophiles

Epoxides are known to undergo facile ring opening with carbon nucleophiles. Organometallics such as organolithiums,³⁸ organomagnesium,³⁹ organocopper,⁴⁰ organoboron⁴¹ and even organoaluminum⁴² compounds are used extensively for the delivery of carbanionic carbon.



Scheme 2.5: Epoxide ring opening with carbon nucleophiles. (Reprinted with permission from: Smith, J. G. *Synthesis* **1984**, 629-656. Copyright 1984 Georg Thieme Verlag Stuttgart · New York.)⁴³

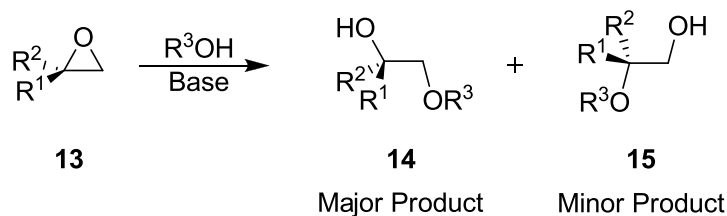
Different organometallic reagents have been shown to give different regioisomers as the major product, and thus the regioselectivity of the reaction can sometimes be controlled by the appropriate choice of the organometallic reagent. Scheme 2.5 shows the different products obtained from the ring opening of styrene oxide with different organometallic reagents.¹⁷ It was observed that the use of dimethyl magnesium (Entry 1) gave **11** as the only product. Organocuprates have also been used to obtain **11** as the major product (Entry 2,3), and it was found that compound **12** was obtained as the major product if mixed cuprates were utilized (Entry 4).^{44,45}

2.3.2 Ring Opening With Heteroatomic Nucleophiles

Due to the strained structure of epoxides, they also undergo facile ring opening with a large range of heteroatomic nucleophiles in acidic, basic as well as neutral conditions to give the corresponding alcohols.^{2,17} Walden inversion is the normal stereochemical outcome of nucleophilic ring opening in both acidic and basic conditions.^{2,16} Unless there exists a functional group that can help stabilize the incipient carbocation via resonance, there is no indication of racemization due to intervention of S_N1 pathway.¹⁶

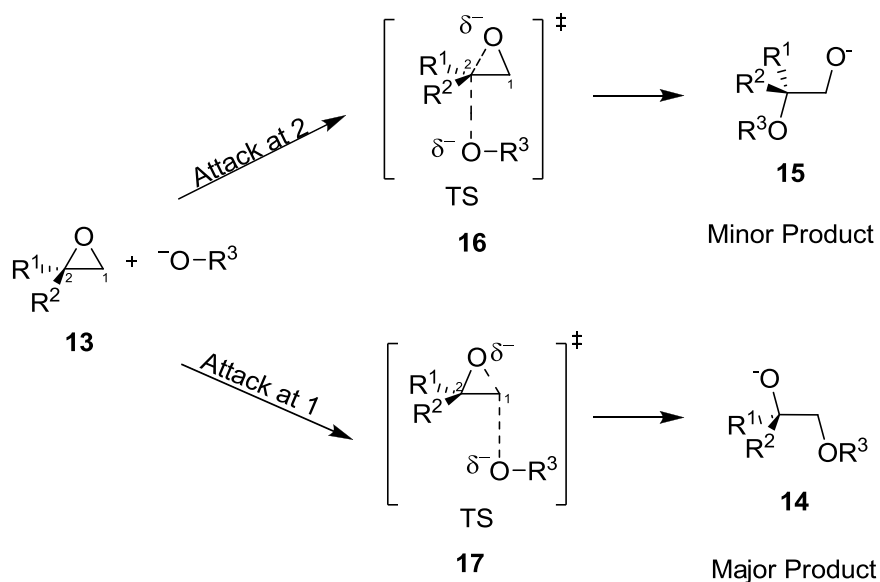
Ring opening reactions of epoxides under acidic and basic conditions can occur via two different pathways. In unsymmetrically-substituted epoxides, nucleophilic ring opening generally proceeds regioselectively, and provides complementary regioselectivities in the presence and absence of acids. In alkyl-substituted epoxides, attack under basic conditions occurs predominantly at the less substituted carbon atom while the opposite regiochemistry is observed in acidic conditions.²

2.3.3 Epoxide Ring Opening Under Basic Conditions



Scheme 2.6: Nucleophilic ring opening under basic conditions

As mentioned above, under basic or neutral conditions, steric interactions play a more significant role, and the nucleophile attacks the epoxide at the least substituted carbon to give the ring opening product (Scheme 2.6).²

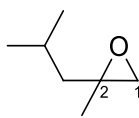


Scheme 2.7: Mechanism of nucleophilic ring opening under basic conditions

Scheme 2.7 shows the mechanism of ring opening of a substituted epoxide by an alkoxide ($^-\text{OR}^3$). Two possible pathways exist: attack at C1, which is the less substituted carbon, (hence less hindered sterically) would give the product **14**; alternatively, attack at C2 would result in attack at the more sterically hindered carbon and would give **15** as the final product (Scheme 2.7). Since steric interactions play the major role under basic or neutral conditions,

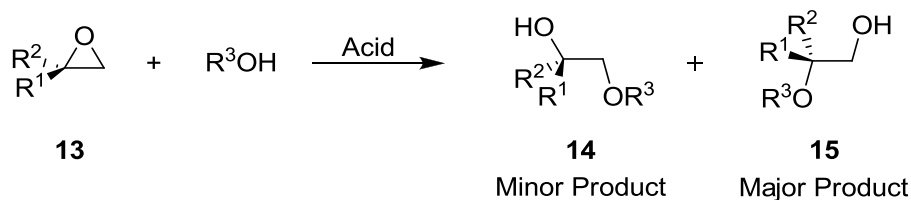
product **14** is obtained as the major product. Table 2.1 shows examples of experimental results obtained for ring opening of epoxides under basic conditions.

Table 2.1: Experimental data of product ratios of epoxide ring opening under neutral and basic conditions²

Entry	Compound	Reagent	Percent yields (attack at 1: attack at 2)	Ref
1		C ₂ H ₅ OH	55.9 : 16.2	46
		C ₆ H ₅ ONa	100 : 0	47
		NaN ₃	Major : Trace	48
2		CH ₃ ONa	Major : Trace	49
3		NH ₃	100 : 0	50
		C ₆ H ₅ -NH ₂	100 : 0	
		CH ₃ -S-Na	100 : 0	

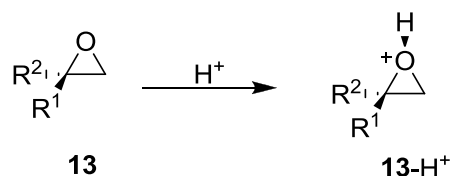
2.3.4 Epoxide Ring Opening Under Acidic Conditions

Ring opening under acidic conditions provide products with regioselectivity complementary to the ones observed in basic conditions.² Thus, attack occurs predominantly at the more substituted carbon (Scheme 2.8).



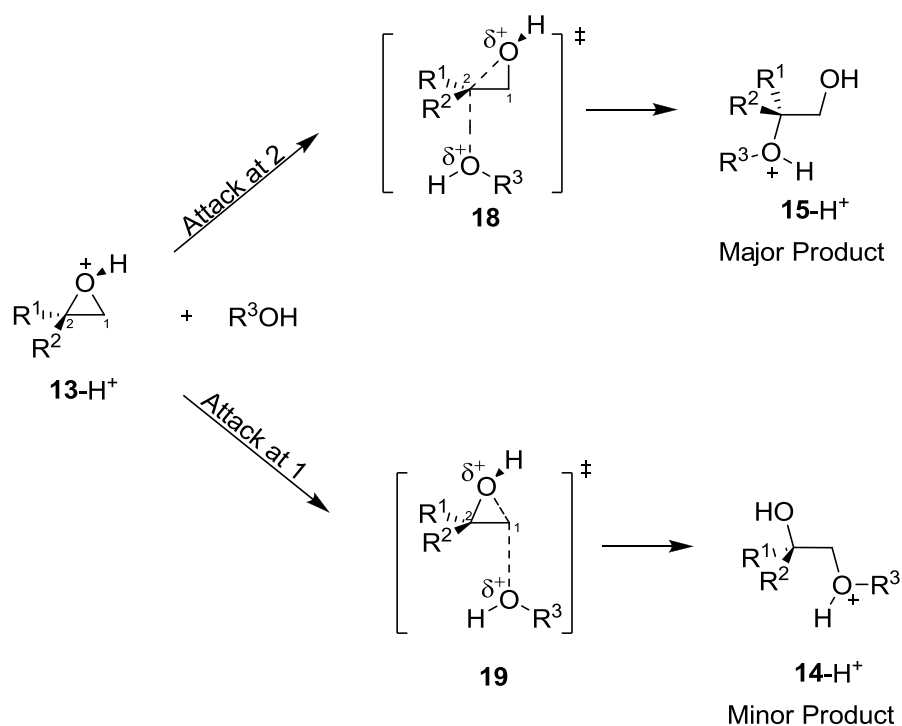
Scheme 2.8: Nucleophilic ring opening under acidic conditions

Under acidic conditions, the ring opening reaction proceeds via a protonated epoxide intermediate **13-H⁺** (Scheme 2.9). Nucleophilic substitution then occurs on this protonated species giving the addition product.



Scheme 2.9: Protonation of epoxide

Under acidic conditions, the attack of the nucleophile is predominantly governed by electronics. In the presence of electron donating groups like alkyl groups, the stabilization provided by the electron donation leads to a greater positive charge transfer to the more substituted carbon, making it the primary site of attack by nucleophiles. (Product **15-H⁺** in Scheme 2.10). Minor products resulting from attack at the less hindered carbon are also usually observed (Product **14-H⁺**). Scheme 2.10 shows a general schematic of acid catalyzed nucleophilic ring opening of epoxides.



Scheme 2.10: Mechanism of nucleophilic ring opening under acidic conditions

In conjugated epoxides like vinyl oxide, benzene oxide and styrene oxide, the hydroxycarbocation and not the protonated oxonium ion is believed to be the reactive intermediate, due to cation stabilization provided by conjugation.^{2,24}

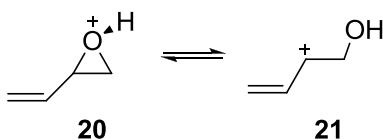
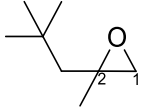
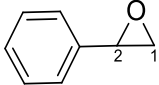


Figure 2.3: Ring opening of protonated vinyl oxide **20** to get the hydroxycarbocation **21**

Finally, for epoxides whose only substituent is an electron withdrawing group (e.g. CF₃, CONH₂ etc.), the major product obtained results from attack at the less substituted carbon. Table 2.2 lists select examples of regioselective ring opening of epoxides under acidic conditions.

Table 2.2: Experimental data of product ratios of epoxide ring opening under acidic conditions²

Entry	Compound	Reagent	Percent yields (attack at 1: attack at 2)	Ref
1		C ₂ H ₅ OH + C ₆ H ₅ SO ₃ H	49 : 51	47
		HCl + H ₂ O (+83 °C)	56 : 44	51
2		CH ₃ OH + H ₂ SO ₄	Trace : Only	49
3		ROH + H ₂ SO ₄	0 : 100	50
4		C ₆ H ₅ CH ₂ NH ₂ + H ⁺ /C ₂ H ₅ OH	35 : 65	52

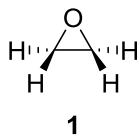
Due to their immense synthetic utility, a number of experimental and theoretical studies have addressed the structures of epoxides. A large number of theoretical studies have been dedicated to the analysis of the structures of various neutral and protonated epoxides,⁵³ and their fate upon ring opening.¹⁸⁻²³ This chapter will focus on the theoretical analysis of some protonated epoxides with emphasis on the gas phase modeling of protonated ethylene oxide, propylene oxide and 2-methyl-1,2-epoxypropane. As such these studies provide insight into the regioselectivity of epoxide opening under acidic conditions.

2.4 Computational Methods

A wide range of computational methods have been used in this study. DFT, Hartree-Fock, post Hartree-Fock methods (MP2,⁵⁴ CCSD,⁵⁵) and composite methods (G2,⁵⁶ G3⁵⁷, G3B3,⁵⁸ and CBS-Q⁵⁹) calculations were performed using Gaussian 03.⁶⁰ DFT investigations employed a variety of exchange (B3⁶¹, mPW⁶² & mPW1⁶², G96⁶³, PBE⁶⁴) and correlation (LYP⁶⁵, P86⁶⁶, PW91,⁶⁷ PBE⁶⁴) functionals. CCSD(T)⁶⁸ single-point calculations at the 6-

311++G**⁶⁹ and aug-cc-pVDZ⁷⁰ basis sets were performed using Gaussian 03. On average, the optimization of **33**-H⁺ with the 18 different DFT functionals finished within one hour versus six hours for MP2 with the same basis set. CCSD(T)/aug-cc-pVTZ single-points, and CCSD(T) and MP2 geometry optimizations using correlation consistent basis sets for protonated isobutylene oxide (**33**-H⁺) and corresponding hydroxycarbocation (**34**) were calculated by Prof. Daniel Crawford using PSI3.⁷¹ All MP2, CCSD, and CCSD(T) calculations were performed 'frozen core' to exclude inner-shell electrons from the correlation calculation. All stationary points were characterized as minima by vibrational frequency analysis, except in the case of CCSD, where cost considerations limited us to the study of **1**-H⁺. Transition structures were characterized by the presence of one imaginary frequency. Since MP2 geometries were shown to closely approximate the CCSD geometries of all 10 protonated epoxides studied, and since the CCSD/6-311++G** ZPVE of **1**-H⁺ differed from the corresponding MP2 ZPVE by only 0.08 kJ/mol (0.04%), MP2 zero-point vibrational energies were used to correct the CCSD electronic energies. Due to the wide range of methods and basis sets employed in this study, ZPVE were calculated from unscaled frequencies.

2.5 Ethylene Oxide



Bond	Electron Diffraction ⁷² (Å)	Microwave Spectroscopy ⁷³ (Å)	X-Ray ⁷⁴ (Å)
C-C	1.47	1.470	1.457
C-O (avg)	1.44	1.434	1.437
C-H (avg)	1.08	1.085	1.1

Figure 2.4: Ethylene oxide

Ethylene oxide **1** is the simplest epoxide; consequently it has been a subject of study for a number of years. Structural analysis of **1** has been performed using microwave spectroscopy,^{2,73,75,76} X-ray^{74,77} and electron diffraction studies.⁷² The different bond lengths obtained using these techniques are shown in Figure 2.4.⁷⁷

A large number of theoretical studies have also addressed the structure of neutral and protonated ethylene oxides. One of the earlier theoretical studies was performed by Radom and coworkers in 1981, which reported the potential surface of $C_2H_5O^+$ at HF/STO-3G and HF/4-31G method and basis.⁷⁸ Calculations were performed on a number of $C_2H_5O^+$ isomers including the protonated epoxide (**1-H⁺**), the hydroxycarbocation **22** and the protonated acetaldehyde **23** (Figure 2.5).

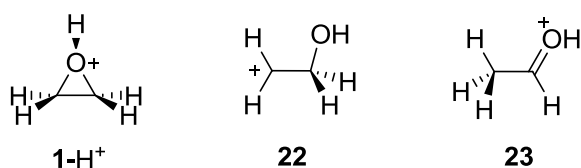
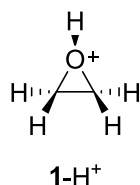


Figure 2.5: $C_2H_5O^+$ isomers **1-H⁺**, **22** and **23**

The protonated ethylene oxide (**1-H⁺**) was found to be a local minimum with a calculated C-O bond distance of 1.543 Å at HF/4-31G and 1.492 Å at HF/STO-3G. Calculations were performed by Ford and Smith in 1987 on the same system at MNDO and HF/6-31G*.¹⁸ Their calculated C-O bond lengths were 1.484 Å at MNDO and 1.498 Å at HF/6-31G*. The effect of electron correlation on these geometries was explored by George and coworkers in 1993 when they performed calculations at MP2/6-31G*.⁷⁹ Table 2.3 shows all the calculated C-O bond distances for **1-H⁺** in the literature.

Table 2.3: Literature data on calculated C-O distances for $\mathbf{1-H^+}$



Method/Basis	C-O distance (Å)	References
HF/STO-3G	1.492	78
HF/4-31G	1.543	78
MNDO	1.484	18
HF/6-31G*	1.498	18
MP2/6-31G*	1.525	79

We calculated this protonated epoxide at B3LYP, MP2 and CCSD (all at 6-311++G**). Our calculated C-O bond lengths are 1.529 Å (B3LYP/6-311++G**), 1.522 Å (MP2/6-311++G**) and 1.517 Å (CCSD/6-311++G**). The B3LYP optimized structure is shown in Figure 2.6.

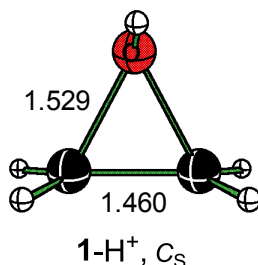


Figure 2.6: B3LYP/6-311++G** optimized geometry of $\mathbf{1-H^+}$. Bond lengths are shown in Å.

Transition structures corresponding to the pyramidal inversion of the epoxide oxygen were also calculated. They were located at RHF/STO-3G and RHF/4-31G method and basis by Radom et al.⁷⁸ Higher-level single-point calculations were also performed. A broad range of values for this inversion barrier were obtained with uncorrected energies ranging from +3.8 kcal/mol (RHF/4-31G//RHF/STO-3G) to +16.5 kcal/mol (RHF/STO-3G//RHF/STO-3G). The calculated energies are shown in Table 2.4. The authors believed that since the calculated barrier was strongly influenced by electron correlation, and inclusion of polarization functions, the best

estimate obtained was +13.9 kcal/mol at the MP3/6-311G**//HF/4-31G level of theory. The same studies were also performed by George and coworkers, who included electron correlation by optimization at MP2/6-31G*.⁷⁹ Incorporation of electron correlation during optimization further increased the oxygen inversion barrier to +17.7 kcal/mol, and gave a structure with C_{2v} symmetry.⁷⁹ Relative energies for the oxygen inversion barrier are summarized in Table 2.4.

Table 2.4: Oxygen inversion energetics of **1**-H⁺

H
 $\text{H} \cdots \text{O}^+ \cdots \text{H}$
 H
0.0
1-H⁺

H
 $\text{H} \cdots \text{O}^+ \cdots \text{H}$
 H
Oxygen Inversion TS
24

H
 $\text{H} \cdots \text{O}^+ \cdots \text{H}$
 H
0.0
1-H⁺

Entry	Method/Basis	Relative Energy ^a (kcal/mol)	Reference
1	RHF/STO-3G //RHF/STO-3G	+16.5	78
2	RHF/4-31G //RHF/STO-3G	+3.8	78
3	RHF/4-31G //RHF/4-31G	+5.0	78
4	RHF/6-31G //RHF/4-31G	+5.2	78
5	MP2/6-31G //RHF/4-31G	+10.4	78
6	MP3/6-31G //RHF/4-31G	+9.3	78
7	RHF/6-31G**//RHF/4-31G	+11.6	78
8	MP2/6-31G**//RHF/4-31G	+14.9	78
9	MP3/6-31G**//RHF/4-31G	+13.9	78
10	MP2/6-31G*//MP2/6-31G*	+17.7	79

^aUncorrected energies.

Our higher-level optimizations at B3LYP/6-311++G** and MP2/6-311++G** showed this structure (**24** in Figure 2.7) to be a C_{2v} -symmetric transition structure with 1 imaginary frequency corresponding to the inversion of oxygen. ZPVE corrected electronic energies relative

to the optimized protonated ethylene oxide ($\mathbf{1-H^+}$) ground state were calculated to be +12.8 and +15.3 kcal/mol for B3LYP/6-311++G** and MP2/6-311++G** respectively. A reduction in C-O bond length was observed in the transition structure (cf. 1.529 Å in $\mathbf{1-H^+}$ and 1.470 Å in **24**, Figure 2.7), which could be attributed to the change in hybridization state of the oxygen atom from sp^3 in the ground state structure to sp^2 in the transition structure. The reaction coordinate with the B3LYP/6-311++G** optimized geometries is shown in Figure 2.7.

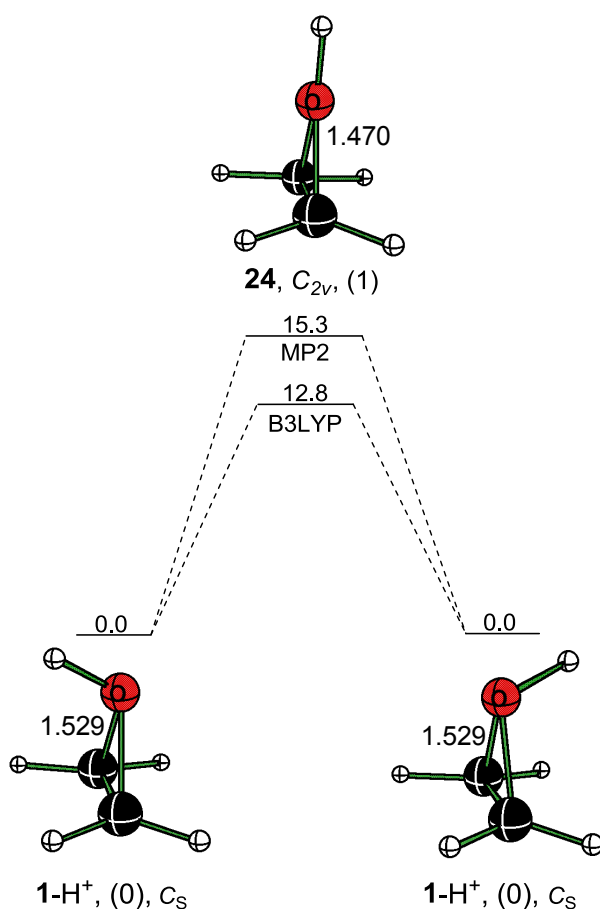
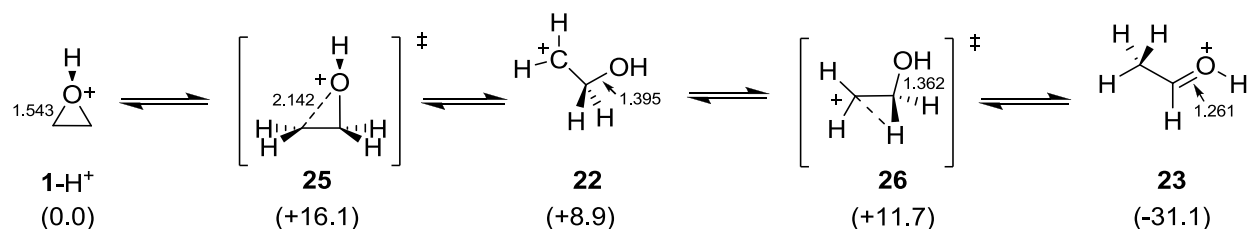


Figure 2.7: Reaction coordinate (kcal/mol) for the pyramidal inversion of oxygen in $\mathbf{1-H^+}$ at MP2 and B3LYP (both at 6-311++G**); the B3LYP optimized geometries are shown, and the number of imaginary frequencies are shown in parenthesis. C-O bond lengths are shown in Å. ZPVE-corrected electronic energies relative to the ground state $\mathbf{1-H^+}$ are depicted.

Another question of considerable interest is the fate of the ethylene oxide ring upon protonation. Experimentally, protonation of ethylene oxide leads to ring opening, and a number of theoretical studies have addressed this phenomenon. Radom and coworkers performed the first of these theoretical studies in 1981,⁷⁸ where they found the hydroxycarbocation **22**, the immediate product of ring opening to be a genuine minimum on the potential-energy surface at both HF/STO-3G and HF/4-31G methods and basis. This hydroxycarbocation **22** was +8.9 kcal/mol higher in energy compared to the protonated ethylene oxide **1-H⁺** at HF/6-31G//HF/4-31G; higher-level single-point calculations at MP2/6-31G**//RHF/4-31G gave an energy difference of +24.8 kcal/mol.

Considerable shortening of the C-O bond was observed (1.395 Å at HF/4-31G and 1.421 Å at HF/STO-3G for **22** compared to 1.543 Å at HF/4-31G and 1.492 Å at HF/STO-3G respectively for the protonated epoxide **1-H⁺**). Transition structure **25** corresponding to the ring opening of **1-H⁺** was also located at both these levels of theory with a very long C-O bond 2.142 Å at HF/4-31G and 2.241 Å at HF/STO-3G (Scheme 2.11). As is typical for these systems, the protonated aldehyde **23** was found to be the lowest energy structure on the potential surface, and was predicted to be more stable than the hydroxycarbocation **22** by 31.1 kcal/mol at HF/6-31G//HF/4-31G. Considerable shortening of the C-O distance at 1.261 Å (HF/4-31G) and 1.282 Å (HF/STO-3G) was observed upon hydride transfer, indicating substantial C-O double bond character in **23**. A transition structure **26** connecting the hydroxycarbocation **22** and protonated aldehyde **23** was also located, and had a small barrier of 2.8 kcal/mol, which was found to disappear at higher levels of theory (Scheme 2.11). Higher-level single-point calculations were also performed with methods including MP2/6-31G* and MP3/6-31G*.



Scheme 2.11: Reaction coordinate of ring opening of **1-H⁺** at HF/6-31G as calculated by Radom and coworkers.⁷⁸ HF/6-31G//HF/4-31G uncorrected electronic energies (kcal/mol) relative to the energy of **1-H⁺** shown in parenthesis.

Contrary results were obtained by Ford et al. in their 1987 study on the same system.¹⁸

Figure 2.8 shows a comparison of the results obtained by these authors.

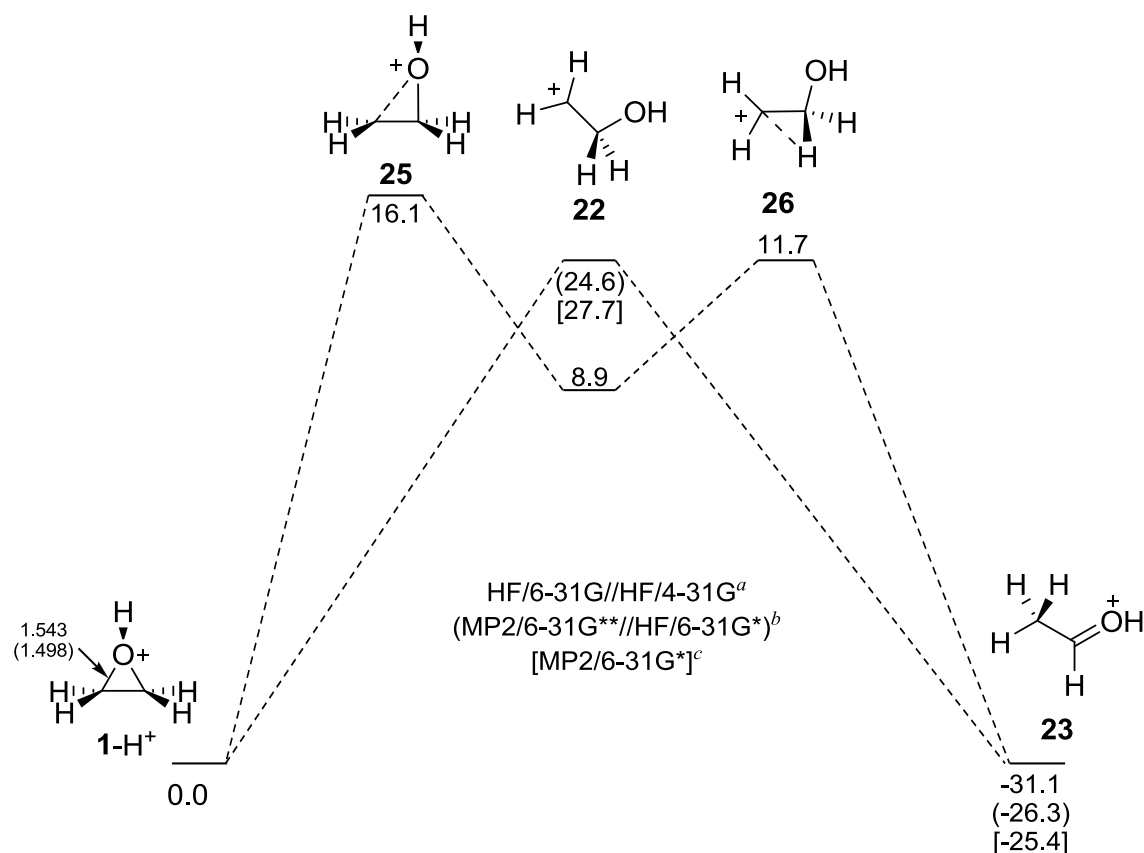


Figure 2.8: Comparison of ring opening data by ^aRadom⁷⁸ and ^bFord¹⁸ and ^cGeorge et al.⁷⁹ All energies in kcal/mol and uncorrected. See figure for details. (Adapted with permission from Coxon et al. *J. Am. Chem. Soc.* **1997**, *119* 4712-4718. Copyright 1997 American Chemical Society)

One of the interesting results observed by Ford et al. was that while the hydroxycarbocation **22** was a local minimum at HF/3-21G and HF/STO-3G, optimization attempts at HF/6-31G* showed no such minima, instead they found the hydroxycarbocation **22** to be a transition structure for the concerted ring opening and hydride shift of the protonated ethylene oxide **1-H⁺** to form the protonated aldehyde **23**, which was the most stable structure along the reaction coordinate. Calculations were also performed by George et al. on this system at MP2/6-31G* in 1993.⁷⁹ Their results were similar to the ones obtained by Ford and are depicted in Figure 2.8. Their studies showed ring opening to occur via a concerted process with the transition structure **22** involving both the C-O bond breaking, and the hydride transfer to get the protonated aldehyde **23** with a barrier of +27.7 kcal/mol at MP2/6-31G*

We followed up the literature calculations using B3LYP/6-311++G** and MP2/6-311++G** for optimizations and frequency calculations. Our results were similar to the ones by Ford et al.¹⁸ and George et al.,⁷⁹ where we found the ring opened hydroxycarbocation **22** to be a true transition structure with one imaginary frequency corresponding to hydride transfer. Note that both C2-H bonds on **22** are of equal length, and the imaginary frequency corresponds to a rotation of the C1-C2 bond and transfer of both H atoms to C2.

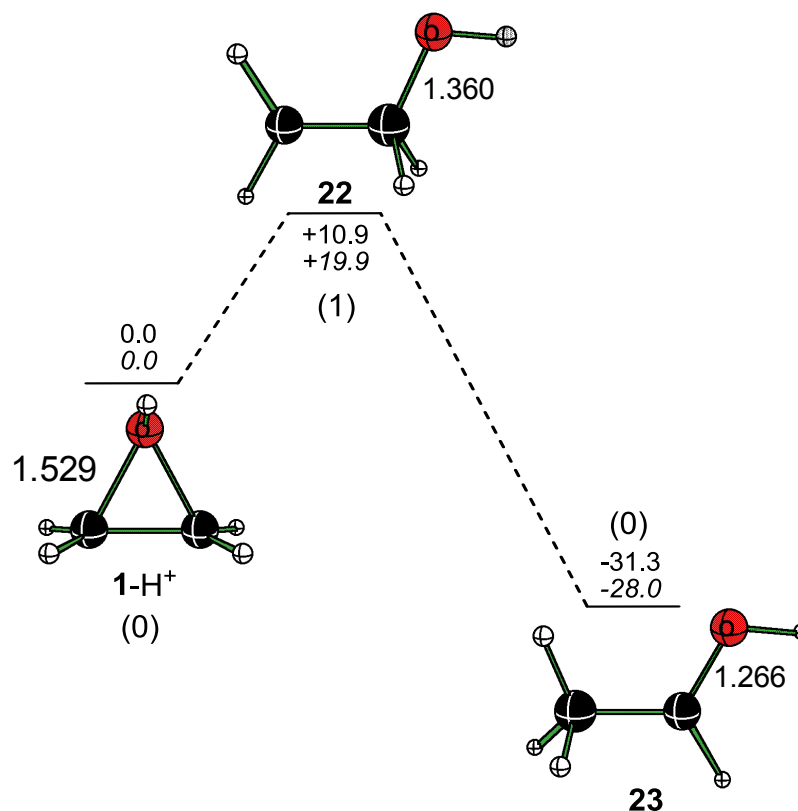


Figure 2.9: Reaction coordinate for ring opening of 1-H^+ at B3LYP/6-311++G**, (MP2/6-311++G** values in *italics*). Note that the transition structure **22** effects the hydride transfer process. All energies ZPVE-corrected in kcal/mol and relative to the energies of 1-H^+ , Number of imaginary frequencies are shown in parenthesis. C-O bond lengths are shown in Å.

The reaction coordinate showing the conversion of the protonated ethylene oxide 1-H^+ to the protonated aldehyde **23** is shown in Figure 2.9. An activation energy of +10.9 kcal/mol was obtained at B3LYP/6-311++G**, while a significantly greater barrier of +19.9 kcal/mol was obtained at MP2/6-311++G**. Again the protonated aldehyde **23** is sufficiently more stable than 1-H^+ (-31.3 and -28.0 kcal/mol at B3LYP and MP2 respectively.)

2.6 Propylene Oxide



Figure 2.10: Propylene oxide (1,2-epoxypropane)

In 1997, propylene oxide **27** and the *cis*- and *trans*- protonated 1,2-epoxypropane (*trans*-**27**-H⁺ and *cis*-**27**-H⁺) were studied by Coxon et al. at MP2/6-31G*.²⁵ The terms *cis* and *trans* correspond to the positions of the proton in reference to the methyl group (Figure 2.11).

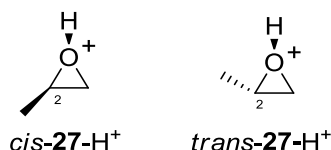


Figure 2.11: Cis and trans protonated propylene oxide

Their analysis showed the *cis*-**27**-H⁺ to be slightly less stable than *trans*-**27**-H⁺, with a relative energy of +0.2 kcal/mol at MP2/6-31G*. Similar results were observed by George and coworkers in 1992, with their results showing relative energies of +0.3 kcal/mol at HF/6-31G* and +0.2 kcal/mol at MP2/6-31G*//HF/6-31G*.²⁴ Compared to **1**-H⁺ the C2-O bond lengths were longer for **27**-H⁺ (cf. 1.562 Å²⁵ for *trans*-**27**-H⁺ and 1.525 Å⁷⁹ for **1**-H⁺ at MP2/6-31G*). This increase in C2-O bond length relative to **1**-H⁺ can be interpreted as evidence of stabilization of the developing positive charge at C2 due to the methyl group. Our B3LYP/6-311++G** optimized geometries are shown in Figure 2.12. The *cis* conformer was found to be slightly less stable than the *trans* conformer with a relative energy of 0.3 kcal/mol at B3LYP/6-311++G**.

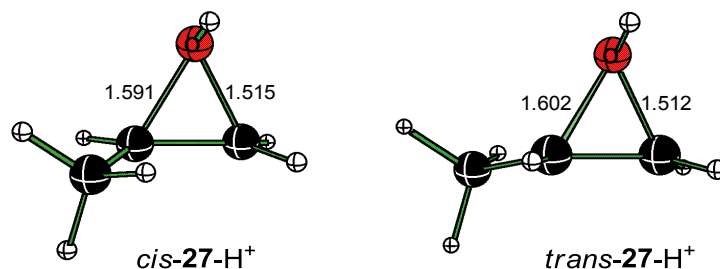


Figure 2.12: B3LYP/6-311++G** optimized geometries of *cis*- and *trans*-**27**-H⁺. Bond lengths are shown in Å.

The barrier for interconversion of the *cis* and *trans* isomers was also calculated by Coxon and coworkers at MP2/6-31G*,²⁵ and involved the same oxygen inversion process as studied by George and coworkers for the protonated ethylene oxide.⁷⁹ There existed a high transition barrier for the interconversion of the *cis*- and *trans*-**27**-H⁺ with ZPVE corrected $\Delta E^\ddagger = +16.9$ kcal/mol at MP2/6-31G* (Figure 2.13)²⁵ which was almost the same as that for the protonated ethylene oxide **1**-H⁺ (Table 2.4, entry 10).

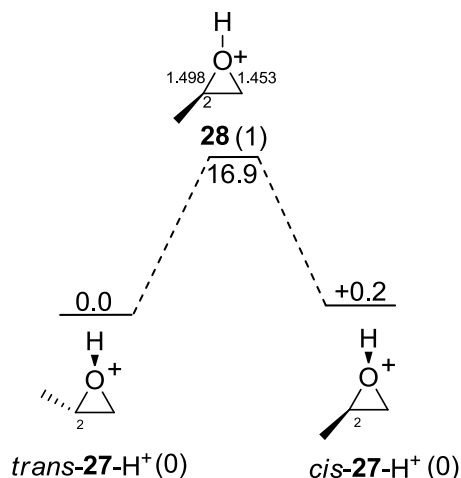


Figure 2.13: Oxygen inversion barrier for **27**-H⁺ at M2/6-31G* as calculated by Coxon et al.. All energies are ZPVE-corrected in kcal/mol and relative to the energies of *trans*-**27**-H⁺. Number of imaginary frequencies shown in parenthesis²⁵

We also calculated the transition barrier for oxygen inversion at B3LYP and MP2 (at 6-311++G**) and found the transition barrier $\Delta E^\ddagger = +14.6$ kcal/mol at B3LYP/6-311++G**

and a higher barrier of +17.3 kcal/mol at MP2/6-311++G**. As seen for **1-H⁺**, a reduction in C2-O bond length accompanied the change in hybridization of the oxygen atom from sp³ in ground state (*cis* and *trans*-**27-H⁺**) to sp² in the transition structure **28** (Figure 2.14).

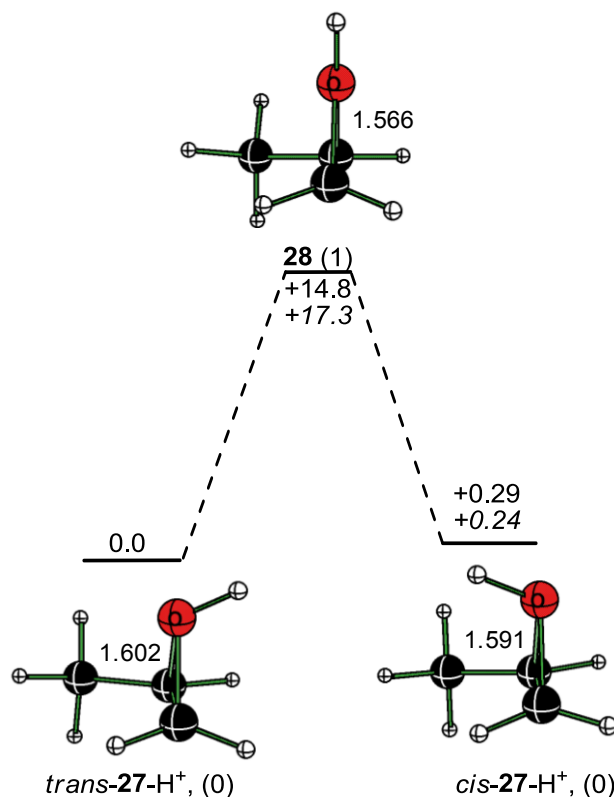


Figure 2.14: B3LYP/6-311++G** (kcal/mol) reaction coordinate for oxygen inversion of **27-H⁺**. All energies relative to energies of *trans*-**27-H⁺**, MP2/6-311++G** energies are shown in italics. Number of imaginary frequencies are shown in parenthesis. C2-O bond lengths are shown in Å.

Ring opening of the epoxide **27-H⁺** results in the formation of the hydroxycarbocation **29**, which is stabilized by the electron donating methyl group. Depending on the relative position of the C2-H proton (H²) and the oxygen, two conformers of the hydroxycarbocation are possible (Figure 2.15): one has a O-C1-C2-H² dihedral of near 0° (**29a**) and the other has a O-C1-C2-H² dihedral of near 180° (**29b**).

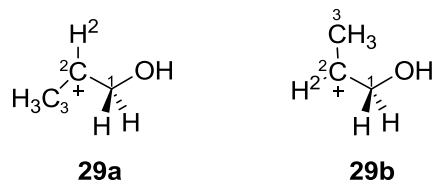


Figure 2.15: Two possible conformers of hydroxycarbocation **29**

In their paper, Coxon and coworkers located both these structures along the potential energy surface at MP2/6-31G*, and referred to the structure **29a** (with a O-C1-C2-H² dihedral angle of 2°) as a minimum. However, careful analysis of their supporting information indicated the presence of an imaginary frequency for this structure. Our multiple attempts to locate this minimum reverted to the protonated aldehyde **30a** as the optimized product.

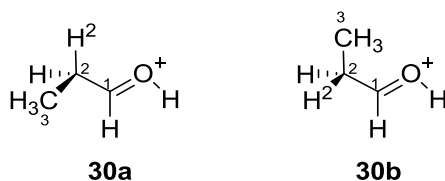


Figure 2.16: Conformers of protonated propanaldehyde **30**

Just like the hydroxycarbocation **29**, two conformations of the protonated aldehyde **30** are possible (Figure 2.16). One has a O-C1-C2-H² dihedral of near 0° (**30a**), and the other has a O-C1-C2-H² of 180° (**30b**). A total of 4 ring opening transition structures were located for **27-H⁺**: two starting from the *trans*-**27-H⁺** (**31a** and **31b**), and two from the *cis*-**27-H⁺** (**31c** and **31d**). Figure 2.17 shows the potential energy surface of ring opening of **27-H⁺** as mapped by Coxon and coworkers at B3LYP/6-31G*.²⁵

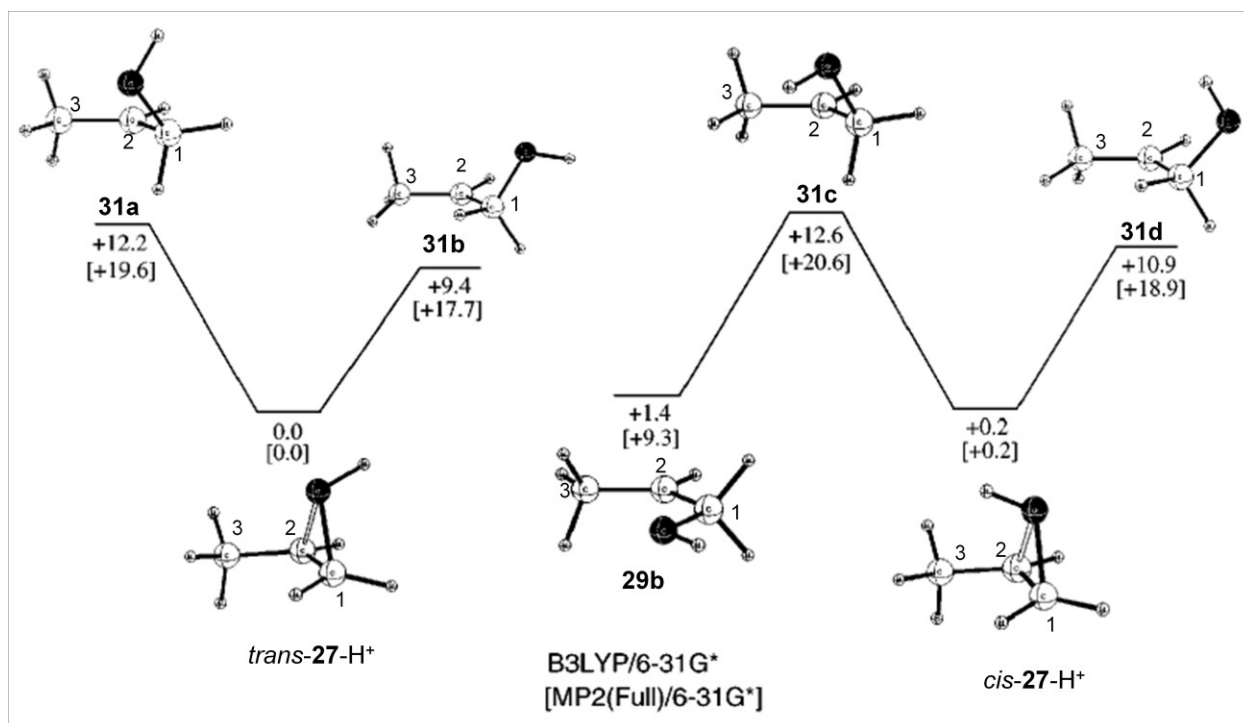


Figure 2.17: Potential energy surface for the ring opening of 27-H^+ at B3LYP/6-31G* (kcal/mol). MP2 values shown in brackets. All energy values are ZPVE-corrected and relative to the energies of $trans\text{-}27\text{-H}^+$. (Reprinted with permission from Coxon et al. *J. Org. Chem.* **1999**, *64*, 9575-9586. Copyright 1999 American Chemical Society).

The highest energy ring opening transition structure **31c** corresponds to the breaking of the C2-O bond in $cis\text{-}27\text{-H}^+$, and the C1-O bond rotating towards C3. This structure was found to give the hydroxycarbocation **29b** as the product. The other three transition structures: two starting from $trans\text{-}27\text{-H}^+$ (**31a** and **31b**), and one starting from the $cis\text{-}27\text{-H}^+$ (**31d**) were reported to collapse directly to the protonated aldehyde **30** (Figure 2.17) via a concerted asynchronous pathway that included both the ring opening and subsequent hydride transfer step. Based on the transition structures, we believe that the structures **31a** and **31c** would give the product **30b** (relative energy of -17.7 kcal/mol at MP2/6-31G*), while the structure **31d** would give the protonated aldehyde conformer **30a** (relative energy of -16.8 kcal/mol at MP2/6-31G*), although the authors do not comment on this point.

We calculated ring opening transition structures for *trans*-**27**-H⁺ at B3LYP/6-311++G**, and found the ring opening to **29b** to be slightly exoenergetic with the ZPVE corrected ring opening electronic energy (ΔE_{ro}) of -2.5 kcal/mol (Figure 2.18). We also located the ring opening transition structure **31a** which had a relative energy of +9.1 kcal/mol. The transition structure **31a** included rotation of the C1-O bond towards C3, and showed no indication of the 1,2-hydride shift to form the protonated aldehyde **30b**. Starting from **29b** we were able to locate a transition structure **32** corresponding to the 1,2-hydride shift with a very small barrier of +0.15 kcal/mol to form the protonated aldehyde **30b**, which was the lowest energy structure along the potential energy surface with a relative energy of -21.9 kcal/mol (Figure 2.18). Unlike the case of **1**-H⁺, the ring opened structure **29b**, and the transition structure for hydride shift **32** are different (cf. Figure 2.9 and 2.18). As observed by Coxon and coworkers, the formation of the protonated aldehyde is accompanied by a shortening of the C1-O bond from 1.378 Å in **29b** to 1.268 Å in **30b**.

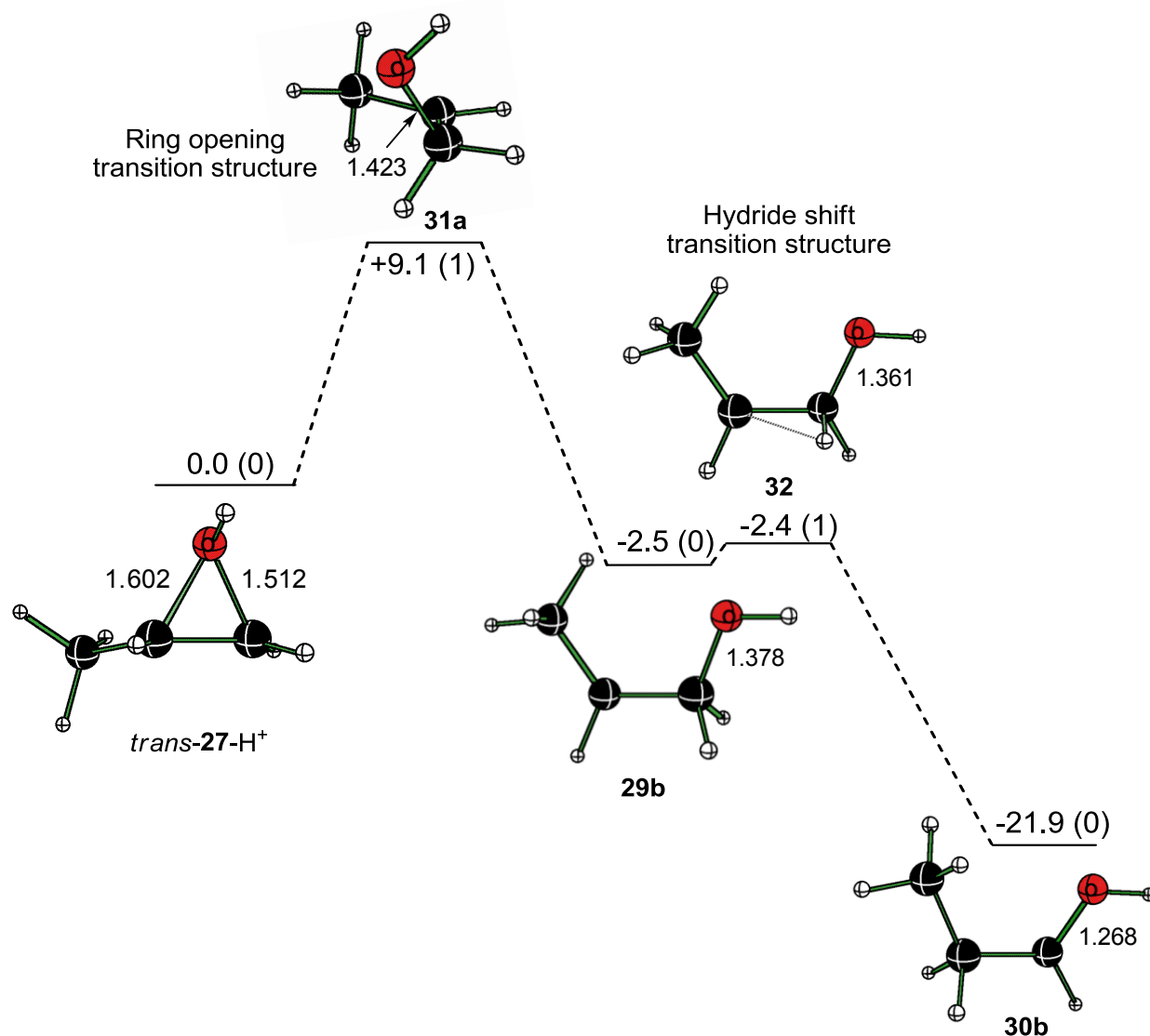
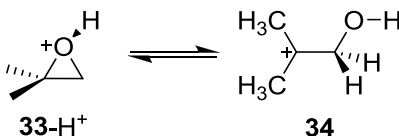


Figure 2.18: Reaction coordinate of ring opening of *trans*-27-H⁺ at B3LYP/6-311++G** (kcal/mol). All energies are ZPVE corrected and relative to the energy of *trans*-27-H⁺ in kcal/mol. Number of imaginary frequencies are shown in parenthesis. Bond lengths are shown in Å.

While we were able to repeat the work of Coxon and coworkers in the locating **29b** at MP2/6-31G*, we could not locate this structure as a true minimum at MP2/6-311++G**, and all attempts to locate this structure gave the protonated aldehyde **30b** upon optimization. Thus at the larger basis set at MP2, *trans*-27-H⁺ opens with hydride migration to give the protonated aldehyde **30b** directly.

2.7 2-Methyl-1,2-epoxypropane (Isobutylene Oxide)



Scheme 2.12: Ring opening of **33-H⁺** to get **34**

Protonated 2-methyl-1,2-epoxypropane **33-H⁺** (Scheme 2.12) was studied at B3LYP/6-31G* by Coxon and coworkers in 1999,²⁶ and by Mosquera and coworkers in 2003.⁸⁰ Unlike for the simplest protonated epoxides **1-H⁺** and **27-H⁺**, no oxygen inversion studies have been reported for **33-H⁺**. Our attempts to locate the oxygen inversion transition structure for this species have thus far been unsuccessful.

Coxon et al. mapped the potential energy surface of C₄H₉O⁺ at the B3LYP/6-31G* method and basis. Ring opening of **33-H⁺** gave the hydroxycarbocation **34**, and this process was found to be more exoenergetic ($\Delta E_{\text{ro}} = -5.5$ kcal/mol) than ring opening of *trans*-**27-H⁺** ($\Delta E_{\text{ro}} = +9.3$ kcal/mol), as would be expected from increased positive charge stabilization imparted by the additional methyl group (Figure 2.19).

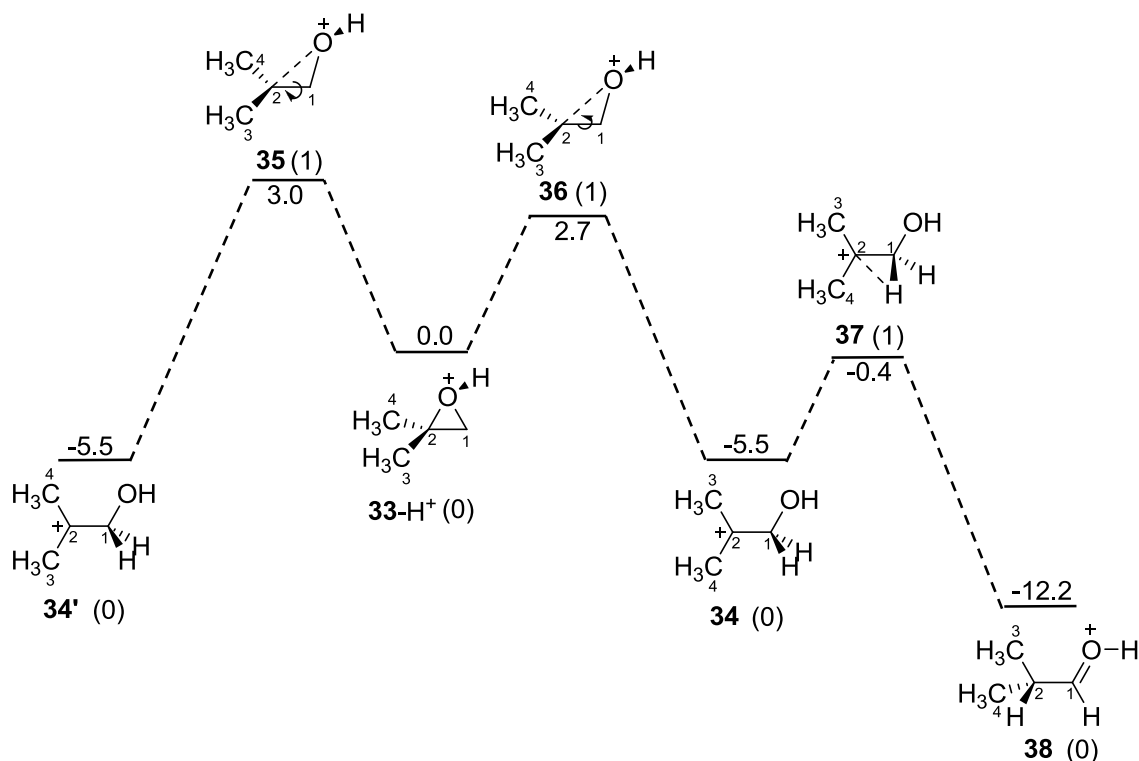


Figure 2.19: B3LYP/6-31G* (kcal/mol) reaction coordinate of **33-H⁺** (kcal/mol) as calculated by Coxon and coworkers.²⁶ Number of imaginary frequencies are shown in parenthesis. All energies are ZPVE-corrected and relative to the energy of **33-H⁺**.

On this potential energy surface, two different ring opening transition structures (**36** and **35**) were located with the C1-O bond rotating towards either the C3 or C4 carbon (**34** and **35** respectively). A small energy difference of 0.3 kcal/mol was observed between the two structures with barriers of $\Delta E^\ddagger$ of +2.7 (**36**) and +3.0 (**35**) kcal/mol relative to the energy of **33-H⁺**. Ring opening of **33-H⁺** gave the hydroxycarbocation **34** with C_1 symmetry and a O-C1-C2-C3 dihedral of 0.1°. This hydroxycarbocation **34** underwent a hydride transfer from C1 to C2 via the transition structure **37** to give the protonated aldehyde **38**, which was the lowest energy structure along the reaction coordinate (relative energy = -12.2 kcal/mol).

Another theoretical study by Mosquera et al. in 2003 explored the effects of protonation on a variety of substituted epoxides at B3LYP/6-311++G**.⁸⁰ A variety of protonated epoxides:

2-methyl-1,2-epoxypropane **33-H⁺**, ethylene oxide **1-H⁺**, *cis* and *trans* propylene oxide **27-H⁺**, *cis* and *trans* protonated 2,3-butylene oxide **39-H⁺**, *cis* and *trans* 2-methyl-2,3-butylene oxide **41-H⁺** were analyzed in their study (Figure 2.20).

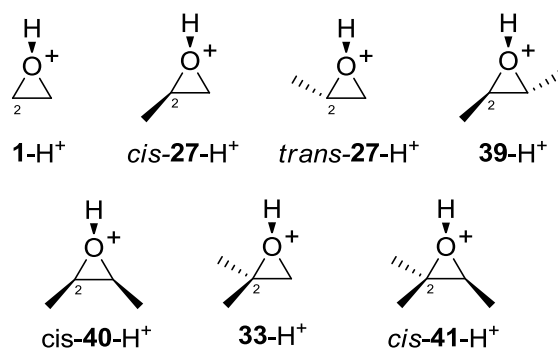


Figure 2.20: Protonated epoxide systems studied by Mosquera and coworkers.⁸⁰

Although C-O distances were not disclosed, *trans*-**27-H⁺**, **33-H⁺** and **41-H⁺** were considered to be substantially carbocationic, and instead of adopting the oxonium ion structures, it was stated that ring opening occurred on protonation. These results for **33-H⁺** at B3LYP/6-311++G** appeared to contradict the results obtained by Coxon and coworkers at B3LYP/6-31G*, and prompted us to further investigate the structure of **33-H⁺**.

Our calculations on this system will be split into two sections. The first section will focus on the structure of protonated cyclic ethers with detailed analysis of the structure of **33-H⁺** (Section 2.7.1). The second section will analyze the energetics of ring opening of the protonated epoxide **33-H⁺** to the hydroxycarbocation **34** (Section 2.7.2).

2.7.1 Modeling of Protonated Cyclic Ethers

Starting from the findings of Mosquera and coworkers, we repeated their B3LYP/6-311++G** calculations on the putative protonated epoxides **1-H⁺**, *cis* and *trans*-**27-H⁺**, **33-H⁺**, *cis* and *trans*-**39-H⁺**. As will be discussed below, our studies demonstrate an unusually

long C2-O bond for **33-H⁺** at B3LYP/6-311++G**; yet this structure is distinct from its *C_s*-symmetric open ring conformer, hydroxycarbocation **34**.

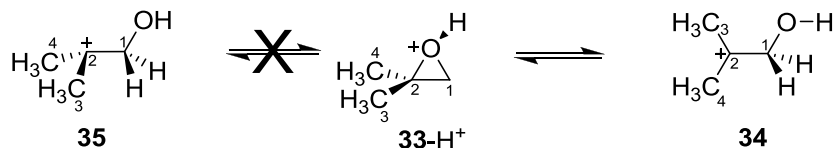


Figure 2.21: Ring opening of protonated 2-methyl-1,2-epoxypropane

Multiple attempts to locate a structure **35** (Figure 2.21) with a O-C1-C2-C3 dihedral near angle 90° proved futile as the structure reverted to the closed form **33-H⁺** for all the methods tested. The greater stability of the hydroxycarbocation **34** could be attributed to the stabilization provided by hyperconjugation between the protons on C1 and the empty *p*-orbital of the C2 carbocation. This stabilization is absent in **35**, and could explain why this structure is not a minimum on the potential energy surface.

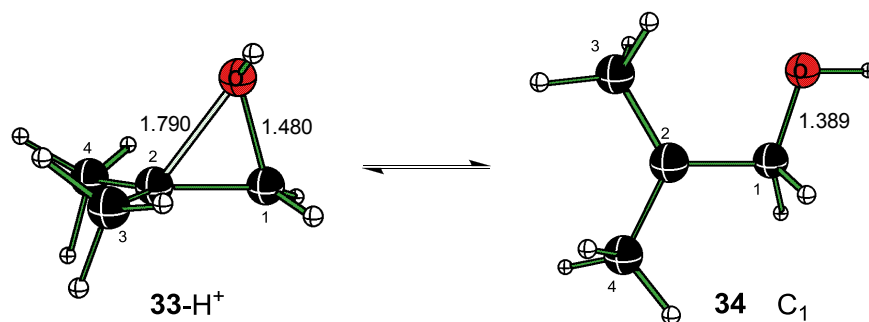


Figure 2.22: B3LYP/6-311++G** optimized geometries of **33-H⁺** and **34**. Bond lengths are shown in Å.

As can be seen in Figure 2.22, the protonated epoxide **33-H⁺** retains a clear cyclic framework, although the 1.790 Å C2-O bond length is quite unusual, and is nearly 0.1 Å longer than previously found with the smaller 6-31G* basis set. At the same basis set, Hartree-Fock predicts a dramatically shorter bond (1.623 Å), as do methods based on *ab initio* treatments of electron correlation with MP2 at 1.598 Å, and CCSD giving a C2-O bond length of 1.599 Å

(Table 2.5). The CCSD/6-311++G** C2-O bond length is nearly 0.2 Å shorter than that predicted by B3LYP.

Table 2.5: Calculated C2-O bond lengths of **33**-H⁺ with B3LYP, MP2 and CCSD methods.

Entry	Method/Basis	C2-O bond length (Å)
1	B3LYP/6-31G*	1.690
2	B3LYP/6-311++G**	1.798
3	CCSD/6-311++G**	1.598
4	MP2/6-311++G**	1.598
5	MP2/cc-pVDZ ^a	1.605
6	MP2/cc-pVTZ ^a	1.595
7	MP2/aug-cc-pVDZ ^a	1.626
8	CCSD(T)/cc-pVTZ(C,O)/cc-pVDZ(H) ^a	1.609

^aCalculations performed by Prof. Daniel Crawford with PSI3.

To confirm the adequacy of the CCSD/6-311++G** geometry for higher-level single-point calculations, with the help of Prof. Crawford, we examined the effects of correlation consistent basis sets and triples excitations. MP2 geometry optimizations using the cc-pVDZ, cc-pVTZ, and aug-cc-pVDZ basis sets gave C2-O bond lengths of 1.605 Å (Entry 5, Table 2.5), 1.595 Å (Entry 6, Table 2.5), and 1.626 Å (Entry 7, Table 2.5) respectively, demonstrating that the use of a valence triple-zeta basis set and diffuse functions cause small opposing changes. Thus we project that the MP2/aug-cc-pVTZ C2-O bond length (if it were available) would be very close to the MP2/6-311++G** C2-O bond length (1.598 Å). To assess the effect of triple excitations, a mixed cc-pVTZ(C,O)/cc-pVDZ(H) basis set was chosen for the computationally-expensive CCSD(T) optimization, since it includes *f*-type functions on the heavy atoms, which are often critical for accurate predictions of molecular structure. Since only a minimal (+0.01 Å)

change in the C2-O bond length is observed vs. CCSD/6-311++G**, we conclude that this latter geometry was sufficiently accurate and suitable for higher-level single-point calculations.⁸¹

Since there was a considerable lengthening of the C2-O bond of **33**-H⁺ on increasing basis set size from 6-31G* to 6-311++G** at B3LYP (cf. Entry 1 and 2, Table 2.5), we decided to explore the basis set dependence of the C2-O bond length of **33**-H⁺ at B3LYP. We increased the basis set size by progressively adding diffuse and polarization functions to the 6-31G* basis set, and assessed the effect of each addition on the C2-O bond length (Table 2.6).

Table 2.6: B3LYP and MP2 calculated C2-O bond lengths for **33**-H⁺ with increasing basis sets

Entry	Basis Set	C2-O (Å)	
		B3LYP	MP2
1	6-31G*	1.692	1.598
2	6-31+G*	1.714	1.603
3	6-31+G**	1.725	1.601
4	6-31++G**	1.726	1.598
5	6-311+G**	1.792	1.598
6	6-311++G**	1.790	1.598

With B3LYP, the **33**-H⁺ C2-O bond progressively lengthens as diffuse functions are added to heavy atoms, and as polarization functions are added to hydrogen. However, the use of a valence triple-zeta basis set appears to cause the largest lengthening (6-31+G** to 6-311+G** and 6-31++G** to 6-311++G**) with C2-O bond length of 1.691 Å at B3LYP/6-31G* (Entry 1, Table 2.6) to 1.790 Å at B3LYP/6-311++G** (Entry 2, Table 2.6).⁸² These variable numbers at B3LYP prompted us to explore the use of an *ab initio* method like MP2 with the increasing basis set approach, to see whether the extremely long C2-O bond would be retained. Unlike B3LYP, MP2 treatment of the C2-O bond length of **33**-H⁺ was more consistent as the basis set size was increased from 6-31G* (1.598 Å) to 6-311++G** (1.598 Å) with a maximum increase of 0.005

Å (C2-O = 1.603 Å) at MP2/6-31+G* (Entry 2, Table 2.6). Figure 2.23 shows a chart of C2-O bond length as a function of increasing basis sets at B3LYP and MP2 methods.

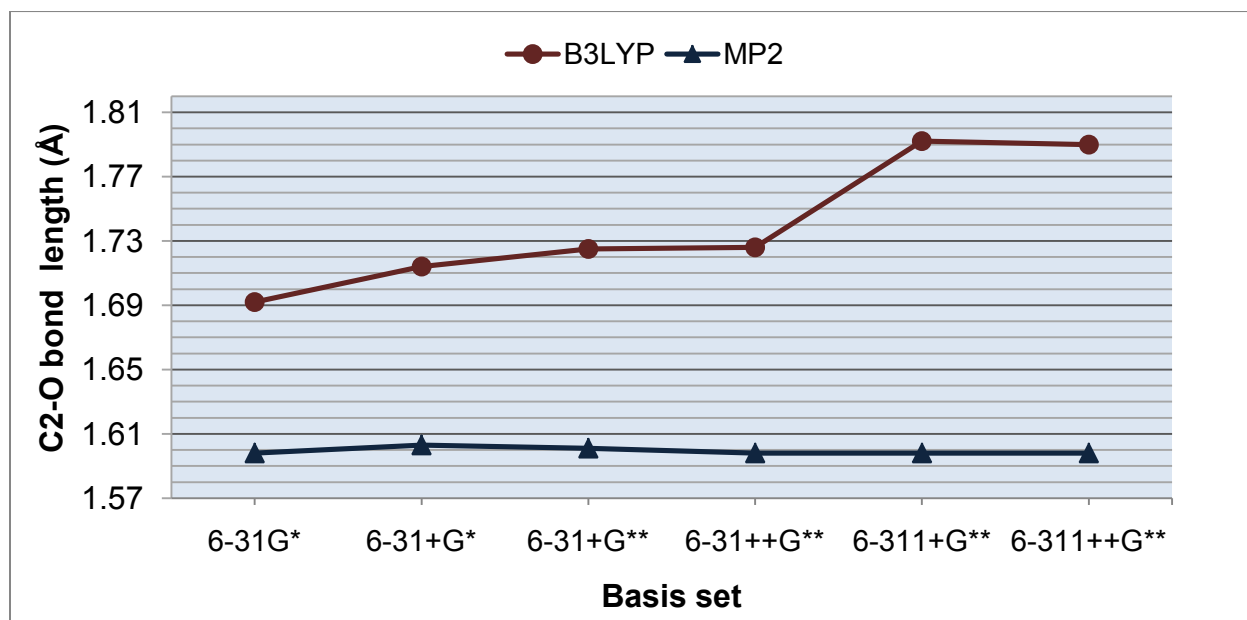


Figure 2.23: C2-O bond lengths of $\mathbf{33-H}^+$ with increasing basis sets at B3LYP and MP2

The poor performance of the B3LYP density functional in describing the C2-O bond length of $\mathbf{33-H}^+$ prompted us to look at other density functionals. We employed five different GGA and hybrid exchange functionals (B3⁶¹, mPW⁶² & mPW1⁶², G96⁶³, PBE⁶⁴) and four different GGA correlation (LYP⁶⁵, P86⁶⁶, PW91,⁶⁷ PBE⁶⁴) functionals. The results obtained are shown graphically in Figure 2.24.

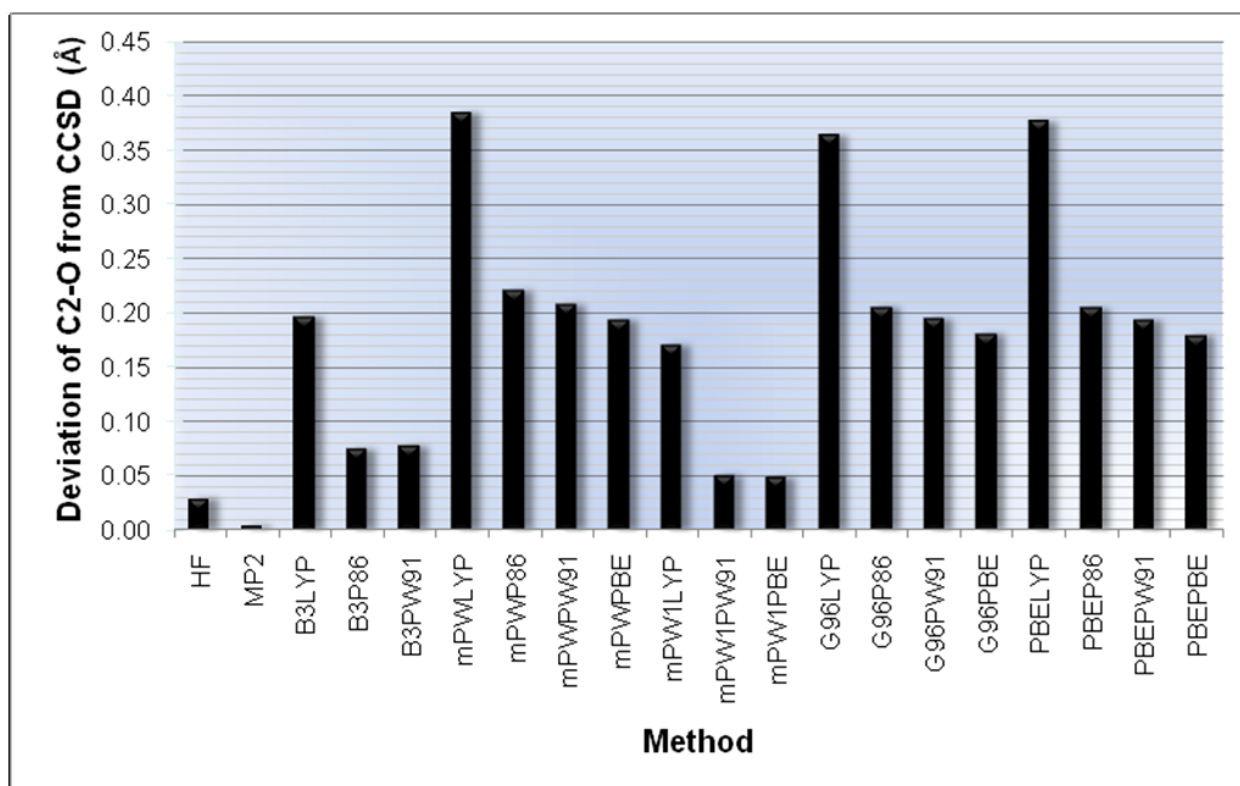


Figure 2.24: Deviation of calculated C2-O bond lengths in **33-H⁺** from CCSD (all at 6-311++G**).

As can be seen in Figure 2.24, DFT methods consistently overestimate the length of the C2-O bond in protonated epoxide **33-H⁺**, and on average were 0.19 Å longer than CCSD. The different C1 and C2 bond lengths obtained on application of different methods to **33-H⁺** have been summarized in Table 2.7. Interestingly, for each of the five exchange functionals examined (B3, mPW, mPW1, G96, PBE), the LYP correlation functional gives the longest C2-O bond. In particular, the mPWLYP, G96LYP, and PBELYP methods gave C2-O bonds 0.379 (Entry 7), 0.358 (Entry 14), and 0.371 Å (Entry 18) longer than that predicted by CCSD. Only two functionals (mPW1PW91 and mPW1PBE) gave C2-O bond lengths within 0.05 Å of that predicted by CCSD. Finally, as mentioned previously, HF and MP2 both perform very well to estimate the C2-O bond length in **33-H⁺**.

Table 2.7: C1-O and C2-O bond lengths calculated at HF, MP2, CCSD and 18 DFT functionals (all at 6-311++G**).

Entry	ab initio method	Exchange functional	Correlation functional	C2-O (Å)	$\Delta(\text{C2-O})$ in 33-H⁺ (Å) ^a	C1-O (Å)
1	HF			1.623	0.024	1.468
2	MP2			1.598	-0.001	1.514
3	CCSD			1.599	0.000	1.504
4		B3	LYP	1.790	0.191	1.480
5			P86	1.669	0.069	1.484
6			PW91	1.671	0.072	1.485
7		mPW	LYP	1.978	0.379	1.481
8			P86	1.814	0.215	1.490
9			PW91	1.801	0.202	1.488
10			PBE	1.787	0.188	1.489
11		mPW1	LYP	1.764	0.165	1.481
12			PW91	1.644	0.045	1.485
13			PBE	1.642	0.043	1.483
14		G96	LYP	1.957	0.358	1.480
15			P86	1.799	0.200	1.489
16			PW91	1.788	0.189	1.476
17			PBE	1.774	0.175	1.488
18		PBE	LYP	1.971	0.371	1.482
19			P86	1.798	0.199	1.492
20			PW91	1.787	0.188	1.491
121			PBE	1.773	0.174	1.492

^a $\Delta(\text{C2-O})$ is defined as C2-O(CCSD/6-311++G**) - C2-O(Method). Significant deviations are highlighted in bold.

The longest C2-O bond length was observed for mPWLYP at 1.978 Å (Entry 7, Table 2.7), while the shortest bond length was observed for mPW1PW91 and mPW1PBE at 1.644 Å (Entry 12, Table 2.7) and 1.642 Å (Entry 13, Table 2.7) respectively. The C1-O bond lengths were considerably shorter in the range of 1.480 Å to 1.490 Å for the different DFT functionals. The calculated C1-O bond length was 1.468 Å for HF. Slightly longer C1-O bond lengths were observed for MP2 and CCSD at 1.514 and 1.504 Å respectively (Entry 2 and 3, Table 2.7). To

ascertain as to what degree this failure stemmed from the charge on the epoxide, we studied the neutral epoxide **33**.

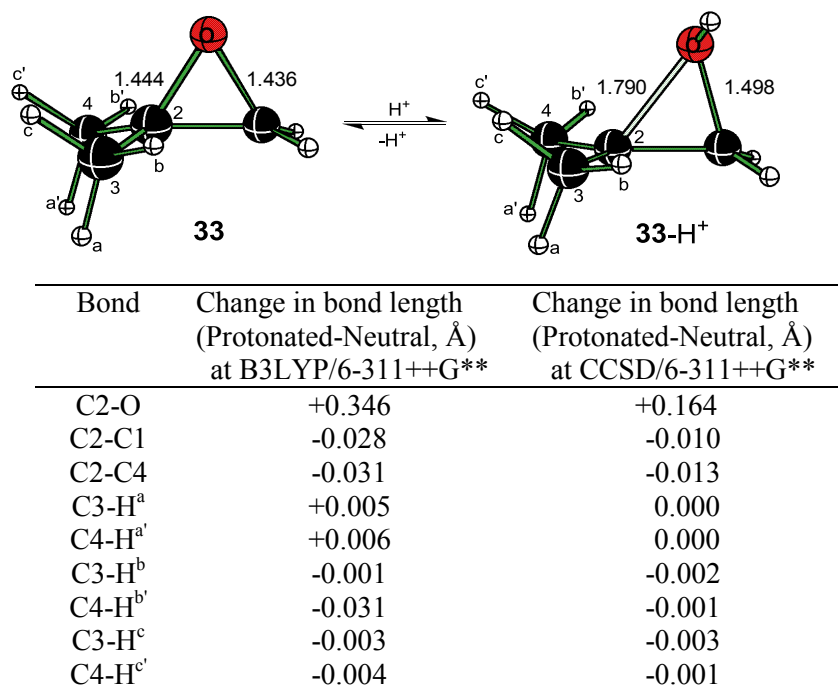


Figure 2.25: Bond length changes upon protonation of **33** to **33-H⁺** at B3LYP/6-311++G** and CCSD/6-311++G**. B3LYP/6-311++G** optimized geometries shown and C-O bond lengths are shown in Å.

As can be seen, the C2-O bond length is shorter for **33** at 1.444 Å, which would be expected due to the absence of the positive charge (Figure 2.25). The CCSD/6-311++G** bond length was 1.434 Å, within 0.01 Å of the B3LYP/6-311++G** value. Along with the changes in C2-O bond lengths upon protonation, changes were also observed in the bond lengths of the exocyclic C-C and C-H bonds. Both the exocyclic C-C bond lengths reduced (average of 0.029 Å at B3LYP and 0.015 Å at CCSD/6-311++G**) consistent with an increase in C3-C2 and C4-C2 bond orders that would accompany hyperconjugation. Also as expected, an increase in the bond lengths of the C-H bonds trans to the oxygen (H^a and H^{a'}), signified the presence of increase in hyperconjugative stabilization upon protonation. Finally, the slight reduction in the

other C3-H and C4-H bond lengths is consistent with a change in hybridization of these carbons upon protonation. As these carbons become more sp^2 -like, the C-H bonds not involved in hyperconjugation would be expected to contract. Greater deviations were observed for the B3LYP compared to CCSD indicating the existence of greater stabilization at B3LYP than CCSD, which mirrored the trends observed in the changes of the C2-O bond length upon protonation.

We then evaluated the ability of the 17 other DFT functionals along with HF, MP2 and CCSD methods (all at 6-311++G**) for modeling **33**. Figure 2.26 shows the deviations of the C2-O bond lengths obtained by different methods from the CCSD values.

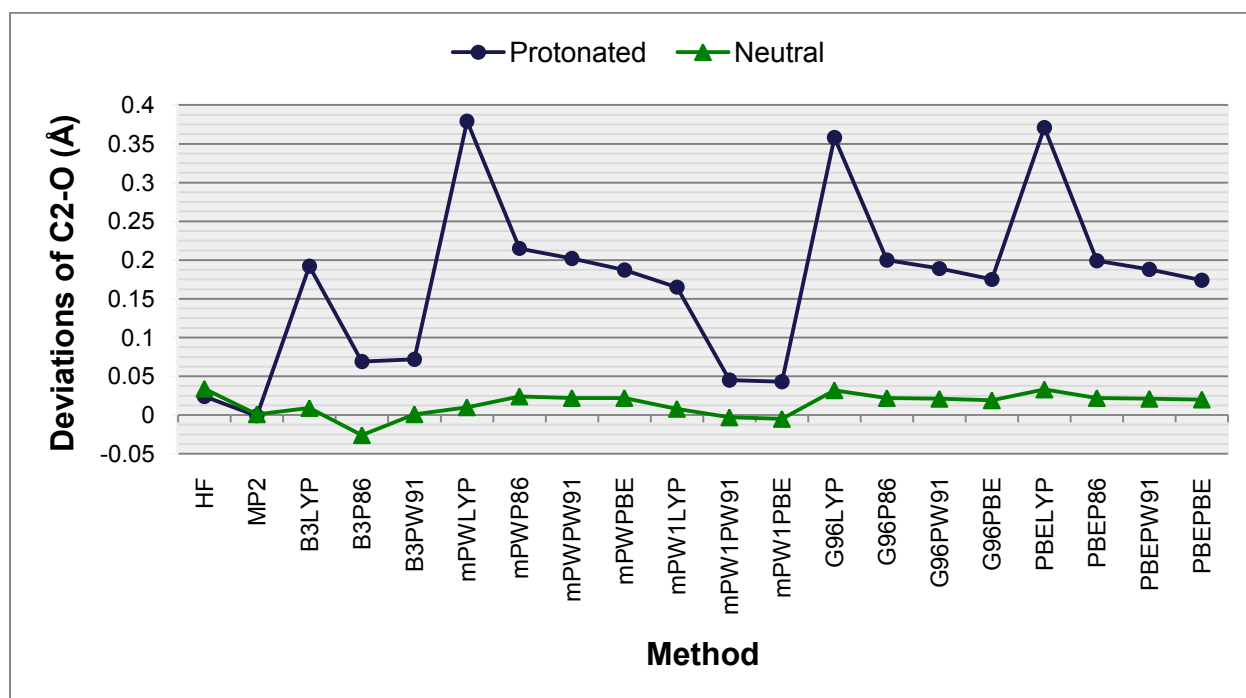


Figure 2.26: Comparison of **33** and **33-H⁺** at different DFT methods to CCSD values (all at 6-311++G**).

In contrast to the protonated epoxide, all 18 functionals performed well in estimating the C2-O bond length of the neutral epoxide **33** (average deviation from CCSD is 0.017 Å; RMS difference is 0.020 Å). Both MP2 and HF again performed well and matched the CCSD bond

length well. These contrasting results for the protonated and neutral epoxides suggest that the difficulty in modeling **33**-H⁺ with DFT methods stems from the C2-O bond, which is disproportionately weakened by hyperconjugative stabilization at C2 of the incipient carbocation. These data have been summarized in Table 2.8, which also shows the deviations of the C2-O bond lengths of **33** and **33**-H⁺ for *ab initio* and density functional methods versus CCSD (all at 6-311++G**).

Table 2.8: C2-O bond lengths and their deviations from CCSD values for **33** and **33**-H⁺ using *ab initio* and density functional methods (all at 6-311++G**).

<i>ab initio</i> method	Exchange functional	Correlation functional	C2-O in 33 (Å)	$\Delta(\text{C2-O})$ in 33 (Å) ^a	$\Delta(\text{C2-O})$ in 33 - H ⁺ (Å) ^a
HF			1.408	-0.026	0.024
MP2			1.443	0.009	-0.001
	B3	LYP	1.443	0.010	0.191
		P86	1.435	0.001	0.069
		PW91	1.435	0.001	0.072
	mPW	LYP	1.468	0.034	0.379
		P86	1.458	0.024	0.215
		PW91	1.457	0.022	0.202
		PBE	1.456	0.022	0.188
	mPW1	LYP	1.442	0.008	0.165
		PW91	1.431	-0.003	0.045
		PBE	1.430	-0.005	0.043
	G96	LYP	1.466	0.032	0.358
		P86	1.456	0.022	0.200
		PW91	1.455	0.021	0.189
		PBE	1.453	0.019	0.175
	PBE	LYP	1.467	0.033	0.371
		P86	1.456	0.022	0.199
		PW91	1.455	0.021	0.188
		PBE	1.454	0.020	0.174

^a $\Delta(\text{C2-O})$ is defined as C2-O(CCSD/6-311++G**) - C2-O(Method). Significant deviations highlighted in bold.

2.7.1.1 Symmetrically and Unsymmetrically Substituted Analogues of 33-H^+

If the weakness of the C2-O bond in 33-H^+ is the salient issue, DFT should be more successful in predicting the structure of protonated epoxides that distribute the charge more equally over C1 and C2, as in these cases neither C-O bond would be disproportionately weakened. To test this hypothesis, we modeled a variety of more symmetrically substituted epoxides. We then compared B3LYP and CCSD/6-311++G** C-O bond lengths for symmetrically (1-H^+ , 39-H^+ , 40-H^+ , 42-H^+) and unsymmetrically substituted epoxides (27-H^+ , 41-H^+). For 27-H^+ , 40-H^+ and 41-H^+ two isomers are possible. The cis isomers direct the OH proton towards the face of the oxirane ring featuring maximum number of methyl groups. The symmetrically and unsymmetrically substituted epoxides modeled are shown in Figure 2.27.

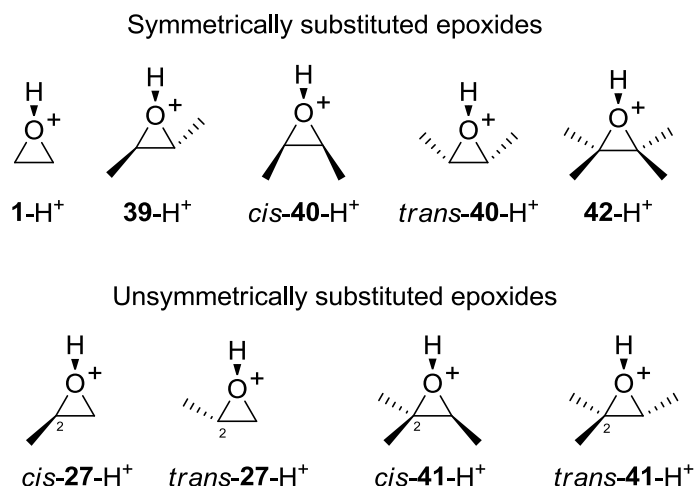


Figure 2.27: Symmetrically and unsymmetrically substituted protonated epoxides

We optimized all these systems at B3LYP, MP2 and CCSD (all at 6-311++G**). Figure 2.28 shows the B3LYP/6-311++G** optimized geometries for all the epoxides studied.

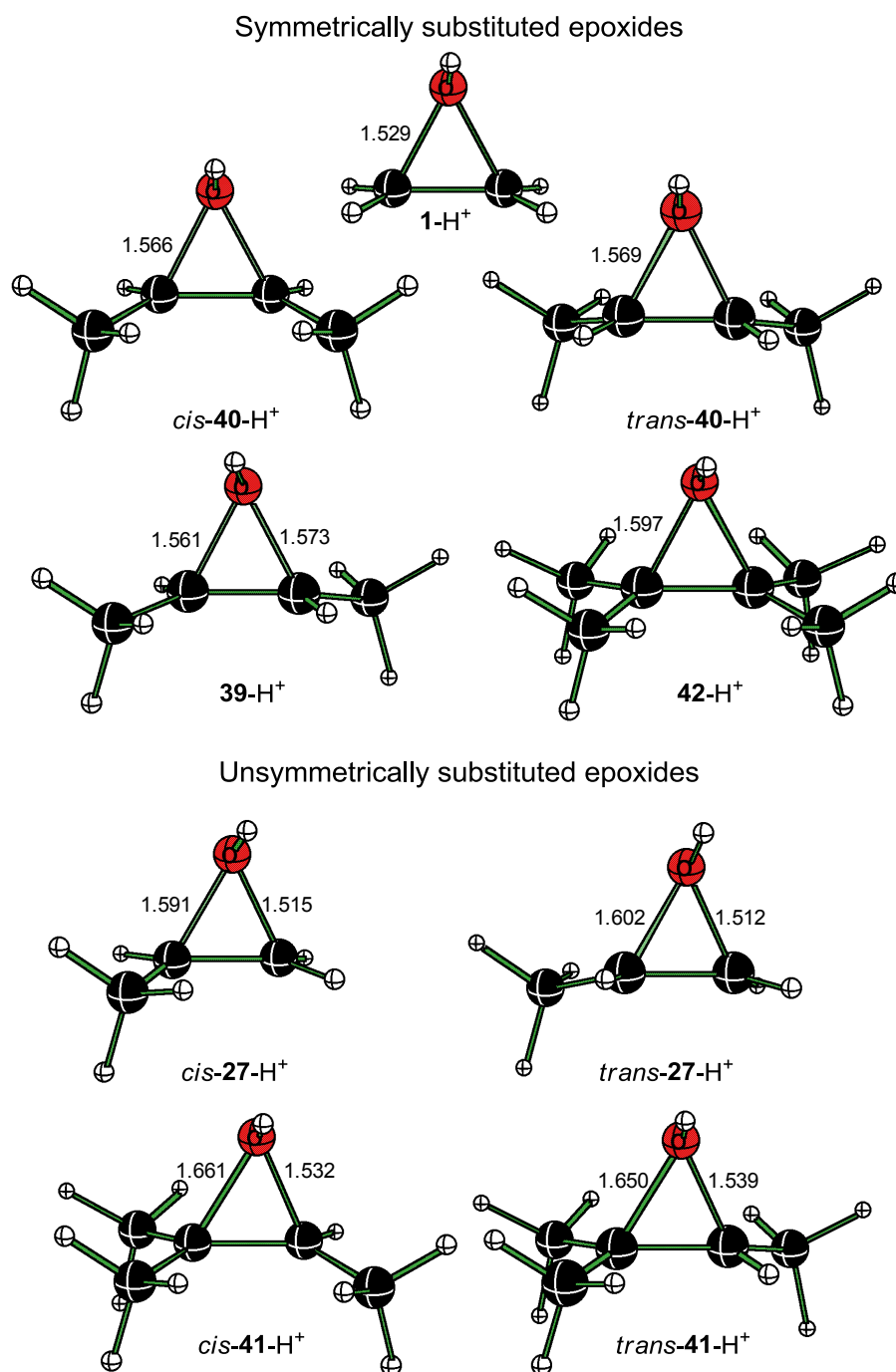


Figure 2.28: B3LYP/6-311++G** optimized geometries of symmetrically and unsymmetrically substituted protonated epoxides. Bond lengths are shown in Å.

As for the case of **33- H^+** , we compared the C2-O bond length obtained for all the systems at B3LYP/6-311++G** to the optimized structures at CCSD/6-311++G**. We also analyzed the

Mulliken charges on the epoxide carbons for all these systems. Figure 2.29 shows the comparison of the B3LYP bond lengths to the CCSD data.

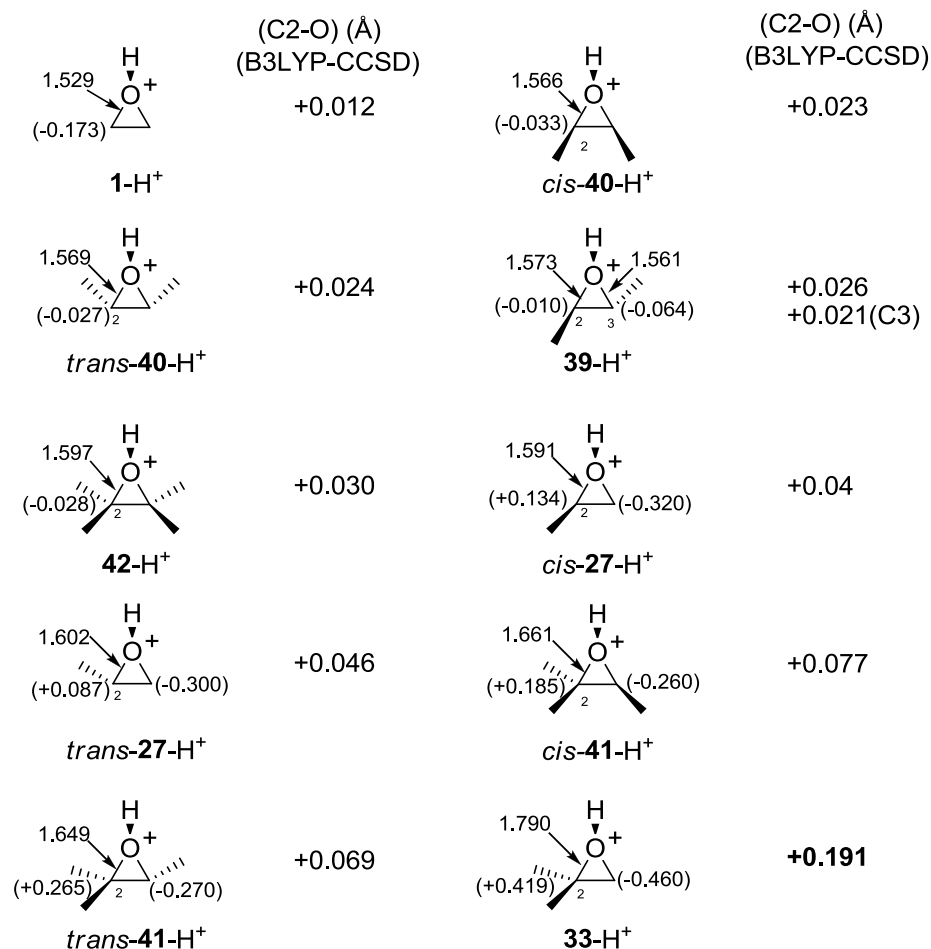


Figure 2.29: B3LYP/6-311++G** bond lengths (C2-O, Å), selected Mulliken charges (in parenthesis), and B3LYP-CCSD differences in C2-O bond lengths (6-311++G**) for protonated epoxides.

As can be seen, B3LYP is quite successful for predicting the C2-O bond length for all the protonated epoxides featuring symmetrical substitution (**1-H⁺**, **39-H⁺**, **40-H⁺**, **42-H⁺**). Small deviations ranging from 0.012 Å for **1-H⁺** to 0.030 Å for **42-H⁺** were observed (Figure 2.29). Thus, the strengthening of the C2-O bond led to a dramatic improvement in DFT performance.

The Mulliken charges on the C1 and C2 carbons were also small in magnitude with both the carbons carrying a slight negative charge (Figure 2.29).

In the case of unsymmetrically substituted protonated epoxides **27-H⁺** and **41-H⁺** the cyclic structure was clearly retained, contrary to the results obtained by Mosquera and coworkers.⁸⁰ However, considerably greater deviations for C2-O bond lengths were observed compared to the symmetrically substituted systems. B3LYP performance deteriorated for these systems, with deviations from CCSD ranging from 0.040 Å for *cis*-**27-H⁺** to 0.077 Å for *cis*-**39-H⁺**. In these cases, Mulliken charges at the oxygen-bearing carbons also begin to diverge, consistent with selective weakening of the C2-O bond. For both these sets of the unsymmetrically substituted epoxides **27-H⁺** and **41-H⁺**, the disparity in substitution at the ring carbons amounts to only one methyl group. A slight positive charge is observed at the C2 carbons in both these cases, while there is a negative charge density at the C1 carbon (Figure 2.29). The protonated epoxide **33-H⁺** is still the most problematic species studied as it features the greatest disparity in alkyl substitution between epoxide ring carbons and gives the maximum deviation of 0.191 Å relative to CCSD. This disparity is also reflected by the Mulliken charges of the oxygen-bearing carbons in **33-H⁺** with a considerable positive charge of +0.419 at the C2 carbon and a significant negative charge of -0.460 at the C1 carbon, indicating disproportionate weakening of the C2-O bond.

We also analyzed all the above mentioned protonated cyclic ethers at MP2/6-311++G** in an attempt to evaluate the performance of a more cost efficient *ab initio* method in modeling these systems. The data obtained are shown in Figure 2.30.

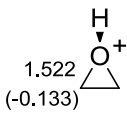
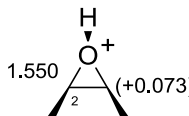
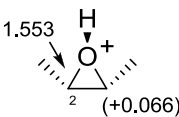
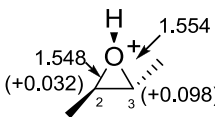
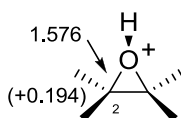
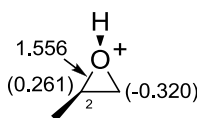
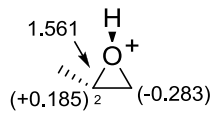
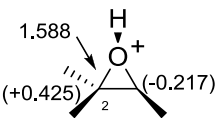
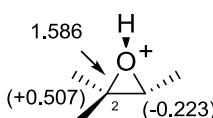
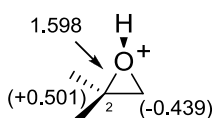
	(C2-O) (Å) (MP2-CCSD)		(C2-O) (Å) (MP2-CCSD)
 1-H⁺	0.004	 <i>cis</i> - 40-H⁺	0.007
 <i>trans</i> - 40-H⁺	0.008	 39-H⁺	0.07 0.08 (C3)
 42-H⁺	0.009	 <i>cis</i> - 27-H⁺	0.005
 <i>trans</i> - 27-H⁺	0.005	 <i>cis</i> - 41-H⁺	0.004
 <i>trans</i> - 41-H⁺	0.006	 33-H⁺	-0.001

Figure 2.30: MP2/6-311++G** bond lengths (C2-O, Å), selected Mulliken charges (in parenthesis); MP2-CCSD differences in C2-O bond lengths (6-311++G**) for protonated cyclic ethers.

As expected, MP2 provides a much better approximation of the CCSD structures than B3LYP: an average deviation in C2-O bond length of +0.005 Å was observed. Here the largest deviation was observed not for **33-H⁺** (-0.001 Å), but for symmetrically substituted **42-H⁺** (0.009 Å). As mentioned, we also analyzed the Mulliken charges at the epoxide ring carbons and just like at B3LYP, the greatest charge discrepancy was observed for **33-H⁺**. Hence, MP2 could be considered a good substitute for the CCSD method for modeling of larger systems where CCSD might prove impractical.

It is interesting to note that the dichotomy seen between MP2 and B3LYP in modeling protonated epoxides mirrors similar behavior in amine-borane complexes.⁸³ The C2-O bonds of **33-H⁺**, **27-H⁺** and **37-H⁺** are weak, and are expected to have dative character like the B-N bonds in amine-boranes; in both systems MP2 outperforms B3LYP for estimation of the dative bond length. In addition, as was found for B-N dative bonds, mPW1PW91 is superior to B3LYP for estimating the length of the C2-O bond in **33-H⁺**.⁸³

2.7.1.2 Ring Expanded Homologues of **33-H⁺**

It seemed feasible to us that the reason the C2-O bond of **33-H⁺** is so difficult to model, is due to the weakness of the bond. This weakness arises from high degree of charge disparity coupled with the ring strain of the protonated epoxide. So, we expected improved B3LYP performance on relief of ring strain. Hence, we studied the trends in the homologous series going from the three membered protonated epoxide **33-H⁺**, to the four membered protonated dimethyl oxetane **43-H⁺**, and finally the five membered protonated dimethyl THF **44-H⁺** (Figure 2.31).

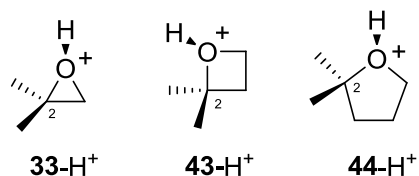


Figure 2.31: Ring Expanded Homologues of **33-H⁺**

The B3LYP/6-311++G** optimized geometries of **33-H⁺**, **43-H⁺** and **44-H⁺** are shown in Figure 2.32.

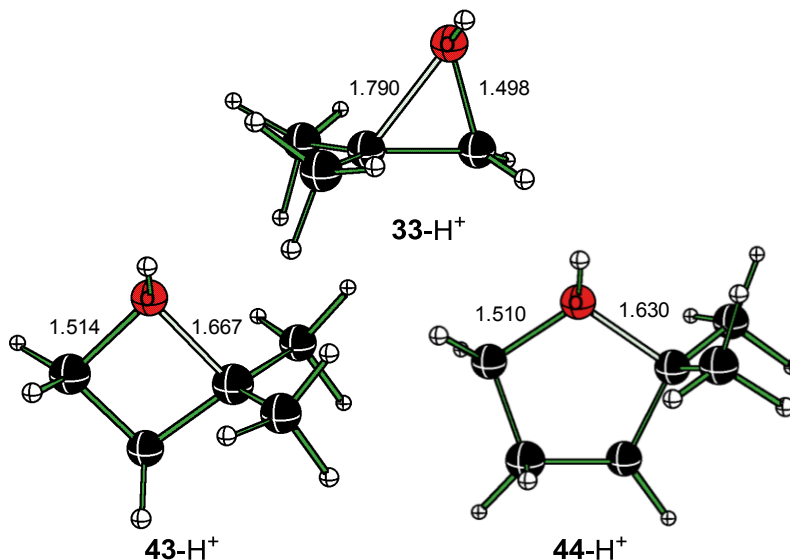


Figure 2.32: B3LYP/6-311++G** optimized geometries of 33-H^+ , 43-H^+ and 44-H^+ . Bond lengths are shown in Å.

Deviations from CCSD C2-O bond lengths decrease significantly with increasing ring size. Going from 33-H^+ (epoxide), to 43-H^+ (oxetane), to 44-H^+ (tetrahydrofuran) the deviations decrease from +0.191 Å to +0.073 Å to +0.061 Å respectively (Figure 2.33).

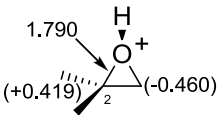
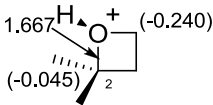
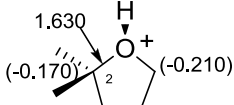
	(C2-O) (Å) (B3LYP-CCSD)	(C2-O) (Å) (MP2-CCSD)
 33-H⁺	+0.191	-0.001
 43-H⁺	+0.073	0.000
 44-H⁺	+0.061	+0.001

Figure 2.33: B3LYP/6-311++G** bond lengths (C2-O, Å), selected Mulliken charges (in parenthesis), and B3LYP-CCSD and MP2-CCSD differences in C2-O bond lengths (6-311++G**) for ring expanded homologues (**43-H⁺** and **44-H⁺**) of **33-H⁺**.

Figure 2.33 shows the B3LYP-CCSD deviations for these structures, along with B3LYP C2 Mulliken charges. As can be seen, the increase in ring size from **33-H⁺** to **44-H⁺** is also accompanied by significant decreases in the positive charge density on the C2 carbon (+0.419 for **33-H⁺**, -0.045 for **43-H⁺** and -0.170 for **44-H⁺**). Note that both these changes (the B3LYP-CCSD C2-O bond lengths and B3LYP C2 Mulliken charges) were expected based on anticipated decreases in ring strain between the three-membered heterocycle **33-H⁺** and the five-membered heterocycle **44-H⁺**. The largest change in both B3LYP-CCSD deviation and C2 Mulliken charge occurs between **33-H⁺** and four-membered heterocycle **43-H⁺**; smaller changes in B3LYP-CCSD deviation and C2 Mulliken charges were seen between the four membered heterocycle and the five-membered heterocycle. When we published this work¹ we did not note this distinction. I thank one of my committee members for pointing out that the large changes observed between the three- and the four-membered heterocycles are in fact *unexpected*. The literature data for the neutral parent heterocycles show that ethylene oxide and oxetane have similarly high ring strain

(cf. Entry 1 and 2, Table 2.9), relative to THF (Entry 3, Table 2.9).⁸⁴ From that perspective one would expect large changes between the three- and five-membered heterocycles, but not between the three- and four-membered heterocycles.

Table 2.9: Experimentally calculated ring strain for the epoxide, oxirane and THF ring in kcal/mol.

Entry	Molecule	Enthalpy of Ring Strain ⁸⁴ (kcal/mol)
1		26.8
2		25.2
3		5.9

Before addressing this apparent contradiction below, I would close this section by noting that as expected, the MP2-CCSD deviations in C2-O bond length for all three heterocycles are quite small (± 0.001 Å, Figure 2.33).

2.7.1.3 Hydrogenolysis of **33**-H⁺ Ring Expanded Homologues

As we have discussed above, we propose that the better DFT treatment of the C2-O bond in four-membered heterocycle **43**-H⁺ relative to three-membered heterocycle **33**-H⁺ is due to reduced ring strain in the former compound. This proposal is at odds with the literature data of the neutral parent heterocycles (Table 2.9). *To address this apparent contradiction we propose that strain in the neutral heterocycle might not be predictive of strain in the protonated heterocycles.*

To test this hypothesis we calculated a reaction of the heterocycles with H₂. The first step is somewhat fanciful: heterolytic cleavage of H₂ to give the protonated epoxide and hydride

anion. The second step is hydride ring opening of the protonated epoxide to give the neutral primary alcohol (Figure 2.34).

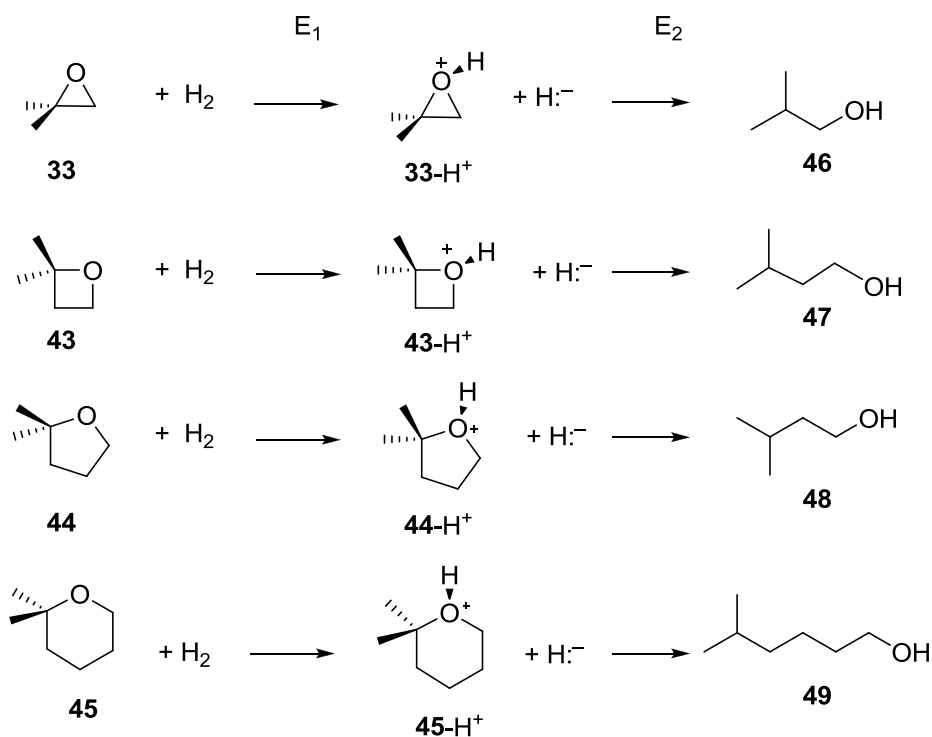


Figure 2.34: Hydrogenolytic ring opening of **33**, **43**, **44** and **45**

Entry	System	E ₁ (ΔE ₁)	E ₂ (ΔE ₂)	E _{Hyd} = E ₁ + E ₂ (ΔE _{Hyd})
1	33	+202.0 (+9.0)	-234.9 (-27.1)	-32.9 (-18.2)
2	43	+194.9 (+1.9)	-225.0 (-17.2)	-30.1 (-15.3)
3	44	+194.5 (+1.4)	-209.7 (-1.9)	-15.3 (-0.5)
4	45	+193.1 (0.0)	-207.7 (0.0)	-14.7 (0.0)

Table 2.10: Energies of B3LYP/6-311++G** (kcal/mol) ring opening hydrogenolysis of **33**, **43**, **44** and **45**; Energies relative to the energies of **45** are shown in parenthesis. For flexible species, an equilibrium conformer search was performed using Molecular Mechanics Force Field 94 (MMFF94) prior to DFT optimizations.

Hydrogenolytic ring opening of the heterocycles is exoenergetic, as expected (Table 2.10). The hydrogenolysis energies ($\Delta E_{\text{Hyd}} = \Delta E_1 + \Delta E_2$), relative to that of 2,2-dimethyl tetrahydropyran **45** reflect ring strain in the heterocycles. These calculations indicated isobutylene oxide **33** and 2,2-dimethyloxetane **43** possess 18.2 (Entry 1, Table 2.10) and 15.3 (Entry 2, Table 2.10) kcal/mol ring strain respectively; in contrast 2,2-dimethylTHF **45** is unstrained at 0.5 kcal/mol (Entry 3, Table 2.10). Thus the calculated values of (ΔE_{Hyd}) for isobutylene oxide **33** and 2,2-dimethyloxetane **43** do indicate that the neutral heterocycles have similar ring strain.

However, examination of ΔE_2 values reveals considerably (9.9 kcal/mol) more strain in the three-membered protonated isobutylene oxide **33-H⁺** than in four-membered protonated 2,2-dimethyloxetane **43-H⁺** (cf. relative ΔE_2 values of -27.1 and -17.2 kcal/mol respectively, cf. Entry 1 and 2, Table 2.10). This strain can reasonably be expected to weaken the C2-O bond in protonated isobutylene oxide **33-H⁺**. While once again, the ring strain in the protonated 2,2-dimethyltetrahydrofuran **44-H⁺** was considerably lower than the strain in the three- and four-membered rings (-1.9 kcal/mol, Table 2.10). Hence, while there exists a trend in the treatment of the C2-O bond by DFT against the ring strains of the protonated heterocycles, this trend is not linear, and a greater improvement in DFT treatment is observed going from the three-membered ring to the four-membered ring system compared to the four-membered to the five-membered ring system. This weakened C2-O bond is also reflected in the relative ΔE_1 values: protonation of isobutylene oxide **33** is 7.1 kcal/mol more endoenergetic than protonation of 2,2-dimethyloxetane **43** (cf. Entry 1 and 2, Table 2.10). Thus, these calculations support our hypothesis that the better DFT treatment of the C2-O bond in **33-H⁺** relative to **43-H⁺** is due to reduced ring strain in the protonated oxetane.

2.7.1.4 Wiberg Bond Index (WBI)

To provide another means of assessing C-O bond strength, Wiberg bond indices (WBI),⁸⁵ which measure the bond order between atoms, were calculated at B3LYP, MP2 and CCSD (all at 6-311++G**) for all the cyclic ethers studied. The B3LYP Wiberg bond indices for the C2-O bonds for all systems are shown in Figure 2.35.

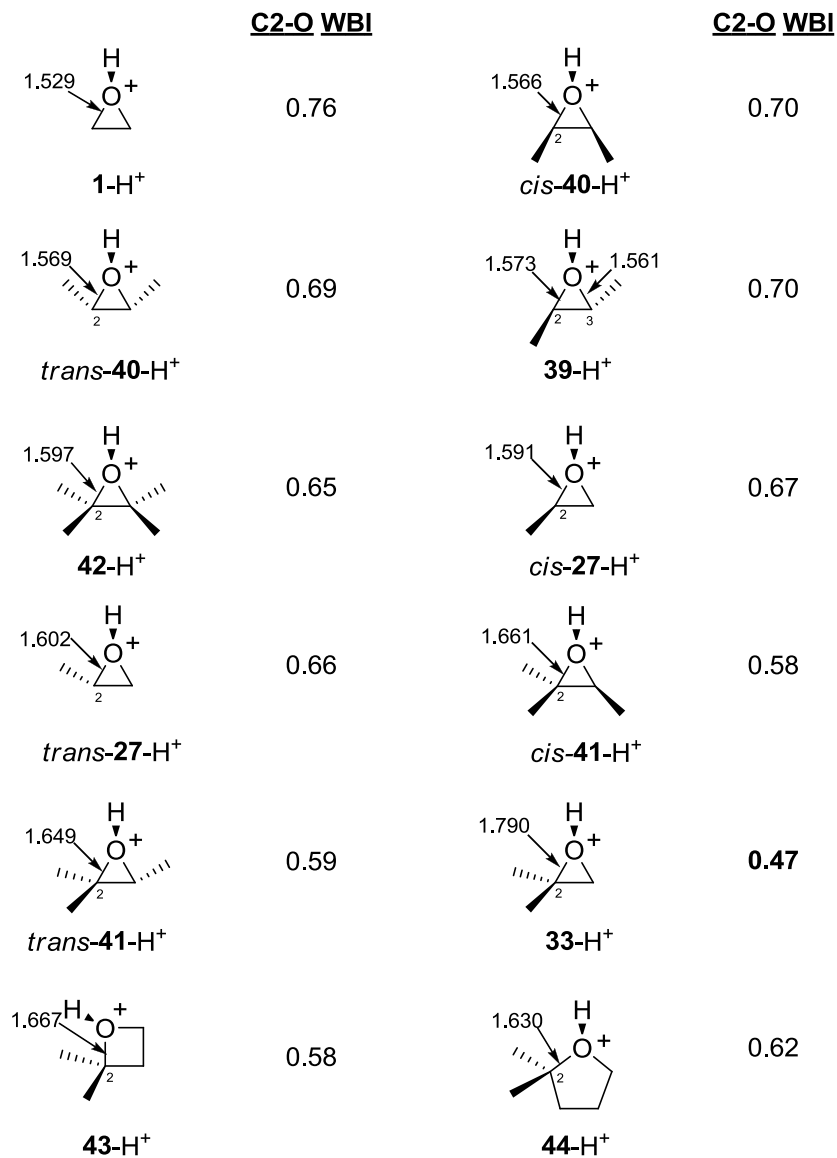


Figure 2.35: C2-O Wiberg Bond Indices at B3LYP/6-311++G**. Bond lengths are shown in Å.

An excellent inverse linear correlation ($R^2 = 0.97$) is seen between C2-O bond length and the C2-O WBI for the twelve compounds. As can be seen, the greatest WBI corresponds to **1-H⁺** which had the shortest C2-O bond, with no methyl substituents. The methyl-substituted symmetrical systems have similar C2-O WBI [**39-H⁺** (0.70), *cis*-**40-H⁺** (0.70) and *trans*-**40-H⁺** (0.70)]. Protonated epoxide **33-H⁺** with the longest C2-O bond (1.790 Å) features the lowest WBI (0.47); the C1-O bond in this species is considerably shorter (1.480 Å) and has a much larger WBI (0.83) (Figure 2.36).

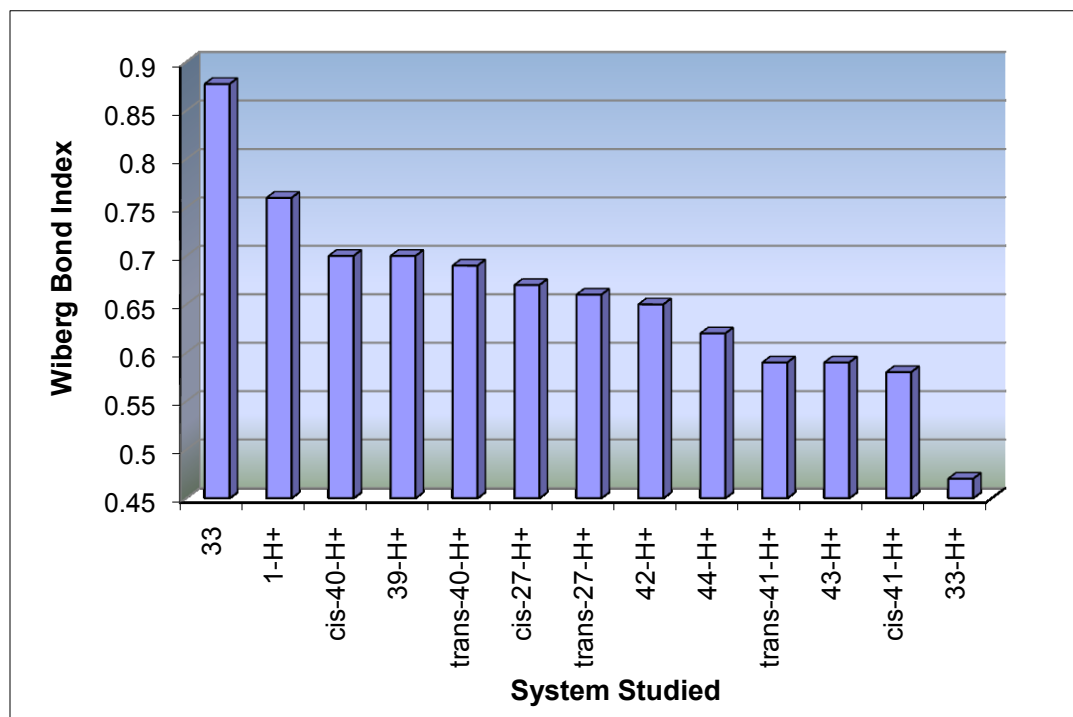


Figure 2.36: C2-O Wiberg Bond Indices for the cyclic ethers studied at B3LYP/6-311++G**

Table 2.11 shows the WBI data along with the corresponding C2-O bond lengths, and the deviations of B3LYP bond length compared to the CCSD data.

Table 2.11: B3LYP/6-311++G** Wiberg NAO bond indices (WBI), C2-O bond lengths, and B3LYP-CCSD differences in C2-O bondlengths (in order of decreasing WBI).

Compound	C2-O WBI	C2-O (Å)	$\Delta(\text{C2-O})$ B3LYP-CCSD (Å)
1-H⁺	0.76	1.529	0.012
<i>cis</i> - 40-H⁺	0.70	1.566	0.023
39-H⁺	0.70	1.573	0.026
<i>trans</i> - 40-H⁺	0.69	1.569	0.024
<i>cis</i> - 27-H⁺	0.67	1.591	0.040
<i>trans</i> - 27-H⁺	0.66	1.602	0.046
42-H⁺	0.65	1.597	0.030
44-H⁺	0.62	1.630	0.061
<i>trans</i> - 41-H⁺	0.59	1.649	0.069
43-H⁺	0.59	1.667	0.073
<i>cis</i> - 41-H⁺	0.58	1.661	0.077
33-H⁺	0.47	1.790	0.191

A reasonable inverse correlation ($R^2 = 0.88$) is evident between the C2-O WBI and the B3LYP-CCSD deviation in C2-O bond lengths. Therefore, as the C2-O bond weakens, B3LYP performance deteriorates. Examination of WBI values also allows the effect of protonation on epoxide C-O bond strength to be assessed. Neutral epoxide **33** features a C2-O WBI of 0.88; the corresponding WBI value of 0.47 in **33-H⁺** represents a near 50% reduction in bond order. Wiberg bond indices at MP2 and CCSD/6-311++G** are slightly higher (0.58), as expected from the 0.19 Å shorter C2-O bond length. Thus it can be inferred that significant bonding still exists between C2 and O, and therefore we do not consider **33-H⁺** to be a ring-opened species.

2.7.2 Energetics of Ring Opening of **33-H⁺**

This section will address the energetics of ring opening of **33-H⁺**. As mentioned at the beginning of Section 2.7, the mechanism of unimolecular ring opening of **33-H⁺** leading to the hydroxycarbocation **34**, followed by a hydride shift to get a protonated aldehyde **38** was studied by Coxon and coworkers at MP2/6-31G* (Figure 2.19).²⁶

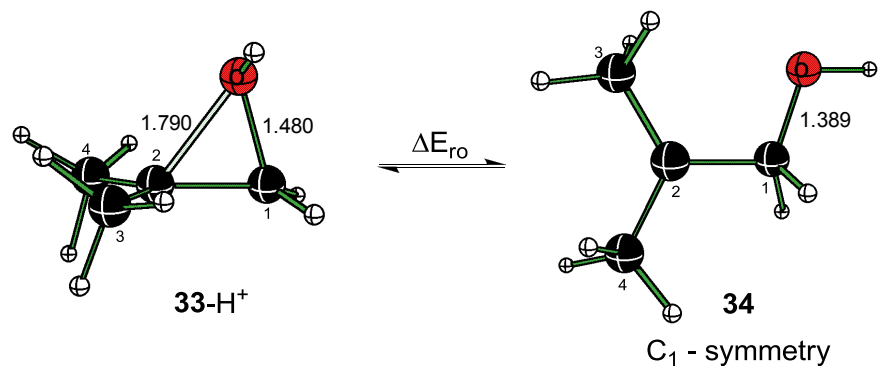


Figure 2.37: B3LYP/6-311++G** optimized geometries for ring opening of **33-H⁺** to **34**. Bond lengths shown in Å.

We followed up the work by Coxon and coworkers by modeling the structures for the protonated epoxide **33-H⁺**, hydroxycarbocation **34** and the structures connecting these at B3LYP/6-311++G** and MP2/6-311++G**. We first located the ring opening transition structure **36** that connects the closed ring **33-H⁺** and hydroxycarbocation **34** at B3LYP/6-311++G** (Figure 2.38). Another transition structure **37** comprising of a hydride shift from C1 to C2 to get the protonated aldehyde **38** was also located. As mentioned in Coxon's work two possible ring opening transition structures exist, one with the O-H proton moving towards C3 or away from C3. Our calculations at B3LYP/6-311++G** showed the energy difference between these two ring opening transition structures (**35** and **36**) to be quite small (0.3 kcal/mol), and the lower energy transition structure **36** corresponded to the structure with the O-H proton moving in the direction of the C3 and is the only structure shown in Figure 2.38. Similar to the reaction coordinate of **1-H⁺** (Figure 2.8), the lowest energy structure along the reaction coordinate corresponded to the protonated aldehyde **38**, which is the product of a 1,2 hydride shift from C1 to C2.

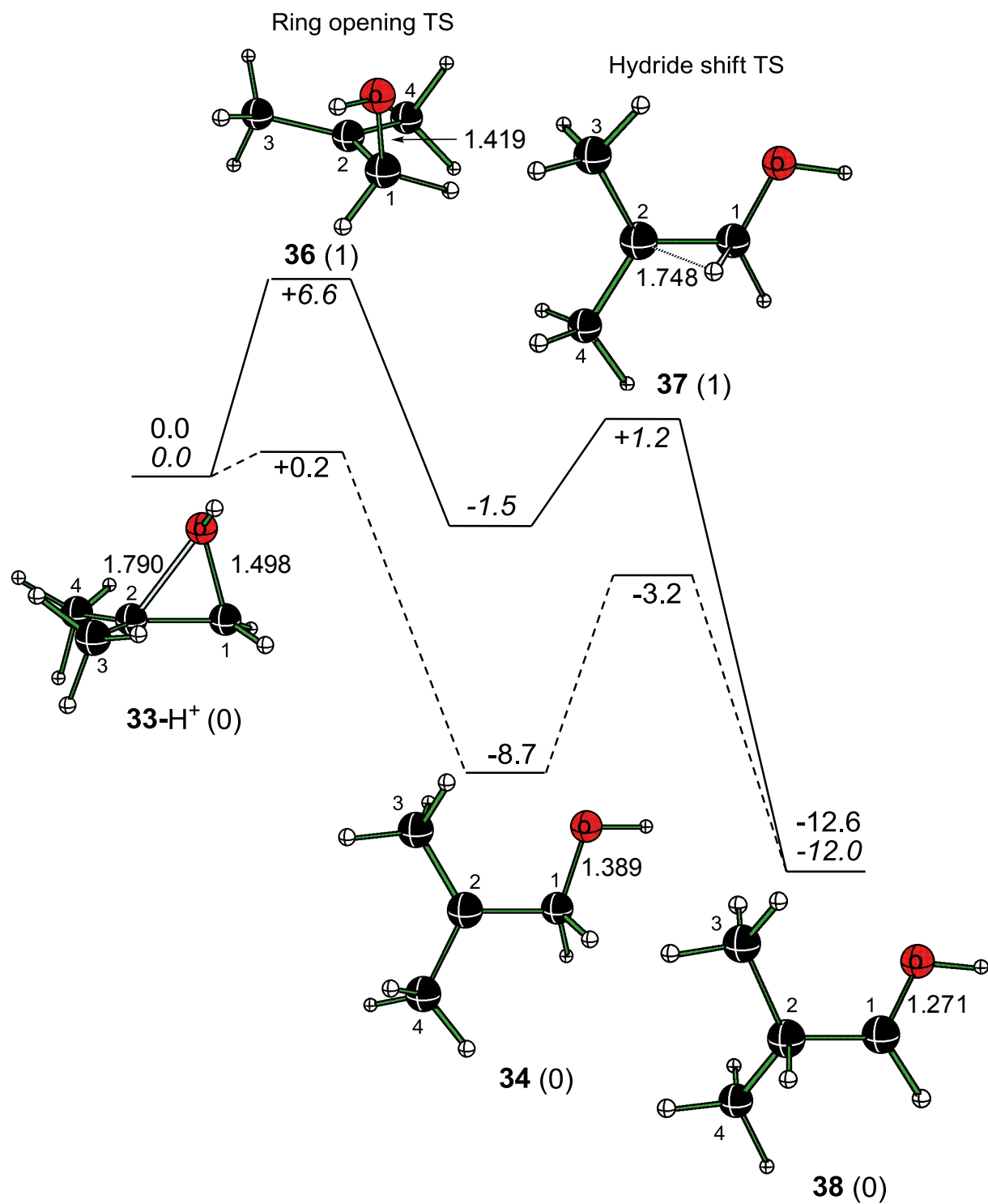


Figure 2.38: B3LYP/6-311++G** (kcal/mol) reaction coordinate for the ring opening of **33-H⁺**. MP2/6-311++G** values shown in *italics*. All ZPVE-corrected energies relative to **33-H⁺**. Number of imaginary frequencies are shown in parenthesis. C-O bond lengths are shown in Å.

Figure 2.38 shows the reaction coordinate of conversion of protonated epoxide **33-H⁺** to the ring opening structure **34** followed by a 1,2 hydride shift to give the protonated aldehyde **38** via a transition structure **37** at B3LYP/6-311++G**. The activation energy for ring opening was small and the transition structure **37** had a relative energy of +0.2 kcal/mol. The hydroxycarbocation **34** obtained is lower in energy than the corresponding protonated epoxide by 8.7 kcal/mol. Formation of the protonated aldehyde **38** occurred via transition structure **37**, which had a barrier of +5.5 kcal/mol relative to **34**. Going from **34** to **38**, considerable shortening of the C2-O bond was observed (cf. 1.389 Å for **34**, 1.271 Å for **38**), indicating an increase in the double bond character. Calculations were also performed at MP2, and as mentioned earlier, the ring opening was considerably less exoenergetic with $\Delta E_{\text{ro}} = -1.5$ kcal/mol. The ring opening transition structure **36** was at a considerably higher energy with MP2 at +6.6 kcal/mol. The conversion of the hydroxycarbocation **34** to the protonated aldehyde **38** was found to be more facile at MP2, with a low transition barrier of 3.7 kcal/mol. Lastly, while there was considerable difference between the relative energies of the hydroxycarbocation **34** between B3LYP and MP2, the energies of protonated aldehyde **38** relative to the protonated epoxide **33-H⁺** for these methods was similar at -12.6 and -12.0 kcal/mol respectively.

Due to the need of frequency calculations in determination of true transition structures, we could not perform CCSD calculations for this reaction coordinate. However, we were able to analyze the effect of CCSD/6-311++G** method and basis on the energetics of ring opening of **33-H⁺** to get **34**. Ring opening energetics were also obtained at HF and with the composite methods G2, G3, G3B3 and CBS-Q. Single-point calculations with larger correlation consistent basis sets were also performed on the CCSD geometries. The results obtained are summarized in Table 2.12.

Table 2.12: Energetics of ring opening of **33**-H⁺ to **34** at B3LYP, *ab initio* and composite methods.

Entry	Method	Basis Set	C2-O (Å)	ΔE_{ro} (kcal/mol) ^a
1	B3LYP	6-311++G**	1.790	-8.7
2	HF	6-311++G**	1.623	-11.8
3	MP2	6-311++G**	1.598	-1.5
4	CCSD	6-311++G**	1.599	-4.4
5	CCSD(T) ^b	6-311++G**	1.599	-3.1
6	CCSD(T) ^b	aug-cc-pVDZ	1.599	-3.9
7	CCSD(T) ^b	aug-cc-pVTZ	1.599	-3.5
8	G2		1.597	-2.1
9	G3		1.596	-2.6
10	CBS-Q		1.591	-2.2
11	G3B3		1.692	-2.6

^aEnergy of ring opening, defined as $E_0(\mathbf{34}) - E_0(\mathbf{33-H}^+)$, where E_0 is the unscaled ZPVE-corrected electronic energy. MP2/6-311++G** ZPVE values were used to correct CCSD and CCSD(T) electronic energies. ^bSingle-point energy calculation at the CCSD/6-311++G** geometry performed by Prof. T. Daniel Crawford: depicted C2-O bond lengths from the CCSD/6-311++G** geometry optimization.

Regarding the energetics of ring opening of **33**-H⁺ to **34**, it is worth noting that the CCSD level of theory indicates the reaction is exoenergetic by only 4.4 kcal/mol. CCSD(T) single point energies at the CCSD/6-311++G** geometries converge well here, giving ΔE_{ro} of -3.1, -3.9, and -3.5 kcal/mol at the 6-311++G**, aug-cc-pVDZ, and aug-cc-pVTZ basis sets, respectively. As a final point of comparison, we calculated **33**-H⁺ and **34** with the G2, G3, G3B3 and CBS-Q methods to get an accurate estimate of ΔE_{ro} : these values (-2.1 to -2.9 kcal/mol) diverge sharply from the B3LYP/6-311++G** value of ΔE_{ro} and approach that obtained at CCSD(T)/aug-cc-pVTZ//CCSD/6-311++G**. It is noteworthy that even at the highest levels of theory, the ring opening of **33**-H⁺ was exoenergetic. This would be a surprise to beginning students of organic chemistry who are always told the importance of filled octets on second-row atoms. While the

Hartree-Fock method gave a very small deviation for the C2-O bond length compared to the CCSD values (cf. Entry 2 and 4, Table 2.12), it significantly underestimates the ΔE_{ro} values, and predicts the ring opening to be more exoenergetic than CCSD by 7.4 kcal/mol. For MP2, the opposite trend is observed, and the ring opening of **33**-H⁺ is more endoenergetic than CCSD by 2.9 kcal/mol (cf. Entry 3 and 4, Table 2.12).

Similar to our analysis for the trends in C2-O bond length upon increase in basis set size, we explored the effects of increasing basis sets on the ring opening energetics of **33**-H⁺ at B3LYP and MP2. Results obtained for ring opening at variable basis sets are shown in Table 2.13.

Table 2.13: C2-O bond length and ring opening energetics of **33**-H⁺ at B3LYP and MP2 with increasing basis set

Basis Set	B3LYP		MP2	
	C2-O (Å)	ΔE_{ro} (kcal/mol) ^a	C2-O (Å)	ΔE_{ro} (kcal/mol) ^a
6-31G*	1.692	-5.6	1.598	+1.7
6-31+G*	1.714	-7.4	1.603	-0.1
6-31+G**	1.725	-8.1	1.601	-0.3
6-31++G**	1.726	-8.0	1.598	-0.3
6-311+G**	1.792	-8.7	1.598	-1.5
6-311++G**	1.790	-8.7	1.598	-1.5

^aAll energies ZPVE corrected from unscaled frequencies.

The trends obtained for electronic energy of ring opening (ΔE_{ro}) at B3LYP mirrored the trends in the C2-O bond lengths, and ring opening became more exoenergetic with increasing C2-O bond length. Ring opening was found to be exoenergetic throughout, ranging from -5.6 kcal/mol (B3LYP/6-31G*) to -8.7 kcal/mol (B3LYP/6-311++G**). The ΔE_{ro} at MP2 was considerably more endoenergetic, and gave values ranging from +1.7 kcal/mol at MP2/6-31G* to -1.5 kcal/mol at MP2/6-311++G**. Since there was no significant variation in the C2-O bond

lengths at MP2, no trend could be followed in the ring opening energies. Ring opening reaction was also evaluated at the different DFT methods that were applied towards the analyses of C2-O bond lengths.

Table 2.14: Ring opening energies ΔE_{ro} and their deviations from CCSD values for the ring opening of **33**-H⁺ to **34** (all at 6-311++G**))

Entry	Ab initio method	Exchange functional	Correlation functional	ΔE_{ro} (kcal/mol) ^a	$\Delta\Delta E_{ro}$ (kcal/mol) ^b
1	HF			-11.8	-7.4
2	MP2			+1.7	+2.9
3		B3	LYP	-8.7	-4.3
4			P86	-8.2	-3.8
5			PW91	-8.1	-3.7
6		mPW	LYP	-7.4	-3.0
7			P86	-7.6	-3.2
8			PW91	-7.5	-3.1
9			PBE	-7.5	-3.1
10		mPW1	LYP	-8.9	-4.5
11			PW91	-8.0	-3.6
12			PBE	-7.9	-3.5
13		G96	LYP	-7.3	-2.9
14			P86	-7.4	-3.0
15			PW91	-7.3	-2.9
16			PBE	-7.3	-2.9
17		PBE	LYP	-7.6	-3.2
18			P86	-7.8	-3.4
19			PW91	-7.7	-3.3
20			PBE	-7.7	-3.3

^aEnergy of ring opening, defined as $\Delta E_{ro} = E_0(\mathbf{34}) - E_0(\mathbf{33-H}^+)$, where E_0 is the unscaled ZPVE-corrected electronic energy. ^b $\Delta\Delta E_{ro} = \Delta E_{ro}(\text{method}) - \Delta E_{ro}(\text{CCSD})$

Table 2.14 summarizes the ΔE_{ro} values obtained using different methods and also shows the deviations of these methods to the values obtained at CCSD/6-311++G**. All the DFT methods overestimated the exoenergeticity of ring opening by 3.4 kcal/mol compared to the CCSD methods. Remarkably, although the various DFT methods give a wide range in C2-O bond

lengths (Table 2.7), they all give values of ΔE_{ro} in the narrow range of -7.3 to -8.9 kcal/mol (Table 2.14).

2.8 Conclusion

Reaction coordinates for the ring opening of protonated ethylene oxide **1-H⁺**, protonated propylene oxide **27-H⁺** and protonated 2-methyl-1,2-epoxypropane **33-H⁺** were calculated at B3LYP and MP2/6-311++G**. Barriers for inversion of the protonated oxygen were calculated for the **1-H⁺** and the **27-H⁺** system at both B3LYP and MP2 methods at B3LYP/6-311++G** and were comparable to the calculated values present in the literature. Reaction coordinates of ring opening of these systems and subsequent collapse to the protonated aldehyde via a hydride shift were also calculated. Results obtained were comparable to the reported literature for the **1-H⁺** system, which showed rearrangement to the protonated aldehyde upon protonation. For **27-H⁺**, literature results were reproduced at B3LYP and with MP2 at smaller basis sets, and indicated ring opening occurred upon protonation, followed by hydride shift to form the corresponding protonated aldehyde. However, our results at MP2/6-311++G** indicated the absence of a hydroxycarbocation intermediate and showed direct rearrangement to the corresponding protonated aldehyde.

We also analyzed the geometries of 12 protonated cyclic ethers using B3LYP, MP2, and CCSD/6-311++G** calculations. Relative to CCSD, B3LYP consistently overestimates the C2-O bond length. Protonated 2-methyl-1,2-epoxypropane (**33-H⁺**) is the most problematic species studied, where B3LYP overestimates the C2-O bond length by 0.191 Å. Seventeen other density functional methods were applied to this protonated epoxide; on average, they overestimated the CCSD bond length by 0.2 Å. The difficulty in using B3LYP to model the structure of **33-H⁺** lies in the extremely weak C2-O bond, which is reflected in the highly asymmetric charge

distribution between the two ring carbons. Protonated epoxides featuring more symmetrical charge distribution and higher cyclic homologues (**43**-H⁺ and **44**-H⁺) featuring less ring strain are treated with greater accuracy by B3LYP. Finally, MP2 performed very well against CCSD in calculations of protonated epoxides and higher homologues, deviating in the C2-O bond length at most by 0.009 Å; it is therefore recommended when computational resources prove insufficient for coupled cluster methods.

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Chapter 3: Computational Studies of Ion Pair Separation of Benzylic Organolithium Compounds in THF: Importance of Explicit and Implicit Solvation

Contributions

This chapter is a modified and expanded version of the published article.¹ Contributions from co-authors of the article are described as follows in the order of the names listed. The author of this dissertation (Ms. Nipa Deora) performed all the calculations, and most of the writing. Dr. Paul R. Carlier was a mentor for this work and the corresponding author for the published article. He provided guidance and crucial revisions to the manuscript.

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3.1 Introduction

Organolithium compounds are ubiquitous in organic synthesis² and enantioenriched configurationally stable organolithium intermediates feature in numerous reactions.³⁻⁹ Figure 3.1 shows examples of select configurationally stable organolithium intermediates: Organolithium **50** was reported as a configurationally stable intermediate by Clayden in 2008 during their study on α -pyridylation of chiral amines,⁷ 2-lithiopyrrolidine **51** was shown to be a configurationally stable intermediate on a macroscopic time scale by Gawley,¹⁰ lithiated durylsulfide **52** was found by Hoffmann to be a stable intermediate with a racemization barrier greater than 13.9 kcal/mol at 263 K,¹¹ and α -alkoxyorganolithium **53** was first reported by Still as stable on a macroscopic time scale.¹² Stability in terms of macroscopic time scale is applicable to systems that can retain configurational stability through sequential quench conditions.¹³

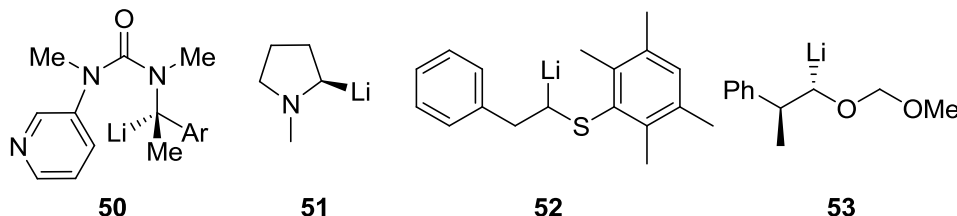


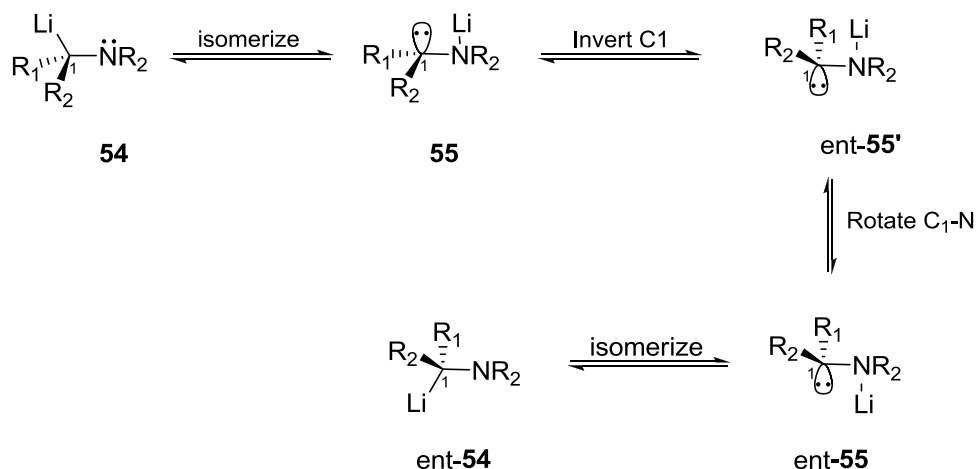
Figure 3.1: Examples of configurationally stable organolithium intermediates

Racemization of the key intermediates in reactions featuring organolithium compounds can occur via a number of mechanisms, including the conducted tour mechanism,^{14,15} radical pathway (SET mechanism),^{10,16} or by an ion pair separation (IPS) mechanism.¹⁷

3.2 Conducted Tour Mechanism of Racemization

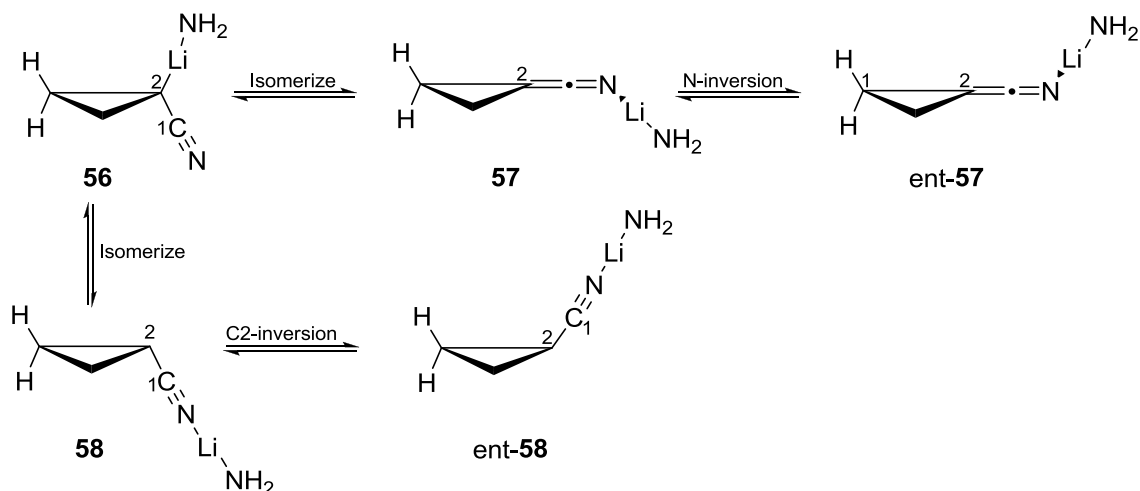
The term “conducted tour” mechanism of racemization was coined by Cram and Grosser in 1964,¹⁸ and is observed in organolithium compounds which have a basic site within the molecule e.g. **54** (Scheme 3.1). The first step is the isomerization of the organolithium species by

transfer of the lithium cation from the carbanion to the basic site within the same molecule to get **55**; this is followed by pyramidal inversion of the carbanion to ent-**55'** followed by rotation of the C-N bond to get ent-**55**. The last step is the re-association of the lithium cation to the other face of the carbanion giving the enantiomer of the starting organolithium compound ent-**54** (Scheme 3.1).



Scheme 3.1: General scheme for a conducted tour mechanism

A computational study addressing the racemization of cyclopropyl nitriles via a conducted tour mechanism was performed by Carlier in 2003 at B3LYP/6-31G* and B3LYP/6-31+G* method and basis (Scheme 3.2).¹⁹

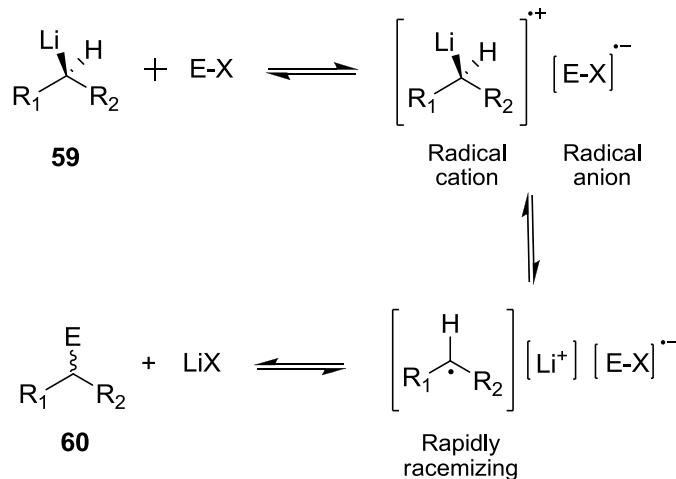


Scheme 3.2: Possible racemization pathways of cyclopropyl nitriles via conducted tour mechanism (Carlier et al, *Chirality* **2003**, 15, 340. Copyright © (2003 and Carlier). Reprinted with permission of Wiley-Liss, Inc. a subsidiary of John Wiley & Sons, Inc.)¹⁹

A C-lithiated nitrile **56** can enantiomerize in two ways, each of which involves a transfer of the lithium cation from the α -carbon to the cyano nitrogen: the first is to get the ketenimine like N-lithiated isomer **57**, and the second way would lead to a pyramidalized N-lithiated isomer **58**. The ketenimine like structure **57** was not located on the potential energy surface during Carlier's theoretical studies, however the C2-inversion transition structure **58*** was located, and found to have a small racemization barrier of $\Delta E = +6.4$ kcal/mol at B3LYP/6-31G* ($\Delta E = +4.3$ kcal/mol at B3LYP/6-31+G*), indicating facile racemization via a conducted tour mechanism.

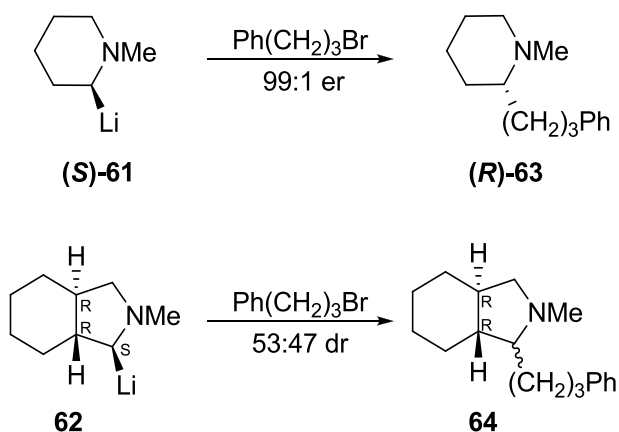
3.3 Single Electron Transfer

Racemization of configurationally stable organolithiums has also been attributed to a single electron transfer mechanism,^{10,16} which proceeds via the formation of radical intermediates which readily racemize. Scheme 3.3 gives a general mechanism for the racemization of organolithium **59** by the SET pathway via the formation of a radical cation dissociation to a rapidly racemizing radical and Li^+ , to the racemized product **60**.



Scheme 3.3: A general SET mechanism for racemizing alkylation of organolithiums

However, while SET is one of the ways in which organolithium intermediates racemize, this mechanism intervenes only in certain cases: e.g. when an $\text{S}_{\text{N}}2$ pathway is less probable due to steric crowding in the substrate, or if the attacking electrophile is easily reduced to give the radical anion.¹⁰ An example of racemization of organolithium intermediates via SET was reported by Gawley in 2006, where he studied the electrophilic substitutions of lithiopiperidines **61** and rigid 2-lithio-*N*-methylpyrrolidines **62** with a variety of electrophiles.¹⁰ One example in their study showed the reaction between 1-bromo-3-phenylpropane with lithiopiperidines (*S*)-**61** and rigid 2-lithio-*N*-methylpyrrolidines **62** (Scheme 3.4).

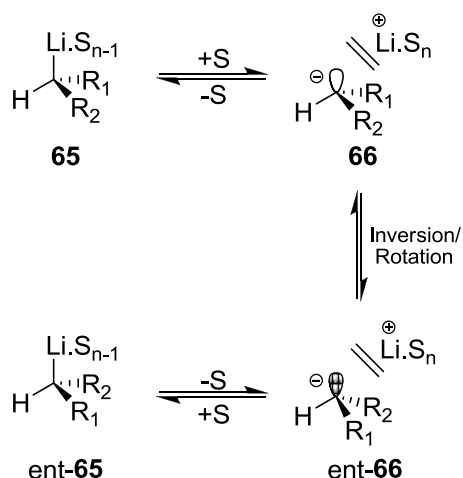


Scheme 3.4: Reaction of 1-bromo-3-phenylpropane with lithiopiperidine **(S)-61** via $\text{S}_{\text{E}}2(\text{inv})$ mechanism, and 2-lithio-*N*-methylpyrrolidines **62** via SET mechanism.¹⁰

Addition of 1-bromo-3-phenylpropane to lithiopiperidine **(S)-61** occurred via $\text{S}_{\text{E}}2(\text{inv})$ mechanism giving 99% of the inversion product **(R)-63**. Conversely, in the case of a rigid system like 2-lithio-*N*-methylpyrrolidines **62**, reaction occurred via a proposed SET mechanism due to severe steric interactions in the $\text{S}_{\text{E}}2(\text{inv})$ transition structure, and a product mixture **64** with a diastereotopic ratio (dr) of 53:47 was obtained.¹⁰

3.4 Ion Pair Separation (IPS)

In ethereal solvents, sufficiently stabilized organolithiums can undergo racemization via ion pair separation. Scheme 3.5 shows a general schematic of the racemization via this mechanism.

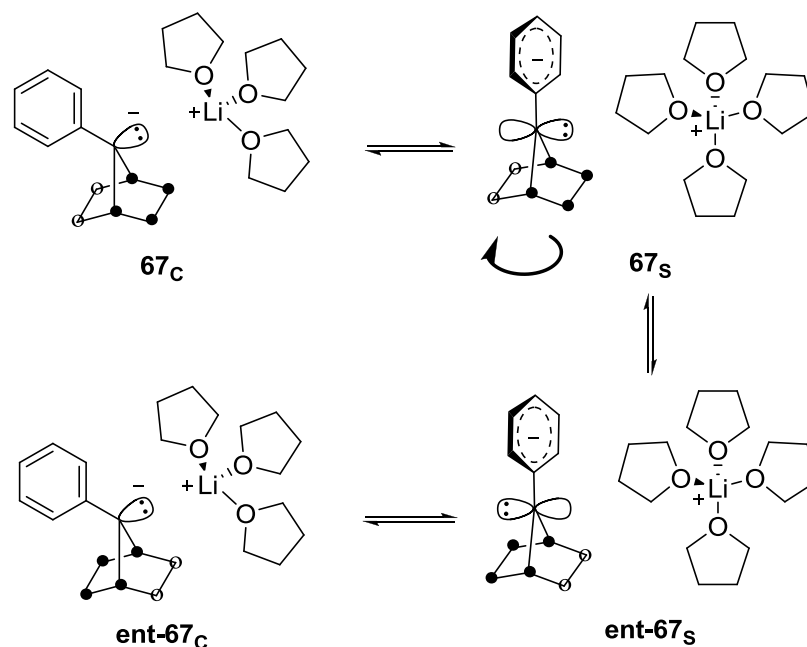


Scheme 3.5: General ion pair separation racemization mechanism of organolithiums

IPS occurs by association of the solvated contact ion pair (CIP) **65** with an additional solvent molecule, resulting in dissociation to a solvent separated ion pair (SSIP) **66**. This, if followed by inversion of the carbanion and reassociation to the solvated lithium fragment (with loss of a solvent molecule) will give the enantiomer **ent-65** of the starting organolithium species **65**.

3.5 Experimental Work on Ion Pair Separation

A study by Peoples and coworkers in 1980 addressed the inversion of 7-phenylnorbornyl lithium **67** in THF using ^{13}C -NMR studies in the temperature range of 183-243 K (Scheme 3.8).¹⁷



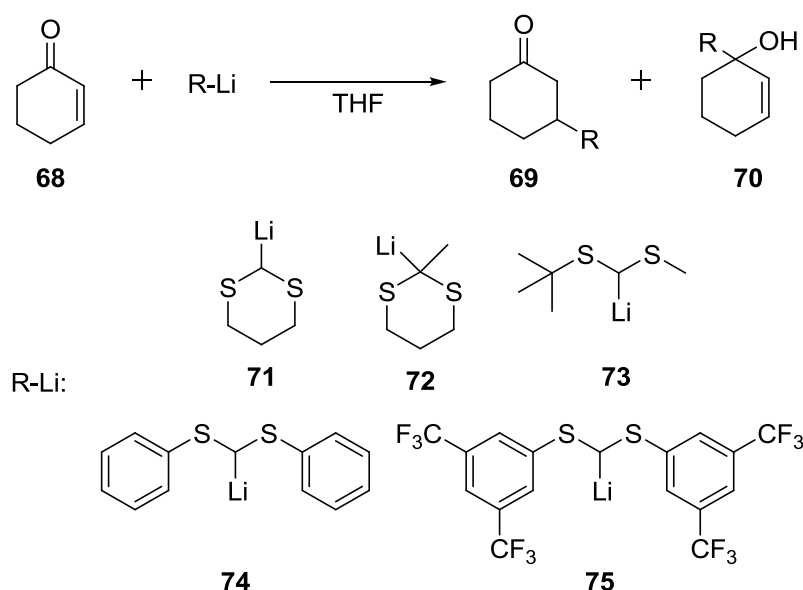
Scheme 3.6: Proposed mechanism for inversion of 7-phenylnorbornyllithium in THF (Reprinted with permission from Peoples, P. R.; Grutzner, J. B.; *J. Am. Chem. Soc.* **1980**, *102*, 4709-4715 Copyright 1980 American Chemical Society.)^{3,17}

Their studies suggested that 7-norbornyllithium **67_c** was pyramidal in solution with a barrier of 11 ± 1 kcal/mol at 298 K, and underwent carbanion inversion after ion pair dissociation. The barrier obtained was proposed to depend on the carbanion inversion along with the ion pair separation process with the latter being the rate determining step.

Extensive experimental work focusing on the relationship of ionization state of organolithium compounds to reactivity has been carried out by Reich and coworkers.²⁰SSIPs can be less²¹ or more²¹⁻²³ reactive than the corresponding CIPs, and this difference in reactivity can lead to changes in the course of reactions.²⁴⁻²⁷ One of the examples highlighting the effects of ionization state was provided by Cohen and coworkers in 1987, where they studied the 1,4-addition versus a 1,2-addition of 1,3-dithianyllithium with α,β -unsaturated ketenes at variable temperatures.²⁸ Their study reported preference of 1,2-addition at higher temperatures (e.g. 10 °C, ascribed to reaction of the CIPs), in contrast to the preferred 1,4-addition at lower

temperatures (e.g. -78 °C, ascribed to reaction via the SSIPs). Note that a temperature dependence of the CIP/SSIP equilibrium is expected based on the expected large $-T\Delta S$ term for ion pair separation. The authors also reported that addition of HMPA increased the preference for 1,4-addition.

Follow up work was performed by Reich et al. in 1999 using Li-NMR techniques. They analyzed the reactions of 2-cyclohexenone **68** with 1,3-dithianyllithium **71**, 2-methyl-1,3-dithianyllithium **72**, *tert*-butylthio(methylthio)methylithium **73**, bis(phenylthio)methylithium **74**, and bis(3,5-bis(trifluoromethyl)phenylthio)methylithium **75**.²⁰



Scheme 3.7: 1,2 versus 1,4-addition of cyclohex-2-enones with 1,3-dithianyllithiums

Their study showed that 1,3-dithianyllithium **71** gave exclusive 1,2 addition product in the absence of HMPA. Li-NMR studies showed **71** to exist only as a CIP in THF solution, and that addition of at least 2 equivalents of HMPA was needed before the corresponding SSIP could be observed in solution. Based on their results, they proposed that the 1,2 addition was the preferred reaction mode for CIPs (Mechanism **1**, Figure 3.2).

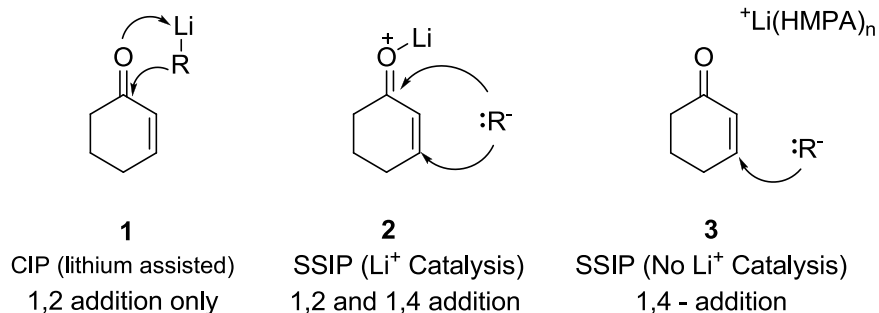
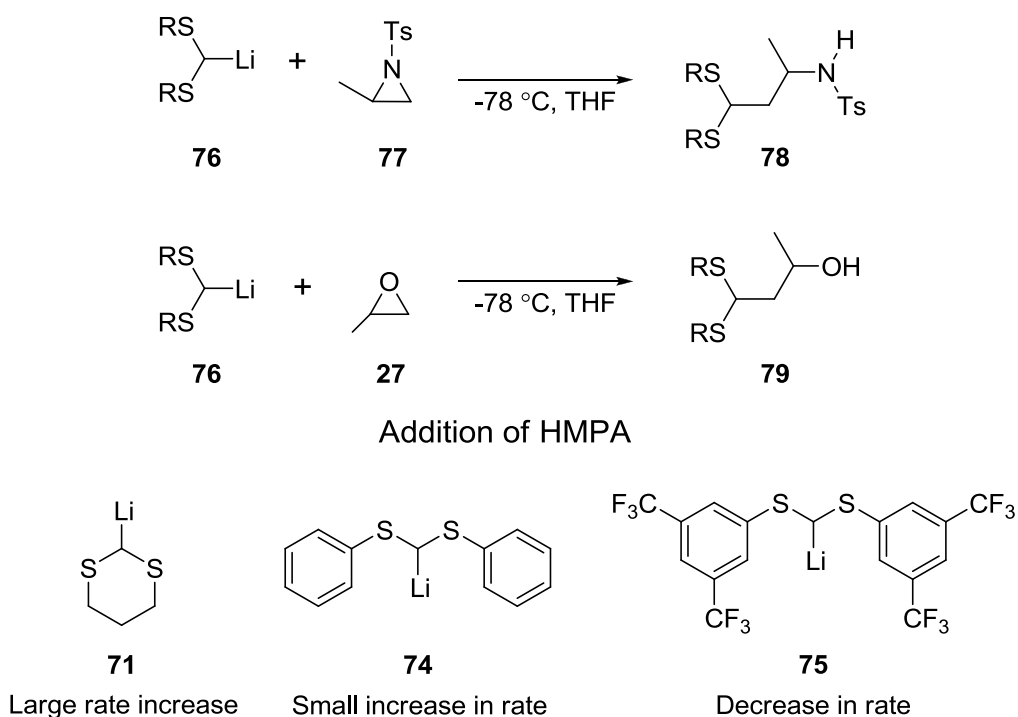


Figure 3.2: Mechanism for 1,4 versus 1,2-addition of cyclohex-2-enones with and without HMPA (Reprinted with permission from Reich, H. J.; Sikorski, W. H.; *J. Org. Chem.* **1999**, 64 14-15. Copyright 1999 American Chemical Society.)

However, reactions of the SSIPs were not as straightforward, and two different pathways intervened in the presence or absence of HMPA. Reactions of systems **73**, **74** and **75** in the absence of HMPA, showed a mixture of 1,2 and 1,4 addition product, and this product mixture was observed even under conditions where SSIPs were barely detectable by Li-NMR (e.g. **73**). This latter result can be rationalized in terms of preferred 1,4-addition for the SSIP and the Curtin-Hammett principle: a minor reactive species at equilibrium disproportionately contributes to the overall product mixture. In the absence of HMPA, it was proposed that both 1,2 and 1,4 addition occurred due to lithium catalysis, wherein the Li⁺ cation complexes the carbonyl oxygen, and the nucleophile R⁻ could attack at position 2 or 4 (Mechanism 2, Figure 3.2). However, in the presence of HMPA, the exclusive formation of the 1,4 addition product was observed for **72**, **73** and **74**. It should be noted that under these conditions, Li-NMR spectroscopy indicates that **72**, **73**, **74** exist as SSIPs. To account for the synthetic outcome in the presence of HMPA, the authors proposed that the Li⁺(HMPA) complex could not participate in lithium catalysis depicted in mechanism 2 in Figure 3.2 above. Furthermore, without Li⁺ coordination of the carbonyl, it was proposed that 1,4 addition was the fastest process. (Mechanism 3, Figure

3.2). Thus according to Reich, both the absence of lithium catalysis and the availability of anSSIP are required for selective 1,4 addition reaction.

Reaction rates have also been shown to be affected by the ionization state of organolithiums. SSIPs have been found to be less or more reactive than the corresponding CIPs as seen in a 2002 study by Reich et al. where they studied the effects of HMPA on the rates of ring opening reactions of propylene oxide **27** and *N*-tosyl-2-methylaziridines **74** by different organolithium reagents.²¹ Three organolithium reagents were used: 1,3-dithianyllithium **71**, bis(phenylthio)methylithium **74** and bis(3,5-bis(trifluoromethyl)phenylthio)methylithium **75** (Scheme 3.8).



Scheme 3.8: Reaction studies by Reich and coworkers on ring opening of propylene oxide **27** and *N*-tosyl-2-methylaziridines **77** by lithiated 1,3-dithianes (Adapted with permission from Reich, H. J.; Sanders, A. W.; Fiedler, A. T.; Bevan, M. J.; *J. Am. Chem. Soc.* **2002**, *124*, 13386-13387. Copyright 2002 American Chemical Society.).²¹

Reaction rates were compared in the absence and presence of HMPA. 1,3-dithianyl lithium **71** was essentially a CIP in solution in the absence of HMPA, and addition of HMPA led to a large increase in reaction rate due to the formation of SSIPs, which were more reactive than the corresponding CIPs. The second organolithium substrate bis(phenylthio)methyl lithium **74** was a weakly bound CIP in THF, and there existed a significant concentration of SSIP even before the addition of HMPA. Thus, addition of HMPA led to a small increase in the rate of the reaction compared to rate increase observed for **71**. In contrast, the bis(3,5-bis(trifluoromethyl)phenylthio)methyl lithium **75** had considerable dissociation in THF with 80% SSIP concentration at -78 °C even in the absence of HMPA, and the addition of HMPA actually led to a decrease in rate due to a decrease in the concentration of Li^+ ions, which is replaced by a greater concentration of the less reactive $\text{Li}^+(\text{HMPA})_n$ complex, hence an overall decrease in the rate of ring opening was observed compared to the rates in the absence of HMPA. Finally, ionizability of alkyl lithiums also plays a significant role in anionic polymerization reactions, wherein the dissociated carbanion is the main propagating species, upon which the rate of polymerization depends.²⁹ Because the ionization state of organolithiums can so dramatically effect reaction stereochemistry and regioselectivity, we propose that a validated computational approach to assess IPS could prove useful for prediction of the reaction outcomes.

3.6 Theoretical Studies on Ion Pair Separation

Numerous theoretical studies of organolithium compounds in ethereal solvents have addressed solvation number and aggregation states.³⁰⁻³³ In 1997, Streitwieser and coworkers studied the aggregated forms of lithium enolate of acetaldehyde **80** with dimethyl ether as the solvent (Figure 3.3).³¹

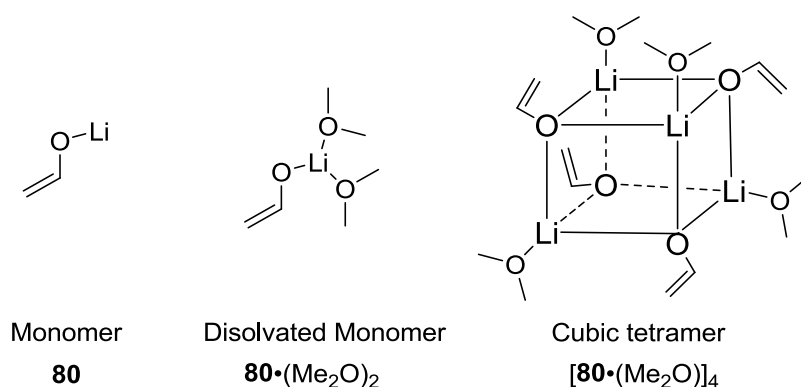
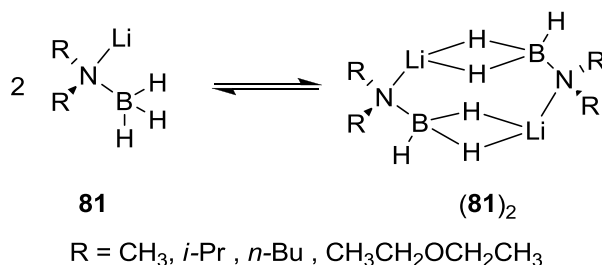


Figure 3.3: Model structures for the lithium enolate of acetaldehyde

They performed B3LYP single-point calculations on PM3 optimized geometries, and compared their data to available experimental data. Their calculations showed that explicit solvation plays a significant role in the determination of the aggregation state of the organolithiums, and concluded that the cubic tetramer $[80\bullet(\text{Me}_2\text{O})]_4$ and the bis(Me_2O)-solvated monomer $80\bullet(\text{Me}_2\text{O})_2$ should be the two dominant species in solution.

Solvation and aggregation states of dialkylaminoborohydrides **81** were studied by Pratt and coworkers in 2003 in the gas phase, with explicit, implicit and a mixed solvation model incorporating both implicit and explicit solvation (Scheme 3.9). Solvation was modeled by use of the Conductor-like Polarized Continuum Model (CPCM) solvation model with solvents THF and dimethyl ether.³⁴



Scheme 3.9: Aggregation of dialkylaminoborohydride

Their gas phase calculations indicated that the dimerization process was significantly exothermic ($\Delta E = -31.0$ to -35.0 kcal/mol). Similarly use of the CPCM model alone overestimated the stability of dimers (**81**)₂ ($\Delta E = -21$ to -25 kcal/mol), as the effects of steric crowding could not be incorporated. Application of the explicit solvation only, showed the dimerization process to be considerably less exothermic and favorable for dimethyl ether solvated systems ($\Delta E = -1.4$ to -3.8 kcal/mol), while the monomers **81** were favored for THF solvated systems ($\Delta E = +4.5$ to $+6.7$ kcal/mol). Application of CPCM on explicitly solvated systems reduced the dimerization energy for the THF solvated system, while an increase in dimerization energy was observed for the dimethyl ether solvated systems. Thus, their study showed that incorporation of both implicit and explicit solvation had significant effect on the predicted aggregation state in solution.

Another study was performed by the same authors in 2009, where they calculated the free energy consequences of successive addition of THF molecules to methyllithium **82**, lithium dimethylamide **83** and lithiated acetaldehyde **80** using DFT methods B3LYP, mPW1PW91 and post Hartree-Fock methods MP2 and G2MP2.³⁵

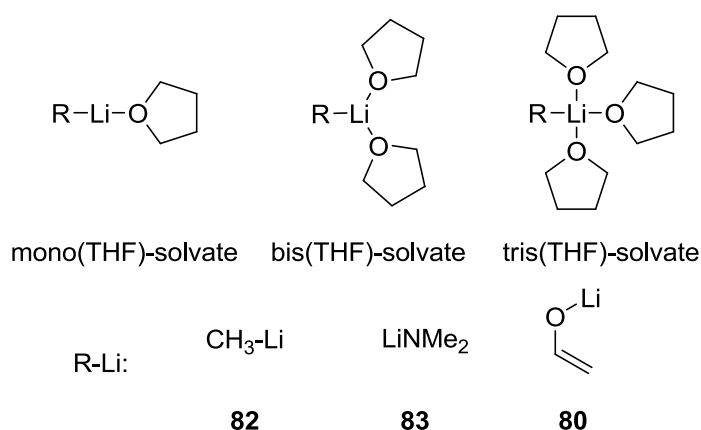
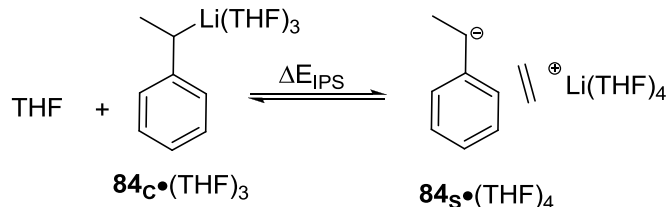


Figure 3.4: Possible solvation states of methyllithium **82**, lithium dimethylamide **83** and lithiated acetaldehyde **80** systems studied by Pratt and coworkers in 2009³⁵

Calculations were performed for successive THF solvation of monomers and dimers of methyllithium **82**, lithium dimethylamide **83** and lithium enolate of acetaldehyde **80**. For the monomeric species, it was observed that while the formation of the mono and bis(THF) solvate was exergonic for all methods studied, the third THF solvation was exergonic only at MP2, and it was suggested by the authors that DFT methods might overestimate the steric strain in trisolvated organolithium species. Thus, the author rationalized the divergent B3LYP and MP2 free energies of the third THF solvation.

To the best of our knowledge, only one theoretical study addressing organolithium ion pair separation has been reported in the literature. Müller et al. studied the conversion of tris(THF)-solvated 1-lithioethylbenzene **84c**•Li(THF)₃ to the corresponding tetrakis-THF solvated separated ion pair **84s**•Li(THF)₄ (Scheme 3.10).³⁶



Scheme 3.10: Ion pair separation of THF solvated 1-lithioethylbenzene

The energies of IPS (ΔE_{IPS}) at B3P86/SVP and B3LYP/TZVP//B3P86/SVP were calculated to be +4.4 and +5.9 kcal/mol respectively. Yet, because no experimental data have been reported for this system, it has not been possible to assess the accuracy of these estimates.

3.7 Experimental Enthalpies of Ion Pair Separation (ΔH_{IPS})

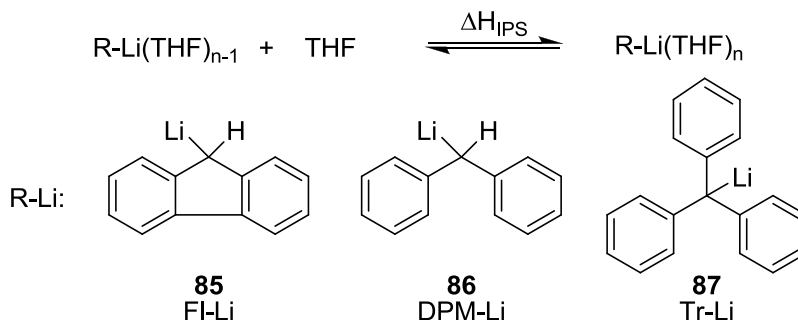


Figure 3.5: Ion pair separation for the systems studied **85-87**

Experimental data is available for the IPS thermodynamics of benzylic organolithium systems, including fluorenyllithium **85**,^{37,38} diphenylmethyllithium **86**,³⁹ and triphenylmethyl lithium **87**⁴⁰ lithium compounds from UV-visible and ¹³C-NMR spectroscopy. Hogen-Esch and Smid used UV-visible spectroscopy to study the effects of temperature, counterion and solvent on ion pair separation of various fluorenyl metal salts in ethereal solvents: dimethyl ether, tetrahydrofuran (THF), methyltetrahydrofuran (MeTHF) and dimethoxyethane (DME).⁴¹ The value for the enthalpy of the ion pair separation process (ΔH_{IPS}) for fluorenyllithium CIP **85_C** in THF was also reported to be approximately -7.0 kcal/mol; however the authors cautioned that this value might be inaccurate due to the high degree of dissociation toSSIP at room temperature. Variable temperature ¹³C-NMR studies which detect the changes in the electron density at the carbanion center upon IPS were performed by O'Brien et al. in 1979, in which they studied IPS of **85** in THF. While the difference between ¹H-NMR shifts of CIP andSSIP protons is small for IPS of these systems; there is a significant difference between the ¹³C-NMR shifts, and thus IPS can be observed experimentally. The IPS of **85** was found to be exothermic with a ΔH_{IPS} of -4.9±1 kcal/mol. The most recent, and in our opinion, the most reliable determination of ΔH_{IPS} of **85** in THF stems from Streitwieser's UV-visible spectroscopic study in 1998. The

temperature range used for this study was 263 K to 328 K, and gave a ΔH_{IPS} of -3.8 ± 1 kcal/mol.³⁷

Buncel and coworkers studied the IPS of diphenylmethyllithium using UV-visible spectroscopy. They observed two sets of peaks, one at 418 nm corresponding to the CIP, and the other set which increased with decreasing temperature at 448 nm corresponding to the SSIP of DPM in THF (Figure 3.6).³⁹

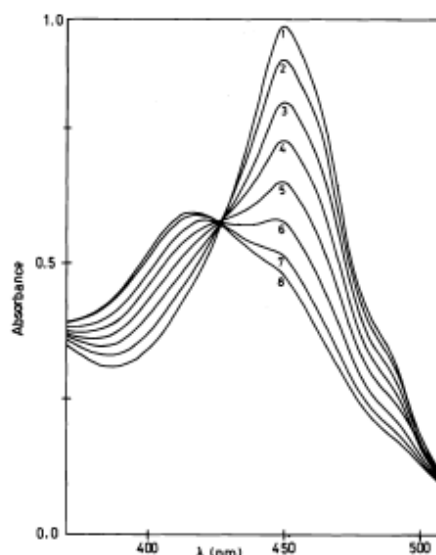
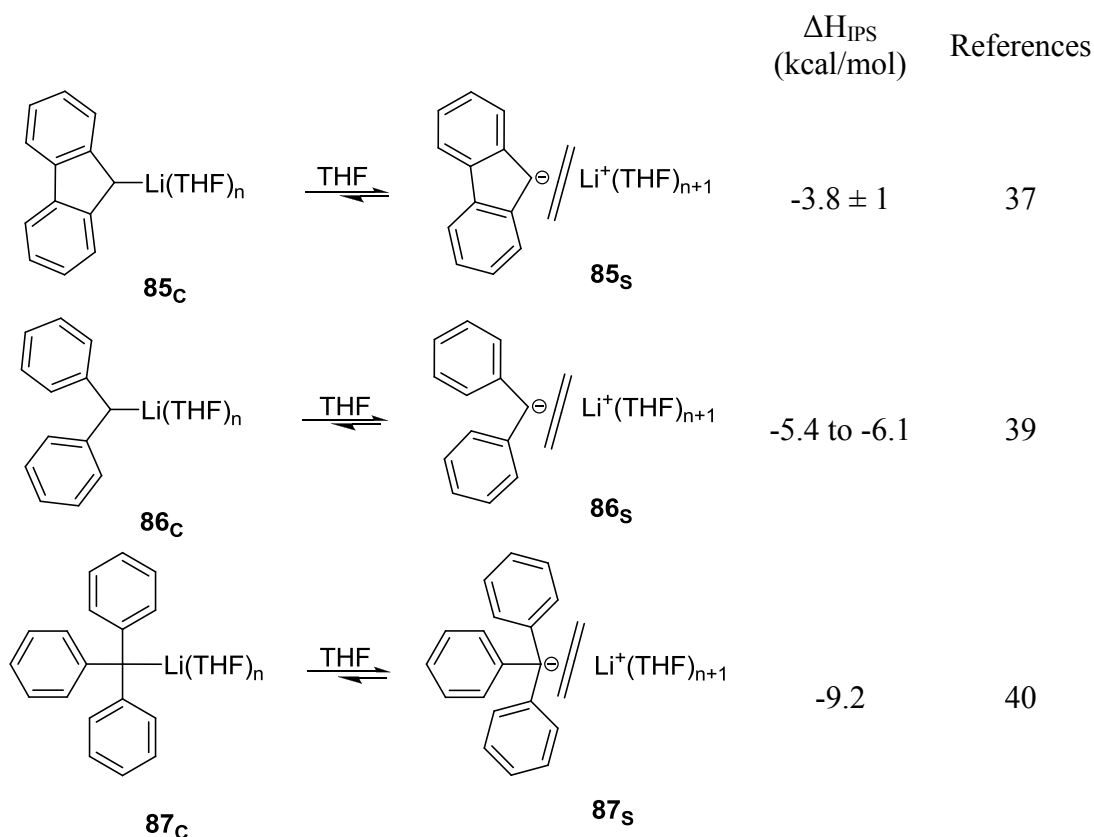


Figure 3.6: UV-Visible spectrum of CIP and SSIPs of DPM-Li **86** in THF at variable temperatures. Spectrum: 1 at 215 K, 3 at 235 K, 5 at 259 K and 8 at 296 K (Reprinted with permission from Buncel, E.; Menon, B. *J. Org. Chem.* **1979**, *44*, 317-320 Copyright 1979 American Chemical Society.)

Figure 3.6 which is taken directly from their study, shows an isosbestic point indicating the presence of an equilibrium between the interconverting species, presumably CIP and SSIP. The data lines from 1 to 8 correspond to the different temperatures employed in their study starting from 215 K to 296 K. A range of ΔH_{IPS} values of -5.4 to -6.1 kcal/mol was obtained for this system; the two values were obtained as a result of different methods used to estimate the absorbance of 100% CIPs in solution, with -5.4 kcal/mol corresponding to the detection of CIPs

by use of a solution of **86** in diethyl ether, and the -6.1 kcal/mol value corresponded to estimation from the DPM-Li spectrum in THF at -64 °C. The presence of a single-point of interconversion between the two absorption peaks indicates the presence of an equilibrium between the CIPs and SSIPs in solution. UV-visible analysis was also performed on trityllithium **87_C** in THF by the same authors using a temperature range of 263 K to 328 K.⁴⁰ The ΔH_{IPS} value obtained in this case was more exothermic at -9.2 kcal/mol. Scheme 3.11 summarizes the ΔH_{IPS} values for the three model systems using UV-Visible spectroscopy.



Scheme 3.11: Experimental data of Ion Pair Separation of organolithium compounds **85-87**

As can be seen, IPS was found to be exothermic in all three cases, with ΔH_{IPS} of -3.8 kcal/mol for Fl-Li, -5.4 to -6.1 kcal/mol for DPM-Li **86_C**, and -9.2 kcal/mol for Tr-Li **87_C**. Therefore, the UV-visible spectroscopic studies of Streitwieser and Buncl indicate that IPS of

87_C is the most exothermic in the series by 4 – 5 kcal/mol, and that **86_C**, and **85_C** have similar values of ΔH_{IPS} . This chapter will assess to what degree modern computational methods can reproduce these experimental solution-phase ΔH_{IPS} values. In particular, we will address the role of both explicit and implicit solvation in correctly modeling the structures of contact and separated ion pairs, and how these solvation models influence the calculated enthalpies of ion pair separation.

3.8 Computational Methods

All calculations were performed using Gaussian 03.⁴² The B3LYP/6-31G* method and basis were chosen for all geometry optimizations to compromise between accuracy and computational economy for the large explicit solvates described in this study (e.g. 84 atoms for **87_S**•(THF)₄, corresponding to 694 basis functions at 6-31G*). All B3LYP/6-31G* stationary points were characterized by vibrational frequency analysis as minima (zero imaginary frequencies) or transition structures (one imaginary frequency). Although molecular dynamics may ultimately provide the best method to determine average equilibrium solvation numbers,^{43,44} a number of recent studies have modeled the thermodynamics of ethereal solvation of organolithiums by locating explicit solvates.^{35,45-47} These and related studies have revealed that Me₂O is not a reliable surrogate for THF,^{33,35,46} and have noted the practical impossibility of exhaustively sampling the large conformational space available to THF-solvated organolithiums.^{35,48} To address this latter concern, multiple initial geometries of the explicit solvates were sequentially constructed and optimized to ensure uniform sampling of the conformational space available to the Li(THF)_n fragments in the fluorenyl, diphenylmethyl, and trityl series (n = 2 – 4). Further details on this iterative optimization procedure are given below. Frequencies were scaled with the B3LYP/6-31G* ZPVE correction factor of 0.9815 to calculate

enthalpic corrections at 298 K.⁴⁹ MP2/6-31G* single-point calculations were performed on B3LYP/6-31G* optimized geometries. To explore basis set size effects, select B3LYP single-point calculations were performed with the 6-31+G* basis set. Select mPW1PW91/6-31G* single-point calculations were also performed to assess the effect of another density functional on the thermodynamics of IPS.

To model bulk solvent effects, continuum solvation models were applied in two ways. First, implicit solvation (THF $\epsilon = 7.58$) was modeled by means of Onsager and PCM single-point calculations on the B3LYP/6-31G* (vacuum) geometries; these dual-level calculations are denoted as B3LYP/6-31G*(Onsager)//B3LYP/6-31G* and B3LYP/6-31G*(PCM)//B3LYP/6-31G*. Van Speybroeck and co-workers have recently used the single-point correction approach to model bulk solvent effects on explicitly solvated lithiated α -aminophosphonates⁵⁰ and lithiated imines.⁵¹ Onsager single-point calculations require specification of a radius (a_0). Since the Volume keyword of Gaussian '03 invokes a Monte Carlo integration method to determine this parameter, a_0 is *not* uniquely determined by the geometry. Uncertainty in a_0 will propagate into uncertainty in energy, and uncertainty in ΔH_{IPS} . In ten identical repeat volume calculations of **85C**•(THF)₃, a standard deviation of 3.7% (0.22 Å) was seen in radius a_0 . This random error must be considered, but may not sufficiently address systematic error stemming from the use of a spherical cavity to contain non-spherical molecules. Therefore, to provide a conservative estimate of the uncertainty in Onsager energy for all the calculated species in the chapter, we allowed a_0 to vary by $\pm 10\%$. Thus for every species in the chapter a specific radius a_0 was determined by a single Volume calculation on the vacuum optimized geometry, and Onsager single-point electronic energies were performed at radii of a_0 , $0.9 \cdot a_0$, and $1.1 \cdot a_0$. The mean Onsager energies and their standard deviations were then determined. Since uncertainty in ΔH_{IPS}

derives only from uncertainties in the energies, a standard formula for propagation of errors in a sum of terms was applied: $\sigma_{\Delta H(\text{IPS})} \approx \sigma_{\Delta E(\text{IPS})} = (\sigma_{E(\text{SSIP})}^2 + \sigma_{E(\text{CIP})}^2 + \sigma_{E(\text{THF})}^2)^{0.5}$. These uncertainties in Onsager energy-based values of ΔH_{IPS} are reported in Table 3.9. PCM single-point calculations were performed with the options surface=SES and radii=pauling; Pauling radii have been recommended for ionic species.⁵¹

To incorporate the effect of a dielectric *during geometry optimization*, we used the Onsager continuum model. The a_0 values determined for the vacuum geometries were used as input in these optimizations, which we denote as B3LYP/6-31G*(Onsager). As described above, single-point Onsager energies on these geometries were determined at $0.9 \cdot a_0$ and $1.1 \cdot a_0$ to assess the uncertainty in ΔH_{IPS} . Note that geometry optimization of the large solvated CIPs and SSIPs under PCM solvation was attempted but proved unsuccessful. Finally, basis set superposition error for IPS was estimated by performing counterpoise calculations on the B3LYP/6-31G* and B3LYP/6-31G*(Onsager) geometries of the tetrakis(THF)-solvated separated ion pairs (**85**_S•(THF)₄ - **87**_S•(THF)₄).

3.9 Modeling of Explicitly Solvated Contact and Separated Ion Pairs

Before the thermodynamics of ion pair separation of **85**_C - **87**_C can be addressed computationally, the resting THF solvation number of these species and of the corresponding separated ion pairs **85**_S - **87**_S must be established. Because these values have not been determined experimentally in solution, we examined ethereal solvates of **85** – **87** that have been characterized by X-ray crystallography. Fluorenyllithium **85** has been characterized as the tris(THF)-solvated CIP (**85**_C•(THF)₃),⁵² and as the bis(Et₂O)-solvated CIP (**85**_C•(Et₂O)₂; note: η^2 -fluorenyl),⁵³ and as a bis(diglyme)-solvated SIP (**85**_S•(η^3 -diglyme)₂) (Figure 3.7).⁵⁴

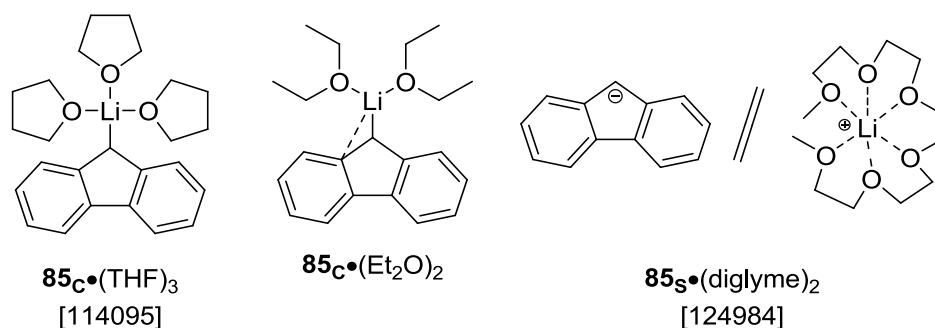


Figure 3.7: Fluorenyllithium compounds with available X-ray crystal structures. Available CCDC numbers shown in brackets.

In order to calculate the solvation state of the fluorenyllithium system, we did a step-wise solvation, starting from the lithium salt **85**, and adding one THF molecule at a time to give the mono **85_C•(THF)**, di **85_C•(THF)₂** and tri solvated **85_C•(THF)₃** CIPs as follows:

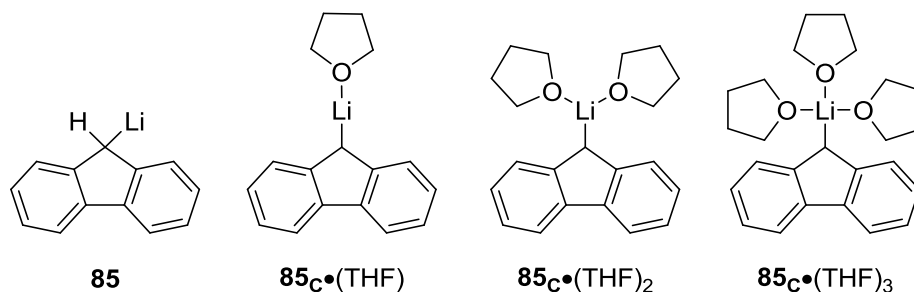


Figure 3.8: Fluorenyllithium **85**: Unsolvated and mono(THF)-solvated to tris(THF)-solvated CIPs

As we will show below, unsolvated **85** features η^5 -coordination of the fluorenyl fragment, and the trisolvated **85** is η^1 -coordinated. With regards to DPM-Li **86**, only a bis(12-crown-4)-solvated SIP (**86_S•(η^4 -12-crown-4)₂**)⁵⁵ has been characterized by X-ray crystallography (Figure 3.9).

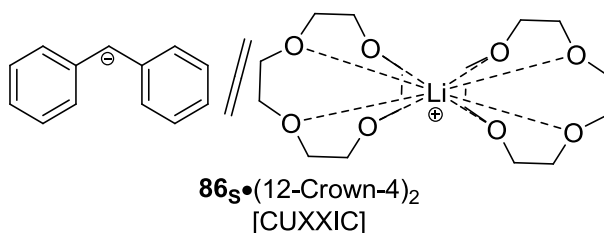


Figure 3.9: Bis(12-crown-4)-solvated diphenylmethyllithium. CSD identifier number shown in brackets

As for fluorenyllithium **85**, stepwise solvation by THF was undertaken for the diphenylmethyllithium **86** to get the mono-, di- and trisolvated CIPs (Figure 3.10). Again, as we will show below, the hapticity of the coordinated DPM decreases upon sequential THF solvation.

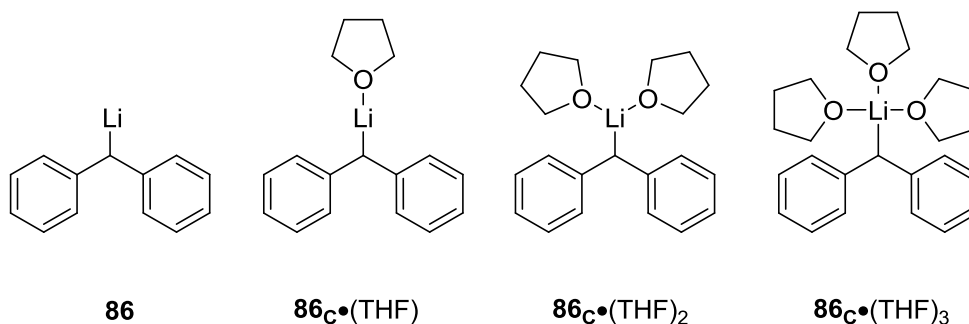


Figure 3.10: Diphenylmethyllithium **86**: Unsolvated and mono(THF)-solvated to tris(THF)-solvated CIPs

Finally, TrLi **87** has been characterized in the solid state as a bis(Et₂O)-solvated CIP (**87_C•(Et₂O)₂**; note: η^3 -trityl),⁵⁶ a tetrakis(THF)-solvated SIP (**87_C•(THF)₄**)⁵⁷ and a bis(12-crown-4)-solvated SIP (**3_S•(η^4 -12-crown-4)₂**) (Figure 3.11).⁵⁵

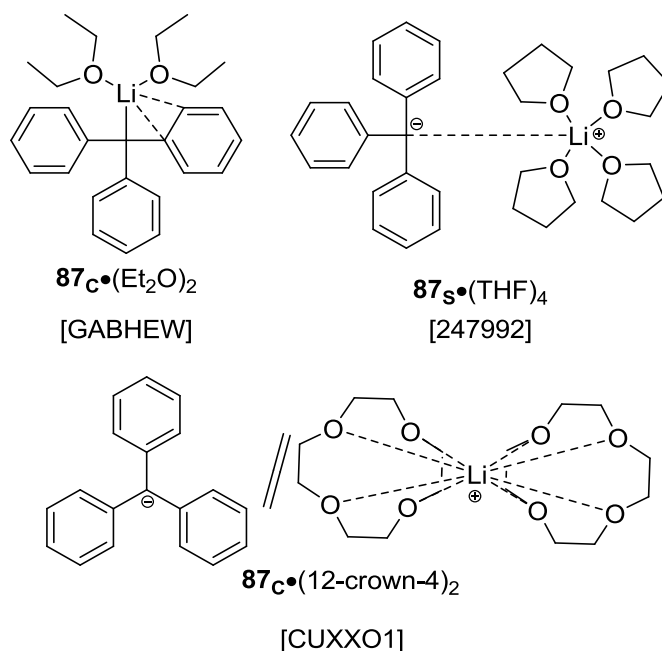


Figure 3.11: Trityllithium compounds with available X-ray crystal structures. Available CCDC or CSD identifier number shown in brackets

A stepwise addition of THF molecules to the trityllithium salt **87** gives the mono-, di- and trisolvated systems (Figure 3.12). The hapticity of the bound trityl fragments in these complexes will be discussed below.

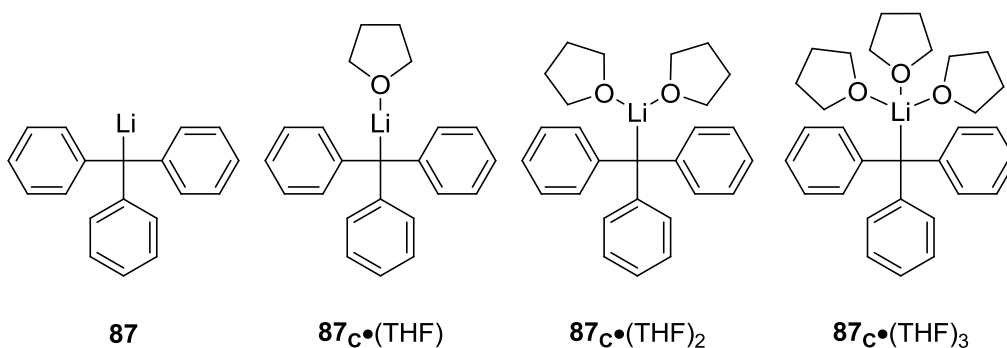


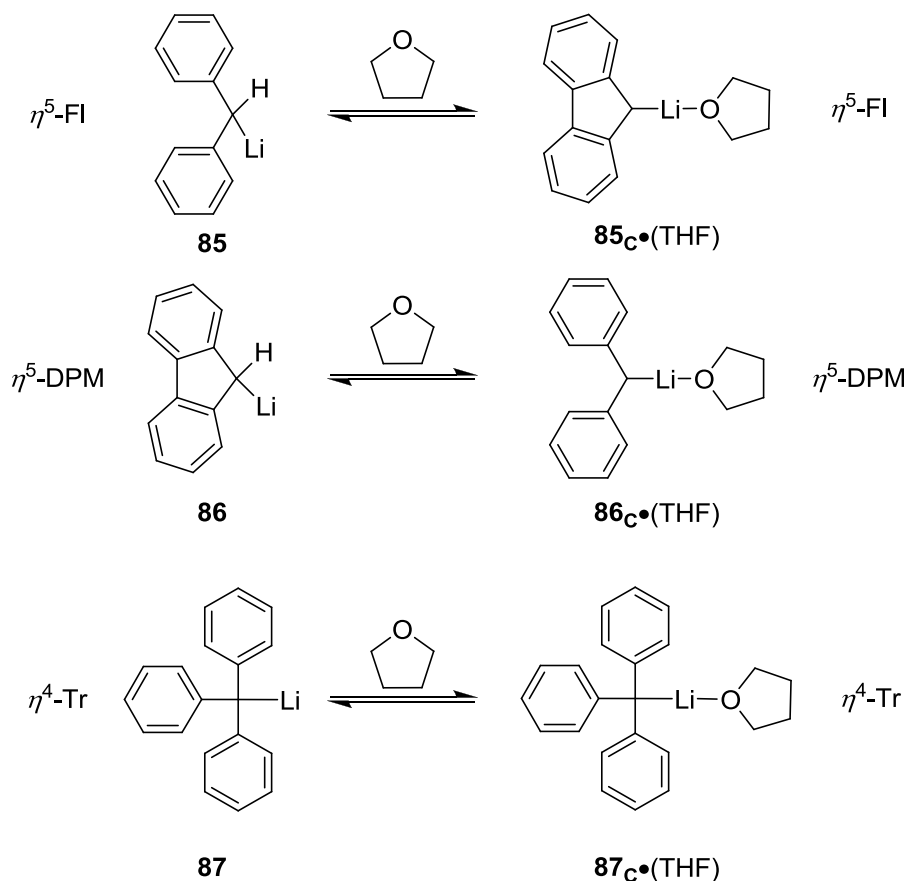
Figure 3.12: Trityllithium **87**: Unsolvated and mono(THF)-solvated to tris(THF)-solvated CIPs

To minimize the chance that the calculated energies of bis- and tris(THF)-solvated **85_C**-**87_C** were biased by different conformations of the Li(THF)_n fragment, we carried out multiple sequential B3LYP/6-31G* optimizations for the bis, tris and tetrakis systems. In this procedure

the THF-solvated lithium fragments of each optimized geometry were swapped between the various carbanion fragments (Fl^- , DPM^- , Tr^-), and the resulting new initial geometries were reoptimized. After three to four generations of optimization, no new lowest energy minima were found (See Figures 3.15, 3.17 and 3.19).

3.9.1 Mono(THF) Solvation

The first step of our study was the mono(THF)-solvation for all three systems. We optimized the three unsolvated lithium salts **85**, **86**, **87** and the corresponding THF monosolvated systems **85_C•(THF)**, **86_C•(THF)** and **87_C•(THF)** at B3LYP/6-31G* (Scheme 3.12).



Scheme 3.12: Formation of mono(THF)-solvated organolithiums from the unsolvated salts **85-86**.

Unsolvated fluorenyllithium **85** possessed an η^5 -coordinated structure with the Li^+ cation

on top of the five membered ring with the average C_{α} -Li distance of 2.153 Å (Figure 3.13). An exhaustive search for different complexation states of lithium was not undertaken due to literature precedence which showed this η^5 structure as the global minimum by Schleyer and coworkers.⁵⁸ Another study by Johnels et al. also found this structure to be lower in energy in comparison to other structures with η^2 and η^3 complexation patterns.⁵³ Similar to fluorenyllithium, an η^5 -coordinated structure was also observed for the unsolvated diphenylmethyllithium **86**, with the average C_{α} -Li distance of 2.209 Å. Trityllithium **87** was found to possess an η^4 -coordinated structure with two of the complexing carbons from one phenyl ring and the third carbon from a second phenyl ring, and the last with the carbanion carbon. The average C_{α} -Li distance was found to be 2.173 Å. The B3LYP/6-31G* optimized structures are shown in Figure 3.13.

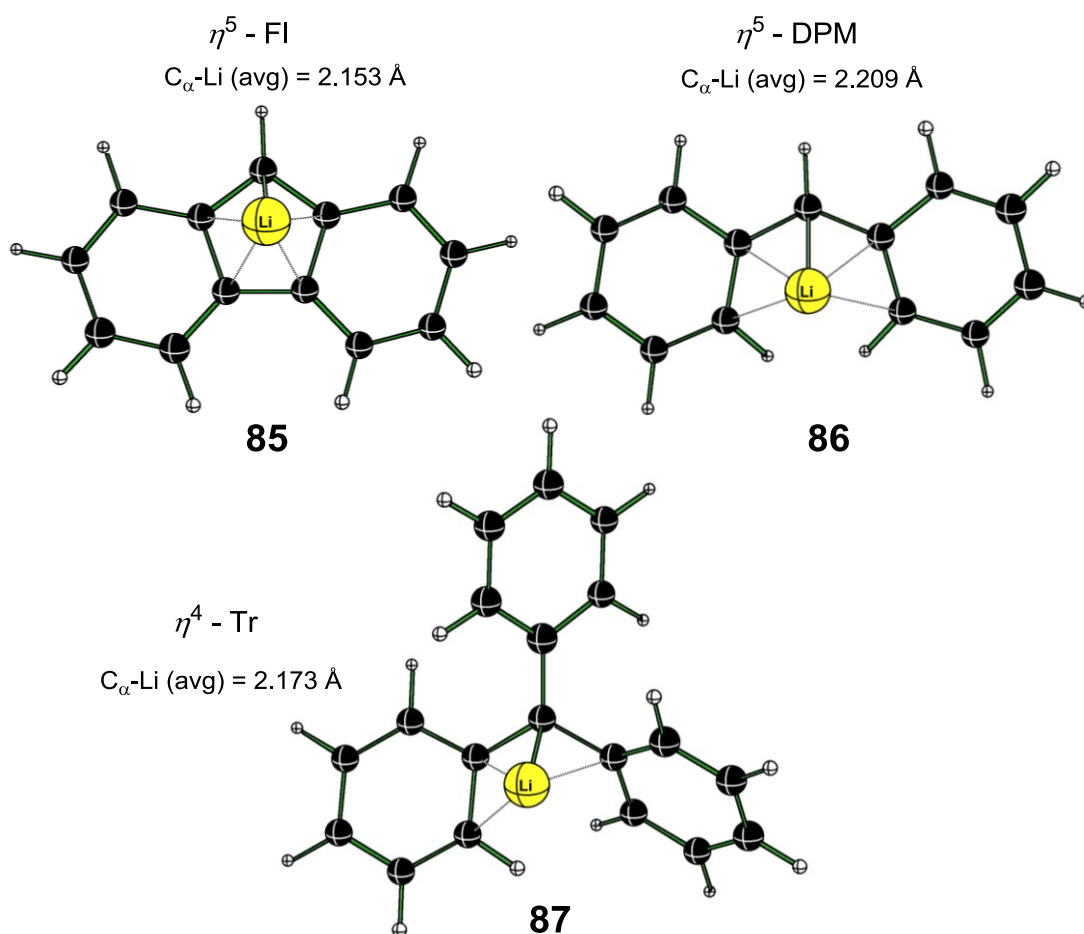


Figure 3.13: B3LYP/6-31G* optimized structures of unsolvated benzylic organolithiums **85-87**.

The monosolvated structures [**85**_C•(THF) - **87**_C•(THF)] were also calculated at B3LYP/6-31G*, and just like the unsolvated lithium salts, the Li⁺ cation possessed multiple close contacts to the carbanionic fragment. Complexation with a THF molecule increased the average C_α-Li distance slightly for all three systems. The fluorenyl **85**_C•(THF) and diphenylmethyl **86**_C•(THF) systems were still η^5 -coordinated structures with average C_α-Li bond lengths of 2.211 Å and 2.284 Å respectively, while the trityl **87**_C•(THF) was again found to be an η^4 -coordinated structure with the average C_α-Li bond length of 2.259 Å (Figure 3.14).

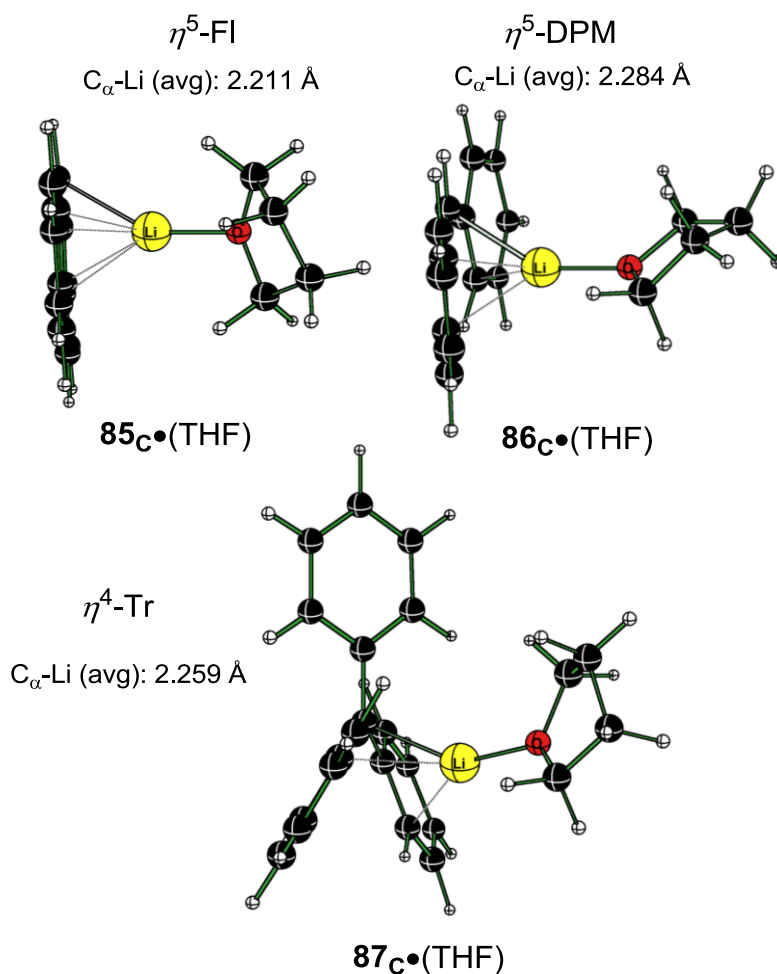


Figure 3.14: B3LYP/6-31G* optimized geometries of mono-THF solvated organolithiums **85**_C•(THF) - **87**_C•(THF).

Energy calculations showed the first THF solvation to be significantly exothermic and

exergonic with almost the same ΔH_{SOLV1} and ΔG_{SOLV1} values for all three systems (Table 3.1).

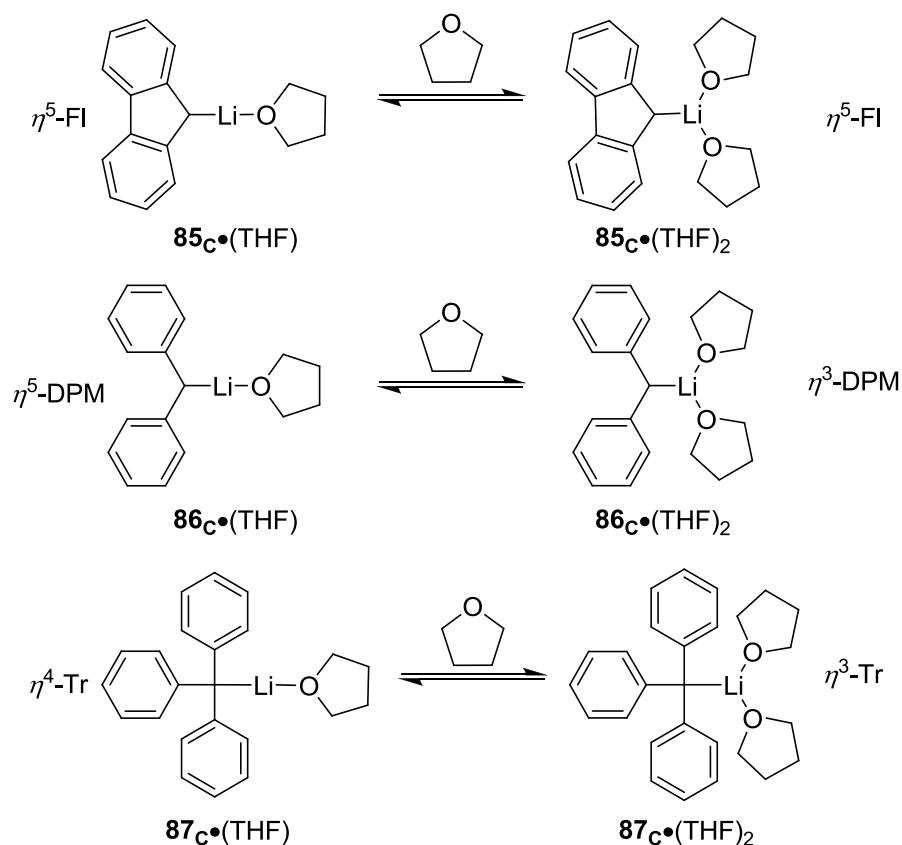
Table 3.1: Enthalpy (ΔH_{SOLV1}) and free energy (ΔG_{SOLV1}) for the first THF solvation of organolithiums **85-87** (298K, kcal/mol).^a

$\text{R-Li} + \text{THF} \xrightleftharpoons{\Delta G_{\text{SOLV1}}} \text{R-Li(THF)}$				
Method/Basis		85 (R = Fl)	86 (R=DPM)	87 (R=Tr)
B3LYP/6-31G*	ΔH_{SOLV1}	-23.4	-22.4	-23.3
	ΔG_{SOLV1}	-12.9	-13.0	-12.9

^aEnthalpy $\Delta H_{\text{SOLV1}} = H(\text{R-Li(THF)}) - [H(\text{R-Li}) + (\text{THF})]$; free energy $\Delta G_{\text{SOLV1}} = G(\text{R-Li(THF)}) - [G(\text{R-Li}) + G(\text{THF})]$; all values in kcal/mol. Free energy and enthalpy corrections (298K) to the absolute energies were determined from B3LYP/6-31G* frequencies, scaled by 0.9815.

3.9.2 Bis(THF) Solvation

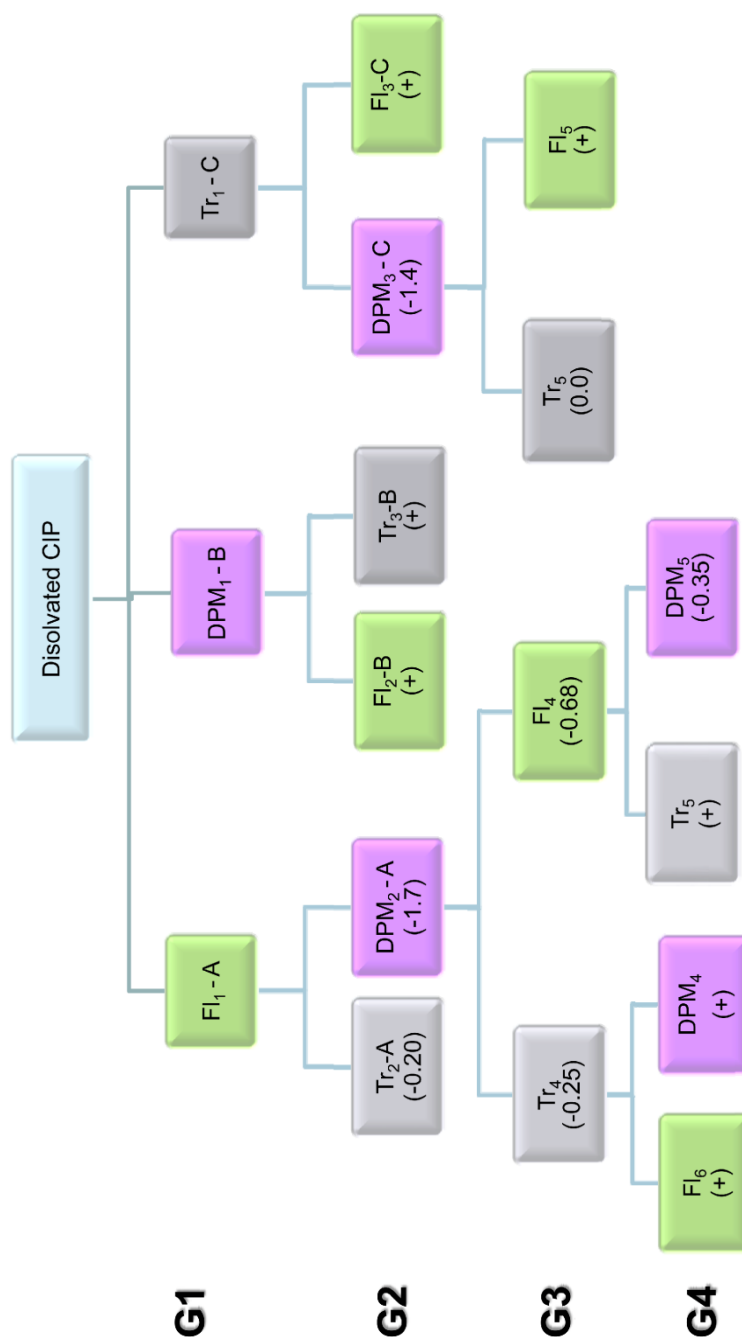
Bis(THF) solvation was studied by an addition of a THF molecule to the mono(THF)-solvated lithium salts for all the three systems (Scheme 3.13).



Scheme 3.13: Formation of bis(THF)-solvated organolithiums $85_{\text{C}}^{\bullet}(\text{THF})_2 - 87_{\text{C}}^{\bullet}(\text{THF})_2$ from mono(THF)-solvated organolithiums $85_{\text{C}}^{\bullet}(\text{THF}) - 87_{\text{C}}^{\bullet}(\text{THF})$

As mentioned earlier, multiple sequential B3LYP/6-31G* optimizations were carried out for the bis(THF)-solvates. In this procedure, the THF solvated lithium fragments of each optimized geometry were swapped between the various carbanion fragments (FI^- , DPM^- , Tr^-), and the resulting new initial geometries were reoptimized. After four generations of optimization, no new lowest energy minimum was found. Figure 3.15 shows the optimization flowchart for the bis(THF) solvated systems.

Figure 3.15: Flowchart for the optimization of $85_{\text{C}}\cdot(\text{THF})_2$ - $87_{\text{C}}\cdot(\text{THF})_2$. Electronic energies relative to the corresponding generation 1 (G1) structure shown in parenthesis (kcal/mol). A positive sign indicates a higher energy minimum that was ignored in subsequent optimizations.



Just like the mono(THF)-solvates, all of the bis(THF)-solvates also showed multiple close contacts between the lithium with the carbanion fragment. While the fluorenyllithium **85C**•(THF)₂ was still η^5 -coordinated, the carbanionic fragments in diphenylmethyllithium **86C**•(THF)₂ and trityllithium **87C**•(THF)₂ both showed reduced hapticity and were both η^3 -coordinated (cf. Figure 3.14 and 3.16). The calculated equilibrium geometries of these bis(THF) solvates parallel the hapticity seen by X-ray crystallography of related bis-solvates **85C**•(Et₂O)₂ (η^2 -fluorenyl)⁵³ and **87C**•(Et₂O)₂ (η^3 -trityl).⁵⁶

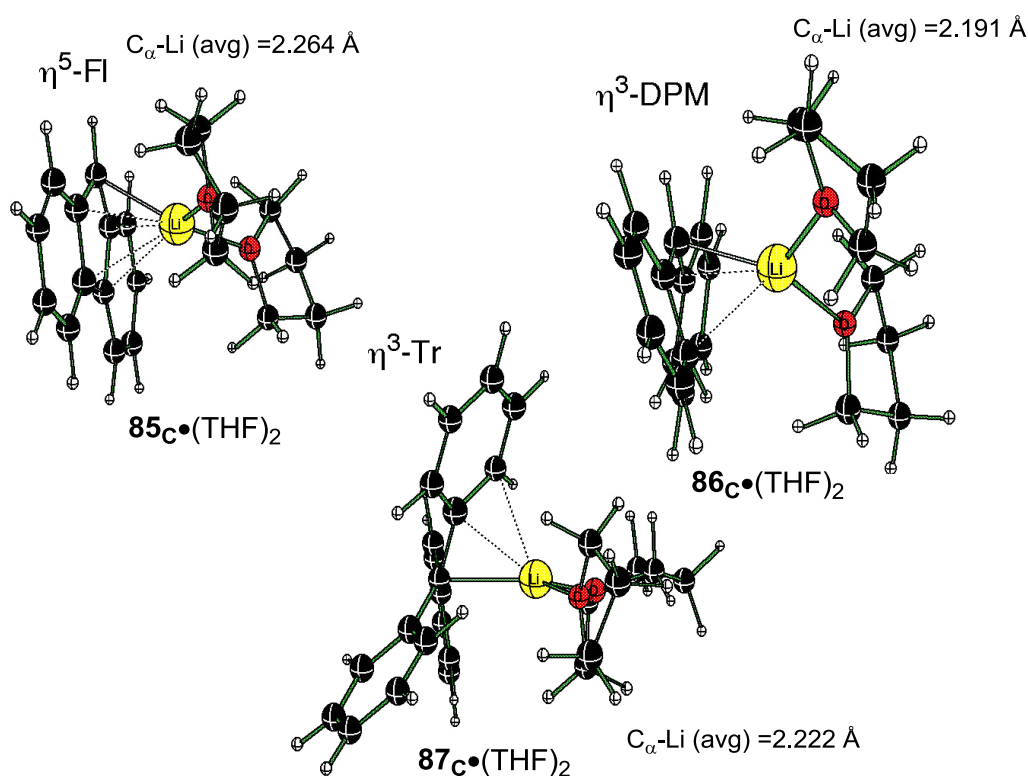


Figure 3.16: B3LYP/6-31G* optimized geometries of bis(THF)-solvated organolithiums **85C**•(THF)₂ – **87C**•(THF)₂.

Solvation by a second THF molecule was exothermic for all three systems, with ΔH_{SOLV2} values ranging from -11.9 kcal/mol for **85C**•(THF) to -14.3 kcal/mol for the **86C**•(THF). While this solvation process was exergonic for all three systems, the ΔG_{SOLV2} values were considerably

smaller than ΔG_{SOLV1} , ranging from -0.6 kcal/mol for the fluorenyl system **85**_C•(THF) to -3.2 kcal/mol for the trityl system **87**_C•(THF).

Table 3.2: Enthalpy (ΔH_{SOLV2}) and free energy (ΔG_{SOLV2}) for the second THF solvation of **85-87** (298K, kcal/mol).^a

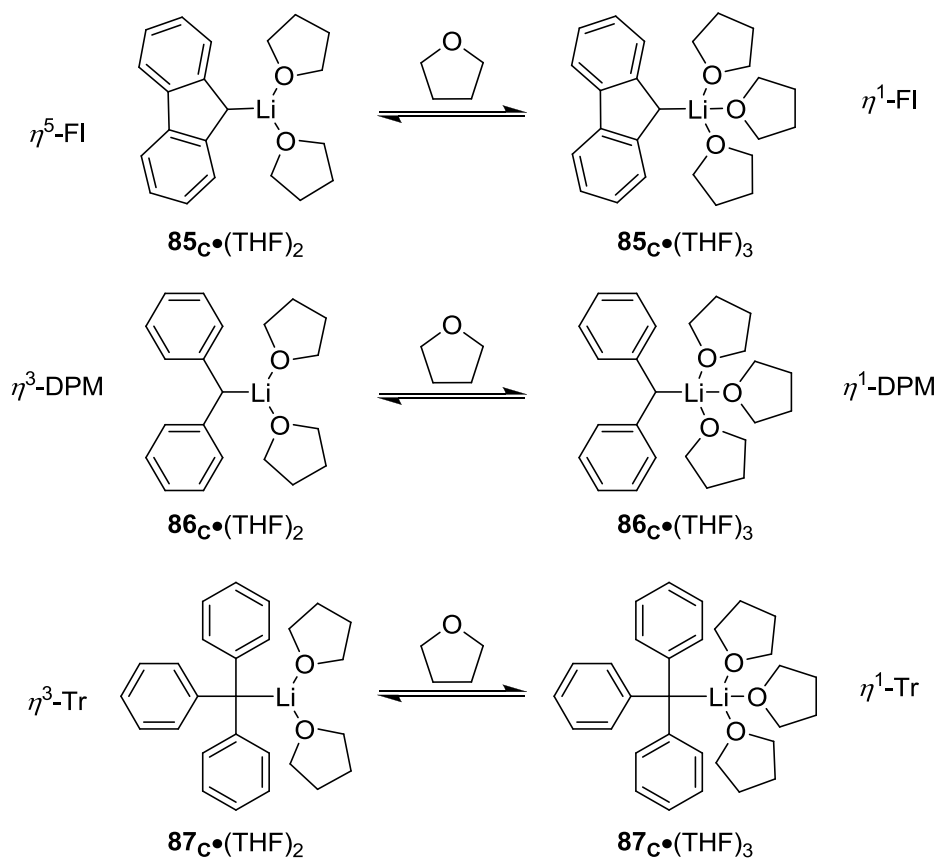
$$\text{R-Li(THF)} + \text{THF} \xrightleftharpoons{\Delta G_{\text{SOLV2}}} \text{R-Li(THF)}_2$$

Method/Basis		85 (R = Fl)	86 (R=DPM)	87 (R=Tr)
	ΔH_{SOLV2}	-11.9	-14.3	-14.0
B3LYP/6-31G*	ΔG_{SOLV2}	-0.6	-1.9	-3.2

^aEnthalpy $\Delta H_{\text{SOLV2}} = H(\text{R-Li(THF)}_2) - [H(\text{R-Li(THF)}) + (\text{THF})]$; free energy $\Delta G_{\text{SOLV2}} = G(\text{R-Li(THF)}_2) - [G(\text{R-Li(THF)}) + G(\text{THF})]$; all values in kcal/mol. Free energy and enthalpy corrections (298K) to the absolute energies were determined from B3LYP/6-31G* frequencies, scaled by 0.9815.

3.9.3 Tris(THF) Solvation

The next step of solvation is the addition of a THF molecule to the bis(THF)-solvate to get a tris(THF)-solvate contact ion pair (Scheme 3.14).



Scheme 3.14: Formation of the tri(THF)-solvated organolithium $85_{\text{C}}\bullet(\text{THF})_3 - 87_{\text{C}}\bullet(\text{THF})_3$ from bis(THF)-solvated organolithiums $85_{\text{C}}\bullet(\text{THF})_2 - 87_{\text{C}}\bullet(\text{THF})_2$

We calculated the minimum energy equilibrium geometries following the multiple optimization method and after three generations no new lower energy minima were obtained (Figure 3.17).

Figure 3.17: Flowchart for the optimization of $85_{\text{C}}\cdot(\text{THF})_3$ - $87_{\text{C}}\cdot(\text{THF})_3$. Electronic energies relative to the corresponding generation 1 (G1) structure shown in parenthesis (kcal/mol). A positive sign indicates a higher energy minimum that was ignored in subsequent optimizations.

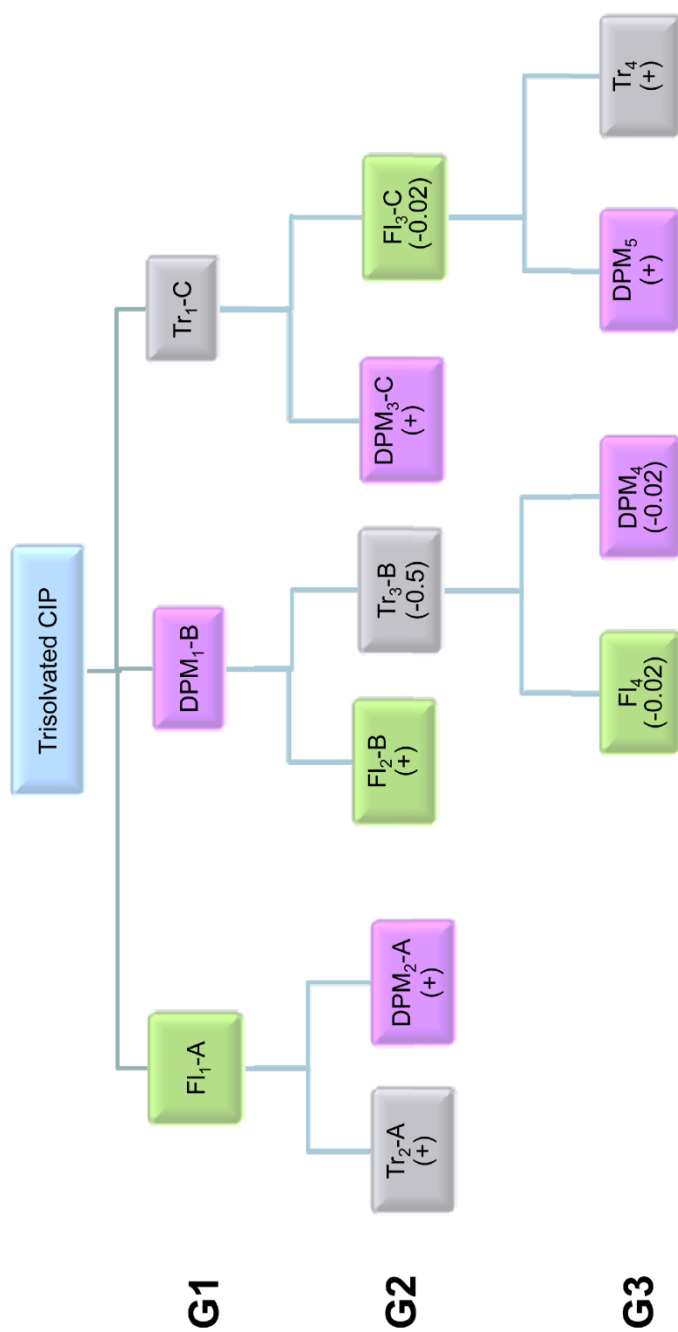


Figure 3.18 shows the B3LYP/6-31G* optimized minimum energy equilibrium geometries of the three tris(THF)-solvates. Several features of the calculated structures of the tris(THF)-solvated CIPs are noteworthy. First, in contrast to the mono and bis(THF)-solvated structures, the calculated tris(THF)-solvates **85_C•**(THF)₃ - **87_C•**(THF)₃ all show η^1 -coordination, as seen in the X-ray structure of **85_C•**(THF)₃.⁵² Consistent with the reduced hapticity seen in the trisolvated structures, significant increases in the C _{α} -Li bond length (0.07 – 0.10 Å) are seen in **86_C•**(THF)₃ and **87_C•**(THF)₃ relative to the disolvates (cf. Figure 3.16 and 3.18). Furthermore, good correspondence is seen between the calculated B3LYP/6-31G* and X-ray geometries of tris(THF)-solvated CIP (η^1 -fluorenyl). The calculated C _{α} -Li bond length of 2.273 Å is within 0.014 Å of the X-ray bond length of 2.287 Å. The calculated Li-O bond lengths (1.993 – 2.014 Å) are within 0.079 Å of those seen by X-ray crystallography (1.914 – 1.956 Å).

Finally, attempts were made to construct CIP species with four coordinated THF molecules. However, in every case the fourth solvent ligand dissociated from the lithium during optimization.

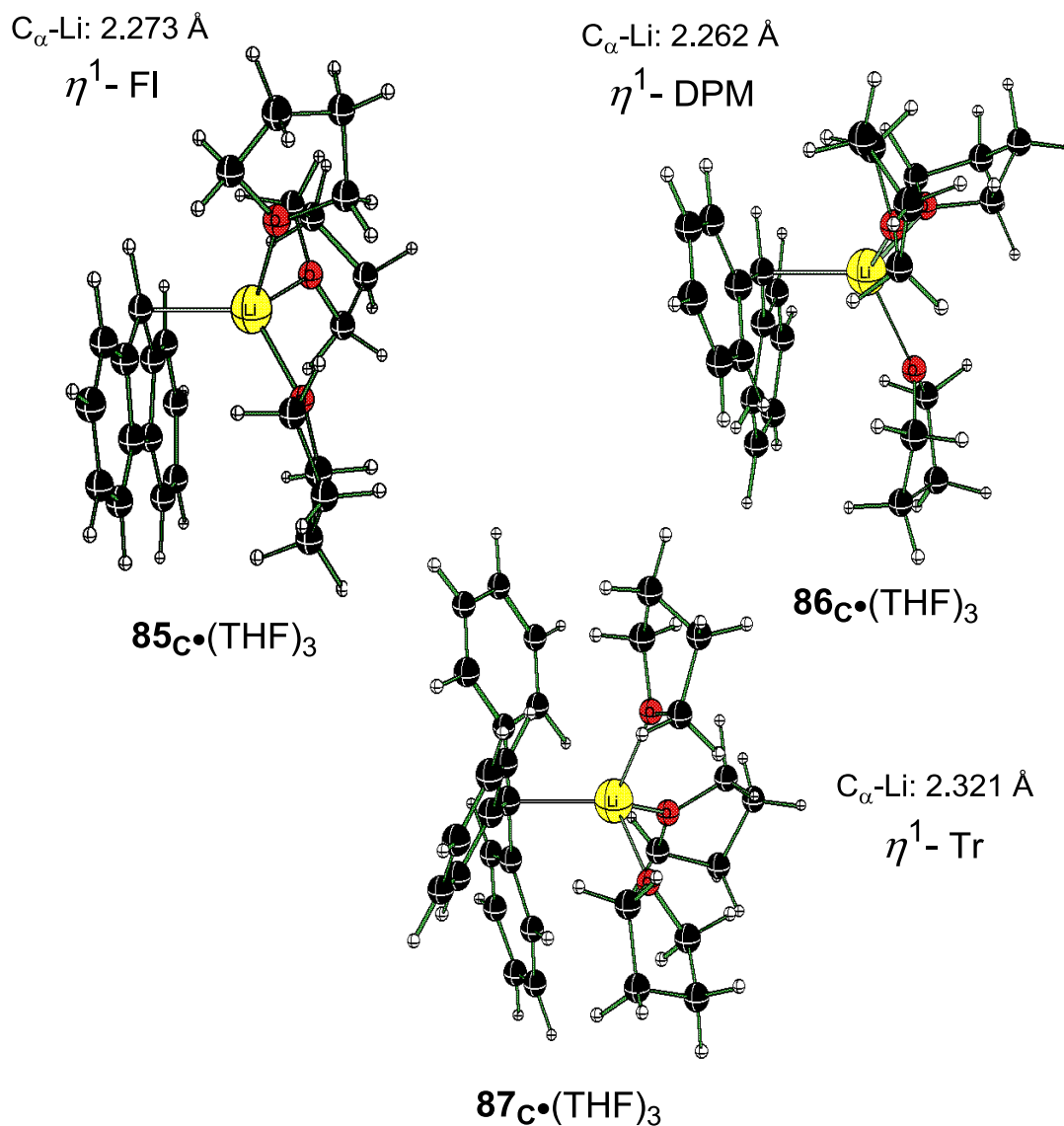
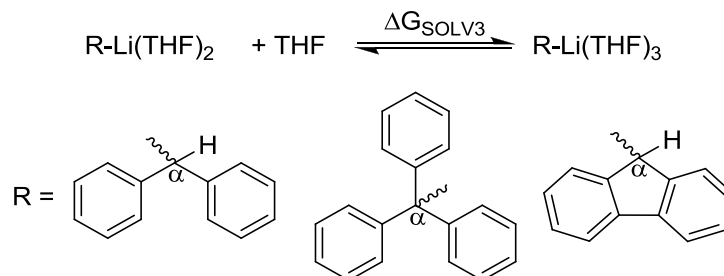


Figure 3.18: B3LYP/6-31G* optimized geometries of tris(THF)-solvated organolithiums **85C•(THF)₃**- **87C•(THF)₃**

With the minimum energy B3LYP/6-31G* geometries of the bis- and tris(THF)-solvated CIPs in hand, we calculated the enthalpy and free energy of the third solvation of **85C** - **87C**. Because previous studies have reported that DFT underestimates the enthalpy of the third ethereal solvation of organolithiums,^{35,46} as recommended we also calculated these terms based on the MP2/6-31G*// B3LYP/6-31G* single-point energies (Table 3.3).

Table 3.3: Enthalpy (ΔH_{SOLV3}) and free energy (ΔG_{SOLV3}) and for the third THF solvation of **85**-**87** (298K, kcal/mol).^a



Method/Basis		85 (R = Fl)	86 (R=DPM)	87 (R=Tr)
B3LYP/6-31G*	ΔH_{SOLV3}	-6.5	-6.7	-7.8
	ΔG_{SOLV3}	+4.8	+2.9	+5.8
MP2/6-31G*//B3LYP/6-31G*	ΔH_{SOLV3}	-12.6	-13.9	-18.7
	ΔG_{SOLV3}	-1.3	-4.4	-5.1

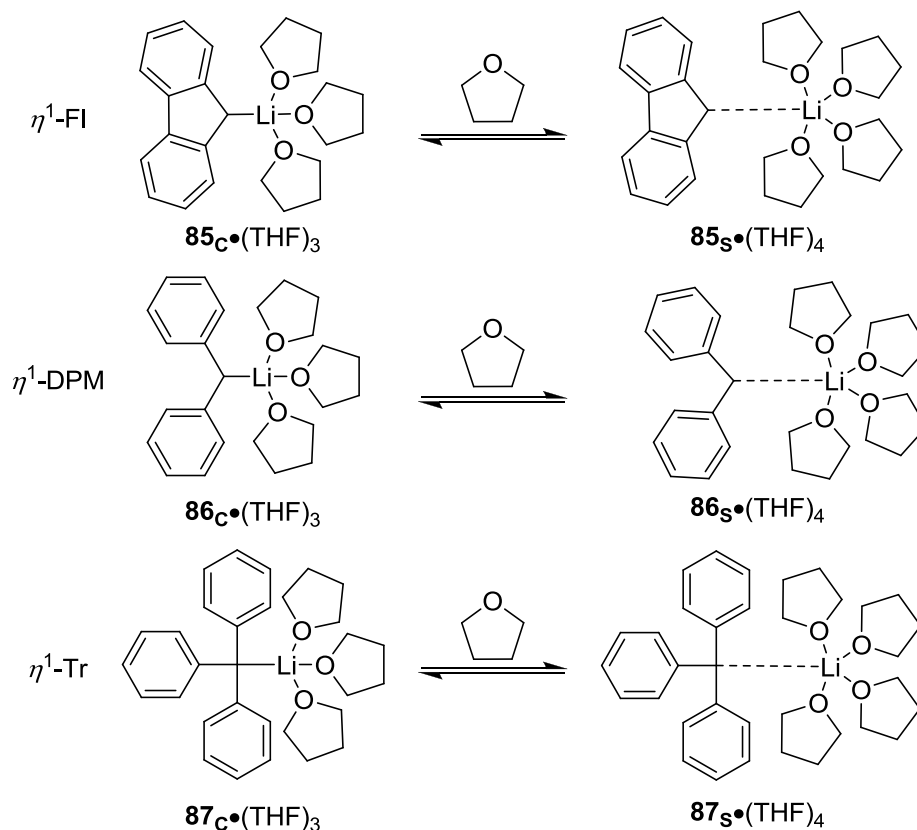
^aEnthalpy $\Delta H_{\text{SOLV3}} = H(\text{R-Li(THF)}_3) - [H(\text{R-Li(THF)}_2) + (\text{THF})]$; free energy $\Delta G_{\text{SOLV3}} = G(\text{R-Li(THF)}_3) - [G(\text{R-Li(THF)}_2) + G(\text{THF})]$; all values in kcal/mol. Free energy and enthalpy corrections (298K) to the absolute energies were determined from B3LYP/6-31G* frequencies, scaled by 0.9815.

Although the third solvation is exothermic for **85_C** - **87_C** at both B3LYP/6-31G* and MP2/6-31G*//B3LYP/6-31G*, the latter ΔH_{SOLV3} values are significantly (6 - 11 kcal) more exothermic. Consequently, the third solvation of **85_C** - **87_C** is *exergonic* only at MP2/6-31G*//B3LYP/6-31G*, due to the large -TΔS term (+9.6 to +13.6 kcal/mol). Thus our results match those of previous workers who reported that DFT underestimates the enthalpy of the third ethereal solvation of organolithiums.^{35,46} Since the MP2/6-31G*//B3LYP/6-31G* based values of ΔG_{SOLV3} are most consistent with the observation of tris(THF)-solvate **85_C**•(THF)₃ in the solid state,⁵⁹ we will consider the trisolvates to be the resting state CIP structures. This conclusion is strengthened by NMR studies of LiHMDS^{60,61} and 2-(α-aryl-α-lithiomethylidene)-1,1,3,3-tetramethylindane⁶² in THF solution, which demonstrate tris(THF)-solvated CIPs in the temperature range employed in studies of **85** - **87**. In addition, Collum's solution studies on

LiHMDS demonstrate that increasing steric bulk of the ether solvent reduces solvation number and energy.⁶¹ In this context, the lower solvation number seen by X-ray crystallography for diethyl ether solvate of **85_C** (i.e. **85_C**•(Et₂O)₂)⁵³ relative to the THF solvate (**85_C**•(THF)₃)⁵² is easily rationalized.

3.9.4 Tetrakis(THF) Solvation

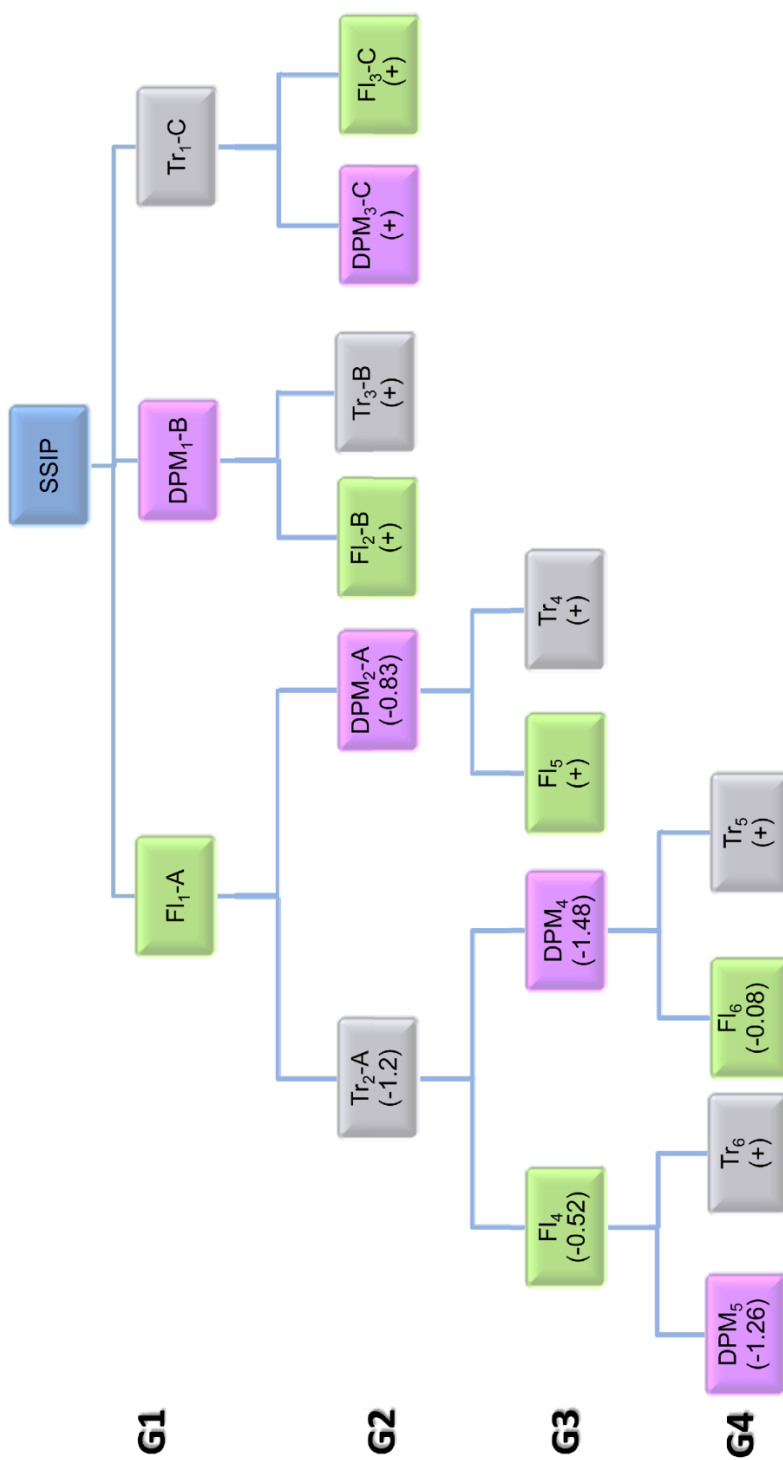
Addition of the fourth THF molecule leads to the formation of the SSIPs as shown in Scheme 3.15.



Scheme 3.15: Ion Pair Separation of trisolvated **85_C**•(THF)₃-**87_C**•(THF)₃

We thus located minimum-energy B3LYP/6-31G* equilibrium geometries of the tetrakis(THF)-solvated SIPs of the fluorenyl, diphenylmethyl, and trityl systems (**85_S**•(THF)₄ – **87_S**•(THF)₄) using the same methodology of sequential B3LYP/6-31G* optimizations.

Figure 3.19: Flowchart for the optimization of $85_S \cdot (\text{THF})_4 - 87_S \cdot (\text{THF})_4$. Electronic energies relative to the corresponding generation 1 (G1) structure shown in parenthesis (kcal/mol). A positive sign indicates a higher energy minimum that was ignored in subsequent optimizations.



After four generations of this procedure no new lower energy minima were located. (Figure 3.19). The B3LYP/6-31G* optimized geometry of the three SSIPs is shown in Figure 3.20.

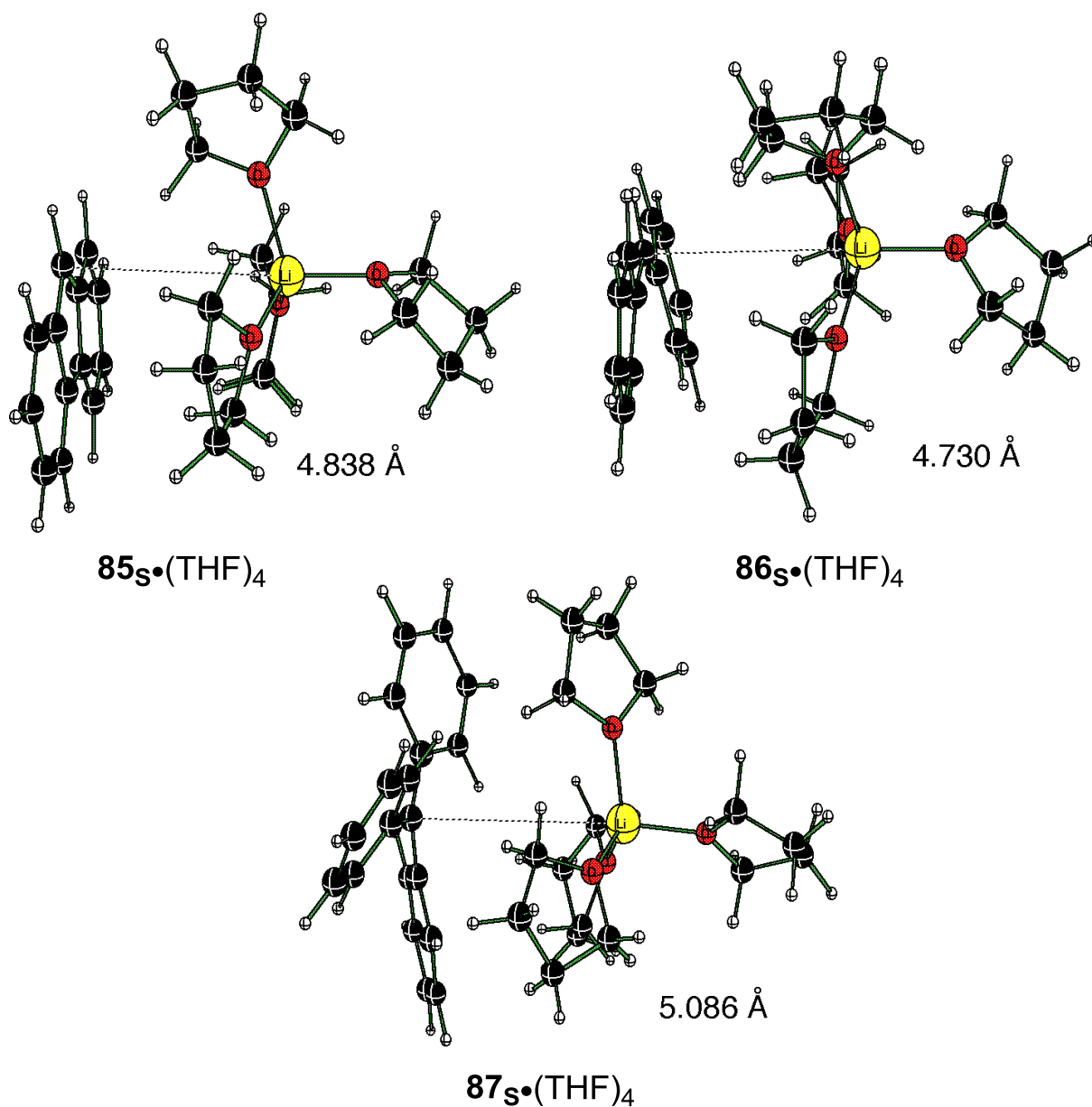


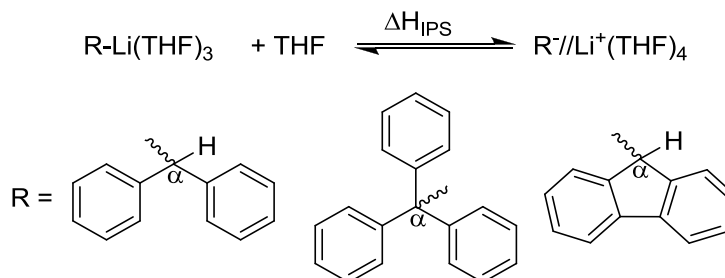
Figure 3.20: B3LYP/6-31G* optimized geometries of tetrakis(THF)-solvated SSIPs **85S•(THF)₄** - **87S•(THF)₄**. C α -Li distances shown in Å

As expected, C_α-Li distances in the tetrakis(THF)-solvated SSIPs **85**S•(THF)₄ – **87**S•(THF)₄ were considerably longer than those in the corresponding trisolvated CIPs, ranging from 4.730 to 5.086 Å for the three systems. However it should be pointed out that the C_α-Li distance of 5.086 Å calculated for **87**S•(THF)₄ in vacuum is considerably shorter than the distance of 6.854 Å observed by X-ray crystallography.⁵⁷ The implications of this large difference in the C_α-Li distance to the proper modeling of solution structures of SSIPs will be discussed below, following our discussion of the thermodynamics of ion pair separation in vacuo.

3.9.4.1 Modeling Enthalpies and Activation Enthalpies of Ion Pair Separation of Explicit Solvates in Vacuo

Based on the minimum energy B3LYP/6-31G* equilibrium geometries of the tris(THF)-solvated CIPs and the tetrakis(THF)-solvated SIPS, the enthalpy of ion pair separation (ΔH_{IPS}) was calculated (Table 3.4).

Table 3.4: Experimental and calculated ΔH_{IPS} (298 K, kcal/mol)^a for formation of SSIPs from tris(THF)-solvated CIPs



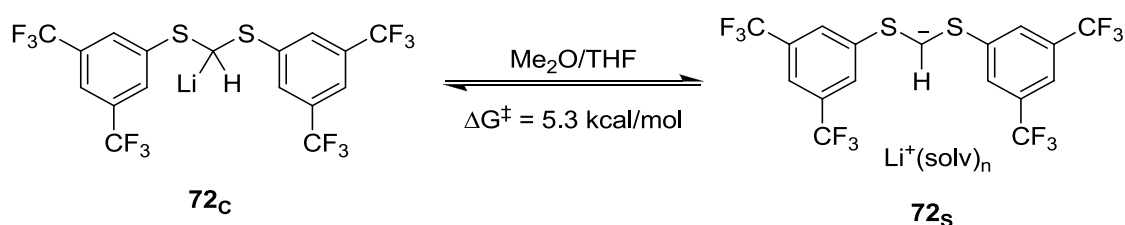
Method/Basis	85 (R = Fl)	86 (R=DPM)	87 (R=Tr)
Experimental	-3.8 ± 1.0^{37}	$-5.4 \text{ to } -6.1^{39}$	-9.2^{40}
B3LYP/6-31G*	+1.9	+1.9	-1.2
B3LYP/6-31+G*//B3LYP/6-31G*	+4.0	+4.1	+1.0
mPW1PW91/6-31G*// B3LYP/6-31G*	+3.6	+3.4	+0.9
MP2/6-31G*//B3LYP/6-31G*	+1.3	+1.9	+0.1

^aEnthalpy value $\Delta H_{\text{IPS}} = H(\text{SSIP}) - [H(\text{CIP}) + H(\text{THF})]$. Enthalpy corrections to absolute energies at 298K were determined from B3LYP/6-31G* frequencies scaled by 0.9815. Experimental values determined by UV-visible spectroscopy as described in the indicated references.

At B3LYP/6-31G*, the ΔH_{IPS} value of **87_C** (-1.2 kcal/mol) was found to be roughly 3 kcal/mol more exothermic than that of **86_C** and **85_C** (both at +1.9 kcal/mol). This basic pattern in ΔH_{IPS} ($\Delta H_{\text{IPS}}(\mathbf{85}) \sim \Delta H_{\text{IPS}}(\mathbf{86}) > \Delta H_{\text{IPS}}(\mathbf{87})$) is also seen in values calculated from B3LYP/6-31+G*, mPW1PW91/6-31G*, and MP2/6-31G* single-point energies (Table 3.4). Thus despite varying basis set size, density functional, and method all these calculations match the experimental observation that ΔH_{IPS} (**87**) is most exothermic. However, the B3LYP/6-31G* ΔH_{IPS} values for **85_C**•(THF)₃ – **87_C**•(THF)₃ are 6 - 8 kcal/mol less exothermic than indicated by experiment. Furthermore, the range of calculated ΔH_{IPS} values (1.8 to 3.1 kcal/mol, depending on the method) is somewhat smaller than that seen in the experimental ΔH_{IPS} values (5.4 kcal/mol).

3.10 Transition Structures for Ion Pair Separation

With the ground state CIPs and SSIPs geometries in hand, we decided to locate the transition structures that interconvert these species. Interconversion of ion pairs has been proposed to occur via an associative mechanism by Reich and coworkers when they studied the IPS of bis(3,5-bis(trifluoromethyl)phenylthio)methyl lithium **72** in THF using NMR spectroscopy. Their calculation showed a relatively low barrier with a $\Delta G^\ddagger$ of 5.3 kcal/mol (Scheme 3.16).⁶³



Scheme 3.16: IPS of bis(3,5-bis(trifluoromethyl)phenylthio)methyl lithium in THF⁶³

Ion pair separation is formally a ligand exchange on lithium. Computational studies addressing the exchange of different ligands on lithium (water,⁶⁴ ammonia,⁶⁴ and DMSO⁶⁵) have been reported by van Eldik and coworkers with the first of these studies reporting the ligand exchange of water and ammonia on lithium at B3LYP/6-311+G**.⁶⁴

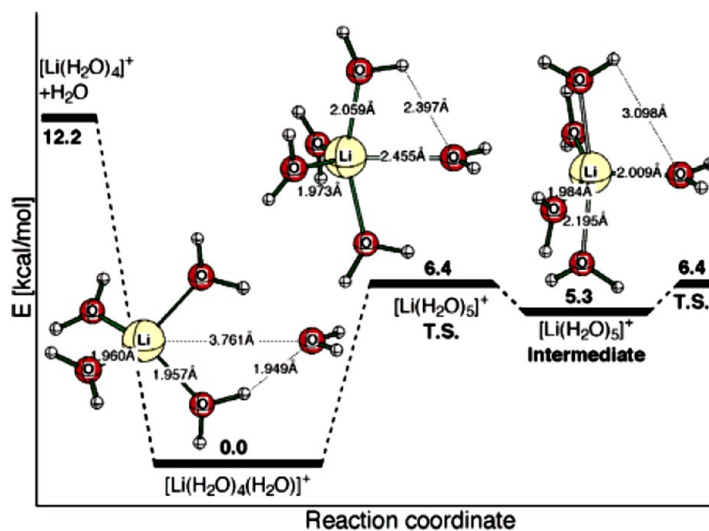


Figure 3.21: Reaction coordinate for ligand exchange of water in the lithium-water complex (Reprinted with permission from Puchta, R.; Galle, M.; Hommes, N. V.; Pasgreta, E.; van Eldik, R. *Inorg. Chem.* **2004**, *43*, 8227-8229. Copyright 2004 American Chemical Society.)

The first structure along the reaction coordinate for the lithium-water system comprised of separated reactants $\text{Li}(\text{H}_2\text{O})_4^+$ and H_2O which had a relative energy of +12.2 kcal/mol (Figure 3.21). The global minimum along this reaction coordinate was the tetrakis(H_2O) $\text{Li}^+/\text{H}_2\text{O}$ precursor complex which was stabilized by hydrogen bonding between the incoming water molecule and a water molecule of the $\text{Li}(\text{H}_2\text{O})_4^+$ complex. This complex then formed a penta-coordinated intermediate $[[\text{Li}(\text{H}_2\text{O})_5]^+ \text{ intermediate}]$ via a transition structure $[[\text{Li}(\text{H}_2\text{O})_5]^+ \text{ TS}]$ which had a barrier of +6.4 kcal/mol. This intermediate was calculated to be a true minimum with zero imaginary frequencies and was +5.4 kcal/mol higher in energy than the precursor $[\text{Li}(\text{H}_2\text{O})_4(\text{H}_2\text{O})]^+$ complex.

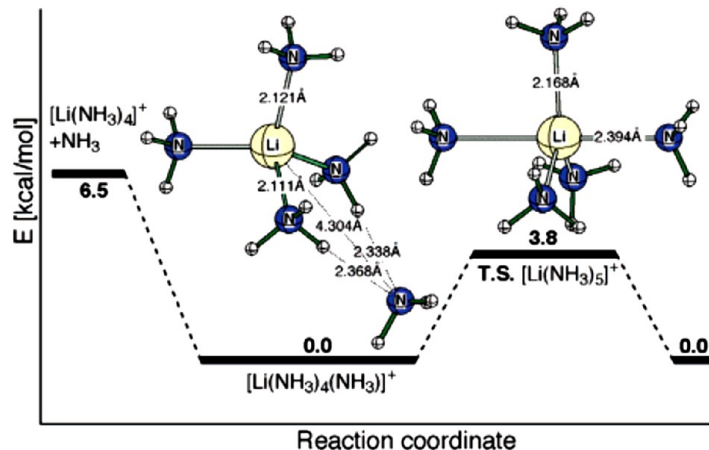
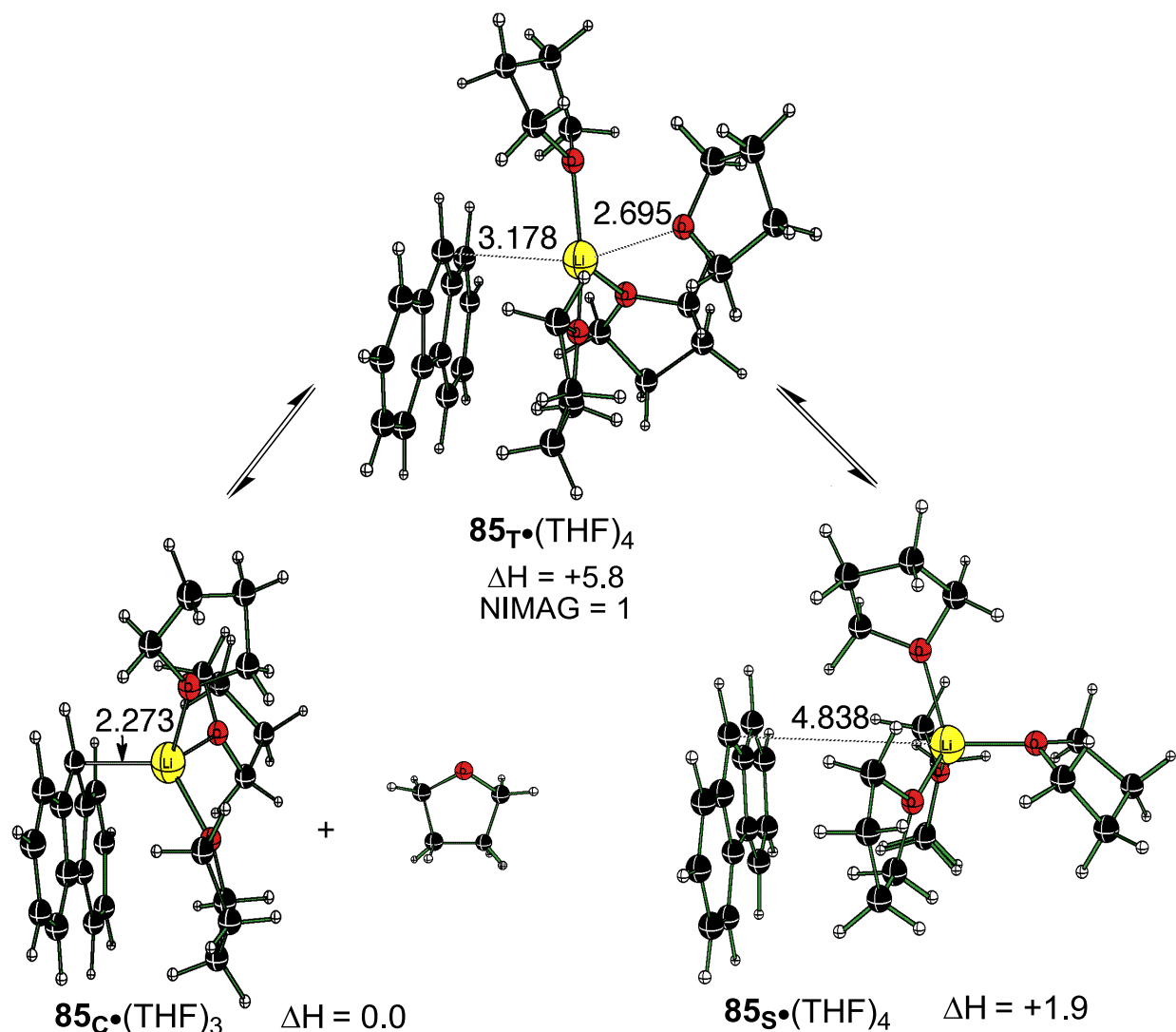


Figure 3.22: Reaction coordinate for ligand exchange of ammonia in the lithium-water complex (Reprinted with permission from Puchta, R.; Galle, M.; Hommes, N. V.; Pasgreta, E.; van Eldik, R. *Inorg. Chem.* **2004**, 43, 8227-8229. Copyright 2004 American Chemical Society.)

Similarly, exchange of NH_3 ligands in $\text{Li}(\text{NH}_3)_4^+$ was studied computationally (Figure 3.22). The highest energy structures along the reaction coordinate again comprised of the separated reactants $\text{Li}(\text{NH}_3)_3^+$ and NH_3 which had a relative energy of +6.5 kcal/mol. The lithium-ammonia precursor complex $[\text{Li}(\text{NH}_3)_4(\text{NH}_3)]^+$ was again found to be the lowest energy structure along the reaction coordinate, however unlike in the case of water, no penta-coordinate minimum was observed for the lithium-ammonia complex. The ligand exchange transition structure $\text{Li}(\text{NH}_3)_5^+$ had a barrier of 3.8 kcal/mol. Exchange of DMSO on $\text{Li}(\text{DMSO})_4^+$ also proceeds through a pentacoordinate associative transition structure.⁶⁵ However, unlike the H_2O and NH_3 systems, the lowest energy structure on the potential structure was the separated $\text{Li}(\text{DMSO})_4^+$ and DMSO. A complex between these species was 3.3 kcal/mol higher in energy. All these exchange reactions had low ligand exchange barriers in the range of 4-7 kcal/mol, and an associative mechanism was found to be feasible in all cases.

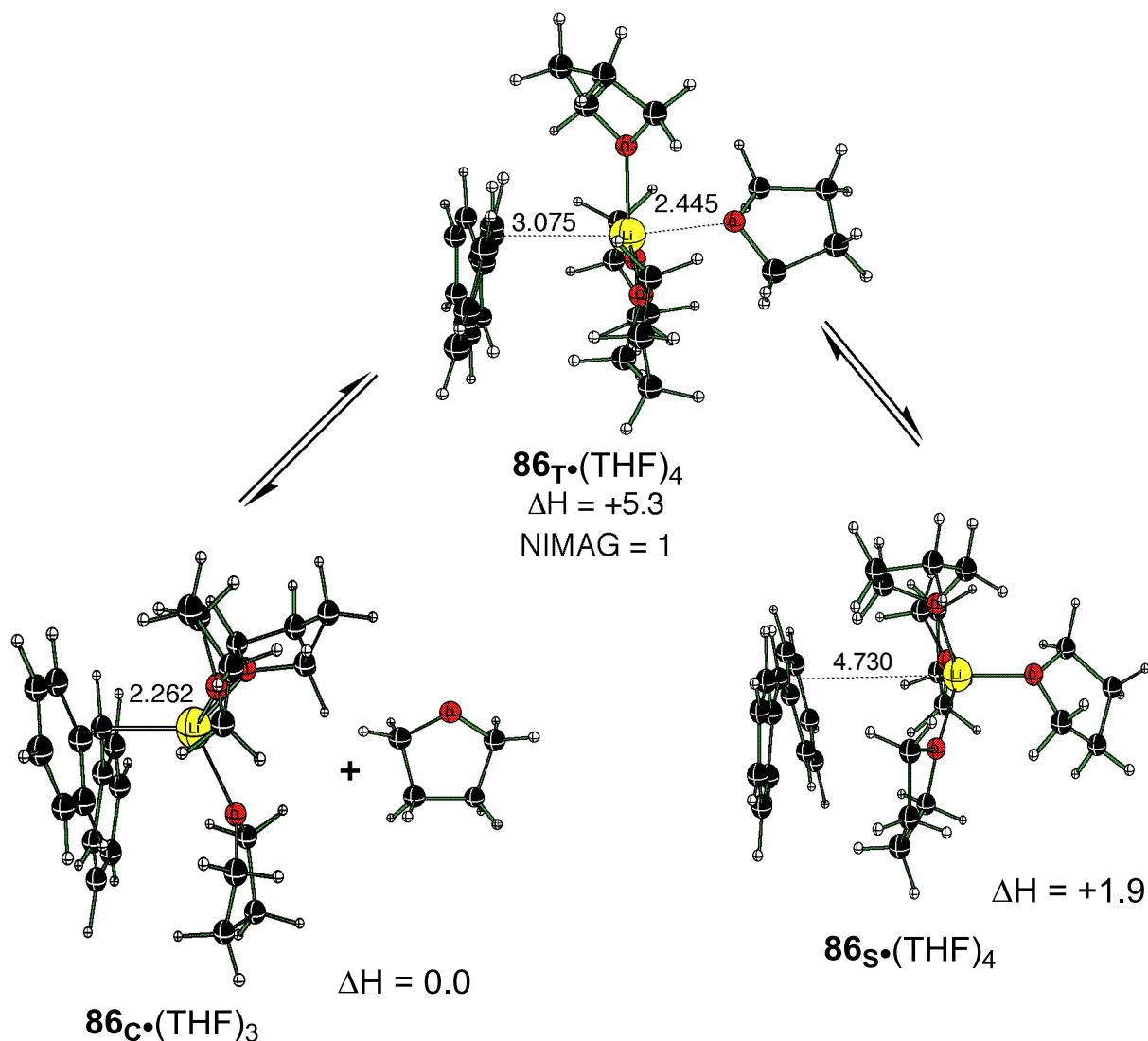
We located transition structures for all three systems $85_{\text{T}} \cdot (\text{THF})_4 - 87_{\text{T}} \cdot (\text{THF})_4$ which interconvert the CIPs and SSIPs. All systems were found to ion pair separate via associative

transition states as precedent in the literature, however unlike in case of the ligand exchange transition structures for the lithium cation, we did not locate a penta coordinate precursor complex or the penta coordinate intermediate structure. The sole imaginary frequency of each of the IPS transition structures corresponded to the simultaneous breaking of the C_α-Li bond and formation of a Li-O bond due to coordination of a fourth THF ligand. Scheme 3.17 shows the reaction coordinate for **85**_C•(THF)₃ at B3LYP/6-31G*.



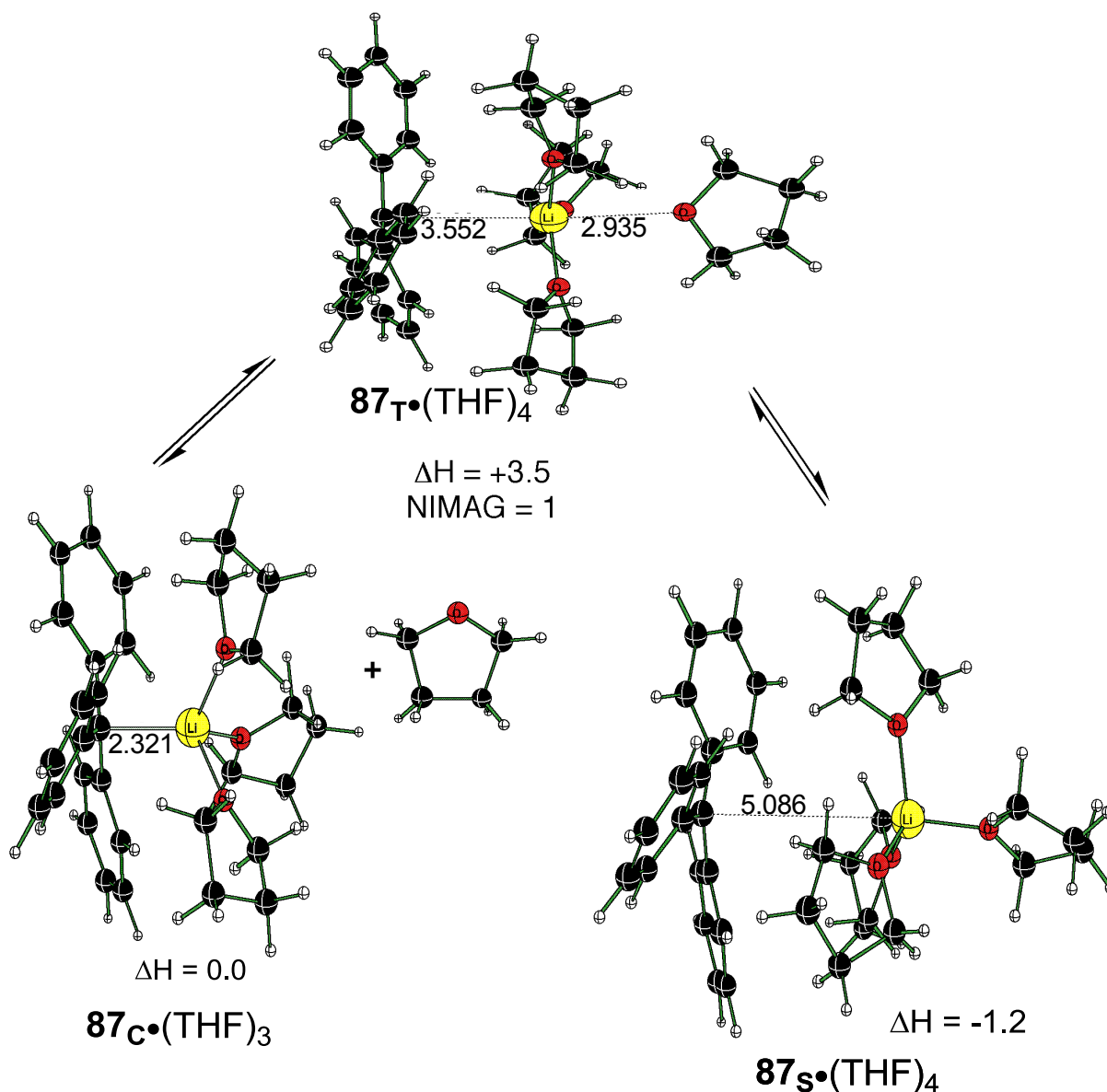
Scheme 3.17: B3LYP/6-31G* reaction coordinate for ion pair separation of **85**_C•(THF)₃. Enthalpies are shown in kcal/mol and are relative to the sum of **85**_C•(THF)₃ and THF. NIMAG = number of imaginary frequencies.

An increase in C_α-Li bond distance was observed (2.273 Å in **85_C**•(THF)₃ to 3.178 Å in **85_T**•(THF)₄). The incoming THF molecule also has a significantly longer Li-O distance compared to the other three THF ligands (2.695 Å vs average O-Li 1.964 Å). A low enthalpy barrier $\Delta H_{\text{IPS}}^\ddagger$ of 5.8 kcal/mol was found for IPS of **85_C**•(THF)₃ (Scheme 3.17).



Scheme 3.18: B3LYP/6-31G* reaction coordinate for ion pair separation of **86_C**•(THF)₃. Enthalpies are shown in kcal/mol and are relative to the sum of **86_C**•(THF)₃ and THF. NIMAG = number of imaginary frequencies.

The same trend was observed for the IPS of $86_{\text{C}}\bullet(\text{THF})_3$ (Scheme 3.18). An increase in the $\text{C}_\alpha\text{-Li}$ distance was observed from 2.262 Å to 3.075 Å, and a larger Li-O distance for the incoming THF was 2.445 Å compared to the average Li-O distance of 2.152 Å for the other three THF ligands.



Scheme 3.19: B3LYP/6-31G* reaction coordinate for ion pair separation of $87_{\text{C}}\bullet(\text{THF})_3$. Enthalpies (ΔH) are shown in kcal/mol and are relative to the sum of $87_{\text{C}}\bullet(\text{THF})_3$ and THF. NIMAG = number of imaginary frequencies.

A similar result was observed for **87_C**•(THF)₃ (Scheme 3.19), with the C_α-Li distance increasing from 2.321 Å in **87_C**•(THF)₃ to 2.935 Å in **87_T**•(THF)₄, and the Li-O distance as 2.935 Å for the incoming THF versus 1.940 Å average O-Li for the other three THF ligands. The enthalpy barrier for IPS ($\Delta H_{\text{IPS}}^\ddagger$) of **87_C**•(THF)₃ was calculated as 3.5 kcal/mol, which was lower than the barriers for IPS for the other two systems (+5.8 kcal/mol for **85_C**•(THF)₃ and +5.3 kcal/mol for **86_C**•(THF)₃). Thus, the low activation barriers for all the three systems support the feasibility of an associative IPS mechanism. To the best of our knowledge, **85_T**•(THF)₄ - **87_T**•(THF)₄ are the first transition structures for IPS of organolithium compounds to be characterized computationally.

3.11 Thermodynamic Cycle

As discussed earlier, our calculated ΔH_{IPS} values in vacuo deviate from experimental solution values in overall exothermicity and range (Table 3.4). Another interesting finding is that whereas application of MP2/6-31G* single-point energies rendered the third solvation of CIPs **85_C** - **87_C** 6 - 11 kcal/mol more exothermic than predicted at B3LYP/6-31G* (Table 3.3, ΔH_{solv3}), values of ΔH_{IPS} at B3LYP/6-31G* and MP2/6-31G*//B3LYP/6-31G* lie within 1.3 kcal/mol of each other (Table 3.4). These observations prompted us to further investigate the ion pair separation process by isolating the key bond breaking, making, and ionic association steps (Figure 3.23).

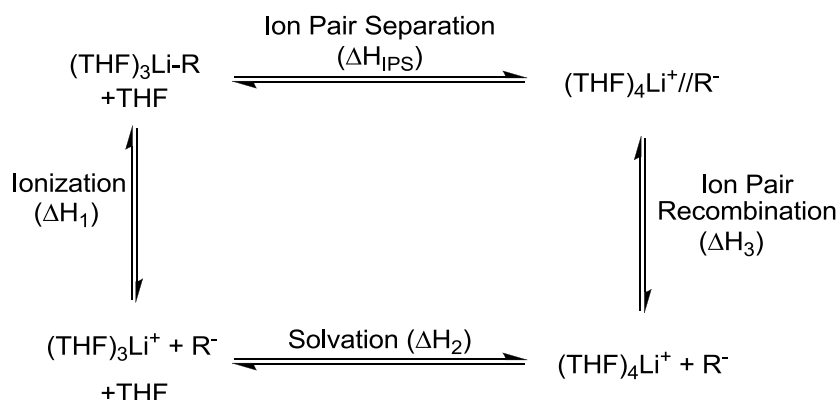


Figure 3.23: Thermodynamic cycle for ion pair separation of THF-solvated organolithiums

The thermodynamic cycle depicted in Figure 3.23 breaks ion pair separation into three steps: 1) ionization (ΔH_1) of the $\text{C}_\alpha\text{-Li}$ bond to give a trisolvated lithium cation $(\text{THF})_3\text{Li}^+$ and carbanion R^- ; 2) solvation (ΔH_2) of the trisolvated lithium cation by a fourth THF ligand to get a tetrasolvated lithium cation $(\text{THF})_4\text{Li}^+$; 3) ion pair recombination (ΔH_3) of the isolated tetrasolvated lithium cation and carbanion R^- to form theSSIP.

Table 3.5: Calculated ΔH_1 , ΔH_2 , ΔH_3 and ΔH_{IPS} for $\mathbf{85C^\bullet(THF)_3}$ - $\mathbf{87C^\bullet(THF)_3}$ in kcal/mol at B3LYP/6-31G* and MP2/6-31G**/B3LYP/6-31G* (values in parenthesis)^a

	85 (R = Fl)	86 (R=DPM)	87 (R=Tr)
ΔH_1^b	+82.5 (+100.7)	+81.2 (+100.6)	+74.7 (+98.7)
ΔH_2^c	-16.3 (-22.8)	-16.3 (-22.8)	-16.3 (-22.8)
ΔH_3^d	-64.2 (-76.6)	-62.9 (-75.8)	-59.5 (-75.8)
ΔH_{IPS}^e	+1.9 (+1.3)	+1.9 (+1.9)	-1.2 (+0.1)

^aSee Figure 3.23 for graphical representations of ΔH_1 , ΔH_2 , and ΔH_3 . Enthalpic corrections to absolute energies determined from B3LYP/6-31G* frequencies scaled by 0.9815. ^b $\Delta H_1 = [\text{H}(\text{R}^-) + \text{H}((\text{THF})_3\text{Li}^+)] - \text{H}(\text{CIP})$. ^c $\Delta H_2 = \text{H}((\text{THF})_4\text{Li}^+) - [\text{H}((\text{THF})_3\text{Li}^+) + \text{H}(\text{THF})]$. ^d $\Delta H_3 = \text{H}(\text{SSIP}) - [\text{H}(\text{R}^-) + \text{H}((\text{THF})_4\text{Li}^+)]$. ^e $\Delta H_{\text{IPS}} = \Delta H_1 + \Delta H_2 + \Delta H_3$.

3.11.1 Ionization

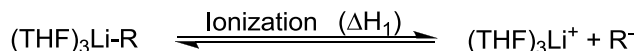
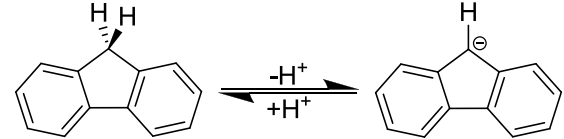
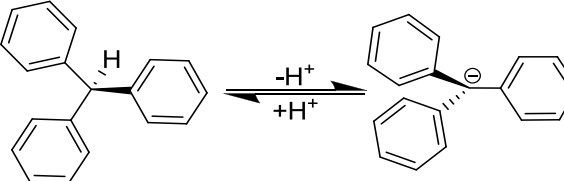
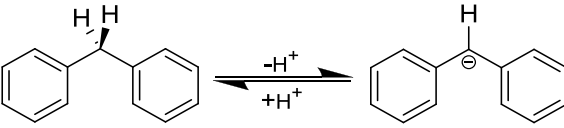


Figure 3.24: Ionization of the CIPs

As can be seen in Table 3.5, the ionization of trityllithium **87_C**•(THF)₃ is least endothermic at +74.7 kcal/mol at B3LYP/6-31G*; the ionization of diphenylmethyllithium **86_C**•(THF)₃ and fluorenyllithium **85_C**•(THF)₃ was 6 - 8 kcal/mol more endothermic at +81.2 and +82.5 kcal/mol, respectively. This trend in ionization enthalpy (ΔH_1) matches the trend in observed experimental values for ΔH_{IPS} : trityl < diphenylmethyl ~ fluorenyl.

In an attempt to assess the relative contribution of electronic effects in these ionization energies (ΔH_1) of **85_C**-**87_C**, we sought to assess the relative stabilities of the carbanionic fragments formed upon ionization. We thus calculated the relative energies for proton loss from fluorene (Fl-H), diphenylmethane (DPM-H), and triphenylmethane (Tr-H, Table 3.6). Fluorene is calculated to be the most acidic; loss of a proton from triphenylmethane is slightly more endoenergetic (relative $\Delta E^a = +1.4$ kcal/mol), followed by diphenylmethane (relative $\Delta E^a = +10.3$ kcal/mol). These calculated energies for proton loss (relative ΔE^a) match the trend in experimental pK_A (DMSO) for the three hydrocarbons (Table 3.6), and confirm that the fluorenyl anion is the most stable of the three, and that the diphenylmethyl anion is the least stable.

Table 3.6: Relative energies for proton loss from Fl-H, DPM-H, and Tr-H and published pK_A values (DMSO)

	Rel. ΔE^a (kcal/mol)	Exptl pK _A
	0.0	22.6 ⁶⁶
	1.4	30.6 ⁶⁶
	10.3	32.3 ⁶⁷

^aElectronic Energy ΔE defined as $E(\text{carbanion} + \text{H}^+) - E(\text{hydrocarbon})$ in kcal/mol at B3LYP/6-31G*. Energies shown are relative to ΔE of fluorene.

In DMSO, Fl-H is the most acidic ($\text{pK}_A = 22.6$),⁶⁶ reflecting aromatic stabilization gained in the carbanion; DPM-H and Tr-H are 8-10 orders of magnitude less acidic ($\text{pK}_A = 32.3$ ⁶⁶ and 30.6⁶⁷ respectively). It should be noted however, that while our Rel. ΔE values explained the trends observed between Fl-H and DPM-H, it does not account for the 10⁸ order acidity decrease from Fl-H to Tr-H. That fluorenyllithium **85**C•(THF)₃ has the most endothermic ΔH_1 among diphenylmethyllithium **86**C•(THF)₃ and trityllithium **87**C•(THF)₃ therefore suggests that steric effects play an important role in ionization of the C_a-Li bond. Bulky trityllithium **87**C•(THF)₃ would enjoy greatest loss of steric compression on ionization, and correspondingly has the least endothermic ΔH_1 value. To further assess electronic effects, we looked at the Mulliken charges at the carbanionic carbon (C_a) for the CIP, SSIP and the corresponding carbanions (Table 3.7).

Table 3.7: Mulliken charges on the anion, CIPs and SSIPs of Fl^- , DPM^- and Tr^-

Mulliken Charges	
	C_α
Fl^-	-0.346
FlLi(THF)_3	-0.477
FlLi(THF)_4	-0.366
DPM^-	-0.418
DPMLi(THF)_3	-0.508
DPMLi(THF)_4	-0.423
Tr^-	-0.147
TrLi(THF)_3	-0.270
TrLi(THF)_4	-0.156

Examining the anions, the greatest C_α charge density was observed for DPM^- and the least for the Tr^- anion, as was expected on the basis of resonance and aromaticity. Within each series, the CIPs had the greatest charge localization on the C_α carbons as expected with significantly greater charge densities than the SSIPs or the anions. For all three systems, there was a slight increase in charge density going from the anion to the SSIPs, which may reflect Coulombic attraction of C_α to the distant solvated lithium cation.

3.11.2 Solvation

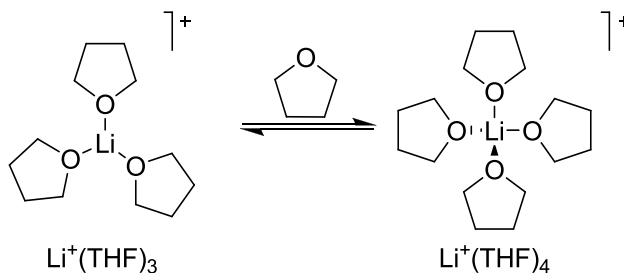


Figure 3.25: Solvation of trisolvated lithium cation to the tetrasolvated lithium cation

Next, we looked at solvation (ΔH_2) of the trisolvated lithium cation by a fourth THF molecule to form the tetrasolvated lithium cation (Figure 3.25). As expected, this process is highly exothermic with ΔH_2 being -16.3 kcal/mol at B3LYP/6-31G* in vacuum. This value, since it is calculated without an anionic fragment, applies equally to the **85** - **87**.

3.11.3 Ion Pair Recombination

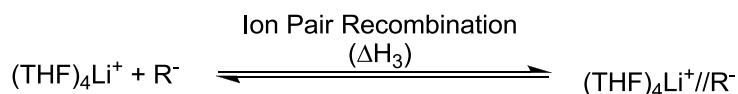


Figure 3.26: Ion pair recombination to theSSIP

Lastly, we looked at the ion pair recombination step (ΔH_3) to assess its contribution to the overall ion pair separation process. As expected, ion pair recombination is highly exothermic, reflecting strong ionic interaction in the SSIP ($\Delta H_3 = -59.5$ to -64.2 kcal/mol; Table 3.5). The trend obtained for ΔH_3 was opposite to the trend of ΔH_1 ; this reversal was expected, as the two are complementary reactions. Thus, just as ionization (ΔH_1) is least endothermic for **87_C**, ion pair recombination (ΔH_3) is the least exothermic for **87_S**.

Finally, we note that the aforementioned trends in ΔH_1 , ΔH_2 , and ΔH_3 at B3LYP/6-31G* are also seen at MP2/6-31G*//B3LYP/6-31G*. As was seen for ΔH_{SOLV3} , the magnitudes of ΔH_1 , ΔH_2 , and ΔH_3 at MP2/6-31G*//B3LYP/6-31G* are considerably larger than they are at B3LYP/6-31G*. However, as Table 3.5 illustrates, the sum of the bond-breaking (ΔH_1), bond-making (ΔH_2), and ionic association steps (ΔH_3) gives nearly identical values of ΔH_{IPS} at both B3LYP/6-31G* and MP2/6-31G*//B3LYP/6-31G*.

3.12 Application of Solvent Continuum Models to the Ion Pair Separation of Explicit Solvates: Comparison to X-Ray Structure

To this point we have attempted to match experimental enthalpies for ion pair separation of **85** – **87** in THF solution by modeling explicit THF solvates in vacuo. These vacuum calculations match the experimental observations that IPS of trityllithium **87_C** is more exothermic than that of diphenylmethyllithium **86_C** or fluorenyllithium **85_C**. However, as noted above, B3LYP/6-31G* values of ΔH_{IPS} are 6 - 8 kcal/mol less endothermic than the experimental values. It should be noted that the B3LYP/6-31G* optimized geometry of **85_C**•(THF)₃ matches the X-ray crystal structure well (cf. Figure 3.18 and 3.27), as we noted earlier (Section 3.9.3).

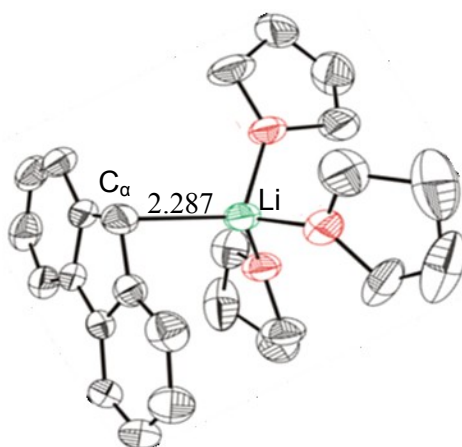


Figure 3.27: Anisotropic displacement ellipsoid drawing (50%) of X-ray crystal structure of **85_C**•(THF)₃ [CCDC No. 114095].⁵² C_α-Li bond length is shown in Å.

The discrepancy in ΔH_{IPS} values, combined with the observation of widely disparate C_α-Li distances in the X-ray (6.854 Å)⁵⁷ and calculated B3LYP/6-31G* (5.086 Å) structures of **87_S**•(THF)₄, suggested that vacuum modeling of SSIPs might not well reflect their solution structures and energies (cf. Figure 3.20 and 3.28).

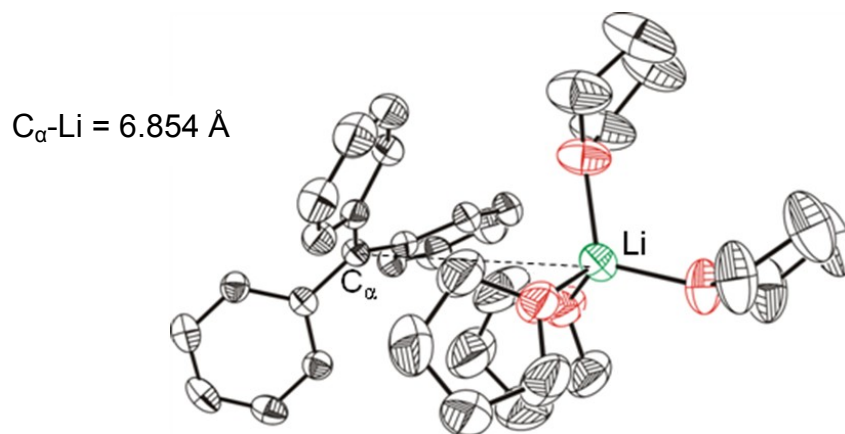


Figure 3.28: Anisotropic displacement ellipsoid drawing (50%) of X-ray crystal structure of **87s•**(THF)₄ [CCDC No. 247992].⁵⁷

It seemed likely that dielectric effects could affect the optimum C_{α} -Li distance in **87s•**(THF)₄, and thus in large part be responsible for the difference seen between the X-ray and calculated vacuum structures.

3.13 Constrained Optimization

To rule out the possibility that the discrepancy in C_{α} -Li distances was due to an extremely flat B3LYP/6-31G* potential surface, we performed constrained geometry optimizations on **87s•**(THF)₄, increasing the C_{α} -Li distance in steady increments from the vacuum value of 5.086 Å to 6.8 Å, close to the value seen by X-ray crystallography. Geometry optimizations were performed at B3LYP/6-31G*. Single-point energy calculations were undertaken at MP2/6-31G*. Incorporation of solvation effects was done by single-point calculations at B3LYP/6-31G*(PCM), B3LYP/6-31G*(Onsager) and MP2/6-31G*(PCM). Relative energies obtained are shown in Table 3.8.

Table 3.8: Relative electronic energies from single-point calculations on the C_α-Li distance constraint from 5.2 to 6.8 Å for **87**_S•(THF)₄. All constrained optimizations at B3LYP/6-31G*^a

C _α -Li (Å)	B3LYP/ 6-31G*	BL3YP/6-31G* (PCM) ^b	B3LYP/6-31G* (Onsager) ^c	MP2/6-31G*	MP2/6-31G* (PCM) ^b
5.086	0.0	0.0	0.0	0.0	0.0
5.2	0.01	-0.25	-0.29	0.51	0.25
5.3	0.10	-0.43	-0.43	0.83	0.30
5.4	0.28	-0.55	-0.52	1.39	0.55
5.5	0.55	-0.56	-0.57	2.11	0.98
5.6	0.89	-0.72	-0.58	.97	1.32
5.7	1.32	-0.67	-0.54	3.92	1.90
5.8	1.85	-0.64	-0.47	4.91	2.38
5.9	2.37	-0.43	-0.35	6.02	3.04
6.0	3.00	-0.54	-0.29	7.18	3.61
6.4	5.36	-0.07	0.15	11.10	5.62
6.8	7.78	0.40	0.44	14.38	6.99

^aAll energies relative to the electronic energy of **87**_S•(THF)₄ at B3LYP/6-31G*

^bPCM calculations done with options: Solvent=THF, Radii=Pauling, Surface=SES

^cRadius (a₀) of 6.52 Å used from B3LYP/6-31G* vacuum optimized geometry of **87**_S•(THF)₄

At B3LYP/6-31G* this 1.714 Å increase in C_α-Li distance raised the energy by nearly 8 kcal/mol; an even larger increase of 14 kcal/mol was seen with MP2/6-31G* single-point energies. These data are shown graphically in Figure 3.29.

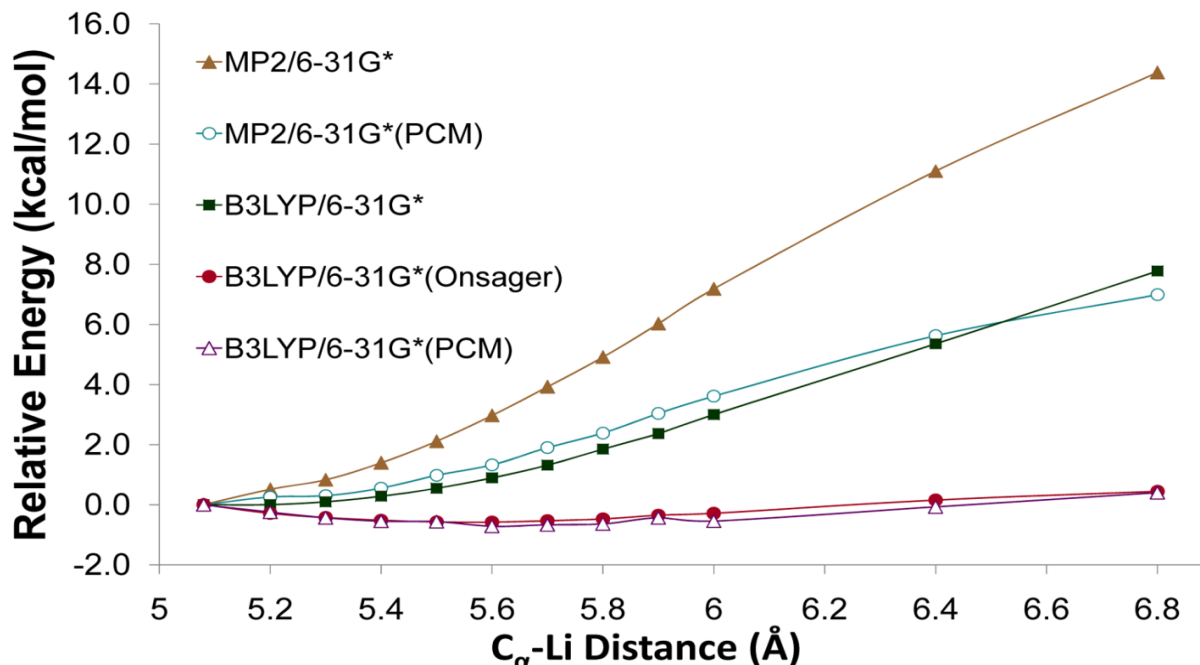


Figure 3.29: Single-point energies of B3LYP/6-31G* constrained optimized geometries of **87_S**•(THF)₄ as a function of the C_α-Li distance constraint, relative to the corresponding energy at the optimized geometry (C_α-Li = 5.086 Å). Onsager and PCM single-points were performed at the dielectric constant of THF ($\epsilon = 7.58$).

Thus in vacuum the potential surface of **87_S**•(THF)₄ along the C_α-Li axis is *not* flat. However, application of B3LYP/6-31G*(Onsager) and B3LYP/6-31G*(PCM) single-point energies (THF $\epsilon = 7.58$) dramatically flattened the potential surface along the C_α-Li axis: increasing the distance by 1.714 Å in these cases raised the energies by only 0.4 kcal/mol (both methods). Such a flat potential surface could easily explain the C_α-Li distance of 6.854 Å seen in the X-ray structure of **87_S**•(THF)₄. Finally, although relative single-point energies at MP2/6-31G*(PCM) are roughly half of those at MP2/6-31G*, at a C_α-Li distance of 6.8 Å the relative energy is still 7 kcal/mol higher in energy than at the 5.086 Å structure. Thus MP2/6-31G*(PCM) single-point energies cannot be used to rationalize the solid state structure of **87_S**•(THF)₄.

Since among all the methods examined, the C_α-Li distance in the X-ray structure of **87**_S•(THF)₄ could only be rationalized in terms of B3LYP/6-31G*(Onsager) and B3LYP/6-31G*(PCM) single-point energies, we used these methods to calculate single-point energies at the B3LYP/6-31G* vacuum geometries of **85**_C•(THF)₃ - **87**_C•(THF)₃, **85**_S•(THF)₄ - **87**_S•(THF)₄, and THF. Because SSIPs are more highly ionized than CIPs, it seemed likely that application of these continuum solvation models might render ΔH_{IPS} more exothermic than seen in vacuum. Happily, this expectation was at least partially realized (Table 3.9).

Table 3.9: Experimental ΔH_{IPS} and calculated ΔH_{IPS}^a from Onsager and PCM single-point calculations at B3LYP/6-31G* and B3LYP/6-31G*(Onsager) geometries. (298 K, kcal/mol)

$$\text{R-Li(THF)}_3 + \text{THF} \xrightleftharpoons{\Delta H_{\text{IPS}}} \text{R}^\cdot/\text{Li}^+(\text{THF})_4$$

Entry	Method	85 (R = F1)	86 (R=DPM)	87 (R=Tr)
1	Experimental	-3.8 ± 1.0 ³⁷	-5.4 to -6.1 ³⁹	-9.2 ⁴⁰
2	B3LYP/6-31G*	+1.9	+1.9	-1.2
3	B3LYP/6-31G*(Onsager)// B3LYP/6-31G*	-1.0 ± 2.4 ^b	-1.8 ± 2.6 ^b	-5.5 ± 3.0 ^b
4	B3LYP/6-31G*(PCM)// B3LYP/6-31G*	+1.8	+0.9	-2.1
5	B3LYP/6-31G*(Onsager)	-2.3 ± 3.4 ^b	-2.8 ± 3.8 ^b	-6.9 ± 4.4 ^b
6	B3LYP/6-31G*(PCM)// B3LYP/6-31G*(Onsager)	+0.8	-0.3	-3.4

^aEnthalpy value ΔH_{IPS} = H(SSIP) - [H(CIP) + H(THF)]. Enthalpy corrections to absolute energies at 298K were determined from B3LYP/6-31G* frequencies scaled by 0.9815. Experimental values determined by UV-visible spectroscopy as described in the indicated references. ^bThe reported uncertainty in Onsager energy-based ΔH_{IPS} values stems from uncertainty in the radii a₀ of the spherical cavities used for the energy calculations on the CIPs, THF, and SSIPs. See Computational Methods section for complete details.

Application of Onsager single-point energies at the vacuum geometries rendered mean ΔH_{IPS} values 3 - 4 kcal/mol more exothermic than the vacuum-based values (Table 3.9, cf. entries 3 and 2). We would stress that thermochemical calculations based on Onsager energies should generally be viewed with caution, due to uncertainty in the Onsager cavity radius a_0 (see Computational Methods section). However, based on our estimates of uncertainty, these calculated enthalpies are distinguishably more exothermic than their vacuum counterparts.

With PCM single-point energies the experimental trend was reproduced and the IPS of **85C**•(THF)₃ was less exothermic than that of **86C**•(THF)₃. Along with the reproduction of the experimental trend, little change was observed for the ΔH_{IPS} value of **85C**•(THF)₃, but the corresponding values for **86C**•(THF)₃ and **87C**•(THF)₃ are 1 kcal/mol lower than the vacuum values (Table 3.9, cf. entries 4 and 2). These increased exothermicities prompted us to look at the effects of incorporating implicit solvation *during* the geometry optimizations.

Since B3LYP/6-31G* optimization under PCM was unsuccessful for these large explicit solvates, B3LYP/6-31G* geometry optimizations were performed with the Onsager solvation model. These Onsager-optimized geometries showed relatively minor changes for all the CIP structures, with an average 0.03 Å increase in C _{α} -Li bond length (Figure 3.30).

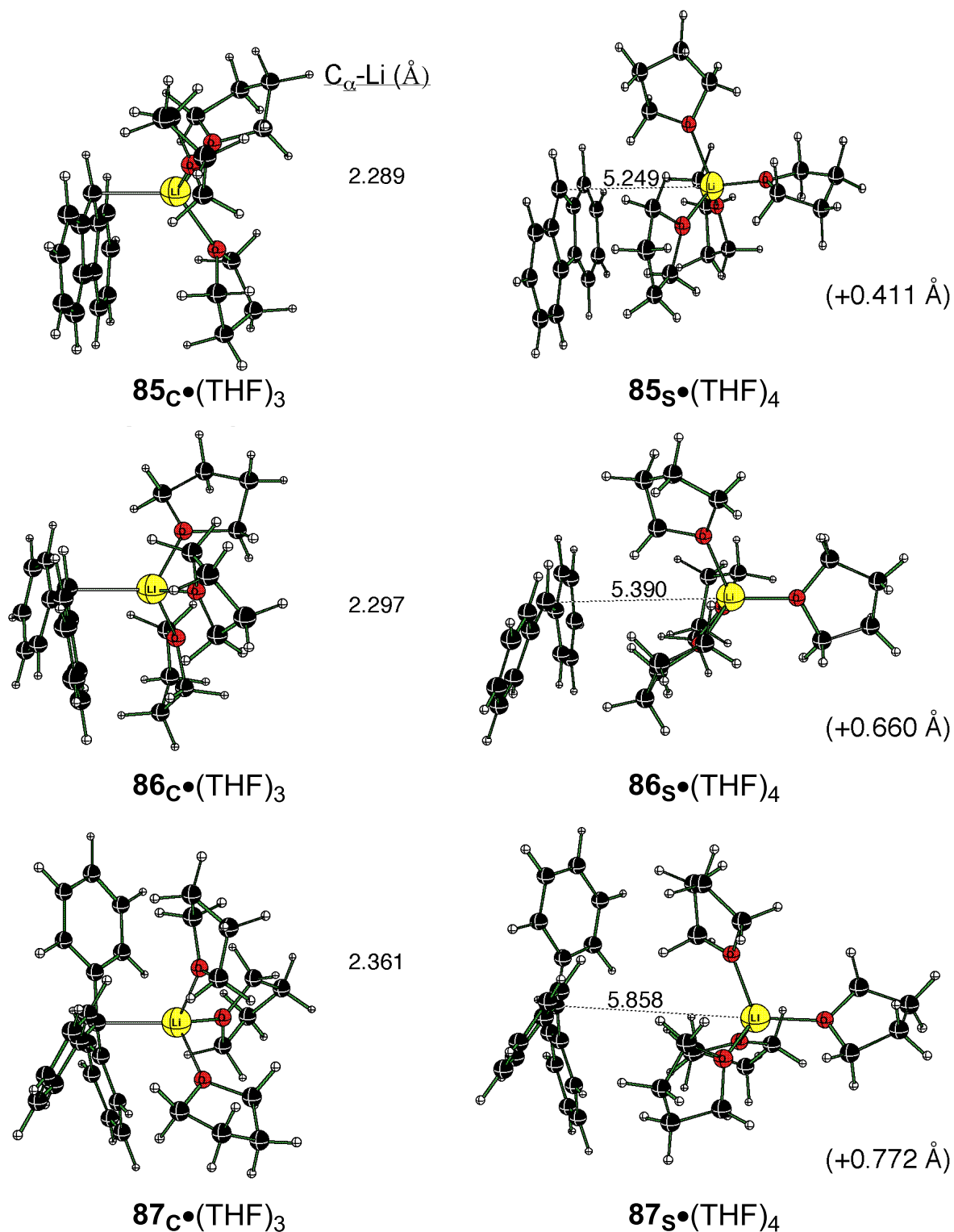


Figure 3.30: B3LYP/6-31G*(Onsager) optimized geometries of CIPs and SSIPs for **85**-**87**. Bond lengths are shown in Å and increases in the C $_{\alpha}$ -Li distance from the vacuum B3LYP/6-31G* geometries are given in parenthesis (cf. Figure 3.18 and 3.20).

In contrast, major changes were observed in the SSIP geometries, with C_α -Li contact distances increasing by 0.411 to 0.585 Å (Figure 3.30). The greatest increase in C_α -Li contact distance (0.585 Å) was seen for **87s**•(THF)₄, which contains the bulkiest carbanion; the smallest increase (0.411 Å) was seen for **85s**•(THF)₄, which contains the smallest carbanion. It is interesting to note that the C_α -Li distance of 5.671 Å seen in the B3LYP/6-31G*(Onsager) optimized geometry of **87s**•(THF)₄ (Figure 3.30) is close to the minima of the B3LYP/6-31G*(Onsager) and B3LYP/6-31G*(PCM) single-point energy curves depicted in Figure 3.29 (C_α -Li = 5.6 Å).

Accompanying the increases in C_α -Li distance for **85s**•(THF)₄ - **87s**•(THF)₄ seen upon incorporating Onsager solvation during optimization, mean ΔH_{IPS} values at B3LYP/6-31G*(Onsager) are rendered 4 – 6 kcal/mol more exothermic than in vacuum (Table 3.9, cf. entries 5 and 2). PCM single-point energies at B3LYP/6-31G* (Onsager) geometries render ΔH_{IPS} values 1.1 to 2.2 kcal/mol more exothermic than in vacuum (Table 3.9, cf. entries 6 & 2). Looking at the values in Table 3.9, the apparent superiority of mean Onsager energies over PCM energies to reproduce experimental ΔH_{IPS} values (Table 3.9, cf. entries 5 vs 6 and 1) is intriguing, but we believe, accidental. Firstly, the PCM cavity is more physical, corresponding much more closely to the shape of the solute than the spherical cavity used in Onsager calculations. Secondly, we would note that B3LYP/6-31G*(PCM)/B3LYP/6-31G*(Onsager)-based values of ΔH_{IPS} (Table 3.9, entry 6) in each case fall within the range of values calculated at B3LYP/6-31G* (Onsager) (Table 3.9, entry 5).

3.14 Stabilization Due to Implicit Solvation

Greater stabilization of the SSIPs compared to the CIPs also invoked a question of which component of the SSIP structure preferentially benefitted from this extra stabilization – the

anionic or the cationic portion. While it is not possible for us to assess this preferential stabilization within the structure, we analyzed the effects of implicit solvation on the different the cationic and anionic fragments: the three carbanions (FI⁻, DPM⁻ and Tr⁻) and the tri and tetrasolvated cations. We performed PCM single-point calculations at B3LYP/6-31G* method and basis. The relative energy stabilization on incorporation of the effects of implicit solvation is shown in Table 3.10

Table 3.10: Stabilization by B3LYP/6-31G*(PCM)//B3LYP/6-31G* calculations for all systems studied

System	ΔE_{PCM}^a		
	FI	DPM	Tr
R-Li(THF) ₃	-10.2	-9.5	-10.5
R ⁻ //Li ⁺ (THF) ₄	-14.5	-14.1	-15.5
R ⁻	-43.6	-42.4	-39.4
Li ⁺ (THF) ₃	-36.7	-36.7	-36.7
Li ⁺ (THF) ₄	-34.5	-34.5	-34.5
THF	-4.1	-4.1	-4.1

^a All calculations at B3LYP/6-31G* (kcal/mol) and $\Delta E_{\text{PCM}} = (E_{\text{vacuum}} - E_{\text{PCM}})$

As can be seen in Table 3.10, both the cationic [Li⁺(THF)₄] and the anionic fragments (R⁻) enjoy considerable stabilization on application of implicit solvation. Even though the lithium cation is explicitly tetrasolvated by four THF molecules, the stabilization provided by PCM solvation model is still considerable ($\Delta E_{\text{PCM}} = -34.5$ kcal/mol). Based on these data, it is clear that both the cationic and anionic fragments of the SSIPs (and not just the anionic fragment) enjoy considerable stabilization upon application of implicit solvation.

3.15 Basis Set Superposition Error

One potential source of error in our calculations of ΔH_{IPS} is the basis set superposition error (BSSE), which is observed in cases where two fragments come together to give a single molecule as is the case in this study. There would be more basis functions employed in the calculation of theSSIP than the basis functions in the corresponding CIP and THF, leading to an artificial lowering in the reaction energy.⁶⁸



Figure 3.31: Ion pair separation

The magnitude of BSSE was estimated by performing a series of counterpoise calculations on the B3LYP/6-31G* and B3LYP/6-31G*(Onsager) geometries of the tetrakis(THF)-solvated separated ion pairs (**85s**•(THF)₄ - **87s**•(THF)₄). For each structure, multiple counterpoise corrections were performed by sequentially designating each of the bound THF molecules as the secondary fragment. These individual corrections were then averaged to give the counterpoise correction for a particular structure.

Table 3.11: Average counterpoise corrections for **85s**•(THF)₄-**87s**•(THF)₄ with one THF molecule as the secondary fragment at the B3LYP/6-31G* and B3LYP/6-31G*(Onsager) optimized geometries.^a

Method	85s •(THF) ₄	86s •(THF) ₄	87s •(THF) ₄
B3LYP/6-31G*	5.4	4.8	5.6
B3LYP/6-31G*(Onsager)	5.2	5.0	4.8

^aAll energies in kcal/mol

BSSE was calculated to be approximately 5 kcal/mol for all three systems, studied at both the vacuum and the Onsager optimized geometries. This means that our calculated values of

ΔH_{IPS} are potentially too exothermic by as much as 5 kcal/mol. Thus, the deviation of our calculated values from experiment may very well be greater than projected in Table 3.9.

3.16 Conclusions

Using DFT methods, we have modeled the reaction of (THF)-solvated benzylic organolithiums **85** - **87** with THF to give the corresponding (THF)-solvated separated ion pairs. Vacuum B3LYP/6-31G* geometry optimizations gave reasonable structures for the bis(THF)- and tris(THF)-solvated contact ion pairs of **85** - **87**, and solvation free energy calculations at MP2/6-31G**/B3LYP/6-31G* indicated that the tris(THF)-solvates **85_C•(THF)₃** - **87_C•(THF)₃** were the resting states of the contact ion pairs. Vacuum geometries of the tetrakis(THF)-solvated separated ion pairs **85_S•(THF)₄** - **87_S•(THF)₄** were located, as were low energy ($\Delta H^\ddagger = 3.5 - 5.8$ kcal/mol) associative transition states **85_T•(THF)₄** - **87_T•(THF)₄** leading to these species. Calculated enthalpies of ion pair separation (ΔH_{IPS}) for **85_C•(THF)₃** - **87_C•(THF)₃** at B3LYP/6-31G* in vacuum ranged from +1.9 to -1.2 kcal/mol.

Application of continuum solvation models (THF $\epsilon = 7.58$) was found to have a significant effect on equilibrium B3LYP/6-31G* C $_{\alpha}$ -Li distances in the SSIPs **85_S•(THF)₄** - **87_S•(THF)₄**, as one might expect for highly ionic species (Figures 3.24). The X-ray crystal structure of **87_S•(THF)₄** cannot be rationalized based on B3LYP/6-31G* or MP2/6-31G**/B3LYP/6-31G* energies; only when implicit solvation models are included at B3LYP/6-31G* can the observed 6.856 Å C $_{\alpha}$ -Li distance⁵⁷ be understood (Figures 3.23). Furthermore, we have shown that application of continuum solvation models (B3LYP/6-31G* (PCM)/B3LYP/6-31G*(Onsager)) renders ΔH_{IPS} values 1.1 to 2.2 kcal/mol more exothermic than the corresponding vacuum values, thus bringing them closer to experiment.

We believe that the principal value of our approach lies in *qualitative* rather than quantitative agreement with experiment. The gap remaining between B3LYP/6-31G*(PCM)//B3LYP/6-31G*(Onsager) and experimental values of ΔH_{IPS} (4.6 to 5.8 kcal/mol) suggests that implicit solvation models may not be able to fully account for the role of bulk solvent. To highlight this point, preliminary calculations estimate the correction for basis set superposition error (BSSE) may further increase this gap by up to 5 kcal/mol. Consideration of explicit solvent molecules outside the primary solvation shell may prove essential, suggesting that use of QM/MM/Monte Carlo^{69,70} or MD^{43,44} methods might be required to achieve closer agreement of calculated ΔH_{IPS} values with experiment.

3.17 References for Chapter 3

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Chapter 4: Conclusion

In this thesis, I applied modern quantum chemical methods to study two distinct classes of reactive intermediates. The first was the gas phase analysis of protonated epoxides which are ubiquitous in organic synthesis, due to their propensity to undergo nucleophilic ring opening and rearrangement to carbonyl compounds and allylic alcohols. The second study focused on ion pair separation of organolithium species, which are important nucleophiles in electrophilic substitution reactions. In both cases, computational methods were used to model the structures of the reactive intermediates (protonated cyclic ethers and organolithium compounds), and to estimate the energetics of unimolecular processes (ring opening of protonated epoxides and ion pair separation of organolithium compounds). However in both cases, the limitations of current available methods also became quite clear.

The first study focused on the gas phase modeling of alkyl substituted protonated cyclic ethers. Ten protonated epoxides were studied using B3LYP, MP2 and CCSD/6-311++G** calculations. Relative to CCSD, B3LYP consistently overestimated the C2-O bond length. Protonated 2-methyl-1,2-epoxypropane (**33**-H⁺) was the most problematic system studied, where B3LYP overestimated the C2-O bond length by 0.191 Å. Seventeen other DFT methods were applied to this system; on average they overestimated the CCSD bond length by 0.2 Å. In contrast, DFT proved significantly more successful in modeling the neutral epoxide **33**. Nine other protonated epoxides featuring varied substitutions were studied, five symmetrically substituted and four unsymmetrically substituted epoxides were modeled. A clear trend was observed, with B3LYP geometries of the symmetrically substituted epoxides having smaller deviations, and the unsymmetrically substituted epoxides having greater deviations. Cyclic homologs of **33**-H⁺ featuring less ring strain were treated with greater accuracy by B3LYP.

Finally MP2 performed very well against CCSD, deviating in the C2-O bond length at most by 0.009 Å.

The superiority of post Hartree-Fock methods relative to DFT was evident in this study. The treatment provided by MP2 and CCSD methods was far less erratic than observed by the 18 DFT functionals studied. The generally poor performance of DFT methods in treating the protonated 2-methyl-1,2-epoxypropane appears to be due to the weakness of the C2-O bond, and better DFT performance was observed in similar species possessing stronger C2-O bonds. Amongst the different DFT methods tried, the LYP functional gave the largest deviations from the CCSD values, while the mPW1PW91 and mPW1PBE showed the smallest deviations from the CCSD results. To a certain degree, this failure could stem from the existence of self-interaction error, which is inherent in all DFT exchange functionals. While this error is alleviated to some extent in hybrid functionals due to the small percentage (~20%) of Hartree-Fock component, it is not completely eliminated. Similar results were observed by Gilbert in the modeling of the weak B-N bond in amine-borane complexes where the performance of MP2 and mPW1PW91 was significantly better than B3LYP.¹ We believe that this work adds to the series of studies that stand as cautionary tales for organic chemists in the indiscriminate use of B3LYP as the method of preference, and highlights the need to benchmark density functional calculations against *ab initio* methods.

The second project focused on the study of ion pair separation in benzylic organolithiums. Ion pair separation (IPS) of THF-solvated fluorenyl (**85_C**), diphenylmethyl (**86_C**) and trityl (**87_C**) lithium was studied computationally. Because of the large size of these species, we had no recourse but to use DFT methods to locate geometries. We chose to use the B3LYP functional because of its widespread use in other studies of organolithium species. Due to the

large number of basis functions employed in this study (694 at B3LYP/6-31G* for **87**•(THF)₄), all geometries were optimized at B3LYP/6-31G*. Minimum energy equilibrium geometries of explicit mono-, bis- and tris-solvated contact ion pairs (CIPs), and tetrakis-solvated separated ion pairs (SSIPs) were thus located at B3LYP/6-31G*. Associative transition structures linking the tris-solvated CIPs and tetrakis-solvated SSIPs were located and found to be 3.5 to 5.8 kcal/mol higher in enthalpy than the CIPs. Calculated enthalpies of IPS (ΔH_{IPS}) were compared to experimental (UV-visible spectroscopy) solution values reported in the literature. Single-point calculations were also performed with another DFT functional mPW1PW91 and an *ab initio* method MP2 (both at 6-31G*). Conformational flexibilities associated with the puckering of the THF molecules (leading to multiple minima) made it practically impossible to compute all possible conformers of these species. To ensure uniform sampling of conformational space, the THF-solvated lithium fragments of each optimized geometry were swapped between the various carbanion fragments (FI⁻, DPM⁻, Tr⁻), and the resulting new initial geometries were reoptimized. This sequential optimization was followed till no new minimum was obtained. Another problem we faced involved the use of ‘Volume’ calculation to get the required input radius (a_0) for the Onsager calculations. Since the Volume keyword of Gaussian '03 invokes a Monte Carlo integration method to determine this parameter, a_0 is *not* uniquely determined by the geometry. Variations in the radius led to significant variations in the energy calculations, and an error analysis was performed to incorporate the energetic consequences of a $\pm 10\%$ change in the input radius.

In vacuum, calculated ΔH_{IPS} values for **85**_C•(THF)₃ - **87**_C•(THF)₃ were calculated to be 6-8 kcal/mol less exothermic than the experimentally determined values in THF solution. Comparison of calculated structures with the published X-ray structures of **85**_C•(THF)₃ and

$87s \bullet (THF)_4$ suggested that in vacuo modeling of the SSIPs was problematic. Application of the Onsager solvation model during optimization at B3LYP/6-31G* produced minor changes for the C_α -Li bond length for CIPs, while significant changes were observed for the C_α -Li contact distances in the SSIPs. An increase in exothermicity of ion pair separation was observed upon using both PCM and Onsager solvation models, highlighting the importance of both explicit and implicit solvation in modeling of ion pair separation. While significant energy and geometry changes were observed upon addition of implicit solvation to the explicitly solvated organolithium systems, the calculated enthalpies of IPS were 5-7 kcal/mol more endothermic compared to the experimental enthalpies. Accounting for basis set superposition error further increased this gap by approximately 5.0 kcal/mol for all the three systems studied, further highlighting the problems associated with modeling of this system.

We believe that for IPS of organolithium compounds to be modeled effectively, it might be useful to test the effects of solvent molecules that lie beyond the primary solvation shell. Thus, a method like QM/MM/Monte Carlo or MD might be required to effectively model this phenomenon.

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Chapter 5: Supplementary Information for Chapter 2

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Computational Methods

Hartree-Fock, hybrid DFT,¹ MP2,² CCSD,³ G2,⁴ G3,⁵ and CBS-Q⁶ calculations were performed using Gaussian 03.⁷ Hybrid DFT investigations employed a variety of exchange (B3,⁸ mPW & mPW1,⁹ G96,¹⁰ PBE¹¹) and correlation (LYP,¹² P86,¹³ PW91,¹⁴ PBE¹¹) functionals. CCSD(T)¹⁵ single-point calculations at the 6-311++G** and aug-cc-pVDZ basis were calculated using Gaussian 03. CCSD(T)/aug-cc-pVTZ single-points, and CCSD(T) and MP2 geometry optimizations using correlation consistent basis sets were calculated using PSI3.¹⁶ All MP2, CCSD, and CCSD(T) calculations were performed 'frozen core' to exclude inner-shell electrons from the correlation calculation. All stationary points were characterized as minima by vibrational frequency analysis, except in the case of CCSD, where cost considerations limited us to the study of **1**-H⁺. Since MP2 geometries were shown to closely approximate the CCSD geometries of all 10 protonated epoxides studied, and since the CCSD/6-311+G** ZPVE of **1**-H⁺ differed from the corresponding MP2 ZPVE by only 0.08 kJ/mol (0.04%), MP2 ZPVE were used to correct CCSD energies. Due to the great number of methods and basis sets employed in this study, ZPVE were calculated from unscaled frequencies.

Table 5.S1: Electronic Energies, ZPVE, C-O bond lengths for all protonated cyclic ethers (except **33-H⁺**), all at 6-311++G**.

Structure	Method	E ₀ (hartrees) ^a	ZPVE (hartree) ^b	C2-O (Å)	C1-O/Cn-O (Å) ^c
1-H⁺	B3LYP	-154.13907	0.07009	1.529	1.529
	MP2	-153.70841	0.07157	1.521	1.522
	CCSD	-153.73667	0.07154	1.517	1.517
<i>cis</i> - 27-H⁺	B3LYP	-193.48275	0.09753	1.591	1.515
	MP2	-192.92102	0.09961	1.556	1.519
	CCSD	-192.96077	nd	1.551	1.512
<i>trans</i> - 27-H⁺	B3LYP	-193.48322	0.09744	1.602	1.512
	MP2	-192.9214	0.09956	1.561	1.518
	CCSD	-192.9612	nd	1.556	1.511
<i>cis</i> - 41-H⁺	B3LYP	-272.16143	0.15226	1.661	1.532
	MP2	-271.34239	0.15519	1.588	1.543
	CCSD	-271.40444	nd	1.584	1.532
<i>trans</i> - 41-H⁺	B3LYP	-272.16186	0.15222	1.649	1.539
	MP2	-271.34299	0.15512	1.586	1.546
	CCSD	-271.40509	nd	1.58	1.535
<i>cis</i> - 40-H⁺	B3LYP	-232.82246	0.12531	1.566	1.566
	MP2	-232.13075	0.12763	1.55	1.55
	CCSD	-232.18188	nd	1.543	1.543
<i>trans</i> - 40-H⁺	B3LYP	-232.82332	0.12516	1.569	1.57
	MP2	-232.13169	0.12753	1.553	1.553
	CCSD	-232.18291	nd	1.545	1.545
39-H⁺	B3LYP	-232.82497	0.12501	1.573	1.561
	MP2	-232.13336	0.12750	1.554	1.548
	CCSD	-232.18455	nd	1.547	1.54
42-H⁺	B3LYP	-311.49409	0.17953	1.597	1.597
	MP2	-310.54927	0.18248	1.576	1.576
	CCSD	-310.62198	nd	1.567	1.567
43-H⁺	B3LYP	-272.16441	0.15428	1.667	1.513
	MP2	-271.34699	0.15729	1.594	1.514
	CCSD	-271.41103	nd	1.594	1.51
44-H⁺	B3LYP	-311.51474	0.18392	1.63	1.51
	MP2	-310.57265	0.18726	1.57	1.508
	CCSD	-310.64737	nd	1.569	1.505

^aElectronic energies.

^bAll B3LYP and MP2 stationary points were shown to have zero imaginary frequencies. CCSD vibrational frequency analysis was performed only for **1-H⁺**; computational cost considerations precluded CCSD vibrational frequency analysis of larger molecules. Zero-point vibrational energies are calculated from unscaled frequencies.

^cC3-O bond lengths for **41-H⁺**, **40-H⁺**, **39-H⁺**, **42-H⁺**; C4-O bond length for **43-H⁺**; C5-O bond length for **44-H⁺**.

Table 5.S2: Electronic Energies, ZPVE, C-O bond lengths, and ΔE_{ro} for **33**-H⁺.

Method	Basis	E_0 (hartrees) ^a	ZPVE (hartrees) ^b	E_0 (ZPVE corrected Energy)	C2-O (Å)	C1-O (Å)	Corrected ΔE_{ro} (kcal/mol) ^c
HF	6-311++G**	-231.34534	0.13320	-231.212144	1.623	1.468	-11.8
MP2	6-31G*	-231.97014	0.12865	-231.841495	1.598	1.518	1.7
	6-31+G*	-231.97836	0.12809	-231.850277	1.603	1.521	-0.1
	6-31+G**	-232.04996	0.12873	-231.921222	1.601	1.52	-0.3
	6-31++G**	-232.05105	0.12870	-231.922352	1.598	1.513	-0.3
	6-311+G**	-232.1326	0.12726	-232.005341	1.598	1.513	-1.5
	6-311++G**	-232.13333	0.12727	-232.006055	1.598	1.514	-1.5
MP2	cc-pVDZ	-232.04141	nd	nd	1.605	1.517	nd
MP2	aug-cc-pVDZ	-232.08581	nd	nd	1.626	1.534	nd
MP2	cc-pV(T/D)Z ^d	-232.23701	nd	nd	1.593	1.511	nd
MP2	cc-pVTZ	-232.28252	nd	nd	1.595	1.511	nd
CCSD	6-311++G**	-232.18422	nd	-232.056952 ^e	1.599	1.504	-4.4
CCSD(T)	cc-pV(T/D)Z ^d	-232.32156	nd	nd	1.611	1.465	nd
CCSD(T) ^f	6-311++G**	-232.2144	nd	-232.087133 ^e	1.599	1.504	-3.1
CCSD(T) ^f	aug-cc-pVDZ	-232.16842	nd	-232.041151 ^e	1.599	1.504	-3.9
CCSD(T) ^f	aug-cc-pVTZ	-232.37999	nd	-232.252716 ^e	1.599	1.504	-3.5
G2				-232.310295	1.597	1.512	-2.1
G3				-232.539823	1.596	1.517	-2.6
CBS-Q				-232.314362	1.591	1.512	-2.2
G3B3				-232.544472	1.691	1.494	-2.9
B3LYP	6-31G*	-232.75433	0.12560	-232.628726	1.692	1.494	-5.6
	6-31+G*	-232.75853	0.12521	-232.633322	1.713	1.492	-7.4
	6-31+G**	-232.77504	0.12474	-232.650296	1.725	1.49	-8.1
	6-31++G**	-232.77521	0.12472	-232.650488	1.726	1.49	-8
	6-311+G**	-232.82396	0.12393	-232.70003	1.793	1.479	-8.7
	6-311++G**	-232.82417	0.12396	-232.700218	1.79	1.48	-8.7
B3P86	6-311++G**	-233.54483	0.12501	-233.419817	1.669	1.484	-8.2
B3PW91	6-311++G**	-232.73566	0.12490	-232.610752	1.671	1.485	-8.1
MPWLYP	6-311++G**	-232.71448	0.11980	-232.594678	1.978	1.481	-7.4
mPWP86	6-311++G**	-232.81289	0.12040	-232.692495	1.814	1.49	-7.6
mPWPW91	6-311++G**	-232.78463	0.12106	-232.663571	1.801	1.488	-7.5
MPWPBE	6-311++G**	-232.69709	0.12102	-232.576068	1.787	1.489	-7.5
mPW1LYP	6-311++G**	-232.68779	0.12464	-232.563151	1.764	1.481	-8.9
mPW1PW91	6-311++G**	-232.76299	0.12582	-232.637166	1.644	1.485	-8
mPW1PBE	6-311++G**	-232.67582	0.12573	-232.550089	1.642	1.483	-7.9
G96LYP	6-311++G**	-232.70845	0.12021	-232.588235	1.957	1.48	-7.3
G96P86	6-311++G**	-232.8087	0.12079	-232.687905	1.799	1.489	-7.4
G96PW91	6-311++G**	-232.78076	0.12144	-232.659324	1.788	1.476	-7.3
G96PBE	6-311++G**	-232.69332	0.12141	-232.571916	1.774	1.488	-7.3
PBELYP	6-311++G**	-232.5371	0.11963	-232.417468	1.971	1.482	-7.6
PBEP86	6-311++G**	-232.63576	0.12028	-232.515482	1.798	1.492	-7.8
PBEPW91	6-311++G**	-232.60733	0.12093	-232.486394	1.787	1.491	-7.7
PBEPBE	6-311++G**	-232.51986	0.12091	-232.398952	1.773	1.492	-7.7

^aElectronic energies.^bAll HF, DFT, and MP2/6-311++G** stationary points were shown to have zero imaginary frequencies. Zero-point vibrational energies are based on uncorrected frequencies; nd denotes that frequencies were not determined.^cEnergy of ring opening, defined as $E_0(\mathbf{33}\text{-H}^+) - E_0(\mathbf{34})$.^dMixed basis: cc-pVTZ at C, O; cc-pVDZ at H.^eCorrected electronic energies (E_0) were calculated using the MP2/6-311++G** ZPVE.^fSingle-point energies at the CCSD/6-311++G** geometry.

Table 5.S3: Electronic energies, ZPVE, and selected bond lengths for **34**

Method	Basis	E ₀ (hartrees) ^a	ZPVE (hartree) ^b	E ₀ (ZPVE corrected energy)	C2-C1 (Å)	C1-O (Å)
HF	6-311++G**	-231.360535	0.12955	-231.230985	1.476	1.312
MP2	6-31G*	-231.962998	0.12417	-231.838827	1.467	1.395
	6-31+G*	-231.973995	0.12360	-231.850396	1.467	1.399
	6-31+G**	-232.045788	0.12408	-231.921713	1.465	1.396
	6-31++G**	-232.046754	0.12398	-231.922770	1.466	1.398
	6-311+G**	-232.129854	0.12215	-232.007703	1.467	1.389
MP2	6-311++G**	-232.130510	0.12209	-232.008414	1.467	1.390
CCSD	6-311++G**	-232.186018	nd	-232.063921	1.474	1.389
CCSD(T) ^c	6-311++G**	-232.214233	nd	-232.092137 ^d	1.474	1.389
CCSD(T) ^c	aug-cc-pVDZ	-232.169387	nd	-232.047290 ^d	1.474	1.389
CCSD(T) ^c	aug-cc-pVTZ	-232.380323	nd	-232.258228 ^d	1.474	1.389
G2				-232.313677	1.465	1.393
G3				-232.543958	1.465	1.393
CBS-Q				-232.317826	1.470	1.388
G3B3				-232.549092	1.471	1.387
B3LYP	6-31G*	-232.759562	0.12193	-232.637632	1.471	1.387
	6-31+G*	-232.767026	0.12184	-232.645189	1.471	1.391
	6-31+G**	-232.784553	0.12140	-232.663153	1.470	1.390
	6-31++G**	-232.784696	0.12140	-232.663299	1.470	1.390
	6-311+G**	-232.834732	0.12089	-232.713841	1.466	1.389
	6-311++G**	-232.834926	0.12090	-232.714028	1.466	1.389
B3P86	6-311++G**	-233.554036	0.12118	-233.432858	1.460	1.380
B3PW91	6-311++G**	-232.744739	0.12105	-232.623690	1.462	1.380
mPWLYP	6-311++G**	-232.723989	0.11745	-232.606539	1.475	1.402
mPWP86	6-311++G**	-232.821953	0.11732	-232.704636	1.469	1.394
mPWPW91	6-311++G**	-232.793481	0.11788	-232.675601	1.468	1.392
mPWPBE	6-311++G**	-232.705836	0.11779	-232.588051	1.467	1.391
mPW1LYP	6-311++G**	-232.698838	0.12149	-232.577344	1.466	1.387
mPW1PW91	6-311++G**	-232.771664	0.12178	-232.649881	1.460	1.378
mPW1PBE	6-311++G**	-232.684246	0.12158	-232.562659	1.460	1.377
G96LYP	6-311++G**	-232.717633	0.11776	-232.599874	1.474	1.400
G96P86	6-311++G**	-232.817276	0.11759	-232.699691	1.468	1.389
G96PW91	6-311++G**	-232.789133	0.11816	-232.670978	1.467	1.389
G96PBE	6-311++G**	-232.701570	0.11807	-232.583506	1.468	1.388
PBELYP	6-311++G**	-232.546894	0.11732	-232.429576	1.474	1.402
PBEP86	6-311++G**	-232.645028	0.11718	-232.527850	1.468	1.393
PBEPW91	6-311++G**	-232.616379	0.11774	-232.498640	1.467	1.391
PBEPBE	6-311++G**	-232.528792	0.11763	-232.411160	1.467	1.391

^aElectronic energies.^bAll HF, DFT, and MP2 stationary points were shown to have zero imaginary frequencies. Zero-point vibrational energies are based on uncorrected frequencies; nd denotes that CCSD frequencies were not determined.^cSingle-point energies at the CCSD/6-311++G** geometry.^dCorrected Electronic energies were calculated using MP2 ZPVE

Table 5.S4: Electronic energies, ZPVE, C-O bond lengths for **33**, all at 6-311++G**

Method	E ₀ (hartrees) ^a	ZPVE (hartrees) ^b	C2-O (Å)	C1-O (Å)
HF	-231.01329	0.1203581	1.408	1.406
MP2	-231.81287	0.114542	1.443	1.443
CCSD	-231.85844	nd	1.434	1.435
B3LYP	-232.49918	0.1125843	1.443	1.436
B3P86	-233.22055	0.1130261	1.435	1.426
B3PW91	-232.41072	0.1129043	1.435	1.427
MPWLYP	-232.38918	0.1092211	1.468	1.457
mPWP86	-232.48991	0.1092516	1.458	1.447
mPWPW91	-232.46002	0.1098077	1.457	1.444
MPWPBE	-232.37287	0.1097353	1.456	1.443
mPW1LYP	-232.36361	0.1131366	1.442	1.435
mPW1PW91	-232.43862	0.1136241	1.431	1.423
mPW1PBE	-232.35176	0.1135365	1.43	1.422
G96LYP	-232.37959	0.1094725	1.466	1.452
G96P86	-232.482	0.1094954	1.456	1.443
G96PW91	-232.45245	0.1100591	1.455	1.439
G96PBE	-232.36538	0.1099791	1.453	1.44
PBELYP	-232.21376	0.1091069	1.467	1.457
PBEP86	-232.31467	0.1091374	1.456	1.447
PBEPW91	-232.28458	0.1097011	1.455	1.444
PBEPBE	-232.19748	0.1096211	1.454	1.443

^aElectronic energies.^bAll HF, DFT, and MP2 stationary points were shown to have zero imaginary frequencies. Zero-point vibrational energies are based on uncorrected frequencies; nd denotes that CCSD frequencies were not determined.**Table 5.S5:** Electronic energies, ZPVE for all transition structures, all at 6-311++G**

Structure	Method	E ₀ (hartrees) ^a	ZPVE (hartrees) ^b
24	B3LYP	-154.1162605	0.06774
	MP2	-153.6818381	0.06935
22	B3LYP	-154.1154414	0.06380
	MP2	-153.6698865	0.06483
28	B3LYP	-193.4596974	0.09475
	MP2	-192.893774	0.09723
31a	B3LYP	-193.4642851	0.09320
	MP2	-192.8919108	0.09519
32	B3LYP	-193.4817041	0.09215
	MP2	-192.9051562	0.09327
36	B3LYP	-232.8213305	0.12139
	MP2	-232.1184589	0.12298
37	B3LYP	-232.8260286	0.12072
	MP2	-232.1264953	0.12238

^aElectronic energies.^bAll DFT, and MP2 transition structures were shown to have one imaginary frequency. Zero-point vibrational energies are based on uncorrected frequencies.

Table 5.S6: Electronic energies, ZPVE, for all protonated aldehydes, all at 6-311++G**

Structure	Method	E ₀ (hartrees) ^a	ZPVE (hartrees) ^b
23	B3LYP	-154.1870065	0.06814
	MP2	-153.7509558	0.06945
30	B3LYP	-193.5172267	0.09658
	MP2	-192.9510028	0.09837
38	B3LYP	-232.8455426	0.12520
	MP2	-232.1525588	0.12738

^aElectronic energies.^bAll stationary points were shown to have zero imaginary frequencies. Zero-point vibrational energies are based on uncorrected frequencies.**Table 5.S7:** B3LYP/6-311++G** Electronic energies and ZPVE for hydrogenolysis

Structure	E ₀ (hartrees) ^a	ZPVE (hartrees) ^b
45 -H ⁺	-350.8432413	0.21327
43	-271.8270184	0.14177
44	-311.1766149	0.17143
45	-350.5031204	0.20079
46	-233.7446368	0.13593
47	-273.0672319	0.16439
48	-312.3918586	0.19267
49	-351.7161043	0.22099

^aElectronic energies.^bAll stationary points were shown to have zero imaginary frequencies. Zero-point vibrational energies are based on uncorrected frequencies.

Table 5.S8: Mulliken charges for all protonated cyclic ethers, all at 6-311++G**

Structure	Method	C2-O Mulliken Charge	C1-O/Cn-O Mulliken Charge ^a	Charge(C2)-Charge(C1/Cn)
1-H⁺	B3LYP	-0.173	-0.173	0.000
	MP2	-0.133	-0.133	0.000
	CCSD	-0.134	-0.134	0.000
<i>cis</i> - 27-H⁺	B3LYP	0.134	-0.322	0.456
	MP2	0.261	-0.320	0.581
	CCSD	0.261	-0.321	0.583
<i>trans</i> - 27-H⁺	B3LYP	0.087	-0.299	0.386
	MP2	0.185	-0.283	0.469
	CCSD	0.184	-0.285	0.469
33-H⁺	B3LYP	0.419	-0.456	0.875
	MP2	0.501	-0.439	0.941
	CCSD	0.512	-0.443	0.955
<i>cis</i> - 41-H⁺	B3LYP	0.185	-0.260	0.445
	MP2	0.425	-0.217	0.642
	CCSD	0.434	-0.216	0.651
<i>trans</i> - 41-H⁺	B3LYP	0.265	-0.272	0.537
	MP2	0.507	-0.223	0.729
	CCSD	0.517	-0.225	0.742
<i>cis</i> - 40-H⁺	B3LYP	-0.033	-0.033	0.000
	MP2	0.073	0.073	0.000
	CCSD	0.074	0.074	0.000
<i>trans</i> - 40-H⁺	B3LYP	-0.027	-0.027	0.000
	MP2	0.066	0.066	0.000
	CCSD	0.065	0.065	0.000
39-H⁺	B3LYP	-0.064	-0.010	-0.055
	MP2	0.032	0.098	-0.067
	CCSD	0.030	0.099	-0.070
42-H⁺	B3LYP	-0.028	-0.028	0.000
	MP2	0.194	0.194	0.000
	CCSD	0.203	0.203	0.000
43-H⁺	B3LYP	-0.050	-0.239	0.189
	MP2	0.223	-0.225	0.448
	CCSD	0.242	-0.230	0.473
44-H⁺	B3LYP	-0.173	-0.213	0.040
	MP2	0.184	-0.237	0.421
	CCSD	0.191	-0.234	0.425

^aC3-O bond lengths for **41-H⁺**, **40-H⁺**, **39-H⁺**, **42-H⁺**; C4-O bond length for **43-H⁺**; C5-O bond length for **44-H⁺**.

Table 5.S9: Wiberg Bond Indices for all systems at B3LYP, MP2 and CCSD, all at 6-311++G**

Compound	Method	Wiberg Bond Index	
		C1-O	C2-O
1-H⁺	B3LYP	0.7569	0.7569
	MP2	0.7162	0.7162
	CCSD	0.7176	0.7176
<i>cis</i> - 27-H⁺	B3LYP	0.7746	0.6685
	MP2	0.7272	0.6549
	CCSD	0.7296	0.6571
<i>trans</i> - 27-H⁺	B3LYP	0.7771	0.6576
	MP2	0.7289	0.6474
	CCSD	0.7310	0.6504
<i>cis</i> - 41-H⁺	B3LYP	0.7397	0.5848
	MP2	0.6865	0.6044
	CCSD	0.6934	0.6045
<i>trans</i> - 41-H⁺	B3LYP	0.7301	0.5929
	MP2	0.6814	0.6064
	CCSD	0.688	0.6078
<i>cis</i> - 40-H⁺	B3LYP	0.6981	0.6981
	MP2	0.6694	0.6694
	CCSD	0.6732	0.6732
<i>trans</i> - 40-H⁺	B3LYP	0.6927	0.6927
	MP2	0.6653	0.6653
	CCSD	0.6693	0.6693
39-H⁺	B3LYP	0.7015	0.6892
	MP2	0.6715	0.6638
	CCSD	0.6756	0.6673
42-H⁺	B3LYP	0.6484	0.6484
	MP2	0.6275	0.6275
	CCSD	0.6324	0.6324
43-H⁺	B3LYP	0.7893	0.5885
	MP2	0.7430	0.6028
	CCSD	0.7457	0.6026
44-H⁺	B3LYP	0.7755	0.6156
	MP2	0.7372	0.6286
	CCSD	0.7384	0.6289
33-H⁺	B3LYP	0.8282	0.4741
	MP2	0.7411	0.5836
	CCSD	0.7476	0.5793
33	B3LYP	0.9156	0.8775
	MP2	0.892	0.8611
	CCSD	0.8941	0.8652

CCSD/6-311++G** Cartesian Coordinates for all species studied and B3LYP/6-311++G**

Cartesian Coordinates for select species

1-H⁺ CCSD/6-311++G** Geometry

C	0.279259431784	-0.825871241645	-0.029645526858
H	0.729248721382	-1.181790130750	-0.951171939938
H	0.498203190211	-1.365169463414	0.885036365365
C	-0.863505261364	0.088442631851	-0.086397503604
O	0.514465449703	0.655421305839	0.199954576836
H	0.906531834055	1.097418157723	-0.573865498149
H	-1.252414639957	0.403717598345	-1.049585303536
H	-1.491817725835	0.227025050148	0.786207944342

24 B3LYP/6-311++G** Geometry

C	-0.833835723313	-0.287681015380	0.000000000000
C	0.623556114966	-0.623888483520	0.000000000000
O	0.179370983357	0.777563056114	0.000000000000
H	-1.388695717229	-0.332362909070	-0.929855104964
H	-1.388695717229	-0.332362909070	0.929855104964
H	1.102783395858	-0.907087872412	-0.929857953449
H	1.102783395858	-0.907087872412	0.929857953449
H	0.398534425960	1.727814107454	0.000000000000

22 B3LYP/6-311++G** Geometry

C	-0.038464164522	-0.180940292271	0.391779519554
H	-0.927030795369	-0.262939157245	1.082840340262
H	0.634010564786	-0.901959457791	0.941084354631
C	-0.438038498893	-0.902639494439	-0.754346559848
H	-0.837994757355	-1.907272290910	-0.629971556373
H	-0.360168961136	-0.488861129159	-1.761253970209
O	0.455332903482	1.069985333560	0.190641040181
H	0.707536701710	1.502628086880	1.017574752010

23 B3LYP/6-311++G** Geometry

C	-0.054267257969	-0.830836302361	-0.895872238783
H	0.581943436257	-0.648666863573	-1.777029058700
H	-1.108935690660	-0.699771304967	-1.130150237539
H	0.172388473568	-1.872288687013	-0.616031859531
C	0.404588229183	0.029667486561	0.173664728747

H	1.443668489516	0.005917436931	0.514898122775
O	-0.397498811066	0.830595589391	0.736493181453
H	-0.011000047444	1.377057598300	1.449612641591

cis-**27**-H⁺ CCSD/6-311++G** Geometry

C	0.224363786882	-0.481931600223	0.204838556404
C	0.479367675200	0.323522403714	1.441328241570
H	-0.217579892895	0.044903905207	2.236653047973
H	0.427560913214	1.400200804038	1.246671921858
H	1.495608886127	0.085930725763	1.778996285218
C	0.382838014599	0.058684088642	-1.147964065694
H	0.513758572469	-0.604335977818	-1.995921723171
H	0.680672970397	1.095917687212	-1.273367763932
O	-1.026973889820	-0.079750125394	-0.619048287373
H	-1.385694408311	0.777069906425	-0.328391271891
H	0.182047217474	-1.563335400477	0.298529409244

trans-**27**-H⁺ CCSD/6-311++G** Geometry

C	0.199338237190	0.470124152260	-0.221651088553
C	1.441487498317	-0.296655458317	-0.542424330611
H	2.259054957353	0.001181362116	0.119095436142
H	1.719671820188	-0.045999613057	-1.573771998399
H	1.272101523338	-1.374273544174	-0.471420676157
C	-1.148038012993	-0.093582622446	-0.348376026173
H	-1.271949050544	-1.120974851806	-0.674384787760
H	-2.008677187508	0.563311881719	-0.430404979470
O	-0.535709418698	-0.084406005799	1.032837163096
H	-0.908455320284	0.619168218992	1.591543926119
H	0.267202271959	1.553518163625	-0.148645553221

28 B3LYP/6-311++G** Geometry

C	-0.854017784058	-0.987300328068	-0.892543114290
H	-0.556527872903	-2.037214128313	-0.875346799845
H	-0.521496640596	-0.507674264217	-1.813144069480
H	-1.952182757719	-0.963160145125	-0.863430141745
C	-0.396279137755	-0.278365916428	0.321662184807
C	0.041837506585	1.151998385248	0.335851898507
O	1.105347319515	0.167566226854	0.334230225089
H	-0.600331509490	-0.723519418696	1.290437595236
H	-0.018255653856	1.719403682107	-0.587414682732

H	-0.021670823547	1.717716671213	1.259478497421
H	2.078443193356	0.135924943689	0.325751986290

31a B3LYP/6-311++G** Geometry

C	0.819261854885	0.58746252936	0.271248787625
C	-0.586837634505	0.594310249549	-0.218392778497
O	1.286738055737	-0.696142948329	-0.127119983894
H	1.407287371011	1.412054830874	-0.135519164702
H	0.834617003882	0.658694458552	1.368492775576
H	1.796344343095	-0.626346163260	-0.945435291914
C	-1.536154618873	-0.422937333339	0.109370585137
H	-2.288902843747	0.155242036300	0.705158368157
H	-2.147472758547	-0.721904357880	-0.754976964850
H	-1.155125453099	-1.262601145019	0.684251486318
H	-0.918269717534	1.400991274197	-0.878370903033

29b B3LYP/6-311++G** Geometry

C	0.785688908058	0.587957122863	-0.002325000000
H	1.175421804107	1.252708183807	0.796422000000
H	1.030743816985	1.170356161183	-0.931042000000
C	-0.654031103650	0.662823897725	0.003144000000
C	-1.521440925115	-0.478879237916	-0.031518000000
H	-1.059799788288	-1.353866165727	-0.498130000000
H	-2.540552958504	-0.265362397281	-0.350981000000
H	-1.577521880709	-0.762847246686	1.050527000000
O	1.268828109831	-0.702350801586	0.014078000000
H	2.232235113050	-0.722939650933	-0.042679000000
H	-1.072453261046	1.669351832294	0.047451000000

32 B3LYP/6-311++G** Geometry

C	0.772677113615	0.575255434811	0.034801750437
H	1.321661645515	1.355468043997	0.575196534718
H	0.610420795210	1.066526908665	-1.014802691503
C	-0.647630728500	0.632039748131	0.118567276496
C	-1.534494465484	-0.498621623764	-0.055623571111
H	-1.044644677155	-1.387240773838	-0.451266273228
H	-2.464485264180	-0.240399675536	-0.566977660972
H	-1.836102062013	-0.736325218158	0.989804312044
O	1.330130599838	-0.664584128334	-0.034266155150
H	2.292511513691	-0.622943617894	-0.105729615586

H	-1.063718267560	1.629546004366	0.261431900796
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30b B3LYP/6-311++G**

C	-1.361509360741	0.815194701441	0.000019816791
H	-1.070321964487	1.381996367961	0.885631800445
H	-1.070453046207	1.381966221769	-0.885654584746
H	-2.446741824969	0.718580178597	0.000102477844
C	-0.736357114070	-0.575950237945	-0.000003667259
H	-1.058240028361	-1.203737023251	-0.853879287046
H	-1.058118325697	-1.203711069018	0.853937630882
C	0.709552379973	-0.673538321289	-0.000133887234
O	1.429287258841	0.371016196819	0.000043409739
H	1.206487734892	-1.648155638454	0.000061117201
H	2.392973953127	0.210694534602	0.000159993725

33-H⁺ CCSD/6-311++G** Geometry

C	0.628318158784	-1.059666594077	0.535689524078
H	0.103238026804	-1.979863490957	0.770019040678
H	1.643137547228	-0.967749806000	0.912788330159
C	-0.124248764368	0.146487949960	0.171347302582
O	0.532072379652	-0.795615559643	-0.942116160163
H	1.362236266079	-0.422846001396	-1.284395600061
C	-1.618778456140	0.083813163819	0.053394759872
H	-1.963831201524	-0.931263219245	-0.158447090490
H	-1.973119966306	0.768110272150	-0.722282024183
H	-2.035281531079	0.404480458592	1.016632929124
C	0.538550893720	1.493002727667	0.255889987280
H	0.231222404100	1.947500980231	1.205796915583
H	0.201362549291	2.143260375146	-0.556635041518
H	1.631405876216	1.421471424407	0.255522379143

33 CCSD/6-311++G** Geometry

H	-1.317556160898	-1.729067058357	0.458659596255
C	-1.284414265567	-0.896732900712	-0.254975512170
H	-1.349460959373	-1.310200835518	-1.268951059015
H	-2.150939502990	-0.252245705693	-0.078116998941
C	-0.000155709372	-0.115465537496	-0.081388477784
C	1.282664105998	-0.898583081513	-0.257261796005
H	2.150431099850	-0.255345848354	-0.081947873527
H	1.345308504802	-1.312143048549	-1.271351066418

H	1.315877284852	-1.730965063312	0.456314215749
C	0.000707537151	1.342006725057	-0.291596068360
O	0.001487921714	0.789214398567	1.031984182747
H	0.922896924942	1.843785994327	-0.580395803876
H	-0.921270574221	1.845115144907	-0.578753346287

34 CCSD/6-311++G** Geometry

C	0.558219581656	-0.826654313867	0.427064507096
H	0.550751421583	-0.819635209114	1.535534679258
H	1.628137599839	-0.814770469280	0.137427304791
C	0.029351128724	0.489462902825	0.024419019442
C	-1.126621000512	0.558616324142	-0.865211056086
H	-0.884946464984	-0.027860383004	-1.768169717559
H	-1.441215327316	1.574086069806	-1.103875297808
H	-1.935761376201	-0.032562850651	-0.403157178203
C	0.685087728895	1.704555061377	0.533235605571
H	1.535800318438	1.508904812084	1.188334767012
H	-0.077831923105	2.307136913162	1.050757469813
H	0.989977084551	2.310403692011	-0.334562211462
O	-0.177866271481	-1.857063094649	-0.143709662409
H	0.181794206460	-2.705077664684	0.130339027289

36 B3LYP/6-311++G**

C	0.892437051465	-0.470525754537	0.583470207998
C	-0.462911020247	0.024277156924	0.151666250255
O	1.698320754627	-0.136186500833	-0.536240539822
H	1.193664148090	0.028411596532	1.512139862852
H	0.908774624589	-1.550842765661	0.736844267964
H	2.397037706533	0.485711698190	-0.297710055562
C	-0.712991641736	1.455081162620	0.050265219304
H	-1.290996832669	1.712114686721	-0.844024189703
H	-1.405990095682	1.669583987212	0.889748546060
H	0.168768971901	2.082340051747	0.157021603723
C	-1.471096582964	-0.945617143661	-0.236024462632
H	-1.498165797793	-1.799520854872	0.452499998000
H	-2.457632215390	-0.532014837137	-0.436984056788
H	-1.074653385701	-1.385584084146	-1.175874947518

37 B3LYP/6-311++G**

C	0.777965684202	-0.683867411722	-0.037661762242
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H	0.262558792990	-0.544314297764	-1.175630105570
H	0.791919379087	-1.765946728985	0.095621156995
C	-0.458038170549	0.000660629807	-0.016881375278
C	-0.490830675758	1.487193464904	-0.019893147098
H	0.440465658103	1.931169969784	-0.368326768257
H	-0.620094562184	1.792286531546	1.028769123966
H	-1.345186728298	1.870399189599	-0.578370506752
O	1.919496221018	0.000143646596	0.099904626480
H	2.698778314948	-0.555607185594	-0.038489310023
C	-1.727668939341	-0.780258489846	0.057998705474
H	-1.582908170514	-1.856032139793	-0.045953532754
H	-2.151628901261	-0.590242651081	1.052456970757
H	-2.458440942342	-0.425231019346	-0.670688565336

38 B3LYP/6-311++G**

C	0.126835115642	-0.540031576559	0.338963137213
H	0.849348919778	-1.353856274154	0.518381044744
C	0.578687167001	0.089049358068	-0.886888023786
H	0.829550147022	-0.514553757968	-1.763563223012
C	-0.004441161004	0.381023227453	1.550263964611
H	-0.764051497087	1.148404459216	1.388203798252
H	-0.301966059967	-0.210119203322	2.416685838477
H	0.940334528926	0.874364790060	1.785332606752
C	-1.217944784184	-1.277460652756	-0.043777767588
H	-1.098039050910	-1.967565506816	-0.880410276384
H	-1.513457098458	-1.851615836116	0.834794608275
H	-2.000369719215	-0.553164563426	-0.272648112831
O	0.653465909633	1.354068270687	-0.989012031133
H	0.932104528110	1.680077589791	-1.866047897917

39-H⁺ CCSD/6-311++G** Geometry

C	-0.587948423659	-0.206429543041	-0.425544743875
C	0.605461870583	-0.156571796818	0.425724255316
H	0.430979808677	-0.218735917724	1.498750075327
O	0.024296513700	1.171682042955	-0.112721631406
H	-0.494288113672	1.638229032477	0.565097987998
H	-0.420170873534	-0.375248556896	-1.486298115971
C	1.991613105138	-0.418478123031	-0.071949889424
H	2.069804743375	-0.224366766635	-1.144938510473
H	2.216364696366	-1.475283612501	0.117445005037
H	2.716865137906	0.192521557045	0.472161443689
C	-1.970317661102	-0.441207002130	0.104343493975

H	-2.708678747569	0.117294556885	-0.478303472807
H	-2.049650981445	-0.181315461486	1.165608799496
H	-2.188451125459	-1.510432384686	-0.003188857008

cis-**40**-H⁺ CCSD/6-311++G** Geometry

C	-0.735233163218	-0.270898277650	0.490102188055
C	-1.606457436023	0.780680981352	-0.129938404440
H	-2.525562677691	0.328856148372	-0.514105044017
H	-1.105512488875	1.339375885186	-0.924247104507
H	-1.881410450343	1.483930872783	0.665445585699
C	0.735233141821	-0.270898373534	0.490102175174
O	-0.000000099839	-1.217892759536	-0.480958968331
H	-0.000000096088	-0.851050953369	-1.382128221871
C	1.606457548113	0.780680752378	-0.129938455513
H	1.881410705398	1.483930598891	0.665445525222
H	1.105512651118	1.339375734952	-0.924247131957
H	2.525562702618	0.328855778212	-0.514105135590
H	-1.209324831772	-0.913761155812	1.226824144474
H	1.209324740194	-0.913761328203	1.226824109534

trans-**40**-H⁺ CCSD/6-311++G** Geometry

C	0.116610682952	-0.905563871829	-0.004662620224
C	1.596004907763	-0.798325769923	-0.206393125058
H	1.909582010703	-1.449621785149	-1.026740104600
H	2.077203357883	-1.148593085646	0.715112687700
H	1.913445500511	0.225696496917	-0.407862652217
C	-0.759697192495	0.174868454739	0.475338732457
O	-0.699959025507	-0.104414189013	-1.042845250910
H	-1.477335050117	-0.593978533446	-1.360093450090
C	-0.314053491215	1.556655733171	0.839849483575
H	-0.122410286130	1.563391748089	1.919960409668
H	-1.111000626519	2.274566049581	0.627796878864
H	0.595379090706	1.850789233881	0.314113840777
H	-0.291191988281	-1.911618959455	0.074552985107
H	-1.727189251655	-0.141124923532	0.861126590267

cis-**41**-H⁺ CCSD/6-311++G** Geometry

C	0.504219606962	-0.254603197256	-0.043982690612
C	0.096533249648	-1.703270281145	-0.022175324968
H	0.575958676269	-2.241485342340	-0.845238819009

H	-0.984795819493	-1.853051931733	-0.065167474564
H	0.460676209361	-2.130769650109	0.919982886441
C	-0.403724159380	0.822542073427	0.386464607493
H	0.073395366043	1.777719344716	0.592824321850
O	-0.270715689530	0.606144483545	-1.124657067912
H	-1.042378197678	0.120096882157	-1.462164918661
C	1.974915766224	0.039685313554	-0.146214812569
H	2.441045900456	-0.266112490066	0.798721424334
H	2.161923606146	1.105247696969	-0.302135691109
H	2.427445402058	-0.537268893637	-0.957626796577
C	-1.774434433443	0.648680923420	0.973030867923
H	-1.667338448284	0.641028982888	2.064319035292
H	-2.258486815968	-0.282370644719	0.668844968743
H	-2.406780542734	1.499601185514	0.702161722956

trans-**41**-H⁺ CCSD/6-311++G** Geometry

C	0.181874279564	-0.526999252980	-0.036535629770
C	-0.325532059491	-1.941290645768	0.064164169217
H	-0.018034828983	-2.526255330842	-0.808072347045
H	-1.413716948794	-1.986078030474	0.181967553994
H	0.128856268716	-2.394001276662	0.953748837918
C	-0.663753884585	0.567036262852	0.472343439036
O	-0.660783656982	0.347888590165	-1.047468114801
H	-1.461832254915	-0.118111182144	-1.340418836801
C	1.651346574432	-0.342623883545	-0.291879763745
H	2.183190259525	-0.608017326026	0.630280735767
H	1.902867004096	0.683762415282	-0.561273879256
H	1.981113080566	-1.017871392250	-1.086357014923
H	-1.624611676743	0.255442317507	0.879765639800
C	-0.196978250635	1.931314767328	0.878965558228
H	0.014419310054	1.901821717337	1.954873028491
H	-0.991668131522	2.662713884374	0.706186030524
H	0.703947218144	2.238861995255	0.346698532151

42-H⁺ CCSD/6-311++G** Geometry

C	-0.070761979693	-0.008486252208	-0.740976373730
C	-0.070761979693	-0.008486252208	0.740976373730
O	1.310106368742	0.011174776608	0.000000000000
H	1.686622458363	0.907272727563	0.000000000000
C	-0.348840286199	1.242679483063	-1.538676815156
H	-1.417229700429	1.244606409922	-1.786466682786
H	0.212826364765	1.215161230903	-2.477323821533
H	-0.123015736636	2.169435239249	-1.009095171880

C	-0.348840286199	1.242679483063	1.538676815156
H	-1.417229700429	1.244606409922	1.786466682786
H	-0.123015736636	2.169435239249	1.009095171880
H	0.212826364765	1.215161230903	2.477323821533
C	-0.228860056032	-1.289050648057	1.521496162745
H	0.219442112912	-1.177490199021	2.512578123234
H	0.218070617876	-2.148482123119	1.023341569552
H	-1.303056431095	-1.472421524938	1.648798217531
C	-0.228860056032	-1.289050648057	-1.521496162745
H	0.218070617876	-2.148482123119	-1.023341569552
H	0.219442112912	-1.177490199021	-2.512578123234
H	-1.303056431095	-1.472421524938	-1.648798217531

43-H⁺ CCSD/6-311++G** Geometry

C	-0.238968539239	0.402080290854	-0.029026060100
C	0.539687661624	-0.259581324464	-1.187152583321
C	0.977328524991	-1.392614758223	-0.253803670814
H	0.761819606114	-2.419790255888	-0.540943193582
H	1.972860061564	-1.285034580232	0.178434427789
H	1.351424126887	0.348419745919	-1.589755313506
H	-0.113808250747	-0.599691339957	-1.992616323232
O	-0.050059356205	-0.966214945719	0.766687014792
H	0.262643266728	-0.905967680170	1.683732349994
C	-1.718059964029	0.622003287529	-0.203386250419
H	-1.850039876798	1.463643066323	-0.894840850066
H	-2.195247678864	0.879157030168	0.747645314958
H	-2.201141569847	-0.259894011461	-0.632852510061
C	0.501785530982	1.489130910613	0.715755851144
H	0.459924224574	2.399281025201	0.106003975729
H	1.557162848264	1.237049161268	0.869677462942
H	0.024238805792	1.706436966734	1.677694821765

44-H⁺ CCSD/6-311++G** Geometry

H	0.064807081606	1.764057982858	0.680631509261
O	0.181734427595	0.815492938235	0.834097003825
C	-0.697639552628	-0.051876394300	-0.133861066749
C	0.286510925036	-1.186628449092	-0.423079888194
C	1.687192843685	-0.552475708409	-0.396054881716
C	1.626317910616	0.394338269221	0.794309774050
H	0.200987328721	-1.959147173010	0.349333609423
H	0.056625299636	-1.640986756266	-1.390964868883
H	1.895283178868	-0.003348330234	-1.319343159413

H	2.474677197428	-1.297339506900	-0.255579448543
H	2.222196317081	1.304404565063	0.713338934769
H	1.790086040877	-0.095507860887	1.754418314217
C	-1.916279477880	-0.442528522521	0.677688149819
H	-2.517126594070	-1.134668335229	0.076221793187
H	-2.535275591830	0.428084227083	0.917435426616
H	-1.624597694593	-0.949216242347	1.602237301389
C	-1.011459927898	0.829849437092	-1.332099697334
H	-1.659021516126	0.266405170179	-2.012417810890
H	-0.109229152653	1.119716150077	-1.880799029904
H	-1.561143641286	1.729530811778	-1.028702941089

45-H⁺ B3LYP/6-311++G** Geometry

H	1300546575421	-0.238849208734	-2.072587931945
C	0.696835310722	0.223556065248	-1.293868753578
C	-1.470232149743	0.231171352652	0.000000000000
C	0.696835310722	0.223556065248	1.293868753578
C	-0.739734464870	-0.242205424039	1.265492580202
O	1.352803023517	-0.253344581972	0.000000000000
C	-0.739734464870	-0.242205424039	-1.265492580202
H	-1.551657900396	1.323860765813	0.000000000000
H	0.808513087177	1.309318634002	1.300693707692
H	-0.769275265289	-1.332655039956	1.346187360752
H	-0.769275265289	-1.332655039956	-1.346187360752
H	0.808513087177	1.309318634002	-1.300693707692
H	-2.489246936913	-0.158251877509	0.000000000000
H	1.300546575421	-0.238849208734	2.072587931945
H	-1.217734552787	0.156043520368	2.165737460118
H	2.310563708363	-0.089803854313	0.000000000000
H	-1.217734552787	0.156043520368	-2.165737460118

45 B3LYP/6-311++G** Geometry

O	0.593213246397	-0.524051218379	-1.190389725781
C	0.790273721913	0.982041012406	0.729065089543
C	-0.877064703348	-0.905363500782	0.729072993034
C	-0.571979655027	0.505293679714	1.253637136391
C	-0.704083719040	-0.957750813891	-0.789252365355
C	0.863590650704	0.816835307010	-0.789259812237
H	1.591868807395	0.392300895266	1.187794805711
H	-0.192954906580	-1.628095388049	1.187803244084
H	-1.353766675690	1.195925077015	0.911825556034
H	-1.467231924948	-0.329221582587	-1.277598563874

H	0.145729983928	1.496629420366	-1.277606222830
H	0.966147444033	2.030707781193	0.992288083311
H	-1.896030137882	-1.209238496235	0.992301670056
H	-0.593110191379	0.523965045029	2.347311043853
H	-0.810763248039	-1.975075154311	-1.170283694458
H	1.859987106773	1.048178042606	-1.170296363895

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Chapter 6: Supplementary Information for Chapter 3

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Table 6.S1: Electronic Energies, ZPVE, Hcorr at 298 K and 1 atm, C_α-Li bond lengths for all CIPs and SSIPs and transition structures, at B3LYP/6-31G* and B3LYP/6-31G*(Onsager)

Cpd	Method	ϵ_0 (hartrees)	ZPVE (hartrees) ^a	H _{corr} (hartrees) ^a
85	B3LYP/6-31G*	-508.36332113	0.174500	0.18546
85_C•(THF)	B3LYP/6-31G*	-740.85255941	0.291439	0.30904
85_C•(THF)₂	B3LYP/6-31G*	-973.322941989	0.408195	0.432477
85_C•(THF)₃	B3LYP/6-31G*	-1205.78487397	0.524765	0.555823
85_C•(THF)₃	B3LYP/6-31G* (Onsager) ^c	-1205.78932662	0.524490	0.555700
85_T•(THF)₄^b	B3LYP/6-31G*	-1438.22627128	0.640900	0.678218
85_S•(THF)₄	B3LYP/6-31G*	-1438.23439635	0.642144	0.680012
85_S•(THF)₄	B3LYP/6-31G* (Onsager) ^c	-1438.24576911	0.641277	0.679535
86	B3LYP/6-31G*	-509.53538887	0.195263	0.207662
86_C•(THF)	B3LYP/6-31G*	-742.02293720	0.311826	0.331133
86_C•(THF)₂	B3LYP/6-31G*	-974.497521103	0.429338	0.454945
86_C•(THF)₃	B3LYP/6-31G*	-1206.96001847	0.546283	0.578538
86_C•(THF)₃	B3LYP/6-31G* (Onsager) ^d	-1206.96506513	0.545957	0.578386
86_T•(THF)₄^b	B3LYP/6-31G*	-1439.40250129	0.662464	0.701081
86_S•(THF)₄	B3LYP/6-31G*	-1439.40923533	0.663055	0.702423
86_S•(THF)₄	B3LYP/6-31G* (Onsager) ^c	-1439.42182766	0.662249	0.701878
87	B3LYP/6-31G*	-740.58055594	0.274223	0.29150
87_C•(THF)	B3LYP/6-31G*	-973.06975813	0.391167	0.41515
87_C•(THF)₂	B3LYP/6-31G*	-1205.54376565	0.508377	0.538972
87_C•(THF)₃	B3LYP/6-31G*	-1438.00808352	0.625480	0.662553
87_C•(THF)₃	B3LYP/6-31G* (Onsager) ^c	-1438.01256065	0.625286	0.662484
87_T•(THF)₄^b	B3LYP/6-31G*	-1670.45262073	0.741584	0.785139
87_S•(THF)₄	B3LYP/6-31G*	-1670.46159473	0.741830	0.785900
87_S•(THF)₄	B3LYP/6-31G* (Onsager) ^c	-1670.47559142	0.741091	0.785602
THF	B3LYP/6-31G*	-232.449453555	0.115154	0.121145
	B3LYP/6-31G* (Onsager) ^c	-232.450122385	0.115164	0.121136

^aThermodynamic corrections based on frequencies corrected by factor of 0.9815

^bAverage Li-O distance of the original bound THF shown; distance to the incoming THF molecules are 2.695 Å [**85_T•(THF)₄**], 3.075 Å [**86_T•(THF)₄**], 2.936 Å [**87_T•(THF)₄**].

^cB3LYP/6-31G*(Onsager) optimizations performed using dielectric for THF ($\epsilon = 7.58$); for the radii (a_0) used, refer Table 6.S8.

Table 6.S2: Electronic Energies, ZPVE, Hcorr at 298 K and 1 atm, all at B3LYP/6-31G*. ^a

Cpd	ϵ_0	ZPVE ^b	H _{corr} ^b
Fl	-501.423187627	0.184983	0.195003
DPM	-502.615367209	0.206424	0.217876
Tr	-733.660876250	0.285996	0.302152
Fl ⁻	-500.833896622	0.170223	0.180175
DPM ⁻	-502.009742189	0.191505	0.202801
Tr ⁻	-733.069363733	0.270879	0.286840
(THF) ₃ Li ⁺	-704.816232435	0.352256	0.372854
(THF) ₄ Li ⁺	-937.293916993	0.468814	0.496211

^aAll energies in hartrees^bZero-point vibrational energies and H_{corr} based on frequencies corrected by a factor of 0.9815**Table 6.S3:** Single-point electronic energies on B3LYP/6-31G* geometries. ^a

Cpd	B3LYP/6-31+G* ^b	mPW1PW91/6-31G*	MP2/6-31G*
85_C •(THF) ₃	-1205.81812420	-1205.49980122	-1201.788526
85_S •(THF) ₄	-1438.27419675	-1437.89229780	-1433.4594143
86_C •(THF) ₃	-1206.99446186	-1206.66752779	-1202.91719
86_S •(THF) ₄	-1439.45001074	-1439.05993078	-1434.5868349
87_C •(THF) ₃	-1438.05018455	-1437.66769049	-1433.237797
87_S •(THF) ₄	-1670.51015704	-1670.06355232	-1664.9098465
THF	-232.459327984	-232.395103217	-231.6699371
Fl ⁻	-500.867098423	nd	-499.1882187
DPM ⁻	-502.044382662	nd	-500.3157709
Tr ⁻	-733.109186061	nd	-730.6406086
(THF) ₃ Li ⁺	-704.830496543	nd	-702.4364563
(THF) ₄ Li ⁺	-937.312388306	nd	-934.1449303

^aAll energies in hartrees; nd designates not determined.^bB3LYP/6-31+G*//B3LYP/6-31G* calculations performed with the option SCF = tight

Table 6.S4: Electronic energies from single-point calculations on the C_α-Li distance constraint from 5.2 to 6.8 Å for **87_S**•(THF)₄. All constrained optimizations at B3LYP/6-31G*.^a

C _α -Li (Å)	B3LYP/6-31G*	BL3YP/6-31G* (PCM) ^b	B3LYP/6-31G* (Onsager) ^c	MP2/6-31G*	MP2/6-31G* (PCM) ^b
5.2	-1670.46158620	-1670.48666519	-1670.47368057	-1664.9090337	-1664.935897
5.3	-1670.46143994	-1670.48696197	-1670.47390122	-1664.9085277	-1664.9358234
5.4	-1670.46114123	-1670.48714157	-1670.47404966	-1664.907629	-1664.9354209
5.5	-1670.46072211	-1670.48716514	-1670.47413379	-1664.9064826	-1664.9347436
5.6	-1670.46016894	-1670.48741008	-1670.47414776	-1664.9051145	-1664.9341895
5.7	-1670.45949588	-1670.48733659	-1670.47407471	-1664.9035978	-1664.9332772
5.8	-1670.45864425	-1670.48728514	-1670.47397499	-1664.9020204	-1664.9325005
5.9	-1670.45782040	-1670.48718541	-1670.47377770	-1664.9002513	-1664.9314621
6.0	-1670.45681474	-1670.48713677	-1670.47367766	-1664.898401	-1664.9305466
6.4	-1670.45305822	-1670.48638270	-1670.47297622	-1664.8921583	-1664.9273387
6.8	-1670.44920307	-1670.48562651	-1670.47251854	-1664.8869274	-1664.925157

^aElectronic energies in hartrees

^bPCM calculations done with options: Solvent=THF, Radii=Pauling, Surface=SES^c B3LYP/6-31G*(Onsager) calculations performed using dielectric for THF (ε = 7.58); radius (a₀) of 6.52 Å used from B3LYP/6-31G* vacuum optimized geometry of **87_S**•(THF)₄

Table 6.S5: Relative electronic energies from single-point calculations on the C_α-Li distance constraint from 5.2 to 6.8 Å for **87_S**•(THF)₄. All constrained optimizations at B3LYP/6-31G*.^a

C _α -Li (Å)	B3LYP/6-31G*	BL3YP/6-31G* (PCM) ^b	B3LYP/6-31G* (Onsager) ^c	MP2/6-31G*	MP2/6-31G* (PCM) ^b
5.2	0.01	-0.25	-0.29	0.51	0.25
5.3	0.10	-0.43	-0.43	0.83	0.30
5.4	0.28	-0.55	-0.52	1.39	0.55
5.5	0.55	-0.56	-0.57	2.11	0.98
5.6	0.89	-0.72	-0.58	2.97	1.32
5.7	1.32	-0.67	-0.54	3.92	1.90
5.8	1.85	-0.64	-0.47	4.91	2.38
5.9	2.37	-0.43	-0.35	6.02	3.04
6.0	3.00	-0.54	-0.29	7.18	3.61
6.4	5.36	-0.07	0.15	11.10	5.62
6.8	7.78	0.40	0.44	14.38	6.99

^aRelative energies (kcal/mol) calculated from Table S7; all energies relative to the electronic energy of **87_S**•(THF)₄ at B3LYP/6-31G*

^bPCM calculations done with options: Solvent=THF, Radii=Pauling, Surface=SES

^cRadius (a₀) of 6.52 Å used from B3LYP/6-31G* vacuum optimized geometry of **87_S**•(THF)₄

Table 6.S6: PCM single-point electronic energies.^a

Cpd	B3LYP/6-31G*(PCM) //B3LYP/6-31G* ^b	B3LYP/6-31G*(PCM) //B3LYP/6-31G*(Onsager) ^b
85_c• (THF) ₃	-1205.80111400	-1205.80233679
85_s• (THF) ₄	-1438.25741135	-1438.25980061
86_c• (THF) ₃	-1206.97510678	-1206.97571010
86_s• (THF) ₄	-1439.43236369	-1439.43441740
87_c• (THF) ₃	-1438.02482793	-1438.02535769
87_s• (THF) ₄	-1670.48626897	-1670.48866628
THF	-232.455945096	-232.455952637

^aAll energies in hartrees.^bPCM calculations done with options: Solvent=THF, Radii=Pauling, Surface=SES.**Table 6.S7:** Counterpoise corrections (hartrees) for the energies of **85_s•**(THF)₄-**87_s•**(THF)₄ at the B3LYP/6-31G* and B3LYP/6-31G*(Onsager) geometries.^a

Geometries		85_s• (THF) ₄	86_s• (THF) ₄	87_s• (THF) ₄
B3LYP/6-31G*	THF1	0.007653092	0.009387079	0.008860078
	THF2	0.006987266	0.008320009	0.008449552
	THF3	0.010603491	0.007061587	0.009346102
	THF4	0.009454078	0.009889168	0.006201623
	Average	0.008674482	0.008664461	0.008214339
Average (kcal/mol)		5.44	5.44	5.15
B3LYP/6-31G* (Onsager)	THF1	0.008675448	0.0088313	0.00857428
	THF2	0.010279061	0.0078513	0.00605542
	THF3	0.006600446	0.0060605	0.00823700
	THF4	0.007859071	0.0090089	0.00806742
	Average	0.008353507	0.0079380	0.00773353
Average (kcal/mol)		5.24	5.0	4.8

^aAll energies in hartrees unless specified otherwise.

Table 6.S8: Onsager single-point energies with variable radii on B3LYP/6-31G* geometries

Cpd	Radius	Radius (Å)	ϵ_0 (hartrees)	$H_{\text{corr}}(298)$ (hartrees)	$H(298)$ (hartrees)	ΔH_{IPS} (kcal/mol)	$\sigma_{\Delta H(\text{IPS})}$ (kcal/mol)
THF	0.9*a ₀	3.31	-232.450416	0.121145	-232.3290185		
	a ₀	3.68	-232.450127108				
	1.1*a ₀	4.05	-232.4499473				
	Average	3.68	-232.4501635				
	St.dev		0.000236471				
85_C• (THF) ₃	0.9*a ₀	5.65	-1205.790563	0.55531	-1205.23370		
	a ₀	6.28	-1205.78878345				
	1.1*a ₀	6.91	-1205.787683				
	Average	6.28	-1205.78901				
	St.dev		0.001453066				
85_S• (THF) ₄	0.9*a ₀	5.85	-1438.248407	0.680012	-1437.56459	-1.18	2.42
	a ₀	6.50	-1438.2440412				
	1.1*a ₀	7.15	-1438.241354				
	Average	6.50	-1438.244601				
	St.dev		0.003559688				
86_C• (THF) ₃	0.9*a ₀	5.25	-1206.966687	0.578538	-1206.38630		
	a ₀	5.83	-1206.9645671				
	1.1*a ₀	6.41	-1206.963273				
	Average	5.83	-1206.964842				
	St.dev		0.0017234				
86_S• (THF) ₄	0.9*a ₀	5.72	-1439.424015	0.702423	-1438.71756	-1.40	2.61
	a ₀	6.35	-1439.419398				
	1.1*a ₀	6.99	-1439.416528				
	Average	6.35	-1439.41998				
	St.dev		0.003777057				
87_C• (THF) ₃	0.9*a ₀	5.70	-1438.014185	0.662553	-1437.34999		
	a ₀	6.33	-1438.01230225				
	1.1*a ₀	6.96	-1438.011147				
	Average	6.33	-1438.012545				
	St.dev		0.001533230				
87_S• (THF) ₄	0.9*a ₀	5.87	-1670.478706	0.7859	-1669.68805	-5.67	2.95
	a ₀	6.52	-1670.473219				
	1.1*a ₀	7.17	-1670.469912				
	Average	6.52	-1670.473945				
	St.dev		0.004441593				

Table 6.S9: B3LYP/6-31G*(Onsager) single-point energies with variable radii on B3LYP/6-31G*(Onsager) geometries

Cpd	Radius	Radius (Å)	E ₀ (hartrees)	H _{corr} (298) (hartrees)	H(298) (hartrees)	ΔH _{IPS} (kcal/mol)	σ _{ΔH(IPS)} (kcal/mol)
THF	0.9*a ₀	3.31	-232.4504206				
	a ₀	3.68	-232.45012239				
	1.1*a ₀	4.05	-232.4499485				
	Average	3.68	-232.4501639	0.121136	-232.3290279		
	St.dev		0.000238773				
85_C• (THF) ₃	0.9*a ₀	5.65	-1205.791261				
	a ₀	6.28	-1205.7893266				
	1.1*a ₀	6.91	-1205.787904				
	Average	6.28	-1205.789497	0.55570	-1205.23380		
	St.dev		0.001684911				
85_S• (THF) ₄	0.9*a ₀	5.85	-1438.251976				
	a ₀	6.50	-1438.2457691				
	1.1*a ₀	7.15	-1438.241883				
	Average	6.50	-1438.246543	0.67954	-1437.56701	-2.63	3.37
	St.dev		0.005090661				
86_C• (THF) ₃	0.9*a ₀	5.25	-1206.967322				
	a ₀	5.83	-1206.9650651				
	1.1*a ₀	6.41	-1206.963429				
	Average	5.83	-1206.965272	0.57839	-1206.38689		
	St.dev		0.001954718				
86_S• (THF) ₄	0.9*a ₀	5.72	-1439.428564				
	a ₀	6.35	-1439.421828				
	1.1*a ₀	6.99	-1439.417134				
	Average	6.35	-1439.422509	0.70188	-1438.72063	-2.96	3.81
	St.dev		0.005745149				
87_C• (THF) ₃	0.9*a ₀	5.70	-1438.014694				
	a ₀	6.33	-1438.0125607				
	1.1*a ₀	6.96	-1438.011241				
	Average	6.33	-1438.012832	0.66248	-1437.35035		
	St.dev		0.00174225				
87_S• (THF) ₄	0.9*a ₀	5.87	-1670.483364				
	a ₀	6.52	-1670.475591				
	1.1*a ₀	7.17	-1670.46998				
	Average	6.52	-1670.476312	0.78560	-1669.69071	-7.11	4.36
	St.dev		0.006720864				

Cartesian Coordinates for all species studied :

B3LYP/6-31G* Geometries (Vacuum)

85_C

C	0.133546910470	0.842114373763	0.159879320444
C	-1.303070550333	0.689728931555	0.001063837436
C	-2.137722231560	1.820229650022	0.220733474378
C	-1.570150593842	3.030961500194	0.565507435636
C	-0.165951715583	3.175023634030	0.719661662602
C	0.676964831684	2.096906223611	0.523487617814
C	0.735339620544	-0.445728557148	-0.114692741765
C	-0.342575904904	-1.365739714727	-0.437169156167
C	-0.018185460718	-2.715600879092	-0.746322352352
C	1.302939217298	-3.117480040063	-0.745363591982
C	2.352748661791	-2.215020829746	-0.429516416545
C	2.076208285395	-0.897489255666	-0.114928359469
H	-3.214747368812	1.731402787711	0.096373025732
H	-2.209842352908	3.896950142604	0.717850419759
H	0.245828836781	4.144193743585	0.987315424426
H	1.753421856610	2.214857240121	0.629568416371
H	-0.808334030632	-3.418346510811	-1.001572606952
H	1.548702211007	-4.146373259203	-0.997017241827
H	3.381125525693	-2.565372796331	-0.443190660922
H	2.884640037724	-0.205961289176	0.113440797990
C	-1.590962894699	-0.676887261194	-0.312141955593
H	-2.568876181467	-1.085640325963	-0.538280731471
Li	-0.635562529082	-0.630605461925	1.564773503425

85_C•(THF)

C	-0.838640706646	1.118754372123	-0.008070361262
C	-0.189610016078	1.070687921537	-1.307881192927
C	0.908484038801	1.939960797494	-1.551830932432
C	1.332154679651	2.806053924981	-0.559858311418
C	0.696834846022	2.846000846478	0.708907522469
C	-0.376418815440	2.013342412246	0.981683901225
C	-1.896500869366	0.134703911607	-0.020550665197
C	-1.879414882024	-0.499877406991	-1.326939017047
C	-2.833240483289	-1.517195638262	-1.602743863898
C	-3.753383276735	-1.872363308333	-0.635176573775
C	-3.766037508187	-1.249292811607	0.640183377740
C	-2.849016634943	-0.259870256022	0.946479385643
H	1.397273901016	1.937545187020	-2.524369082260
H	2.159940515396	3.483355525635	-0.758833639721
H	1.045779915259	3.548388675036	1.461346554151

H	-0.874598886505	2.061936041450	1.948500294652
H	-2.847796830762	-1.997165773493	-2.579098773396
H	-4.490034166356	-2.641766029355	-0.854706451474
H	-4.507744854349	-1.549568955222	1.375445635163
H	-2.871659877661	0.226055197983	1.920218166478
C	-0.802981647438	0.047379522328	-2.091905048158
H	-0.568153760008	-0.193771181352	-3.122460387348
Li	0.058389232160	-0.904657497913	-0.354444995673
O	1.666502731765	-1.473117977074	0.453513590343
C	2.902621886879	-1.192393219854	-0.263054868601
C	1.843897182970	-1.208887421373	1.877025997664
C	3.757355994275	-0.386883653815	0.712118975568
H	3.367003193961	-2.148810782076	-0.531834825440
H	2.644903145834	-0.644220504081	-1.173403864609
C	3.343735284550	-0.980478999764	2.067826281492
H	1.262369403537	-0.314643407544	2.129427453380
H	1.451879686997	-2.067537716474	2.428948344148
H	3.485292564379	0.672720659969	0.656743021764
H	4.826987129265	-0.484851428352	0.505349497548
H	3.552866488993	-0.315453814871	2.910409566040
H	3.859468442396	-1.931141340575	2.246257112688

85c•(THF)₂

C	0.007207799196	-1.324928400517	-1.854033677872
H	-0.196178378922	-1.204080329131	-2.912753114325
Li	-0.130729787530	0.375543047823	-0.366080171099
O	1.142360519610	1.840455469414	0.011012585577
C	1.949226843536	2.436418266611	-1.034631945512
C	1.798994840226	1.986818589549	1.295145377654
C	3.293549200253	2.766876299900	-0.384442325940
H	2.034996469067	1.713663161470	-1.850292364388
H	1.433468007727	3.336157777951	-1.393995015950
C	2.893945552940	3.030490874207	1.075984475827
H	1.043011946866	2.291293253144	2.026118730751
H	2.216086807981	1.015930739171	1.584027432993
H	3.787610727621	3.619623908790	-0.859725317420
H	3.957970783228	1.898737475473	-0.445387157868
H	2.490960909994	4.043990944782	1.189972913537
H	3.724611671759	2.912009656867	1.777951537685
O	-1.839742591368	1.311884063196	-0.029348105397
C	-2.877252925301	1.407005871622	-1.035178989667
C	-2.427031689442	1.308392891096	1.297068620733
C	-4.198494445645	1.211341091923	-0.290033805257
H	-2.811888758520	2.398178994691	-1.502378136254

H	-2.688549291757	0.638928946495	-1.789699120852
C	-3.872534601961	1.768679302626	1.104095614520
H	-2.375642334771	0.289856073045	1.698149191772
H	-1.834719526737	1.979074011781	1.927577135271
H	-4.431558954561	0.143877374865	-0.224175448414
H	-5.032715706520	1.723927508665	-0.778396099105
H	-4.535695689136	1.387391185456	1.886075418032
H	-3.933057567975	2.863581549021	1.107222463654
C	1.299840106565	-1.309830205580	-1.247294766371
C	1.165859031625	-1.656626289252	0.154896705659
C	2.594517538928	-1.036803820279	-1.759350936466
C	2.303866277805	-1.706264097855	0.983759104666
C	3.694249611009	-1.103065924535	-0.919419814246
H	2.724716323301	-0.809527107382	-2.816187652809
C	3.556299348375	-1.431581171958	0.452616937597
H	2.205024457741	-1.988285521619	2.030979283996
H	4.688260816233	-0.921529386000	-1.323585166846
H	4.440325998920	-1.491571058348	1.082450125328
C	-0.921763421872	-1.784766509670	-0.873254946688
C	-2.307381001591	-2.086617625900	-0.930806384728
C	-0.229087027308	-1.945277725173	0.391974391672
C	-2.967988576750	-2.510628042993	0.210069221267
H	-2.840356911081	-2.016719068942	-1.877718488819
C	-0.935171207291	-2.364281384534	1.537901081798
C	-2.291523310991	-2.641909290971	1.449422718659
H	-4.024056090790	-2.767385051821	0.153180668350
H	-0.411723566659	-2.496471108058	2.483528906035
H	-2.835623860175	-2.986655524618	2.325064003658

85C•(THF)₃

C	-1.885401350264	1.793120692653	0.416110289407
C	-1.009612172306	1.949113303869	-0.725264169065
C	-0.244933140472	3.136110877204	-0.829232698669
C	-0.309817555327	4.094760003918	0.174383696301
C	-1.130802490665	3.912535049815	1.309712222327
C	-1.920284213014	2.771687904732	1.421868347113
C	-2.608927403114	0.558468348363	0.235810553248
C	-2.156584182429	-0.029489105317	-1.006490296239
C	-2.770224603347	-1.227084363189	-1.446861170957
C	-3.756798348847	-1.827803373623	-0.674070493352
C	-4.171803805631	-1.263165618517	0.552128092038
C	-3.605189849479	-0.071464407975	0.996760719360
H	0.370774668174	3.312984067708	-1.710589869311
H	0.267664039383	5.012603816165	0.077228610677
H	-1.166377459534	4.679274218485	2.079591396805

H	-2.581893989744	2.651636182738	2.278987239940
H	-2.498810995961	-1.657937992291	-2.409632462657
H	-4.232251987104	-2.740653817068	-1.028031762603
H	-4.954184575667	-1.746132550146	1.132328633557
H	-3.956173826265	0.384424349104	1.922048027495
C	-1.127416622648	0.795411677527	-1.566692649876
H	-0.767744619699	0.731659783520	-2.590967337375
Li	0.528123195860	-0.206145043486	-0.373969627979
O	0.284763877967	-0.973338937252	1.451174208650
C	-0.471741526014	-2.209063951047	1.563822185958
C	0.190100002290	-0.220337237818	2.686810598423
C	-0.763437513599	-2.377240673384	3.054744904617
H	-1.391107442687	-2.109093293417	0.979563699064
H	0.139388996091	-3.014095191365	1.144215484171
C	-0.884843733093	-0.918679215261	3.520881705696
H	1.169594768138	-0.252383302603	3.183639209575
H	-0.059689823133	0.814324454978	2.440219115878
H	0.071036866107	-2.877855402724	3.561361117652
H	-1.671707547667	-2.960727921125	3.230957004423
H	-0.725255983021	-0.790494318569	4.595928781338
H	-1.872513321474	-0.525572955659	3.262919770516
O	1.244902458620	-1.824649159467	-1.344402578945
C	2.471418624106	-2.468498103856	-0.939641354989
C	0.612610571249	-2.572526078469	-2.412184433612
C	2.813650020505	-3.437899927502	-2.070940819206
H	3.216941525488	-1.688606273736	-0.768517894584
H	2.301326351480	-3.000765627571	0.006381442439
C	1.416902908099	-3.869358569328	-2.544960354957
H	-0.435719790471	-2.727600936227	-2.147210236008
H	0.658263876370	-1.969311423060	-3.327217190950
H	3.435583494877	-4.272754852481	-1.734242358642
H	3.347933222403	-2.916830175424	-2.874435513351
H	1.012352189361	-4.642161280798	-1.880796221642
H	1.406289745010	-4.262628669144	-3.565689788257
O	2.294423982939	0.784388108033	-0.309191492852
C	2.830302513657	1.304433756207	-1.550067918026
C	2.702648103832	1.627641062655	0.795385910295
C	3.557201362894	2.606024640845	-1.191946109382
H	3.514905618238	0.553105941727	-1.964103687763
H	2.003938514742	1.452007955744	-2.251278101618
C	3.924701671467	2.387858287791	0.284214294273
H	1.881034460474	2.309261716406	1.042964161082
H	2.910347082197	0.975769878726	1.648274429007
H	2.874901111213	3.456862037731	-1.285303461362
H	4.424081927285	2.787658879331	-1.834319237587
H	4.091966082590	3.322159560473	0.828102491824

H	4.827711071914	1.771778298751	0.373205993019
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85s•(THF)₄

C	-3.219391343988	0.702864161992	0.431426736192
Li	1.477142357407	0.511047132969	-0.714470228507
O	1.061691997623	-1.155411170672	-1.644354468277
C	0.327164404671	-1.168644451414	-2.891353147614
C	0.859431155092	-2.453634711917	-1.025452026277
C	0.590023441064	-2.564508292216	-3.449483327905
H	-0.739425944297	-1.010951345818	-2.688764726876
H	0.716255169436	-0.350273258579	-3.502342136334
C	0.582108001843	-3.445673187922	-2.178567557520
H	1.769103579544	-2.677745103635	-0.460296234718
H	0.005176904563	-2.394757202765	-0.343562628019
H	1.567879233382	-2.596285398826	-3.944086198027
H	-0.170157426879	-2.868139257296	-4.174749295174
H	1.331089509419	-4.241491649579	-2.229614651378
H	-0.399318482206	-3.902297875339	-2.031712585808
O	1.220194837285	0.616649960266	1.218620915689
C	0.498224462896	1.721653006848	1.819486965069
C	1.017318179638	-0.504661947768	2.115155857184
C	0.768056750740	1.598624949186	3.325324637224
H	0.883702716313	2.639278949771	1.367067748067
H	-0.568339860213	1.612156555440	1.593154945762
C	1.079233072741	0.090318768836	3.531771137145
H	0.035666369954	-0.947644387225	1.916725835893
H	1.803856458387	-1.233956523327	1.900803680486
H	-0.106823671849	1.912684989095	3.898346376499
H	1.621509990701	2.217133909256	3.622630126629
H	0.338434160448	-0.389408118233	4.175369495897
H	2.070026311296	-0.046719147047	3.977102725543
O	3.456260029532	0.789639150028	-0.939920025278
C	4.187544554680	0.102376958621	-1.989120205546
C	4.333886381476	1.014231297962	0.184233798680
C	5.551778225662	-0.289095035364	-1.387749162744
H	3.583474457338	-0.760313298676	-2.282587401483
H	4.287701089969	0.773320001747	-2.849833032062
C	5.327266489958	-0.142000763495	0.127906436456
H	4.840803488673	1.982899362943	0.065296854260
H	3.705481165200	1.040409684506	1.075965212895
H	6.332024438506	0.402744217321	-1.723221326848
H	5.855612162030	-1.298668569040	-1.678310042683
H	6.249381106883	0.063389317920	0.679433486747
H	4.872939110159	-1.048157113453	0.545125670842

O	0.638697008473	1.994697271228	-1.673736904330
C	1.289118902501	3.172680319715	-2.173422902337
C	-0.786064463461	2.244108531571	-1.776645656982
C	0.471886899694	4.336881070529	-1.600781593380
H	2.330738046108	3.135248469376	-1.847801871578
H	1.256234304638	3.166178874764	-3.273565984208
C	-0.961657062661	3.749341612225	-1.485759135805
H	-1.107053717236	1.992023581578	-2.795823116314
H	-1.298679544819	1.591004668812	-1.064810606174
H	0.519806449827	5.223540807177	-2.239810794367
H	0.855145831057	4.616932554928	-0.614176330963
H	-1.650186993744	4.206646257764	-2.202085046469
H	-1.375668226042	3.907980902807	-0.486467165870
C	-3.149903645345	-0.513884262247	-0.294841826197
C	-3.354658486767	-0.831770549408	-1.662341574571
C	-2.843063576952	-1.598295360293	0.624968862464
C	-3.268410053961	-2.150289291222	-2.092072427578
H	-3.621454347398	-0.046746955201	-2.370146865828
C	-2.752896912068	-2.917533790512	0.158226892717
C	-2.964791267117	-3.199234548486	-1.191443315447
H	-3.461303567508	-2.386291688565	-3.137941363344
H	-2.551270775499	-3.730792524434	0.855588827288
H	-2.939175759225	-4.227402277231	-1.546458368826
C	-3.003975933314	0.401414331537	1.802402050540
C	-2.749277202830	-1.021702128501	1.941169492770
C	-3.018967841668	1.199488283043	2.974454672772
C	-2.509603733664	-1.577390526395	3.207186336292
C	-2.781216425278	0.619974661361	4.213548254669
H	-3.238406657043	2.264766704544	2.905395301009
C	-2.518776492289	-0.765638211276	4.339674402042
H	-2.334902367279	-2.648449458155	3.309721920379
H	-2.814822846604	1.238160141135	5.109596551250
H	-2.356403299474	-1.198176759156	5.324395534454
H	-3.547145509796	1.660419505061	0.037565988663

85_T•(THF)₄

H	4.459853752532	1.790609758611	-1.553576192053
C	3.853649908110	1.968220386763	-0.665620965500
C	2.338716475641	2.450720815608	1.676670441646
C	3.284653015285	0.888045442425	0.024941627365
C	3.676197810798	3.268902607192	-0.196957628713
C	2.926887581839	3.499002767458	0.980365409795
C	2.488557266453	1.118642659107	1.216096697357
H	4.140358521175	4.104821368856	-0.715257575670
H	2.823836655710	4.516153112821	1.355323217144

H	1.791328368151	2.652155504589	2.598226133862
C	3.358926228207	-0.538403620475	-0.167130458198
C	3.299234314573	-3.330143840493	0.072869065795
C	4.015222174406	-1.335352172630	-1.117530993369
C	2.615191091534	-1.155083080543	0.916993201528
C	2.626953936887	-2.568868633769	1.019587008968
C	3.979651017089	-2.723665858243	-1.008345196359
H	4.572915628896	-0.869648397582	-1.929611762238
H	2.135844347488	-3.060882091113	1.859621195268
H	4.501545087834	-3.342523170566	-1.734416792573
H	3.313836769810	-4.414738976992	0.169384435026
C	2.040086192936	-0.132510077121	1.723533465609
H	1.591496055378	-0.285948980089	2.699998968353
Li	-0.715378249221	-0.175673173783	0.140256627685
O	-0.537249234176	1.516370350158	-0.807798635015
C	0.283880582864	1.642572892766	-2.002725692586
C	0.477166287565	3.150607964574	-2.234648232044
C	-0.645311605860	3.787364206589	-1.397007841468
C	-0.734145788386	2.822167974171	-0.219261920296
H	-0.262298710783	1.156649805626	-2.819733860870
H	1.232595091763	1.127083685616	-1.834172482064
H	1.454942028795	3.458228740453	-1.852860575049
H	0.419727248586	3.414043315852	-3.295303990180
H	-1.591440586301	3.803594973549	-1.952590643009
H	-0.413322585057	4.809050664209	-1.081747942344
H	-1.707591798669	2.806670175977	0.279961422369
H	0.059850461478	3.012085965146	0.511691787284
O	-3.340200757080	0.320483985629	-0.215312404227
C	-3.958782786987	1.195217073047	-1.178995512575
C	-5.478888794111	1.124031825677	-0.937111675684
C	-5.567948884948	0.577423646745	0.497231786248
C	-4.357517905620	-0.353763640268	0.536150809804
H	-3.681921036047	0.877729932505	-2.191743109205
H	-3.563832086735	2.204948320975	-1.021647568771
H	-5.966861279516	2.095212362621	-1.061518377791
H	-5.948716672929	0.423770471899	-1.637352544388
H	-6.511153816084	0.063548639077	0.706568346251
H	-5.447281723950	1.385230036414	1.228719654025
H	-4.596230175928	-1.322787750651	0.067024603892
H	-3.956036451265	-0.542285659151	1.533676150572
O	-0.750193714966	-1.635329265840	-1.180337635178
C	-1.879115247399	-1.889310994793	-2.048322263753
C	-1.399904170901	-2.922614502174	-3.072128423527
C	0.104161351610	-2.623281873658	-3.154554366606
C	0.440507018946	-2.302493661677	-1.702437268073
H	-2.165093002324	-0.946047863405	-2.528526185779

H	-2.719812459144	-2.233513038407	-1.438994948984
H	-1.563954864601	-3.939834386544	-2.697240214287
H	-1.920296578704	-2.827602957031	-4.030221173189
H	0.289260025858	-1.752983241846	-3.796071943283
H	0.694409005700	-3.459929561660	-3.538607371948
H	1.291743060263	-1.635534525269	-1.565438991914
H	0.618275458468	-3.207243966294	-1.114219752254
O	-1.378967959216	-0.730940027938	1.918322138603
C	-1.316173771108	0.149638976378	3.069426426164
C	-0.991676995572	-0.743501914140	4.272732998845
C	-1.512238129908	-2.118886651301	3.825060465397
C	-1.189365151755	-2.106092374001	2.332397448191
H	-2.293785064966	0.637467557171	3.170011126997
H	-0.551629422751	0.908192162895	2.881963765856
H	0.090380601703	-0.783904520019	4.434184097130
H	-1.459514193804	-0.382558114667	5.193421108342
H	-2.594891423717	-2.194746398949	3.983691221757
H	-1.031569053617	-2.950903706796	4.347886753155
H	-1.855746772558	-2.727193595963	1.727308626927
H	-0.151628472108	-2.395614525884	2.134763303350

86c

C	3.987514097826	0.550860934783	0.196567934783
C	3.712908097826	-0.833618065217	0.163300934783
C	2.433962097826	-1.303394065217	-0.040882065217
C	1.310118097826	-0.428897065217	-0.238377065217
C	1.624274097826	0.973729934783	-0.232729065217
C	2.940048097826	1.429814934783	-0.016297065217
H	4.998093097826	0.912131934783	0.360505934783
H	4.522790097826	-1.546721065217	0.300927934783
H	2.251167097826	-2.375576065217	-0.054878065217
H	0.900124097826	1.708041934783	-0.561370065217
H	3.125404097826	2.501497934783	-0.046491065217
C	-0.000011902174	-1.016110065217	-0.271341065217
H	-0.000101902174	-2.102401065217	-0.224237065217
C	-1.310044902174	-0.428715065217	-0.238415065217
C	-2.434007902174	-1.303314065217	-0.041768065217
C	-1.624191902174	0.973922934783	-0.231817065217
C	-3.712953902174	-0.833691065217	0.162546934783
H	-2.251196902174	-2.375489065217	-0.056527065217
C	-2.940050902174	1.429853934783	-0.015294065217
H	-0.900082902174	1.708571934783	-0.559790065217
C	-3.987551902174	0.550804934783	0.196779934783
H	-4.522888902174	-1.546861065217	0.299506934783
H	-3.125314902174	2.501574934783	-0.044744065217
H	-4.998168902174	0.911931934783	0.360796934783
Li	0.000036097826	0.378602934783	1.290882934783

86c•(THF)

C	-0.991612810390	-3.806216861097	0.112086966224
C	-0.426323163364	-3.421198598692	1.346442393792
C	-0.502400908509	-2.117250302933	1.791115188930
C	-1.152776035719	-1.077115642763	1.040473708831
C	-1.756323876414	-1.509089091806	-0.187497384337
C	-1.664156196067	-2.840780101223	-0.624293060473
H	-0.930066315363	-4.834221304884	-0.232350738774
H	0.076396015384	-4.162814808874	1.964351659172
H	-0.053649804938	-1.849550589867	2.745652001905
H	-2.410124544961	-0.850592391849	-0.744033668854
H	-2.157921954309	-3.114422438772	-1.554870836935
C	-1.038589481424	0.269695416097	1.516607221707
H	-0.549977875009	0.357762273722	2.484719363047
C	-1.351209553945	1.529939664979	0.905688267174
C	-0.940974437155	2.726942097251	1.587870916721
C	-1.921120382808	1.744294410256	-0.394428302065
C	-1.061459597504	3.981973181771	1.029641580189
H	-0.520468811122	2.622293381035	2.585965778305
C	-2.026402601941	3.031975074226	-0.948649987803
H	-2.392665571693	0.936597206819	-0.938620252576
C	-1.596175771993	4.157870563418	-0.263564608475
H	-0.738339903543	4.849078016871	1.602269317105
H	-2.482611331760	3.134848838486	-1.931383042171
H	-1.689049874302	5.148888593396	-0.697508820343
Li	-0.075614821227	0.251398368666	-0.396513339883
O	1.622500429035	-0.100685504553	-1.131574100171
C	2.768374222904	0.791425191479	-1.068774486476
C	2.062684069695	-1.477715662073	-1.299560323535
C	3.995666661673	-0.088804767345	-1.328677925115
H	2.631428787054	1.581468825903	-1.812894680181
H	2.789529417505	1.243829865448	-0.070572917585
C	3.522018770187	-1.472794783411	-0.855729895695
H	1.407763602968	-2.114548466215	-0.700461061785
H	1.959860364241	-1.747587269076	-2.358199491945
H	4.879818590229	0.271508065576	-0.795314482810
H	4.231827578500	-0.111621265859	-2.398624304788
H	3.586470179978	-1.552391112546	0.235492202477
H	4.093309039184	-2.296135217689	-1.293984819811

86c•(THF)₂

C	0.128601917883	-1.388668255409	-1.246553073152
H	-0.244905803142	-1.353797391281	-2.270765657986
Li	-0.379345095380	0.386975043482	-0.067119216187
O	0.960433893699	1.588681342196	0.683120165466
C	1.682813883046	2.401048120272	-0.284684026297
C	1.795234341931	1.343110229808	1.843456651056

C	3.103600230496	2.546163967093	0.266884973403
H	1.655539679594	1.890660335158	-1.251662946036
H	1.165359679212	3.364707359253	-0.363222826561
C	2.887470468938	2.408235919510	1.782053842635
H	1.157500290227	1.407690280735	2.729972550679
H	2.216322150475	0.334624287579	1.764702081921
H	3.560611042006	3.498349931739	-0.018968121867
H	3.735253931527	1.732568419094	-0.104221067592
H	2.530897172894	3.351653550001	2.212825642538
H	3.791049746356	2.105228072566	2.319033786130
O	-1.991118844229	1.448146342533	-0.277783494970
C	-2.947950754073	1.222271241520	-1.344344966609
C	-2.678360424637	1.875839844656	0.928575801977
C	-4.313702135704	1.181604867739	-0.662600672859
H	-2.869919713175	2.051451734821	-2.059421574599
H	-2.680847912150	0.287124181878	-1.841346577892
C	-4.120010622108	2.163217632100	0.503548407559
H	-2.627831034625	1.059096550232	1.658254030564
H	-2.152638371506	2.748659556418	1.326287181631
H	-4.508716202275	0.172251315752	-0.284981539473
H	-5.126023249904	1.466190301039	-1.338043293301
H	-4.829515356428	2.007209348403	1.321316267822
H	-4.220827178405	3.198548825053	0.156887613771
C	-0.837565864104	-1.819315864775	-0.277440338096
C	-0.682733967619	-1.728624450029	1.146764136258
C	-2.141062577905	-2.234421866354	-0.711800367218
C	-1.729509262676	-2.026410795213	2.026952358638
H	0.277950178833	-1.451967264772	1.570307890129
C	-3.165470589080	-2.525885607475	0.171876169701
H	-2.308230020062	-2.346413832677	-1.781715604013
C	-2.981714697172	-2.422747112273	1.563477400708
H	-1.545894343175	-1.956254616443	3.098014831152
H	-4.123642982880	-2.861524145316	-0.221849134277
H	-3.783747129320	-2.669109823466	2.252999344447
C	1.571675187907	-1.313934151783	-1.142501785008
C	2.354194974742	-1.807089056142	-0.060734878832
C	2.310524228177	-0.731478176563	-2.214319076925
C	3.744284837902	-1.689495564408	-0.044206449364
H	1.870895551920	-2.350210192383	0.744396849562
C	3.694234592748	-0.619305893085	-2.191492264638
H	1.760063754126	-0.374122186215	-3.083858938188
C	4.436165712487	-1.083417376900	-1.095471569458
H	4.295836234839	-2.100953445204	0.799675518516
H	4.205348700143	-0.171319118130	-3.041915632060
H	5.519309188203	-1.000074555832	-1.078678031303

86c•(THF)₃

C	-1.589994080189	-2.409221990566	0.102295014151
C	-1.358108080189	-1.676498990566	-1.100474985849
C	-2.525708080189	-1.439637990566	-1.889026985849
C	-3.787271080189	-1.886389990566	-1.519033985849
C	-3.979081080189	-2.606554990566	-0.330847985849
C	-2.859827080189	-2.859640990566	0.465302014151
C	1.631301919811	-2.705609990566	-0.473963985849
C	1.246770919811	-1.633260990566	-1.332199985849
C	2.324569919811	-1.035885990566	-2.057949985849
C	3.649064919811	-1.419127990566	-1.893612985849
C	3.997927919811	-2.442695990566	-1.001419985849
C	2.963616919811	-3.088242990566	-0.318687985849
H	-2.405368080189	-0.914464990566	-2.835631985849
H	-4.632448080189	-1.693612990566	-2.178343985849
H	-4.962658080189	-2.971868990566	-0.049251985849
H	-2.971310080189	-3.423412990566	1.390502014151
H	2.082782919811	-0.266200990566	-2.789462985849
H	4.421182919811	-0.926232990566	-2.482736985849
H	5.032933919811	-2.746267990566	-0.872085985849
H	3.192613919811	-3.924924990566	0.340180014151
C	-0.092839080189	-1.128401990566	-1.538698985849
H	-0.181646080189	-0.545358990566	-2.459827985849
Li	-0.044652080189	0.556715009434	-0.030478985849
O	0.942878919811	0.249208009434	1.692804014151
C	2.397744919811	0.216928009434	1.631301014151
C	0.484612919811	-0.512623990566	2.829499014151
C	2.860740919811	-0.574724990566	2.860407014151
H	2.682721919811	-0.274251990566	0.698166014151
H	2.762683919811	1.249679009434	1.626494014151
C	1.637985919811	-1.450097990566	3.177546014151
H	0.260961919811	0.175119009434	3.658480014151
H	-0.433627080189	-1.027879990566	2.537229014151
H	3.079917919811	0.096594009434	3.699435014151
H	3.759008919811	-1.160061990566	2.646509014151
H	1.604523919811	-1.790337990566	4.217129014151
H	1.621479919811	-2.323157990566	2.517630014151
O	0.845404919811	2.300680009434	-0.560484985849
C	0.742361919811	3.431435009434	0.331254014151
C	1.831654919811	2.564808009434	-1.589609985849
C	1.351780919811	4.604247009434	-0.434033985849
H	-0.311251080189	3.553829009434	0.590482014151
H	1.304170919811	3.216298009434	1.250734014151
C	2.471131919811	3.909486009434	-1.225314985849
H	2.538302919811	1.731822009434	-1.610614985849

H	1.312164919811	2.608327009434	-2.554536985849
H	1.715224919811	5.395219009434	0.228965014151
H	0.612681919811	5.042015009434	-1.115605985849
H	3.348657919811	3.757055009434	-0.585906985849
H	2.791840919811	4.469586009434	-2.108491985849
O	-1.826591080189	1.395643009434	0.437735014151
C	-2.621593080189	1.897954009434	-0.667785985849
C	-2.699596080189	0.952364009434	1.504187014151
C	-4.088600080189	1.724918009434	-0.255375985849
H	-2.352773080189	2.950697009434	-0.819801985849
H	-2.367638080189	1.327592009434	-1.565021985849
C	-4.009635080189	1.702406009434	1.278962014151
H	-2.839210080189	-0.131979990566	1.425918014151
H	-2.207316080189	1.191171009434	2.451516014151
H	-4.465613080189	0.765945009434	-0.624075985849
H	-4.725993080189	2.524296009434	-0.645374985849
H	-4.862557080189	1.200208009434	1.744928014151
H	-3.944981080189	2.720020009434	1.683331014151
H	0.870466919811	-3.287060990566	0.032379014151
H	-0.763603080189	-2.618357990566	0.771485014151

86s•(THF)₄

C	-3.160890003793	0.087116608499	0.211336495711
Li	1.494286381648	0.372990588206	-0.579303292864
O	0.988868996820	-0.985814271212	-1.895550304670
C	0.085579501595	-0.709646739360	-2.992861888187
C	0.987555170199	-2.424260891483	-1.703711667727
C	0.378269900269	-1.826992274850	-3.990212103210
H	-0.949604942379	-0.753526399702	-2.633035717596
H	0.315414260891	0.296375720755	-3.351616535311
C	0.622765548799	-3.046634401308	-3.071999430536
H	1.986598248675	-2.695697422129	-1.347799299523
H	0.240747811705	-2.682243891312	-0.946518752947
H	1.275114660084	-1.587865982726	-4.573648820190
H	-0.450619861325	-1.985931434302	-4.685593052082
H	1.415865272183	-3.694646353257	-3.457144147945
H	-0.288451710443	-3.640465125398	-2.965682990344
O	1.262535363397	0.049014680132	1.335172800485
C	0.696501718125	1.053915119285	2.221870497203
C	1.124511082121	-1.256989067233	1.958751807259
C	0.936499147941	0.498661268945	3.619896063652
H	1.216395269706	1.992789603871	2.012215172934
H	-0.372451160888	1.166708762544	2.015142050314
C	0.676299567179	-1.003783103447	3.410051945104

H	0.391352415765	-1.842904046400	1.396273119413
H	2.103198056980	-1.747581797260	1.895541069660
H	0.254842603767	0.940457744475	4.350852874133
H	1.970597342350	0.683340670074	3.936994185758
H	-0.394031350124	-1.200970477374	3.510070072010
H	1.215391981210	-1.634740783490	4.123050523250
O	3.479111516240	0.576705009639	-0.790909106182
C	4.159172179154	0.185221961029	-2.011188119968
C	4.401799723522	0.488383560262	0.313356810975
C	5.511857333089	-0.422032100125	-1.583946051372
H	3.504905324814	-0.526498164878	-2.520738243115
H	4.283223939213	1.068511074695	-2.648180190048
C	5.341525794715	-0.650821362004	-0.070329354200
H	4.946420749465	1.438571348299	0.415918409605
H	3.806225683356	0.315742436465	1.211374750595
H	6.326320220573	0.285921244800	-1.771071037405
H	5.741026722944	-1.341967808068	-2.128928761744
H	6.288811840190	-0.622804022275	0.475974835524
H	4.860222951799	-1.615662379223	0.126751623955
O	0.757395211736	2.098605510952	-1.121316221301
C	1.490674142842	3.317277877052	-1.319602864065
C	-0.644232205773	2.465134827595	-1.148446296957
C	0.740916422308	4.370112988544	-0.490093175997
H	2.520804280042	3.132993305203	-1.008000231120
H	1.481639787359	3.572833453765	-2.390015164993
C	-0.716679704187	3.831664416672	-0.440537350954
H	-0.959527216573	2.540088228124	-2.198673382929
H	-1.212530187209	1.667697109873	-0.661193825395
H	0.812375043226	5.363834979358	-0.942159492963
H	1.162878888188	4.434947822967	0.517852897069
H	-1.420514523512	4.497859186827	-0.947870394106
H	-1.061072312063	3.710384366633	0.588888356629
C	-2.992374794471	-1.222400421147	-0.320339148021
C	-3.383083357503	-1.473992707824	-1.680611206884
C	-2.432853386137	-2.361833073308	0.350392596293
C	-3.265490282082	-2.716340913443	-2.283376750493
H	-3.825891988371	-0.651713919718	-2.241718007315
C	-2.317332239491	-3.604825107039	-0.267844556955
H	-2.085565388183	-2.265607272321	1.371895505359
C	-2.730508433499	-3.815892920765	-1.589297349645
H	-3.612157642726	-2.840964469058	-3.309009110635
H	-1.904966875500	-4.435450249157	0.305395822535
H	-2.674500399394	-4.799424543924	-2.048137818552
C	-3.072682762252	0.596506315023	1.540767670370
C	-2.933986190867	-0.166339867838	2.746125965048
C	-3.169201134889	2.014292993006	1.749284875892

C	-2.842410697476	0.437372027779	3.999295984981
H	-2.982043646977	-1.247894660434	2.701905202492
C	-3.067536903808	2.603519085771	3.000262405261
H	-3.348572871734	2.645674682952	0.879603880698
C	-2.879041042717	1.827119889310	4.155829010134
H	-2.763497975686	-0.200775430601	4.879461452099
H	-3.152413904110	3.686655097384	3.083999543051
H	-2.809992112424	2.286656580271	5.137950318895
H	-3.511859692833	0.819150087373	-0.518593034064

86T•(THF)₄

C	1.015784907381	-2.494945855098	-2.682751192652
C	1.078469509904	-2.445181390964	-1.254057089587
C	2.160346480754	-2.577797735668	-3.473062291441
H	0.051228655308	-2.540206507699	-3.174113688417
C	2.405402929174	-2.527743090035	-0.718393730188
C	3.441939676991	-2.617923848697	-2.914586568526
H	2.042934058464	-2.632017250131	-4.554876819174
C	-0.031638432494	-2.388245597040	-0.348751490824
C	3.539063245276	-2.608087937398	-1.513421542201
C	-1.441146649148	-2.460572037388	-0.598184827854
H	2.516170511486	-2.558345352436	0.365633209610
H	4.327860809315	-2.691551098882	-3.539272666508
H	0.242321818985	-2.671766962588	0.669063005026
C	-2.115420938863	-2.058286167943	-1.795319136307
C	-2.307245771142	-2.963587942310	0.427319834434
H	4.516673432308	-2.681155845967	-1.037817951371
C	-3.682238633186	-3.068934592212	0.270785429407
C	-3.495423676510	-2.174189170667	-1.945579818035
H	-1.852204245943	-3.322691093960	1.350500806186
H	-1.546026011686	-1.629902653306	-2.612444030113
C	-4.307827782115	-2.678475381111	-0.923783532017
H	-4.277508343859	-3.484130862476	1.083243581168
H	-3.946038559480	-1.863641733880	-2.887811928065
H	-5.380439070683	-2.787312484838	-1.058525492235
Li	0.067966264272	0.574222288208	0.469770689388
O	1.204733259421	1.135610146374	-1.065537423212
O	0.735830780226	0.014697752533	2.290237100490
O	0.524033502745	2.824928955744	1.310312914714
O	-1.871112922591	1.032494333839	0.450690933369
C	0.825193505858	1.113054533605	-2.463170454954
C	2.653262045028	1.109421559888	-0.958652705548
C	0.231043596110	-1.064401248791	3.100020721690
C	2.014913716288	0.361277296703	2.845846271283

C	0.552049907007	3.952041204707	0.429743383968
C	-0.260204256806	3.247833650906	2.431031630880
C	-2.813261538117	0.510732263618	1.428095964023
C	-2.590996806683	1.457428739781	-0.729267514424
C	2.008907838383	1.739967293704	-3.192972436750
H	0.667689582723	0.075683896708	-2.776182445243
H	-0.107508014673	1.676402603187	-2.557356775609
C	3.197242248238	1.178959839992	-2.394596998514
H	2.948652980574	1.975035975409	-0.352751379774
H	2.952517000655	0.185896949659	-0.456091932563
C	1.460100746733	-1.912118113714	3.487305356908
H	-0.256552694212	-0.638279898884	3.988920611962
H	-0.508720918008	-1.598492180405	2.504013359988
C	2.668595956032	-0.981482703549	3.194558852589
H	2.549816491745	0.952315567526	2.101835349567
H	1.863256322079	0.978766655833	3.744565697293
C	0.748562371149	5.175011951693	1.344479150570
H	1.353195841188	3.791544094320	-0.292602505897
H	-0.403784184033	4.018907076686	-0.114262147102
C	0.159782204968	4.706536502848	2.704504477321
H	-1.326503027890	3.184121632639	2.169104810126
H	-0.060670366361	2.557159628532	3.252351781849
C	-4.216032515250	0.732497114349	0.840570337759
H	-2.604578758569	-0.549538902753	1.587900305022
H	-2.652845733644	1.066926532662	2.359312389216
C	-3.985089965409	1.816806273500	-0.224348794370
H	-2.041662711536	2.299794573024	-1.160793816340
H	-2.625461197821	0.628331146171	-1.445263659376
H	1.968029137017	2.834513020897	-3.125616703640
H	2.038187620155	1.461723872563	-4.250562808626
H	4.093404761263	1.803278021815	-2.465174767011
H	3.446803844432	0.172883184281	-2.744379633883
H	1.513922502851	-2.820325648549	2.881864037796
H	1.413345371347	-2.213403762187	4.538048032715
H	3.239793253152	-1.354334198683	2.339767878327
H	3.352434941519	-0.892434289875	4.043991646479
H	0.246041617819	6.062526805242	0.948339058245
H	1.811533514871	5.414103882984	1.444993078342
H	-0.691329286894	5.314515651409	3.025745067932
H	0.916154930553	4.756367646378	3.493300704499
H	-4.940021395611	1.031172028361	1.604929641500
H	-4.568531311589	-0.190579510055	0.371030481654
H	-3.984106549905	2.818111297891	0.223986455156
H	-4.734055885936	1.797939644576	-1.021647829599

87c

C	-0.035657816321	-0.018134976880	-0.158549413745
C	1.379308681531	-0.426041888920	-0.024710760358
C	4.093442805489	-1.235970779100	0.383988610229
C	1.915904516685	-1.592559009354	-0.631205255230
C	2.272842614024	0.307558510817	0.809040032104
C	3.599781845588	-0.085136859991	0.999153952287
C	3.235946906739	-1.983507856453	-0.431959678450
H	1.279313663817	-2.175558862078	-1.290564069450
H	1.924175834972	1.234914452362	1.261479099688
H	4.247714604217	0.517218402829	1.631695386308
H	3.607195184797	-2.874312375705	-0.933495788034
H	5.124610831051	-1.543818696280	0.530864909010
C	-1.094019219486	-1.008538245877	-0.092769606315
C	-3.271621335454	-2.862091965235	0.342595259970
C	-2.442039695817	-0.725592735880	-0.487463467830
C	-0.909932189019	-2.306224491620	0.513723501922
C	-1.978159954444	-3.193906446338	0.718161358829
C	-3.478403389383	-1.616190493836	-0.279506954666
H	-2.645197786417	0.213591963048	-0.990154067161
H	0.093786496179	-2.687216350032	0.699155990948
H	-1.768643919368	-4.166068601037	1.159773671785
H	-4.475351025910	-1.346721223743	-0.622123148564
H	-4.095184064447	-3.552627601320	0.495663820481
C	-0.322430893368	1.430417566978	-0.297173333198
C	-0.782719999959	4.234828933097	-0.529547862815
C	-1.397790234180	2.068529155107	0.365690625472
C	0.512598319458	2.260623269393	-1.079323629213
C	0.291665324136	3.631545772310	-1.188067221454
C	-1.626630093040	3.438409717198	0.247384599253
H	-2.073286220907	1.475964917869	0.978872498176
H	1.344386155431	1.810284176775	-1.613858379188
H	0.956631448365	4.231449444253	-1.805358067961
H	-2.465283092954	3.886538328498	0.775690830811
H	-0.959544486727	5.302961561555	-0.621291020999
Li	0.044053072941	-0.744900863163	1.755627931130

87c•(THF)

C	0.064756280726	-0.203695010843	-1.117393731749
C	0.333576607812	1.249893127460	-1.127988227631
C	-0.312378084195	2.150566233294	-2.015542101449
C	1.252040286185	1.841174547841	-0.215208336068
C	-0.071999298841	3.521484500494	-1.983781615449
H	-0.996112669286	1.750614083985	-2.758372405665
C	1.500377932250	3.212508801834	-0.194696422010

H	1.800029832590	1.194405694247	0.466109842558
C	0.835066871594	4.072052544653	-1.073242364549
H	-0.584651109208	4.165785676369	-2.694914310249
H	2.222602828017	3.611732380660	0.514812424040
H	1.026474506959	5.141324412204	-1.056793491068
C	-1.267049626837	-0.712323265286	-1.416457926583
C	-2.459363149521	0.059918091682	-1.187351735838
C	-1.506896592786	-2.056207667073	-1.844359974226
C	-3.743038465067	-0.476255342029	-1.345023103198
H	-2.382834267284	1.125714476460	-0.972458930716
C	-2.783012322391	-2.570544049909	-1.998886352577
H	-0.654171444392	-2.684039147110	-2.079369627963
C	-3.927027682237	-1.796570062110	-1.739583784601
H	-4.603076800648	0.166928566657	-1.168951863348
H	-2.895204102856	-3.595868955125	-2.345976431996
H	-4.922678227137	-2.210373156754	-1.867735994149
C	1.197670768070	-1.124987935076	-0.871776921843
C	2.501799482545	-0.831720844244	-1.336934309814
C	1.060419579575	-2.329588975304	-0.135978073440
C	3.584715818704	-1.668030743256	-1.076743330715
H	2.657360733758	0.071272491918	-1.920052914919
C	2.141623823623	-3.173287252516	0.113782371683
H	0.078049793183	-2.616259552740	0.233732322338
C	3.418999075080	-2.849960382806	-0.349958611837
H	4.566726551010	-1.400763464362	-1.461418516903
H	1.983194165153	-4.088443934037	0.680884942572
H	4.263056755992	-3.505911768031	-0.155056941551
Li	-1.077535656643	0.201474046301	0.595110439101
O	-0.868895515870	0.354279290056	2.458526441073
C	-0.862071744373	1.646095057774	3.133127582420
C	-0.079923984666	-0.611038231038	3.211320838488
C	-0.166824283638	1.406130764781	4.475517266954
H	-0.309441222432	2.350979121299	2.501829306370
H	-1.897944355119	1.983860114055	3.230475985106
C	0.770110953055	0.228875570494	4.160478093472
H	-0.769055123399	-1.269801448737	3.753812153860
H	0.498570678723	-1.201388068380	2.495595451440
H	-0.896658828332	1.119823189282	5.241273943387
H	0.362449773658	2.296048499704	4.827421064196
H	1.072692095082	-0.330670074596	5.050107666052
H	1.674958064856	0.579437530777	3.651588104084

87c•(THF)₂

C	0.429642468102	-1.213660626964	-0.654863381405
Li	-0.409842081143	0.572671565794	0.365190656094
O	0.530835419279	1.566590362175	1.761519536589
C	1.630026340367	2.472385717614	1.489542848243
C	0.553570359121	1.143266568446	3.153004280978

C	2.542146676587	2.390081495319	2.714383943855
H	2.114627969204	2.150448737630	0.563706578277
H	1.222350689538	3.482592006251	1.352687140266
C	1.547386274034	2.078135654737	3.843504748178
H	-0.465336448536	1.216296505502	3.542829371697
H	0.867630149170	0.095073156175	3.189346486183
H	3.104690239236	3.314358167242	2.875387889564
H	3.259831920039	1.570561160652	2.597419854370
H	1.047305155458	2.995100732580	4.177350671743
H	2.016546716430	1.611183910634	4.714246927821
O	-1.805588037000	1.844857091483	-0.149879484241
C	-2.622582388862	1.845111526481	-1.355646219157
C	-2.408530150302	2.688601255722	0.861624613238
C	-3.964375385998	2.434998170861	-0.927322800059
H	-2.125532433551	2.468160152986	-2.107648940222
H	-2.675868340559	0.822111111844	-1.729653844072
C	-3.543155667561	3.436651078065	0.158543937036
H	-2.786916338792	2.046417563605	1.667700763775
H	-1.634087445408	3.342585259594	1.270886202137
H	-4.608058089652	1.655911671085	-0.501883247434
H	-4.498506311244	2.899309585797	-1.761310707733
H	-4.352203382589	3.702249722380	0.845408138315
H	-3.168329818716	4.359868629770	-0.298772733792
C	-0.124371458745	-1.712568011142	0.600003130165
C	0.653207777863	-2.422395886924	1.568734444885
C	-1.476948021201	-1.455615590898	1.004593564426
C	0.142323826891	-2.808843373217	2.799280497917
H	1.672151583602	-2.695422601965	1.316938213161
C	-1.979616488378	-1.848361997966	2.247617806312
H	-2.163460825409	-0.983614492637	0.305384926481
C	-1.180357172324	-2.520108714718	3.170512754740
H	0.782735919482	-3.368296094935	3.479149057251
H	-3.020799530455	-1.633626503503	2.482967974330
H	-1.574157364307	-2.833414868954	4.132985435414
C	1.901443217916	-1.173052952866	-0.849600459473
C	2.789795171191	-0.701554437337	0.148212902439
C	2.508579548376	-1.606401699798	-2.052695579192
C	4.169697460962	-0.658937053990	-0.041200980794
H	2.379888270906	-0.370769692925	1.098247542443
C	3.886499801497	-1.551830768059	-2.249626505399
H	1.878812828655	-1.999377540546	-2.844917259872
C	4.736240072288	-1.077648024001	-1.247329735416
H	4.807922542327	-0.289766971541	0.759972717588
H	4.301791018297	-1.901146908926	-3.192782336392
H	5.811604653321	-1.041216785379	-1.399519688255
C	-0.422195017243	-1.057339424670	-1.852959131019

C	-0.090170409581	-0.122934899046	-2.872669405078
C	-1.598622912826	-1.816926649425	-2.082082582237
C	-0.865835527030	0.038197607782	-4.016326538361
H	0.810989618053	0.474285527623	-2.758177011592
C	-2.384807449273	-1.641563292091	-3.220343991998
H	-1.881811325879	-2.578208771857	-1.361709644512
C	-2.032789043085	-0.711443358477	-4.202475078707
H	-0.560360148512	0.764312123403	-4.767316906052
H	-3.271411708958	-2.259280997372	-3.350763293540
H	-2.641703992699	-0.583731701491	-5.093355169120

87C•(THF)₃

C	-0.050557178627	-1.201783589688	-1.157493896004
Li	-0.004110804011	0.516493505877	0.401545966381
O	0.270026505971	0.018849915704	2.374266439196
C	1.503662571390	0.361019635867	3.052227577319
C	-0.446208785276	-0.993472723739	3.130720579011
C	1.469884515890	-0.373858298834	4.396728890138
H	2.338005396975	0.026828836150	2.426000715085
H	1.555218142867	1.449269620236	3.156272577155
C	0.586866260914	-1.590754750518	4.082201073775
H	-1.260530859596	-0.505521404144	3.683885808408
H	-0.869733828379	-1.706674721184	2.424047415558
H	0.998791650538	0.249545585621	5.166196737923
H	2.471682637630	-0.641051889069	4.746186487509
H	0.127554447829	-2.034175304878	4.970654089226
H	1.166064085139	-2.369661140366	3.573372400478
O	1.449259805004	1.932685192791	0.221980738258
C	1.200023648126	3.312815181487	0.577063753644
C	2.797943808433	1.795938244309	-0.291271963688
C	2.508140153587	4.074332935101	0.306721973810
H	0.358680836114	3.687553086759	-0.012973320086
H	0.917886160714	3.340007924788	1.636414108469
C	3.564166320980	2.957882760727	0.331855097210
H	3.157870764665	0.802976502672	-0.020651511896
H	2.778774643599	1.873063314193	-1.385697978917
H	2.688712834851	4.861381745486	1.045003476362
H	2.479917707058	4.544015938388	-0.683032328516
H	3.852392049951	2.717870803638	1.362492738258
H	4.470991376860	3.209678087297	-0.225908057104
O	-1.652524497298	1.699917814169	0.544618758173
C	-2.365658712409	2.331640041946	-0.553569079523
C	-2.481889432358	1.683711343148	1.730669053339
C	-3.817659630377	2.439538323729	-0.089506949653

H	-1.925519700787	3.323260447488	-0.725159158673
H	-2.225076610236	1.723911166648	-1.447445077828
C	-3.659626782082	2.611942962830	1.428705013761
H	-2.814906068268	0.653501076558	1.904559008162
H	-1.871812246093	2.004795232365	2.579741738482
H	-4.359504603065	1.514207692414	-0.316050095488
H	-4.346625810098	3.268625152101	-0.568662506463
H	-4.556498835318	2.341607824754	1.994162210386
H	-3.404595973099	3.650605681110	1.671722335874
C	1.407741649502	-1.426117539442	-1.137600251559
C	2.106359512477	-1.776806570504	0.053413926858
C	2.225985465070	-1.302836084330	-2.293706547462
C	3.485734543500	-1.969322029606	0.087167875998
H	1.540858902180	-1.905241341435	0.970864278752
C	3.606138321974	-1.480623265344	-2.255080071921
H	1.756881456967	-1.078817044808	-3.246076458385
C	4.262229931298	-1.811859682323	-1.065204998368
H	3.959634769457	-2.245315290700	1.028180093772
H	4.175598963666	-1.380808372468	-3.177479878570
H	5.338220731179	-1.961143865244	-1.040716305016
C	-0.641950458521	-0.437312165080	-2.277156266187
C	-0.025331414473	0.730790250575	-2.804767501093
C	-1.862452540675	-0.805489244173	-2.903425981464
C	-0.580721373625	1.467036545654	-3.847977619390
H	0.915110787014	1.063527126096	-2.377336272677
C	-2.426526507893	-0.059198066101	-3.935756336942
H	-2.367251808557	-1.709058870392	-2.577535339704
C	-1.797843951472	1.090235068520	-4.423661791897
H	-0.058494636437	2.351205597654	-4.209942898555
H	-3.361586148507	-0.395732461306	-4.379980052950
H	-2.235267268997	1.666142133106	-5.234704258333
C	-0.927817107681	-2.072763702731	-0.351586347139
C	-0.528405983479	-3.350302293018	0.127407477451
C	-2.251134280371	-1.686267451289	0.008629931999
C	-1.357464143642	-4.146065841067	0.914596550959
H	0.450326947883	-3.730138081970	-0.146394159994
C	-3.083603501457	-2.489292449974	0.783716182719
H	-2.628359200804	-0.730925946794	-0.342799681104
C	-2.646228568983	-3.728765333080	1.261919733684
H	-0.996447846204	-5.119336447368	1.242530407322
H	-4.087562602395	-2.139733223572	1.019859258986
H	-3.293941442130	-4.355302347082	1.868959533614

87s•(THF)₄

C	-2.809480388081	0.081157535171	0.506758581124
Li	2.174337264941	-0.078808194937	-0.496708289082
O	1.576813349535	-1.452070678215	-1.765579785698
C	0.273830666575	-1.504791693228	-2.430965755276
C	2.274819589162	-2.701646049819	-1.955936348506
C	0.239621189151	-2.836749445931	-3.184411724143
H	-0.499314166021	-1.452962848073	-1.661025354796
H	0.198255607476	-0.634976061129	-3.089684745273
C	1.201413944086	-3.708368119478	-2.363419157461
H	3.030255554384	-2.575553757685	-2.744897627158
H	2.785640953201	-2.951591528760	-1.020906021915
H	0.607853475517	-2.717184154148	-4.210512816421
H	-0.772885826044	-3.245665145009	-3.218664875500
H	1.612933900131	-4.551844220103	-2.926204639824
H	0.684800692121	-4.095923109323	-1.479474741270
O	2.070110406793	-0.609152707185	1.387471165764
C	1.770820524174	0.311265563199	2.475637000141
C	1.855421620551	-1.975944346165	1.828989132272
C	1.838472851062	-0.531952920038	3.744758026346
H	2.514280922513	1.114090753110	2.439967978851
H	0.769997472159	0.729857312996	2.328586440049
C	1.293045396281	-1.880954703583	3.251297893693
H	1.170920416031	-2.459686463697	1.126648004759
H	2.823784516653	-2.493695606719	1.804448167373
H	1.230695077785	-0.101344027011	4.544358819933
H	2.873728897069	-0.629314599856	4.094737560835
H	0.199300450495	-1.847162521951	3.233258174433
H	1.602374785977	-2.727014020553	3.872329228536
O	4.121025528761	0.089921380670	-0.883532458242
C	4.573845173552	0.518226747301	-2.191259491264
C	5.229577221897	0.040468708792	0.041398699575
C	6.028990996978	0.957824477625	-2.004683646681
H	4.489268653484	-0.331089297560	-2.880131366453
H	3.911072655327	1.316731675597	-2.536323433908
C	6.485811317574	0.079507121052	-0.828961471178
H	5.176211877508	0.910586918056	0.709511217727
H	5.130045505576	-0.867206861889	0.642061262298
H	6.078997298517	2.018118248990	-1.731078528759
H	6.625540892739	0.814346176593	-2.910050271433
H	7.351453743484	0.483844383422	-0.296544294630
H	6.739749218942	-0.928004228998	-1.178396277176
O	1.480087750319	1.710752786365	-0.856112279278
C	2.046342988094	2.927557439026	-0.324686415461
C	0.079514167530	1.940098521746	-1.230544406845

C	0.850673780105	3.787392512042	0.078287135364
H	2.705611986231	2.661414598142	0.507601435216
H	2.647445147330	3.416803069108	-1.105026263758
C	-0.172061009452	3.433049101681	-1.012066538944
H	-0.047327476617	1.632748020956	-2.271051808665
H	-0.550467384673	1.314521058806	-0.592371991717
H	1.096129533801	4.853116850296	0.115856406545
H	0.480298968588	3.480697400527	1.062748332363
H	0.036853282837	3.999303234753	-1.927502839772
H	-1.207982926877	3.625868335668	-0.723771054420
C	-3.314555970709	1.135440696072	-0.380419117242
C	-4.023745849812	2.268304828327	0.108268097062
C	-3.126075064992	1.112617473925	-1.791895371148
C	-4.474038742372	3.286616659931	-0.726614732640
H	-4.235039980180	2.331188926479	1.171405560961
C	-3.589702235003	2.125008824439	-2.627869861396
H	-2.599559614596	0.272024335098	-2.235168738531
C	-4.263839640217	3.234844477861	-2.109387802531
H	-5.018998395168	4.123274604842	-0.292266239903
H	-3.414084564840	2.048775651599	-3.700211926477
H	-4.625371513439	4.025841107625	-2.761152760826
C	-2.761047916407	-1.300051536239	0.042614813958
C	-1.855297929895	-2.267741509382	0.575379388351
C	-3.616670522462	-1.801028966033	-0.984995531264
C	-1.813127441488	-3.587371418294	0.133598946986
H	-1.177297268359	-1.961746919474	1.365027023522
C	-3.558409468938	-3.114061375836	-1.437375635913
H	-4.359656102714	-1.136308744510	-1.413418217460
C	-2.655280621154	-4.036320868512	-0.890800377850
H	-1.112836863623	-4.279496607998	0.602190277359
H	-4.252637219163	-3.432987810818	-2.213494147992
H	-2.632730652189	-5.069553443264	-1.227056686366
C	-2.417553915731	0.416502680593	1.873341262284
C	-2.539941878276	-0.498129627692	2.961864773675
C	-1.892713099445	1.694712934062	2.234492370019
C	-2.160165777283	-0.175683453875	4.260741131795
H	-2.981505018704	-1.471987758353	2.775204191833
C	-1.524222906149	2.018627826694	3.537599114362
H	-1.796755227620	2.454092781073	1.464310652604
C	-1.638380638096	1.086234592662	4.575804857513
H	-2.304476488807	-0.913228190095	5.049232777763
H	-1.141579840785	3.017458774195	3.745852604282
H	-1.365645498401	1.343665912201	5.595976247372

87_T•(THF)₄

C	2.526078986301	0.009609044521	-0.446583986301
C	2.865406986301	-0.764202955479	0.746717013699
C	3.509108986301	-2.285912955479	3.117078013699
C	2.361705986301	-2.078107955479	0.984322013699
C	3.728535986301	-0.271068955479	1.769466013699
C	4.029536986301	-1.001956955479	2.914340013699
C	2.679294986301	-2.814526955479	2.122993013699
H	1.705397986301	-2.521869955479	0.243222013699
H	4.188137986301	0.703269044521	1.638861013699
H	4.705908986301	-0.570412955479	3.650619013699
H	2.267157986301	-3.816864955479	2.237236013699
H	3.757353986301	-2.859370955479	4.005972013699
C	2.576350986301	1.472539044521	-0.405724986301
C	2.664072986301	4.357439044521	-0.327146986301
C	2.287830986301	2.222608044521	0.772349013699
C	2.926545986301	2.263582044521	-1.538671986301
C	2.959201986301	3.654033044521	-1.501365986301
C	2.340117986301	3.613777044521	0.812441013699
H	2.021586986301	1.686391044521	1.677336013699
H	3.247592986301	4.197958044521	-2.399588986301
H	2.118259986301	4.125401044521	1.748690013699
H	2.705564986301	5.442861044521	-0.296978986301
C	2.247765986301	-0.673350955479	-1.709421986301
C	1.686958986301	-2.018667955479	-4.204341986301
C	2.788308986301	-1.952442955479	-2.034621986301
C	1.420005986301	-0.107681955479	-2.725216986301
C	1.158559986301	-0.752068955479	-3.932036986301
C	2.509800986301	-2.602157955479	-3.232990986301
H	3.466396986301	-2.425882955479	-1.331915986301
H	0.981238986301	0.868619044521	-2.548945986301
H	0.526836986301	-0.258179955479	-4.669994986301
H	2.967162986301	-3.571847955479	-3.423881986301
H	1.484369986301	-2.522151955479	-5.145705986301
Li	-0.949758013699	-0.037355955479	0.285557013699
O	-3.868719013699	0.053361044521	0.585030013699
O	-1.362187013699	1.383354044521	-0.962513986301
O	-0.817636013699	0.362401044521	2.176141013699
O	-1.217521013699	-1.924026955479	-0.119630986301
C	-1.049409013699	-2.557675955479	-1.421817986301
H	-0.263947013699	-2.027031955479	-1.960841986301
H	-1.997807013699	-2.464036955479	-1.968005986301
C	-1.292750013699	-2.931065955479	0.923020013699
H	-0.362134013699	-2.899045955479	1.499339013699
H	-2.130572013699	-2.677325955479	1.579428013699

C	-0.465984013699	2.126466044521	3.673635013699
H	-0.913335013699	2.691071044521	4.497336013699
H	0.132674986301	2.815629044521	3.070894013699
C	0.398920986301	0.934820044521	4.156706013699
H	0.166829986301	0.663425044521	5.191151013699
H	1.465856986301	1.164560044521	4.105877013699
C	-2.337580013699	2.467428044521	-2.840037986301
H	-2.412947013699	2.386294044521	-3.928495986301
H	-3.262381013699	2.927147044521	-2.470035986301
C	-1.114870013699	3.272117044521	-2.371679986301
H	-0.232639013699	3.030653044521	-2.973775986301
H	-1.267664013699	4.354488044521	-2.413206986301
C	-5.954645013699	-0.800467955479	-0.094175986301
H	-5.859677013699	-0.720675955479	-1.183638986301
H	-6.743705013699	-1.525254955479	0.127867013699
C	-6.205250013699	0.581102044521	0.533555013699
H	-6.868234013699	1.214017044521	-0.063498986301
H	-6.656645013699	0.468499044521	1.525813013699
C	-1.463486013699	-4.266018955479	0.194781013699
H	-2.524419013699	-4.467960955479	0.001803013699
H	3.202328986301	1.760614044521	-2.460023986301
H	-1.059485013699	-5.103347955479	0.771410013699
C	-0.714450013699	-4.017100955479	-1.123447986301
H	0.365529986301	-4.133952955479	-0.988038986301
H	-1.028325013699	-4.684744955479	-1.931113986301
C	-1.518463013699	1.455825044521	2.789956013699
H	-2.360140013699	1.064638044521	3.380950013699
H	-1.910326013699	2.087037044521	1.989732013699
C	0.033757986301	-0.219616955479	3.196358013699
H	-0.533515013699	-1.005839955479	3.711958013699
H	0.889354986301	-0.664901955479	2.689661013699
C	-0.925544013699	2.771809044521	-0.942227986301
H	-1.565326013699	3.322610044521	-0.238332986301
H	0.106643986301	2.799350044521	-0.592914986301
C	-2.108142013699	1.107700044521	-2.175221986301
H	-1.500518013699	0.446844044521	-2.803558986301
H	-3.029367013699	0.592885044521	-1.889082986301
C	-4.608887013699	-1.171937955479	0.527312013699
H	-4.020741013699	-1.881575955479	-0.059888986301
H	-4.745083013699	-1.582705955479	1.540732013699
C	-4.783144013699	1.163741044521	0.650420013699
H	-4.545337013699	1.843779044521	-0.176950986301
H	-4.631733013699	1.706917044521	1.591367013699

THF

C	-0.737926640695	-0.213182814980	-0.996713729760
H	-0.821085444799	-1.295193303790	-1.155097602492
H	-1.338976497587	0.288720109024	-1.761361137916
C	0.737926640695	0.213182814980	-0.996713729760
H	0.821085444799	1.295193303790	-1.155097602492
H	1.338976497586	-0.288720109024	-1.761361137916
C	-1.162723109699	0.153631011171	0.430645297290
H	-1.958392773641	-0.490286594996	0.823633800526
H	-1.513157909150	1.196263862821	0.483180772508
C	1.162723109699	-0.153631011171	0.430645297290
H	1.513157909150	-1.196263862821	0.483180772508
H	1.958392773641	0.490286594996	0.823633800526
O	0.000000000000	0.000000000000	1.251513690548

(THF)₃ Li⁺

Li	-0.012257647270	-0.017618312593	0.001082104235
O	-1.781580040716	-0.691569022842	0.007972624814
C	-2.231167120874	-1.863812420829	0.753569872179
C	-2.895499149761	-0.125570151953	-0.746982547795
C	-3.616884306683	-2.190967488024	0.200937918941
H	-1.495354616264	-2.659467329204	0.607688041973
H	-2.265834842581	-1.599199703861	1.816836758370
C	-4.146752568876	-0.803365928288	-0.193420467605
H	-2.879465607500	0.959176338383	-0.609897275020
H	-2.741708515867	-0.354766280191	-1.808077953111
H	-4.244908093578	-2.696761646304	0.938789963533
H	-3.537362550070	-2.837974349841	-0.679593688097
H	-4.517240664608	-0.267048247428	0.687127624148
H	-4.952659824436	-0.844748405716	-0.930629510488
O	1.460169947894	-1.207522146991	0.024177035555
C	2.621882377631	-1.053181709068	0.894306274002
C	1.639656747969	-2.369125919340	-0.843086639627
C	3.698694473719	-1.951066135793	0.291333008250
H	2.885826154443	0.007753349421	0.917002731619
H	2.340554963536	-1.374429752581	1.904252283441
C	2.866509181917	-3.099933247195	-0.299846382483
H	0.721354622180	-2.962207438666	-0.810703421342
H	1.796633895016	-2.008166539235	-1.866157909133
H	4.422750711193	-2.285406769798	1.038781531349
H	4.242998928198	-1.421469344336	-0.498455494666
H	2.577160662466	-3.808253518582	0.484196878304
H	3.393197333006	-3.654608120269	-1.080614205435
O	0.280234277179	1.852936151734	-0.011794061297

C	1.181099060680	2.552349752413	-0.923725197845
C	-0.355146705080	2.809383692283	0.890265623328
C	1.325867071936	3.960248522788	-0.350325798695
H	2.118868373270	1.991489622451	-0.968287749377
H	0.721447140979	2.560880774653	-1.919087419871
C	-0.044564423509	4.186241971702	0.307251095405
H	-1.422576963857	2.575545934757	0.933550617798
H	0.080082938599	2.679622362728	1.888173019155
H	1.558336241049	4.697525760296	-1.122999223208
H	2.123643411596	3.989903229610	0.400018787202
H	-0.791754765926	4.463315535758	-0.444550947337
H	-0.029977298298	4.964183988358	1.074884906591

(THF)₄Li⁺

Li	-0.006981158982	-0.006947001519	0.017958474803
O	1.062044633342	0.892046316731	1.400561707729
C	1.990679106707	0.215011036761	2.288175380243
C	1.170918262457	2.332653585873	1.573832076606
C	2.968037911937	1.291757672161	2.754722911895
H	1.427584146561	-0.210149639950	3.128415980766
H	2.456935227779	-0.599768988153	1.726643164305
C	2.070848911880	2.538927934037	2.793325938672
H	1.611209172730	2.755396025881	0.663097374532
H	0.164154400252	2.740489474016	1.701185084512
H	3.776832002976	1.419868215240	2.026104304983
H	3.417664948467	1.053880505611	3.722333523096
H	2.631983434169	3.475527967132	2.739286874421
H	1.475506760416	2.553602059584	3.713016548884
O	-0.961422683167	1.316450402410	-1.073191725912
C	-2.150919376764	2.040469193534	-0.654914438229
C	-0.685732646336	1.585905123201	-2.473593070118
C	-2.542983096360	2.927877723385	-1.839704894151
H	-2.929147083102	1.306451290103	-0.414832443232
H	-1.911863428921	2.606087871709	0.250834015314
C	-1.988875320268	2.143425602151	-3.039457413980
H	0.128226419665	2.319502069836	-2.538593584865
H	-0.358379829212	0.649796624942	-2.932487228983
H	-2.055338559887	3.906074723399	-1.765209463043
H	-3.622332492162	3.092784504429	-1.892703998835
H	-1.826769905891	2.766336336454	-3.923106268901
H	-2.666934653745	1.328077320980	-3.316653303497
O	1.228456782936	-1.015129378056	-1.133263590382
C	1.137786448047	-2.431014053397	-1.455305515377
C	2.502180719069	-0.484578185484	-1.587008530389

C	2.341922657563	-2.732808443955	-2.349100596966
H	1.169952999178	-2.997987487004	-0.517478215183
H	0.175736595761	-2.610369280436	-1.944030597054
C	3.376757403472	-1.705686917333	-1.863425636969
H	2.333063433713	0.105806155240	-2.496524357926
H	2.886666215399	0.175133186356	-0.804283000152
H	2.093328386221	-2.556684073797	-3.401525615653
H	2.681410976861	-3.767209559670	-2.250449134642
H	4.158259764273	-1.499885640330	-2.599603218518
H	3.859239730032	-2.050580195811	-0.941679150592
O	-1.337247916460	-1.198897358266	0.834374770953
C	-2.372773799052	-1.885059313728	0.083304225375
C	-1.577011881646	-1.350280827361	2.261658726602
C	-3.502670686396	-2.132112149297	1.080222505743
H	-2.651875399679	-1.247368839874	-0.760395734964
H	-1.962944358682	-2.826835230170	-0.303265180630
C	-2.727548639985	-2.350898046524	2.389107691253
H	-0.650149234108	-1.691505985719	2.731446311346
H	-1.840507784487	-0.367605555928	2.669996073678
H	-4.125200633792	-2.986126800428	0.800481388425
H	-4.148910169197	-1.250010406358	1.155747749811
H	-2.342896042187	-3.375556839776	2.438879693497
H	-3.331903941621	-2.173628269651	3.282591524337

FI⁻

H	0.021582230392	1.458489011731	-3.351051951046
C	0.025009237892	1.646175494445	-2.276465555144
C	0.033930809467	2.177916066754	0.502940251146
C	0.008311888164	0.556433481350	-1.369118277050
C	0.045598189823	2.949858695041	-1.801650579712
C	0.050199690570	3.227481232345	-0.413833737378
C	0.013131328098	0.850002436044	0.056927432331
H	0.058382495955	3.778801978902	-2.510486721373
H	0.066615455533	4.259632324998	-0.066562594743
H	0.037321843399	2.393013014408	1.572727193901
C	-0.013645015988	-0.846148595631	-1.551424811349
H	-0.021082171659	-1.366259946969	-2.505029091356
C	-0.006340022226	-0.412316249437	0.745568520169
C	-0.047900266830	-3.111603019996	1.505098847817
C	-0.022671785786	-1.452223494397	-0.273322309181
C	-0.011329271850	-0.756274831912	2.103648881190
C	-0.031903039898	-2.095201580611	2.489884735563
C	-0.043650016862	-2.804971762557	0.151798340169
H	0.000820112186	0.026621536652	2.863680435986

H	-0.035524498269	-2.362054808388	3.545810320010
H	-0.056549154372	-3.606731471658	-0.587788609436
H	-0.064016660599	-4.156278868296	1.818390586618

FI-H

C	-1.480132000022	-2.610036996419	1.250875100782
C	-0.300185898758	-2.097107078774	0.708148245043
C	-0.266477989496	-0.759123602724	0.308892224448
C	-1.407527046056	0.057828778443	0.452880094243
C	-2.579667736629	-0.458053252797	0.993742266859
C	-2.611447091762	-1.799017486449	1.393161973386
H	-1.520255170698	-3.649525276565	1.565671792399
H	0.575139890611	-2.732750157533	0.600151648336
H	-3.462336029400	0.167369384828	1.106961752233
H	-3.522030260149	-2.213634138935	1.817349272879
C	-1.111313156761	1.456457956933	-0.051494409954
H	-1.242780275127	2.213693759012	0.734237468369
H	-1.779468719897	1.747100207091	-0.874395160193
C	0.332166774332	1.351470215836	-0.502762789489
C	1.158044664404	2.321320672870	-1.059445607710
C	0.812561567350	0.043253382792	-0.283842233582
C	2.472397986112	1.981344653686	-1.399479072830
H	0.792761439708	3.331472367589	-1.230434385112
C	2.124578870017	-0.294044870898	-0.623815557349
C	2.949805641489	0.684077652356	-1.182563664633
H	3.127470782822	2.730954377941	-1.835332755195
H	2.501726502830	-1.300134690901	-0.458154568702
H	3.972944333987	0.435234018343	-1.451834480286

DPM-H

C	-2.876770654146	-2.382809753674	0.511506533879
C	-1.527307451560	-2.547029097955	0.836109663851
C	-0.695092664329	-1.435964562654	0.959258593816
C	-1.193547341852	-0.139269801161	0.765068309844
C	-2.545853924248	0.011848313650	0.438563412428
C	-3.383664491077	-1.099295216104	0.312228917835
H	-3.525355994750	-3.249380833698	0.414117277111
H	-1.122507634188	-3.543800319039	0.992186673435
H	0.356104397594	-1.572615634282	1.202070202938
H	-2.949377724483	1.010522798549	0.284751046570
H	-4.431087198301	-0.958848622064	0.057520092188
C	-0.288334982021	1.072145406097	0.924893022810

H	0.035757605797	1.148230652572	1.971354286254
H	-0.876290550459	1.978030637320	0.725679464416
C	0.944260627650	1.065711462115	0.034115497217
C	0.820332911496	0.965445771562	-1.359468608200
C	2.227133121317	1.177957633208	0.581756876451
C	1.946829698745	0.982400769826	-2.179854901657
H	-0.168556825379	0.866395519491	-1.800914906389
C	3.359556850465	1.193852171926	-0.236646618198
H	2.341902491826	1.257247252880	1.660803182254
C	3.222713617240	1.096633966883	-1.620741800449
H	1.829930771531	0.904964546147	-3.257857693531
H	4.346757315778	1.281203824096	0.210016575780
H	4.101191438952	1.108287795711	-2.260459598789

Tr-H

C	-0.255122434974	-0.636216207920	0.268694311272
H	-0.634685016295	-1.585885519821	0.668596103831
C	-0.330273255473	-0.767524717322	-1.256625796807
C	-0.574861377809	-1.022879305169	-4.052244831764
C	0.610889516399	-0.184870812096	-2.113281420839
C	-1.395439845436	-1.482349100365	-1.824724218154
C	-1.518817305674	-1.611676724595	-3.207005824203
C	0.488198257233	-0.309180833521	-3.500051106616
H	1.451757729583	0.361126589520	-1.696176307462
H	-2.136905347673	-1.939652618403	-1.172772158990
H	-2.349693022499	-2.174702906119	-3.624653034546
H	1.231638302490	0.149696965766	-4.147029685899
H	-0.666474340686	-1.124338762017	-5.130450510729
C	-1.185611787350	0.449440994694	0.821314543686
C	-2.867002917451	2.416419050508	1.937088002617
C	-1.693960292433	0.310242252579	2.121460936149
C	-1.536795210610	1.589445596074	0.089118977068
C	-2.368420515090	2.566523805342	0.643501368803
C	-2.526397790914	1.280780793735	2.676218930999
H	-1.429675948850	-0.569468910913	2.704748994988
H	-1.168590692373	1.710956735563	-0.925147320651
H	-2.630214516635	3.443284712365	0.056461148148
H	-2.912313380692	1.149145661155	3.683948333326
H	-3.518623355702	3.173526136366	2.365327478426
C	1.182116119841	-0.512485746420	0.786979621720
C	3.849580007065	-0.379024912950	1.686127370187
C	1.960909068127	-1.673013510826	0.908809806879
C	1.762359070912	0.715469912820	1.125640987900
C	3.086246724114	0.782015601577	1.569154127351

C	3.280144922655	-1.610886598809	1.354066522546
H	1.526050555774	-2.635704054398	0.647828432931
H	1.174947543564	1.625924102105	1.053238190244
H	3.516518848811	1.746084026252	1.828583801281
H	3.862790308335	-2.524111308637	1.445366321500
H	4.877026614055	-0.327258072812	2.036676360843

DPM

C	0.304143168119	0.513097712011	-0.789288838508
H	0.639889866868	1.079425556820	-1.660585976005
C	-0.928964135505	0.968101283938	-0.248593914363
C	-1.730329989576	0.309378222373	0.743327334732
C	-1.499004835730	2.190070023426	-0.745224770592
C	-2.934020938735	0.838630275436	1.195635898112
H	-1.422309970178	-0.659817098574	1.117862722833
C	-2.698499414631	2.707021397961	-0.284981483370
H	-0.947313428468	2.730160230413	-1.514880917820
C	-3.443831111835	2.048116052246	0.707368504861
H	-3.497211841567	0.282180215962	1.946757229106
H	-3.065248099199	3.645644158174	-0.703740316386
H	-4.382079904801	2.457471360223	1.075585500923
C	1.183978937107	-0.537869874392	-0.413139546109
C	2.279529572107	-0.873552810688	-1.280377293066
C	1.137312370447	-1.309739288196	0.795994903319
C	3.191207600415	-1.875860447969	-0.994092358837
H	2.381826758868	-0.310305322308	-2.208122209583
C	2.060318353780	-2.312491907244	1.072046428919
H	0.394912844888	-1.073420528199	1.549320036822
C	3.098752002794	-2.630166239751	0.187860672237
H	3.993295040442	-2.080202491559	-1.705278662871
H	1.971081599582	-2.856380374840	2.013975019452
H	3.809607661032	-3.423162101018	0.409894349513

Tr⁻

C	0.000198985388	-0.000134072512	0.000250118911
C	1.277640601057	-0.000284579612	-0.703852585004
C	3.803330549188	0.000151040984	-2.096555352831
C	1.454303831945	-0.616691455480	-1.977676666152
C	2.449108392187	0.616088131192	-0.173190965062
C	3.667046516093	0.610382127283	-0.843599323308
C	2.671199591688	-0.610478040276	-2.650000422524
H	0.606163763233	-1.122185774354	-2.430486696319
H	2.379387620163	1.121546262839	0.785723281571

H	4.523178423650	1.108032901820	-0.387292906581
H	2.742239316999	-1.107828488236	-3.617690355208
H	4.756006023476	0.000458590977	-2.621975303153
C	-0.028980785483	0.000050546558	1.458586398110
C	-0.087423022361	0.000201916998	4.342205464572
C	0.985238307771	-0.616726489967	2.248964160479
C	-1.074295632216	0.616997602288	2.207239451514
C	-1.103583589309	0.611125248483	3.597173762689
C	0.958115771196	-0.610724280759	3.638973662307
H	1.801554001444	-1.122519712908	1.741314779845
H	-1.869354873333	1.122778638818	1.666916715023
H	-1.926956363878	1.109067841485	4.109956365051
H	1.760098834234	-1.108524875763	4.184731354928
H	-0.109436771267	0.000222347848	5.429934498540
C	-1.248236468478	0.000061240818	-0.754099928817
C	-3.716373923527	-0.000281168061	-2.246424447877
C	-1.374175592882	0.617264184691	-2.033562127562
C	-2.439724160509	-0.616953239078	-0.270939860213
C	-3.629964074312	-0.611274442464	-0.989395043689
C	-2.563297860563	0.611106544376	-2.753847460138
H	-0.508896251795	1.123409487804	-2.451874731854
H	-2.408056717319	-1.122909168354	0.689732625267
H	-4.503430414244	-1.109449081584	-0.567846404283
H	-2.595911242498	1.109157654889	-3.723236485826
H	-4.647349970106	-0.000541518068	-2.809399749433

B3LYP/6-31G*(Onsager) Geometries

85_C•(THF)₃

C	-2.070281542591	1.599446175704	-0.679492673384
C	-0.808644067774	1.643271332417	-1.387026489189
C	-0.104450458720	2.870488348543	-1.431071531019
C	-0.608796759790	3.985341343988	-0.773167097503
C	-1.822860039781	3.924355369515	-0.052945026732
C	-2.550158179955	2.738221106895	-0.014391977310
C	-2.609372536688	0.272522786509	-0.845476439196
C	-1.669058715847	-0.478034739139	-1.649456140428
C	-2.002641302012	-1.805710900336	-2.010045447885
C	-3.190612126294	-2.370503781994	-1.562576909720
C	-4.088694498772	-1.641536156029	-0.751898932772
C	-3.799574776845	-0.324636301696	-0.403880296935
H	0.821257567993	2.948521892724	-2.000095595997
H	-0.065610686592	4.927624194684	-0.822290213657
H	-2.194487637510	4.810743625817	0.455764496088
H	-3.499329193961	2.700109836004	0.519580076329

H	-1.341930662830	-2.377559577754	-2.659960784628
H	-3.439760385287	-3.390347001547	-1.850335838862
H	-5.013185533872	-2.105689559164	-0.416263612183
H	-4.508064219943	0.246984763275	0.195479224305
C	-0.533735262286	0.348058621306	-1.933392571158
H	0.215378155089	0.137706560442	-2.693275984821
Li	0.670563418056	-0.239590893457	-0.077211428086
O	-0.232933737595	-0.570705440913	1.653698882743
C	-0.943572152473	-1.827160684283	1.821585735526
C	-0.793417035236	0.438131792140	2.532126135581
C	-1.742307297914	-1.673164380369	3.115044270851
H	-1.598425314953	-1.975996300882	0.957246224866
H	-0.200786456037	-2.629102872188	1.857027173996
C	-2.073094203526	-0.173259305597	3.105156724659
H	-0.060079599824	0.651313168054	3.321312429819
H	-0.972954817899	1.341697776740	1.945134638941
H	-1.125981672374	-1.927912623313	3.985646647128
H	-2.631545207431	-2.310201944674	3.126188628950
H	-2.315845593418	0.224951230569	4.095193676489
H	-2.914124846468	0.021310018906	2.432250680659
O	1.696546327377	-1.941457081080	-0.333062757747
C	2.733793877021	-2.344281425990	0.591864769092
C	1.583114486910	-2.906427311441	-1.407877679931
C	3.564491118501	-3.382750156980	-0.159470497788
H	3.283650398235	-1.447026267773	0.884196368009
H	2.265740617185	-2.776524149640	1.486674526425
C	2.494950946542	-4.074172223863	-1.019814310476
H	0.530445395990	-3.181239073384	-1.509813862571
H	1.912004956879	-2.424911905859	-2.337239764748
H	4.089169303452	-4.066733716346	0.513531991919
H	4.310348830115	-2.890923101094	-0.794991341441
H	1.944406114101	-4.810145267501	-0.422266998998
H	2.906724089806	-4.588744973817	-1.892732876753
O	2.260664964056	0.948668265999	0.292702735195
C	3.215830915118	1.211974026882	-0.763294401987
C	2.299177764202	2.014787597178	1.273115239563
C	3.785948488532	2.606199646439	-0.483923803748
H	3.993500521223	0.438855396764	-0.722642406642
H	2.697991934558	1.139930381734	-1.724371714585
C	3.631183144082	2.725487848139	1.040218928902
H	1.447713575430	2.682390271659	1.097264421792
H	2.208909942763	1.559069218540	2.262964527169
H	3.182373798914	3.370727312733	-0.984947769638
H	4.820268946182	2.707348981091	-0.825113254097
H	3.618645119735	3.761013945611	1.392394460517
H	4.444353169453	2.199594720275	1.553957766854

85s•(THF)₄

C	-3.068085265570	-0.230479045988	1.692338863351
Li	1.885419040419	0.000922259572	-0.029571270623
O	1.688488261079	1.864456618491	-0.583584440188
C	1.273158408353	2.890918744903	0.365274160330
C	1.591513939379	2.375044297434	-1.934985092577
C	1.154900554270	4.179257843829	-0.448567918277
H	0.307085879913	2.598755027021	0.788776362088
H	2.025411528634	2.937927190482	1.157841794679
C	0.753312014444	3.648138182530	-1.832517389380
H	2.603996783121	2.582810277978	-2.306456977202
H	1.138072001074	1.600949818036	-2.560488914299
H	2.117045388900	4.702578382373	-0.496177190021
H	0.411131260637	4.858235381390	-0.022979708647
H	0.965061499650	4.349555032148	-2.645135068090
H	-0.314960217542	3.404840781276	-1.841490680134
O	0.625241800627	-1.291628931080	-0.790768336444
C	-0.021450304347	-2.316681112296	-0.000171827329
C	-0.240617630237	-1.079458332196	-1.931041934731
C	-0.534307169767	-3.330501990895	-1.028071353269
H	0.727136236152	-2.712322883081	0.690788520271
H	-0.848514202928	-1.866778733008	0.562812252816
C	-0.805116928618	-2.468507878604	-2.291105705394
H	-1.041355907291	-0.386577084263	-1.647900609094
H	0.371706813263	-0.633642781913	-2.719672022095
H	-1.438860218630	-3.828869282942	-0.671953133336
H	0.226676351573	-4.091398850202	-1.231317964313
H	-1.873908851212	-2.401216031665	-2.506673460150
H	-0.300830138778	-2.888764470501	-3.166814180733
O	3.705406086007	-0.599972118313	-0.502934025727
C	4.861780028322	0.266864879880	-0.671220552146
C	4.001907371509	-1.923860505337	-1.017654310606
C	5.983546201695	-0.626221809343	-1.210645150719
H	4.589917443358	1.059834942589	-1.376849762133
H	5.096097116602	0.723254630467	0.295346248208
C	5.205752138161	-1.735426259255	-1.936484871875
H	4.240522964484	-2.586453230583	-0.174742288809
H	3.100052178158	-2.290604243668	-1.513114838311
H	6.569975381446	-1.048714145431	-0.387403187281
H	6.668940398345	-0.080261224059	-1.864159513612
H	5.785153558567	-2.654023424768	-2.062693227368
H	4.881519624913	-1.396279408604	-2.927316772205
O	1.755601831758	-0.053175319080	1.932473991989
C	2.865815686214	-0.295014404404	2.816822379923
C	0.601777382997	0.123328963439	2.781130516576

C	2.302084599395	-1.170806222922	3.952571002077
H	3.653267662674	-0.766164785207	2.226192752822
H	3.234091508846	0.667041453550	3.200510510539
C	0.766589938271	-0.936250287831	3.880367516450
H	0.622134327831	1.140392572429	3.197884482513
H	-0.296425146891	0.007148108223	2.170191854847
H	2.725454064177	-0.881276263309	4.918396829374
H	2.544183066893	-2.225177483087	3.791773493517
H	0.347191913616	-0.596283174309	4.831600947833
H	0.246694709622	-1.856882853301	3.599355196909
C	-2.939805190772	1.060112372050	1.119034665982
C	-2.512469097653	2.308017488609	1.641616509005
C	-3.377679143940	1.008930792750	-0.267337620369
C	-2.511203487820	3.437811742838	0.834031455048
H	-2.206550904806	2.386136352760	2.684992228537
C	-3.354347971646	2.165514395081	-1.059561461684
C	-2.924228978657	3.376381585876	-0.519257496003
H	-2.200795326597	4.394807450272	1.252511875220
H	-3.687946255372	2.123499688197	-2.096828512573
H	-2.926224817500	4.279285434943	-1.126484974841
C	-3.608013848706	-1.092735445815	0.703711180664
C	-3.800014138516	-0.342344959486	-0.526533702217
C	-3.973444754855	-2.463169413709	0.718078596335
C	-4.328947414586	-0.971606525441	-1.662923351074
C	-4.494291142227	-3.057251568777	-0.423357441640
H	-3.850636792372	-3.049625038536	1.628608575087
C	-4.674852672894	-2.320803234231	-1.619306377749
H	-4.476487631388	-0.403431257976	-2.581905589907
H	-4.774627491573	-4.109896682975	-0.399127509004
H	-5.089046345070	-2.809265194765	-2.499171413819
H	-2.885089104728	-0.488566530977	2.731090135327

86_C•(THF)₃

C	-1.590487795549	1.627222063327	-1.792269684858
C	-0.162888877197	1.637212211241	-1.790326256453
C	0.424774053255	2.939822807203	-1.783368192171
C	-0.329360620935	4.105474747286	-1.781454530846
C	-1.731292378590	4.059303100674	-1.790985591826
C	-2.341453142780	2.802645545912	-1.795918298786
C	-0.717526366877	-1.349083896944	-2.858819938148
C	0.488473714124	-0.843700175547	-2.287485652820
C	1.582687301058	-1.765071391802	-2.297380111297
C	1.469002816052	-3.066931244962	-2.765390976119
C	0.254799166017	-3.546284912056	-3.277703510807

C	-0.821757330056	-2.657087263805	-3.331134650998
H	1.511531530523	3.010292854576	-1.804542531182
H	0.181479770021	5.067489915073	-1.791786738720
H	-2.322496021663	4.970911018364	-1.798375248649
H	-3.428377333459	2.730008580416	-1.798965403889
H	2.548221773195	-1.415049628203	-1.935329594148
H	2.342604167350	-3.716935515009	-2.741652131200
H	0.161109803968	-4.567115942108	-3.637886682529
H	-1.768295728291	-2.981561194768	-3.762716215826
C	0.698055222492	0.477376482406	-1.741715342714
H	1.757688947810	0.736394218488	-1.663405446458
Li	0.317708633043	0.030448138791	0.479718896753
O	-1.143680714703	-1.278331689960	0.880681849424
C	-0.873834415397	-2.686914556947	0.629957362469
C	-2.567617271002	-1.049414697417	0.893486752610
C	-2.242104838796	-3.368095391269	0.491799683284
H	-0.287490689011	-2.752798989680	-0.289470053730
H	-0.286158291633	-3.079852795269	1.466066181124
C	-3.163029631537	-2.204020526840	0.092052501216
H	-2.927523742823	-1.054610616144	1.932467879259
H	-2.748935284715	-0.063591397961	0.458198012006
H	-2.562764411936	-3.798843296060	1.447352321629
H	-2.219841960792	-4.168910988338	-0.252301522110
H	-4.216155049068	-2.382582743609	0.329975739107
H	-3.069621422206	-2.001248030012	-0.980058759297
O	1.790338630610	-0.818694243574	1.573100742445
C	1.596788247190	-0.946060041530	3.003124161605
C	2.957728513037	-1.572788763120	1.161518420821
C	2.929323075743	-1.453467912848	3.548632648993
H	1.291461838207	0.029973129470	3.385157616737
H	0.785497183483	-1.662434703197	3.188908054441
C	3.415489232258	-2.350277685783	2.399755916557
H	2.674890293944	-2.210086380850	0.319819758116
H	3.722040816043	-0.861967838482	0.822824939144
H	2.817645498831	-1.986201192567	4.497209686835
H	3.622644386523	-0.618947074812	3.706037495821
H	2.920350182574	-3.327367153749	2.445141342244
H	4.495976910360	-2.519865864938	2.408998846903
O	0.064802517169	1.631383471924	1.665710900658
C	1.127355167566	2.618100109702	1.720109554571
C	-1.197838334112	2.250216131305	2.011543053526
C	0.453734741449	3.952362240952	2.060079485029
H	1.838309260120	2.303813079092	2.493928048597
H	1.633570700904	2.633988594053	0.751185428451
C	-0.822264418654	3.507507097731	2.791185241824
H	-1.739053293956	2.493805687984	1.089635903115

H	-1.772961188385	1.523720056705	2.592570988591
H	0.192893409024	4.482885716207	1.138507068299
H	1.096344019623	4.598698631782	2.665155020175
H	-1.614103110770	4.261995326825	2.772707862044
H	-0.606880622895	3.261255529723	3.837499402447
H	-1.569506411081	-0.691474798562	-2.981807094731
H	-2.119440266119	0.681744620861	-1.761907071080

86s•(THF)₄

C	-3.220681304207	0.367054922150	0.866409996979
Li	1.929331518839	-0.340954249413	0.113779812878
O	2.236265248851	1.587869630758	0.024896718823
C	1.707734085024	2.480956733287	1.050966637344
C	2.705677217621	2.360218015069	-1.105864846232
C	2.080594536094	3.893976160128	0.602456811908
H	0.622360983364	2.349756969345	1.098595969704
H	2.153895495719	2.192341929096	2.007056867225
C	2.103090750962	3.752191993349	-0.926535566691
H	3.803228122075	2.388990768765	-1.085155361180
H	2.384289626523	1.854443508230	-2.021173906231
H	3.069744997633	4.178178252102	0.979711379413
H	1.348048506837	4.627979026898	0.947127051327
H	2.691674927193	4.526648490679	-1.427044990175
H	1.079533213586	3.779406059310	-1.316111147687
O	0.592442238675	-0.974153596226	-1.174634348338
C	-0.406992862705	-1.977348627498	-0.862670784571
C	0.137752951114	-0.218958249799	-2.327905875227
C	-0.964579404479	-2.382766988203	-2.221564144220
H	0.101756934922	-2.780267673106	-0.322724156141
H	-1.185703103597	-1.536028321951	-0.229501353781
C	-1.011262446794	-1.031875165841	-2.961166751541
H	-0.194254128474	0.771285918159	-1.997402020431
H	0.999689356230	-0.108179789752	-2.994799803574
H	-1.951979369963	-2.844869076077	-2.139936725000
H	-0.282438555511	-3.083018358365	-2.718382899196
H	-1.972888077595	-0.546199703352	-2.773161108319
H	-0.887181577671	-1.140814693364	-4.042855112313
O	3.626321745726	-1.293821101888	-0.207035177094
C	4.939066895450	-0.772988852380	0.151899011538
C	3.774933674126	-2.367310142397	-1.170095665396
C	5.959463887257	-1.598039381735	-0.643798238735
H	4.958389119853	0.288320770660	-0.116544676963
H	5.065552184260	-0.861899403581	1.235511813524
C	5.128787617913	-2.120869345223	-1.827293406677

H	3.756312314031	-3.329594369045	-0.640381248980
H	2.917876401618	-2.315794219342	-1.845617689086
H	6.332589938044	-2.434043781744	-0.042580807998
H	6.820900553184	-1.000650029856	-0.953205826276
H	5.548739825796	-3.023928928209	-2.278471966005
H	5.040062375421	-1.356954011720	-2.608622056157
O	1.332614092367	-0.820427797489	1.919432972143
C	2.069361318796	-1.658762445175	2.826662515223
C	0.105592661647	-0.450546677696	2.592069384768
C	1.002355324507	-2.560724155936	3.449160505887
H	2.829460359435	-2.181596064074	2.243499702154
H	2.562787025236	-1.033976432345	3.585921188086
C	-0.238995636807	-1.634916502729	3.525787135195
H	0.281045242658	0.470455306022	3.161968361290
H	-0.649658197295	-0.253260153028	1.827751741626
H	1.306708553182	-2.950547864707	4.424638088433
H	0.807660589929	-3.414197952972	2.791649395730
H	-0.412734368889	-1.281596144408	4.546779536068
H	-1.145104935349	-2.151347182610	3.197355690099
C	-2.726058220226	1.683149046068	0.635636893355
C	-2.347714248047	2.493297500584	1.759803428110
C	-2.521277938445	2.312139796893	-0.637737964360
C	-1.866651863311	3.786842919561	1.630958867883
H	-2.473917812464	2.070967928243	2.756411382393
C	-2.033406211888	3.611338526704	-0.754506041164
H	-2.727835752490	1.759854589024	-1.546979666925
C	-1.705668808466	4.382017398038	0.367574430870
H	-1.619359778737	4.351106536327	2.530076922526
H	-1.911021739693	4.034240880783	-1.751986451587
H	-1.351679920697	5.404635525922	0.266860952145
C	-3.884076034440	-0.561520958512	0.011545409511
C	-4.386023941320	-0.302333312566	-1.306266978337
C	-4.136916422737	-1.891782840353	0.488300451851
C	-5.024317478234	-1.282938929294	-2.062122766066
H	-4.327510186785	0.701539062230	-1.710506187512
C	-4.771199772494	-2.858923388718	-0.274060302405
H	-3.803408814634	-2.143280138014	1.495091349151
C	-5.219957004714	-2.580193732266	-1.576618908305
H	-5.387287059352	-1.019656038329	-3.056256359080
H	-4.918652332506	-3.852818333430	0.148448353697
H	-5.705306099931	-3.342866107936	-2.180491882627
H	-3.155313923734	0.042059023476	1.906677452759

87c•(THF)₃

C	-0.048102072084	-1.224210871801	-1.181328639059
Li	-0.005243203969	0.523754281202	0.404589267035
O	0.291640869928	-0.004592310950	2.354866137538
C	1.4870783587829	0.402834434809	3.065714891303
C	-0.423608278010	-1.007553353052	3.124323679180
C	1.417931734430	-0.273464721845	4.438360551222
H	2.356294836601	0.066241432576	2.488318486946
H	1.505198591931	1.495055659307	3.122759298227
C	0.587256831009	-1.530872459356	4.141395430039
H	-1.274938309732	-0.525225601076	3.623012514252
H	-0.796013698979	-1.761764143439	2.430964786676
H	0.895179498474	0.366921097508	5.158263968887
H	2.410866907921	-0.491951551610	4.842045623959
H	0.105616237213	-1.950741267695	5.029298545227
H	1.211986087449	-2.310720624289	3.690378097219
O	1.424058975678	1.944537152046	0.209615203061
C	1.171077860293	3.323966415606	0.575357672939
C	2.789147203898	1.805183333493	-0.257377609583
C	2.483651730132	4.084279318409	0.332593769072
H	0.339196779958	3.703484565040	-0.024555544624
H	0.873575483830	3.341840600423	1.630425289678
C	3.537916227055	2.967367762135	0.386368358595
H	3.138405999786	0.812279195363	0.028438210116
H	2.804840235507	1.877852429749	-1.352562527426
H	2.647416856202	4.872851197004	1.072471464498
H	2.478149307986	4.550968223219	-0.658933929275
H	3.797723931415	2.728084296601	1.424458668852
H	4.459819628902	3.219710553340	-0.145672922532
O	-1.665427135112	1.667197941015	0.544108565610
C	-2.383249262260	2.321233573939	-0.536609536135
C	-2.441087237886	1.730155542848	1.766062090277
C	-3.808710857494	2.513034589084	-0.020491858462
H	-1.899245152190	3.285486220728	-0.741165256032
H	-2.306822844079	1.693653892884	-1.425059335413
C	-3.582577943357	2.709310226077	1.486062460884
H	-2.815828057175	0.723364911299	1.986885959373
H	-1.779007876644	2.044573224121	2.577399717019
H	-4.405671247087	1.612103155374	-0.205035534016
H	-4.313360046102	3.358703641883	-0.496691847986
H	-4.468726788355	2.497213246624	2.091306459240
H	-3.267989258555	3.738320537948	1.695368723969
C	1.410298046433	-1.443641053309	-1.159376408785
C	2.104612023745	-1.803389518807	0.031721361495
C	2.232732905862	-1.310562961031	-2.311518051193

C	3.483070149384	-1.997917691631	0.068220649279
H	1.537005481012	-1.929024054735	0.948238222855
C	3.612715087044	-1.490633632818	-2.269601300749
H	1.767316271675	-1.072175878745	-3.262400341764
C	4.263849296237	-1.834355102809	-1.080883794523
H	3.954222629996	-2.274765955421	1.010184606838
H	4.186663239292	-1.377548212390	-3.188120613854
H	5.340476187863	-1.978928325717	-1.051723818376
C	-0.642464428601	-0.454876781624	-2.293852662657
C	-0.027865357505	0.715886685632	-2.819335495591
C	-1.865524206914	-0.820363558348	-2.918316584185
C	-0.587639864429	1.456289139943	-3.856660779097
H	0.911028713911	1.050903521865	-2.390251540925
C	-2.432713029432	-0.070253757148	-3.946084708051
H	-2.371807559214	-1.722611706367	-2.590623480443
C	-1.805821134538	1.080944311986	-4.431995814275
H	-0.069726408949	2.345624265988	-4.211886213542
H	-3.372105950680	-0.402645385536	-4.385314369639
H	-2.248542446509	1.664174215608	-5.235070830937
C	-0.921755243149	-2.105749534093	-0.382624663376
C	-0.522310192418	-3.392585836616	0.070129114542
C	-2.240633027278	-1.721612855142	-0.006179657041
C	-1.348325162687	-4.200678840029	0.848149183551
H	0.457114179028	-3.765985423964	-0.210914531220
C	-3.070339254026	-2.536652064949	0.758690240367
H	-2.612797934239	-0.753644130336	-0.327179621748
C	-2.634300432428	-3.787225089071	1.209065848988
H	-0.985330766287	-5.178224307391	1.161956716714
H	-4.068736472649	-2.185316503901	1.014336454804
H	-3.277992533690	-4.419856015223	1.814296959813

87s•(THF)₄

C	3.129362963782	0.116433186375	0.199391420688
Li	-2.513088362597	-0.084809639182	-0.327854759006
O	-2.354050801890	1.854852827364	-0.596619084503
C	-1.207392214776	2.539546102037	-1.181839054532
C	-3.284984867460	2.827286887144	-0.071327113946
C	-1.444512847946	4.040675058694	-0.964377741063
H	-0.309581038501	2.188317385578	-0.665329222860
H	-1.147353543148	2.267983626144	-2.240691482967
C	-2.441484467530	4.067670914581	0.205937419174
H	-4.064388385309	3.028519199557	-0.818958671078
H	-3.753523308774	2.396072889626	0.817611286978
H	-1.892062451847	4.497133710300	-1.854306330416

H	-0.510042251937	4.561700016394	-0.740306588499
H	-3.041175777531	4.981547101124	0.243053625786
H	-1.914377943544	3.961390926765	1.161017657942
O	-2.044203693310	-0.532745503582	1.528499001043
C	-1.549290970084	-1.836913484782	1.935997414988
C	-1.892953201499	0.416753007431	2.614072573034
C	-1.443598854501	-1.775336578178	3.458047071901
H	-2.257155768656	-2.589148906297	1.574081944883
H	-0.570066270674	-2.003471123305	1.473854639853
C	-1.074491879965	-0.301697720351	3.689404530936
H	-1.404542668246	1.311472315800	2.217640988496
H	-2.893819781474	0.686410562246	2.976045141322
H	-0.684842665212	-2.462990785772	3.840059510783
H	-2.406425963735	-2.015666533941	3.923973136811
H	-0.001786339328	-0.157462103995	3.523242213741
H	-1.319443273340	0.051156983723	4.695593909966
O	-4.387584855477	-0.599512586597	-0.619407040048
C	-5.114167240207	-0.269420511492	-1.836852031499
C	-5.311213423172	-1.093349736746	0.385773433656
C	-6.562082985334	-0.709997536108	-1.598576596663
H	-5.032380105843	0.812195820980	-1.995432730566
H	-4.634154498808	-0.783516354086	-2.675193841465
C	-6.689631079636	-0.623386608096	-0.069584783056
H	-5.249068847701	-2.189237070458	0.415351403191
H	-4.993788979631	-0.695503408109	1.352872214704
H	-6.711820398266	-1.741481920176	-1.936014499361
H	-7.279849603327	-0.077020641611	-2.126726991246
H	-7.496971713924	-1.242671498284	0.329939857699
H	-6.865601132731	0.411234222475	0.246444780000
O	-1.401210133829	-1.143729593138	-1.547032791927
C	-1.761679800635	-2.487296777285	-1.940705420811
C	-0.019762057760	-0.869004590310	-1.936003057462
C	-0.433878281952	-3.222322810240	-2.100248216004
H	-2.416944131483	-2.900025704891	-1.168789490518
H	-2.316044981767	-2.450884443268	-2.888659782208
C	0.464638203394	-2.118569754603	-2.678760149696
H	-0.010802496931	0.027593218414	-2.561496522830
H	0.561435243038	-0.673936653236	-1.029391842420
H	-0.518171084380	-4.099776644662	-2.748362192765
H	-0.061070830920	-3.548794629648	-1.122370202939
H	0.290690056152	-2.017189511820	-3.756394784064
H	1.532226230341	-2.290001783039	-2.524273537525
C	3.683084142408	-0.355441135368	-1.066971366517
C	4.550085170887	-1.484435076054	-1.151775542486
C	3.401074013953	0.272857646670	-2.316140041070
C	5.066820093205	-1.942523037394	-2.358995924987

H	4.824174788357	-1.998042261580	-0.234967798061
C	3.930547963395	-0.180350904196	-3.520206631911
H	2.740036122422	1.134617430434	-2.327612091128
C	4.770574398150	-1.299036802552	-3.566620238386
H	5.725725104922	-2.810930827768	-2.355053866755
H	3.667434339821	0.338965395752	-4.441038726952
H	5.173978811880	-1.659180531281	-4.510031533857
C	2.846862923969	1.534951638868	0.393658792947
C	1.833467325602	2.004010562846	1.282082670661
C	3.565136176388	2.566110204692	-0.281161385028
C	1.573922176931	3.357404904958	1.479861494195
H	1.243513778428	1.274332779998	1.828895378742
C	3.290328128948	3.916044467489	-0.095790385358
H	4.368645166045	2.283859176835	-0.954812141119
C	2.291349491627	4.341389816228	0.788998810274
H	0.793780027491	3.649140448622	2.182687092944
H	3.880797970200	4.653676256029	-0.638691722919
H	2.088857092942	5.397914808712	0.944798117736
C	2.895282216830	-0.830596619000	1.287676175806
C	3.023094046805	-0.470229101836	2.661228598508
C	2.528014287959	-2.190230653049	1.061564744115
C	2.795664661436	-1.370842661566	3.696849075355
H	3.328309837719	0.542991325764	2.905560285181
C	2.311844701515	-3.092566097858	2.099447809062
H	2.417172294644	-2.536290258324	0.037668142851
C	2.435409243965	-2.699758285201	3.437891678165
H	2.921773570672	-1.035182393590	4.725735002360
H	2.032530471727	-4.117844193318	1.859220389214
H	2.269207341840	-3.405435148133	4.247915275890

THF

C	-0.000035664057	0.767963045731	-0.996919365611
H	-1.016117512135	1.148460426744	-1.155764820717
H	0.648778196128	1.205261385695	-1.761722306512
C	0.000035664057	-0.767963045731	-0.996919365611
H	1.016117512135	-1.148460426744	-1.155764820717
H	-0.648778196128	-1.205261385695	-1.761722306512
C	0.470148578079	1.074233969017	0.430291477329
H	0.072193070427	2.017741738102	0.822814854588
H	1.569155573572	1.121696848222	0.482864313909
C	-0.470148578079	-1.074233969017	0.430291477329
H	-1.569155573572	-1.121696848222	0.482864313909
H	-0.072193070427	-2.017741738102	0.822814854588
O	0.000000000000	0.000000000000	1.252893822107

B3LYP/6-31G* C_α-Li distance constrained optimized geometries for 3s•(THF)₄**C_α-Li distance = 5.2 Å**

C	2.891343815586	0.182996969034	0.225502519503
Li	-2.279171051798	-0.081415078373	-0.260138315520
O	-1.999325718487	1.823588183637	-0.647799693880
C	-0.811335050738	2.416966178452	-1.264993745481
C	-2.841036946283	2.864491775867	-0.105487213294
C	-1.023438642656	3.931523284024	-1.214068105202
H	0.060824952454	2.110237243697	-0.682783682660
H	-0.732084818976	2.026001547052	-2.283199075345
C	-1.945353151612	4.096788560715	0.002939691723
H	-3.684421330982	3.037730366534	-0.789234100167
H	-3.235658370315	2.517023027930	0.854395843497
H	-1.518565676191	4.289693709568	-2.124765477962
H	-0.074245784400	4.459814466361	-1.096928685602
H	-2.517204743931	5.029711268263	-0.007239683046
H	-1.352662516322	4.060135417669	0.922706133920
O	-1.961857060684	-0.554980195958	1.616622410384
C	-1.428215760063	-1.841756293643	2.038196953148
C	-1.764657192247	0.425439968900	2.670992046294
C	-1.343832488650	-1.763641104266	3.559060793657
H	-2.110836678169	-2.615981005810	1.673058542674
H	-0.437994326958	-1.983345946859	1.592852885132
C	-0.976099882815	-0.287407979409	3.774787074356
H	-1.233464310648	1.282438103860	2.247741572483
H	-2.755404959619	0.749035817354	3.016921247538
H	-0.586406231342	-2.444123788188	3.955932366263
H	-2.312861929836	-2.000632657836	4.015638243030
H	0.100787967115	-0.154573268264	3.631310538584
H	-1.239162680264	0.082190911073	4.770398797254
O	-4.217163186221	-0.365582145400	-0.575493459979
C	-4.790437418971	-0.116842934971	-1.882674196528
C	-5.193150987093	-0.983200516808	0.292901603348
C	-6.150732221838	-0.819885710276	-1.880825260434
H	-4.891311435112	0.967386361595	-2.013766337510
H	-4.096564230988	-0.498229640922	-2.637086375477
C	-6.541441236109	-0.768566085761	-0.395059687719
H	-4.957346197430	-2.051390839254	0.390961301640
H	-5.114195788991	-0.516253629262	1.277895643686
H	-6.047318355767	-1.859473026115	-2.212624332666
H	-6.874051713590	-0.326565073998	-2.536223006127
H	-7.279267264887	-1.525674214703	-0.114599565316
H	-6.948540319238	0.216423643276	-0.138715297009
O	-1.395514674812	-1.294456811704	-1.512094345698

C	-1.729083435435	-2.690622330644	-1.664060709443
C	-0.036751177295	-1.054509354639	-2.014229204725
C	-0.391075121979	-3.411572912521	-1.809156042348
H	-2.310558885821	-2.998793144440	-0.789284361906
H	-2.351949435518	-2.818066095927	-2.561479577621
C	0.432439937027	-2.386243525763	-2.603219976374
H	-0.085380347152	-0.253595696571	-2.755232767305
H	0.583689284597	-0.728696093891	-1.174981747701
H	-0.489171961119	-4.377164149588	-2.314539029107
H	0.056365386936	-3.579741970268	-0.823140538475
H	0.185635556990	-2.445514320775	-3.669849662198
H	1.512550570486	-2.511612779433	-2.498880044178
C	3.347793904475	-0.221365518862	-1.107602729963
C	4.214923164773	-1.331927226497	-1.311910141155
C	2.951006022503	0.452228599436	-2.298755336821
C	4.620980138556	-1.741473836683	-2.578327671932
H	4.585533480461	-1.868971092107	-0.444110585608
C	3.369498130604	0.049501888926	-3.564105017157
H	2.294330766150	1.313900672861	-2.217968451529
C	4.204721706831	-1.059975917031	-3.728062451767
H	5.293116110568	-2.593581623147	-2.667158630732
H	3.030940458862	0.607461980706	-4.436316912304
H	4.531729902683	-1.374713206525	-4.715578370873
C	2.623379726606	1.587169346322	0.512406986475
C	1.705351686326	2.011599281674	1.521335675763
C	3.254597827665	2.655454957534	-0.193873136322
C	1.450158743379	3.352692742150	1.794634780122
H	1.193177713030	1.254830398371	2.106528389495
C	2.982813023230	3.993187028070	0.068322642496
H	3.994855879102	2.413723120977	-0.949684217537
C	2.073430394773	4.372498480906	1.065420309386
H	0.755326735673	3.605914352984	2.595865495318
H	3.512951017371	4.757435141396	-0.498161220538
H	1.885186028038	5.419744721121	1.286877246192
C	2.742018953727	-0.823138171333	1.274323439482
C	2.948707335067	-0.533963401868	2.656037582682
C	2.386363070270	-2.178726875790	1.001797925017
C	2.796034189268	-1.490214501646	3.654726671525
H	3.269642512370	0.464842333907	2.935142864349
C	2.245572333118	-3.136871569560	2.002352562189
H	2.240171091176	-2.480827938231	-0.031102908803
C	2.435529724031	-2.809923812684	3.350430926678
H	2.992459414181	-1.207909690775	4.688215736507
H	1.984006935990	-4.157491482855	1.723958629057
H	2.341608122183	-3.561316128428	4.130211485537

C_α-Li distance = 5.3 Å

C	2.928376675514	0.173849885123	0.239100967600
Li	-2.341648533318	-0.043348473959	-0.280187525968
O	-2.011044074671	1.856846289538	-0.649221362178
C	-0.783226317990	2.435681749043	-1.201081504904
C	-2.864417362950	2.910089744836	-0.151295344818
C	-0.955061201785	3.954513610020	-1.112669255423
H	0.056550115924	2.085541807988	-0.596012035493
H	-0.672069578848	2.075399212412	-2.227619759813
C	-1.945529797189	4.112315728923	0.050513151619
H	-3.647037944824	3.122394779774	-0.893831634987
H	-3.341408121551	2.553352189536	0.766757578530
H	-1.384500931566	4.354620672796	-2.039015036396
H	-0.000057046507	4.450450924985	-0.923628787749
H	-2.490022887621	5.061338882828	0.032736980670
H	-1.414599338226	4.033480280244	1.005244880186
O	-1.961311595311	-0.513843337857	1.587486868075
C	-1.416042973912	-1.792474355352	2.015918690343
C	-1.744824354284	0.480841253680	2.625461364813
C	-1.346304706384	-1.707173699239	3.536718051031
H	-2.087209613494	-2.574322423399	1.645867984175
H	-0.419536060916	-1.926492345105	1.581793333364
C	-0.978697996884	-0.229918900270	3.747710507455
H	-1.190025858787	1.317363385604	2.191281004180
H	-2.729694707349	0.834345165013	2.957519451275
H	-0.593512914341	-2.386395564344	3.944503360582
H	-2.320240689714	-1.940186025038	3.984852477588
H	0.100841217499	-0.099780961090	3.623789052210
H	-1.258164336544	0.146951286726	4.736128054318
O	-4.280528878303	-0.309761572714	-0.561892693229
C	-4.844711577590	-0.156727647285	-1.887470625558
C	-5.224041065249	-0.971466222766	0.313708047904
C	-6.074307644106	-1.064739259383	-1.913956250352
H	-5.115054199165	0.896784881397	-2.033182259807
H	-4.072831268440	-0.426804248892	-2.613061314444
C	-6.548065280417	-1.001025694608	-0.453187581177
H	-4.855565090737	-1.983355337460	0.525037134609
H	-5.270698199039	-0.414287859305	1.253335406877
H	-5.789073162602	-2.089116326050	-2.180474597461
H	-6.828671892263	-0.725020245759	-2.629265843055
H	-7.177569222994	-1.847315794945	-0.163965436495
H	-7.114536611600	-0.079610777847	-0.275438573141
O	-1.461446658905	-1.250156078791	-1.548821415125
C	-1.785563805580	-2.650662859282	-1.685762001947
C	-0.096113558841	-1.011347884417	-2.035071205954

C	-0.443703901569	-3.366874827703	-1.820447320758
H	-2.367158948768	-2.952452609093	-0.808705614272
H	-2.406044054302	-2.790984792001	-2.582808818314
C	0.379338763678	-2.343146893678	-2.617104289077
H	-0.136407302699	-0.209651224680	-2.775631710711
H	0.516122933439	-0.687269623613	-1.189006395065
H	-0.536168625502	-4.335595823771	-2.320835634987
H	0.000609424559	-3.528604061537	-0.831968628207
H	0.135442572161	-2.407789527530	-3.684075049964
H	1.459575976696	-2.463766964170	-2.508773828308
C	3.347297919616	-0.236551962164	-1.103743434898
C	4.176796905610	-1.371980802535	-1.328673449533
C	2.949554562055	0.454369329480	-2.285077985199
C	4.547584885245	-1.787620155479	-2.603799756981
H	4.547231578740	-1.923244056146	-0.469836852490
C	3.333420379702	0.044978680447	-3.559256018856
H	2.321069486001	1.335356024741	-2.189470034821
C	4.131375268230	-1.088785847600	-3.743130637894
H	5.192390863817	-2.658920550920	-2.708077714664
H	2.996594005824	0.617077718079	-4.422980222246
H	4.431531715486	-1.408233356626	-4.737643447460
C	2.688180695806	1.581937530335	0.532458901611
C	1.783618112692	2.019875738534	1.547859398396
C	3.333807684637	2.640170278917	-0.175146276393
C	1.552449378820	3.364568728837	1.824795120770
H	1.261269010227	1.271251730253	2.134749022763
C	3.087361921319	3.981817399790	0.091697470153
H	4.064597166605	2.386502526871	-0.936291950276
C	2.190704386854	4.374668813027	1.095067665021
H	0.864880715474	3.628023203539	2.628946981788
H	3.627370160921	4.738053410919	-0.476189750667
H	2.022206095965	5.424587490529	1.319924634062
C	2.761751848348	-0.832488491936	1.284768036278
C	2.985920319944	-0.553186639634	2.665882767146
C	2.366787409734	-2.177010721146	1.010990391600
C	2.813396969054	-1.507452822478	3.663097624529
H	3.335604823759	0.435934207108	2.944989513574
C	2.207161809765	-3.133914783532	2.009994856666
H	2.202006061458	-2.471663017292	-0.021218213261
C	2.415117307321	-2.816130946269	3.357607224925
H	3.023597515357	-1.233427215050	4.696078600916
H	1.915153569107	-4.146067115360	1.730826844448
H	2.306458901575	-3.567071239269	4.135934457141

C_α-Li distance = 5.4 Å

C	2.972801742353	0.167457903498	0.244028586341
Li	-2.397628141708	-0.033412130946	-0.283339648433
O	-2.061450671663	1.870208538573	-0.630903469622
C	-0.818362205241	2.451903857033	-1.145089583733
C	-2.918014831681	2.919021525714	-0.128298982205
C	-0.987773657869	3.969548879229	-1.040728151713
H	0.006193643604	2.093000321667	-0.523945869001
H	-0.682929923848	2.103865788110	-2.172751056566
C	-1.997859491864	4.114350512260	0.107196524070
H	-3.688153576157	3.146586022408	-0.879153362629
H	-3.410638456284	2.549527974300	0.776444266105
H	-1.400758546516	4.382426835232	-1.968931460174
H	-0.034367987413	4.459861851920	-0.829660163343
H	-2.538288129990	5.065736411670	0.094273798944
H	-1.484911642258	4.019859833614	1.070560717304
O	-1.982312716740	-0.508496630582	1.577135463493
C	-1.405208508846	-1.780705311057	1.981281283173
C	-1.746691034536	0.482162650309	2.615301826940
C	-1.326606907100	-1.714782074602	3.502098126930
H	-2.061619749583	-2.570994383682	1.603368022666
H	-0.408613396367	-1.886360921692	1.539051673209
C	-0.973298004574	-0.236171822806	3.729029650848
H	-1.189440971913	1.315954926046	2.178774681028
H	-2.725723358456	0.842367575096	2.956293599829
H	-0.563702990468	-2.390255810740	3.897100127954
H	-2.295562693532	-1.963885851629	3.952297927123
H	0.104946382683	-0.094279401963	3.606985230155
H	-1.255524738314	0.126350000931	4.721987597274
O	-4.329117910068	-0.308886283952	-0.573970271224
C	-4.882690879048	-0.146658639268	-1.903248972307
C	-5.268959782375	-1.001702747578	0.281907096206
C	-6.092252318141	-1.079954872970	-1.957010529579
H	-5.173730048539	0.903110483310	-2.035249685401
H	-4.097663289194	-0.389115767219	-2.624511367140
C	-6.583154752192	-1.048395012762	-0.500853315061
H	-4.881260337611	-2.008102022449	0.484406323842
H	-5.338688327039	-0.457814861298	1.227882693684
H	-5.782396022737	-2.093819667365	-2.235954532855
H	-6.845925513175	-0.745274309042	-2.675394299230
H	-7.197279842550	-1.912254561210	-0.231264586136
H	-7.171346516829	-0.142155564021	-0.316024067766
O	-1.483270688430	-1.228708273067	-1.543485206897
C	-1.802876519379	-2.628385082685	-1.700883942260
C	-0.110694907407	-0.982803640803	-2.005917008486

C	-0.458597792694	-3.340598903583	-1.834645890040
H	-2.390357492933	-2.943114280313	-0.832194040122
H	-2.416328367796	-2.758173443080	-2.604244572110
C	0.370364251774	-2.303510200783	-2.607251765680
H	-0.139743441970	-0.166252356482	-2.730388302878
H	0.491848229061	-0.677832245849	-1.145689479794
H	-0.545321304981	-4.301415629580	-2.351004635151
H	-0.022699799000	-3.517970749633	-0.845036892108
H	0.134966033884	-2.349731544573	-3.677069512957
H	1.449817741019	-2.424855917173	-2.492577359274
C	3.374450151847	-0.260836169249	-1.098059499997
C	4.192232706783	-1.405735691886	-1.318467452253
C	2.970066479020	0.419815525683	-2.283186611964
C	4.546441117286	-1.838914592281	-2.592396309470
H	4.566851211544	-1.950363438771	-0.457174115296
C	3.338179939423	-0.006852134718	-3.556372004641
H	2.349706162197	1.306896695136	-2.191064030944
C	4.124833259105	-1.149301816622	-3.735417932722
H	5.182723975140	-2.716871709214	-2.693191075712
H	2.997404374661	0.558358075425	-4.423114758048
H	4.412671639734	-1.482210986264	-4.729166769762
C	2.734931198804	1.579090613970	0.521116801793
C	1.833170548790	2.031487170320	1.532846524522
C	3.380247278462	2.627012560129	-0.201963013743
C	1.604047066964	3.380301426657	1.791557671287
H	1.312096369073	1.291789382282	2.132413978104
C	3.136151199052	3.972272446453	0.047062668641
H	4.108858383401	2.361634162225	-0.961250265228
C	2.241878719349	4.379681172454	1.046857005429
H	0.917883044841	3.655497612472	2.593024066305
H	3.675535662945	4.720124551873	-0.532382167492
H	2.075595978839	5.432766922507	1.258355494207
C	2.799390361523	-0.826837007733	1.299826392326
C	3.030838058727	-0.534708158346	2.677145465355
C	2.389010143506	-2.169820233479	1.041731526659
C	2.851639892850	-1.476170075398	3.685178544139
H	3.390912757251	0.454073709780	2.944045011524
C	2.222831806554	-3.114084626059	2.051693327807
H	2.217381232484	-2.474051545656	0.013279965513
C	2.439171047943	-2.784008748144	3.395037513857
H	3.067658601021	-1.193099687448	4.714512360979
H	1.918564698528	-4.125898147280	1.784653971413
H	2.325648400870	-3.525348832702	4.181850316449

C_α-Li distance = 5.5 Å

C	3.019324395791	0.175511774586	0.251539669561
Li	-2.449638668756	-0.043668019692	-0.289193750037
O	-2.103866862656	1.863215122922	-0.616732692777
C	-0.855000041657	2.442302399329	-1.119815912531
C	-2.953009436971	2.912013280563	-0.101722845536
C	-1.005462511123	3.959429368712	-0.980569219939
H	-0.033067227790	2.059423333694	-0.509260254175
H	-0.725016656470	2.116478531195	-2.155459646888
C	-2.021162395344	4.091458565043	0.164217095197
H	-3.713978941725	3.162963627955	-0.854499236872
H	-3.457528607716	2.530611640538	0.791476349142
H	-1.407269337863	4.398863535482	-1.901358257260
H	-0.047028092128	4.432348605929	-0.752684010585
H	-2.550496510282	5.049107696424	0.167995512493
H	-1.516012406288	3.971284578419	1.128947847400
O	-2.001872334552	-0.520895224347	1.564042970644
C	-1.408096034464	-1.790238421941	1.952284671977
C	-1.752232446660	0.466456002338	2.602450787770
C	-1.315656132362	-1.734840840227	3.472440602813
H	-2.059856073231	-2.583876923092	1.573706371317
H	-0.414094646712	-1.882593066819	1.500844301555
C	-0.967158108063	-0.256001351358	3.705761945301
H	-1.198107025796	1.300776954891	2.162811259381
H	-2.726844459914	0.827604036861	2.954513461444
H	-0.545371669924	-2.408468372281	3.856092044962
H	-2.279376952040	-1.991800443664	3.929382674671
H	0.109609601344	-0.108587376097	3.576975812826
H	-1.243385522849	0.098873991643	4.703141155768
O	-4.374780885622	-0.324865371147	-0.589830268753
C	-4.920070656008	-0.145012568845	-1.920373906962
C	-5.322967036619	-1.022830572298	0.253097679252
C	-6.127836784501	-1.078937332689	-1.994035262516
H	-5.211522254319	0.906094459485	-2.040180118063
H	-4.130066944575	-0.377131807264	-2.639599435406
C	-6.630427708483	-1.063940321906	-0.541520672164
H	-4.936812502235	-2.030348342531	0.452306205962
H	-5.401491287648	-0.484949020527	1.201869893176
H	-5.814448116810	-2.089217037718	-2.281810686084
H	-6.876262448291	-0.737110060223	-2.714523573792
H	-7.244641985323	-1.932054947382	-0.286251702216
H	-7.222498108437	-0.161249006397	-0.351872693079
O	-1.505414428955	-1.227356261700	-1.542864386215
C	-1.814440475810	-2.628392343835	-1.711220402896
C	-0.128500048295	-0.971203195857	-1.987109310514

C	-0.464426899512	-3.331654572609	-1.835035677946
H	-2.408677908589	-2.951751719641	-0.850248865755
H	-2.417894784577	-2.756812715242	-2.621403635300
C	0.366768454571	-2.284870933358	-2.591832741253
H	-0.153125145173	-0.149455452969	-2.705745031893
H	0.462129620404	-0.669156951069	-1.117580255658
H	-0.539916312744	-4.289556554509	-2.358496923012
H	-0.037851577690	-3.513359093126	-0.842108939188
H	0.143116774035	-2.325089723146	-3.664378448708
H	1.445631114305	-2.400718484821	-2.466737115660
C	3.400506944481	-0.266412534361	-1.091420893280
C	4.202421260911	-1.422221324026	-1.314377613410
C	2.988432163476	0.410503356878	-2.276288680863
C	4.533979593605	-1.868944196975	-2.589743079855
H	4.583017961254	-1.964639737413	-0.454266073427
C	3.333981390217	-0.030045529413	-3.551040265138
H	2.380632902987	1.306043602996	-2.182218097417
C	4.104522060845	-1.183227794421	-3.732227954963
H	5.158743586024	-2.754935653816	-2.692482005401
H	2.988254693918	0.532944904613	-4.417310239959
H	4.374762567881	-1.526985474911	-4.727233768739
C	2.785509734041	1.590999426385	0.514837487049
C	1.876529167322	2.056949232992	1.513453029375
C	3.442751895513	2.627815295973	-0.212910770102
C	1.651758075854	3.409565160534	1.756282921169
H	1.346951049872	1.325418699800	2.115998999342
C	3.203634864260	3.976698173791	0.020348880246
H	4.175892195005	2.350024851348	-0.963546402715
C	2.302045043889	4.398047325777	1.007770413596
H	0.959044557167	3.696767119622	2.547816205224
H	3.751499476075	4.716220978587	-0.561771786100
H	2.139313376021	5.454033784761	1.207456159355
C	2.836019947498	-0.807473602191	1.315291056833
C	3.064086826507	-0.502099749991	2.690573167637
C	2.416923743340	-2.150467134429	1.070400303766
C	2.875693749683	-1.431551140838	3.707825763779
H	3.428582249183	0.487495263158	2.948359673862
C	2.241551345586	-3.082650489232	2.089995573171
H	2.245655881257	-2.464911204505	0.044937193925
C	2.456368136848	-2.740081919601	3.430488433736
H	3.089751218512	-1.138575609966	4.734811753461
H	1.931548767141	-4.095266534833	1.832598588093
H	2.336725545110	-3.472469905205	4.224756372751

C_α-Li distance = 5.6 Å

C	3.069142004985	0.176713744382	0.254396447104
Li	-2.499901955953	-0.044538018964	-0.290387328293
O	-2.151856208226	1.866251388797	-0.599350598140
C	-0.899141773300	2.446706995032	-1.090602334944
C	-2.997865052558	2.911661144266	-0.072578725190
C	-1.037974680252	3.961990037521	-0.920814995950
H	-0.079344347312	2.045859023195	-0.488477123806
H	-0.770952442582	2.141063078440	-2.132625968437
C	-2.059889368285	4.079888976123	0.220195914310
H	-3.751771631276	3.180782656416	-0.826161198339
H	-3.511180762678	2.518244849683	0.810367369360
H	-1.430526047777	4.423347842932	-1.834720185428
H	-0.076654972101	4.421984220834	-0.678413235047
H	-2.582726460033	5.040901469967	0.238040283343
H	-1.562769730861	3.939207568434	1.186444312606
O	-2.031337471725	-0.527824156384	1.558313292303
C	-1.423217852796	-1.794222685796	1.933739954020
C	-1.769928776066	0.457940835296	2.595506272684
C	-1.313541232296	-1.744654543129	3.452804806291
H	-2.072970237372	-2.591078640820	1.558685331940
H	-0.433417994872	-1.877053152001	1.471060772543
C	-0.969669203123	-0.264970147151	3.687793465735
H	-1.222517844035	1.294279410591	2.151104846658
H	-2.740668560212	0.817149157092	2.959822143323
H	-0.534828044673	-2.414984744206	3.825003618740
H	-2.270669849503	-2.008510130723	3.919521157305
H	0.105047383460	-0.111937956776	3.548770049439
H	-1.237224622385	0.084718251826	4.689330566087
O	-4.417520563609	-0.342859737698	-0.599697678271
C	-4.963168712452	-0.151953020914	-1.928878186546
C	-5.359520017375	-1.061420636622	0.233202592820
C	-6.165259034724	-1.092275434715	-2.013803868383
H	-5.260422566957	0.898697566126	-2.037106438826
H	-4.171502309778	-0.371615493737	-2.650257458178
C	-6.667125463519	-1.099713010567	-0.560953521568
H	-4.965699015172	-2.069123225613	0.415881357644
H	-5.440628692786	-0.539022944034	1.190316986606
H	-5.846043651499	-2.096742961808	-2.315139895585
H	-6.916193967909	-0.745502991992	-2.729272467184
H	-7.275781485525	-1.974976583384	-0.317090671436
H	-7.264513362158	-0.203284850610	-0.358735924801
O	-1.522170138538	-1.210764716925	-1.540068251139
C	-1.828674194594	-2.610855480796	-1.723176152709
C	-0.140099794471	-0.951007989328	-1.966346867520

C	-0.477546254535	-3.312121248344	-1.846855045312
H	-2.426734345586	-2.943328395667	-0.868273368873
H	-2.427512157904	-2.730983223528	-2.637462022007
C	0.357963610476	-2.256372829097	-2.585965346702
H	-0.155724195978	-0.118008968329	-2.672091150680
H	0.443481014628	-0.664189428899	-1.086843208008
H	-0.549472278470	-4.263875438856	-2.381862082364
H	-0.056634466216	-3.505430849718	-0.853659373118
H	0.139601906933	-2.282180993572	-3.660043102838
H	1.436067104324	-2.374719026810	-2.457146128575
C	3.439031609039	-0.278716786037	-1.086928898466
C	4.229325754364	-1.443081451407	-1.306424821177
C	3.025366782713	0.393822297345	-2.273720444443
C	4.549814869179	-1.900864541166	-2.580732349788
H	4.609931450041	-1.983037093849	-0.444695607741
C	3.360603310050	-0.057488003781	-3.547428744444
H	2.425756242746	1.295064790326	-2.181286167379
C	4.120296714358	-1.218459941774	-3.725213567715
H	5.166065386300	-2.793054113352	-2.681311567994
H	3.014942835174	0.502765578518	-4.415525594240
H	4.382348668683	-1.570806228664	-4.719428330909
C	2.841847853863	1.596522479242	0.502515933266
C	1.920442483574	2.078692953053	1.481204650563
C	3.518853548825	2.620016170144	-0.225467543824
C	1.701555786223	3.435692018968	1.705551376553
H	1.376252915259	1.357241851524	2.083440466628
C	3.285887297799	3.972909268373	-0.011014285871
H	4.260594082147	2.327601034135	-0.962144672412
C	2.371190148725	4.410980272715	0.956945650184
H	0.997673846294	3.736681986349	2.481977650657
H	3.847812612503	4.702401922638	-0.592351686242
H	2.212812859447	5.470269209438	1.142367368424
C	2.866728425819	-0.794826608832	1.323681852229
C	3.081396525969	-0.477727423140	2.698904670604
C	2.438795629738	-2.136961487071	1.087507589935
C	2.874933282521	-1.395744633672	3.722760657151
H	3.450294395569	0.511685783755	2.951172558189
C	2.245207235913	-3.057513776123	2.114268410292
H	2.275306265944	-2.460285379522	0.063509292248
C	2.448779532826	-2.703998043085	3.453743314507
H	3.079878016197	-1.094205745454	4.749163806054
H	1.930474015445	-4.070311852097	1.863184398585
H	2.316279987482	-3.428029823105	4.253641014731

C_α-Li distance = 5.7 Å

C	3.121537131108	0.178222841878	0.257828658656
Li	-2.547504740557	-0.047351867190	-0.290859389918
O	-2.194271604390	1.866776441081	-0.584395728969
C	-0.932052528745	2.447655755796	-1.050205484670
C	-3.044384417269	2.909700732889	-0.058518469236
C	-1.072249841866	3.961946319520	-0.876716705019
H	-0.122779140171	2.044841638778	-0.434908382919
H	-0.784713764533	2.145513324981	-2.090554762766
C	-2.108516144705	4.075392700790	0.251774460212
H	-3.790587783148	3.184286780602	-0.817617613196
H	-3.566699377011	2.511133395983	0.816896808162
H	-1.453372767550	4.426892794145	-1.793598023332
H	-0.113278455637	4.420290055877	-0.621696171029
H	-2.630394724115	5.036916199555	0.267894929534
H	-1.624799862502	3.929615343748	1.224168913751
O	-2.061753055429	-0.531607687825	1.555988319053
C	-1.445233826591	-1.796352538920	1.923525769152
C	-1.786321544699	0.455751174146	2.588240642678
C	-1.308178428804	-1.743981441160	3.440288562880
H	-2.100369231543	-2.595045324151	1.562007165512
H	-0.463792925538	-1.879269708144	1.443072361892
C	-0.964690503126	-0.263046320520	3.667099529464
H	-1.249866020890	1.294118219876	2.134360891292
H	-2.752033181736	0.811693320820	2.968702969707
H	-0.520346622848	-2.410681012924	3.799628388274
H	-2.255911673621	-2.010285644952	3.924402787942
H	0.107001804151	-0.106857606319	3.509707251323
H	-1.215888897783	0.086991291402	4.672711618228
O	-4.457911389350	-0.357738361656	-0.611787571247
C	-4.999509328872	-0.163101015774	-1.942295419266
C	-5.401640326482	-1.080752589859	0.215668480893
C	-6.201862097469	-1.102453563419	-2.033419565143
H	-5.295453577493	0.888063328533	-2.048539376564
H	-4.205912482696	-0.381610289316	-2.661956240852
C	-6.707249364053	-1.115458710301	-0.581735657864
H	-5.007940531230	-2.089221209177	0.394162108698
H	-5.484820994626	-0.562814516800	1.175001005283
H	-5.882626634603	-2.105896779214	-2.338043062000
H	-6.950958953478	-0.752372696226	-2.749178764916
H	-7.316557920548	-1.991643250900	-0.342915312441
H	-7.305019141184	-0.219802358901	-0.377271049327
O	-1.536208654579	-1.203244097221	-1.530037576040
C	-1.837277030202	-2.603737357864	-1.721428490730
C	-0.153700808809	-0.936765593822	-1.950329442667

C	-0.483757231054	-3.299241027143	-1.852132803917
H	-2.431845006390	-2.944419711185	-0.867296443835
H	-2.437699980367	-2.720255415797	-2.635081125371
C	0.347733735351	-2.234565827765	-2.582646353085
H	-0.169153408074	-0.096193912974	-2.647056412340
H	0.428414632072	-0.658838718274	-1.066934601349
H	-0.552930886343	-4.246606246041	-2.395193242077
H	-0.061240562651	-3.499861082483	-0.861046908890
H	0.127978507440	-2.250995657893	-3.656641528544
H	1.426299087854	-2.351177634901	-2.456341392776
C	3.479920807703	-0.286263272031	-1.083217205936
C	4.260716623205	-1.457165576287	-1.301781941171
C	3.061907278454	0.382703536217	-2.270512828468
C	4.569527372249	-1.923562219861	-2.575849968973
H	4.643008962118	-1.995231241153	-0.439547947294
C	3.385713339406	-0.077266816905	-3.544042167981
H	2.468703447173	1.288188312565	-2.178408003500
C	4.136884421892	-1.243998456208	-3.720914079788
H	5.178999810517	-2.820451768401	-2.676073701274
H	3.037810683322	0.480641639970	-4.412789021270
H	4.390100820140	-1.603013045288	-4.715055096217
C	2.893178514981	1.599663880979	0.495907537825
C	1.962668642959	2.088461366965	1.462374109080
C	3.576146083918	2.617523782289	-0.234140644947
C	1.740672694693	3.447146338038	1.673745051470
H	1.413609686675	1.371166457106	2.065430515445
C	3.340291162767	3.971843486079	-0.032764487919
H	4.323653140134	2.319086362864	-0.962675038404
C	2.416328524960	4.416753638265	0.923261146078
H	1.029109720482	3.753893919288	2.440913486958
H	3.906407147817	4.697249044680	-0.615144183607
H	2.255548756327	5.477423406071	1.098666384986
C	2.904156364228	-0.786671180342	1.329530585560
C	3.111436573275	-0.464367685895	2.704805556065
C	2.464425686599	-2.125795788859	1.097148562871
C	2.888728994514	-1.374945720469	3.731773643637
H	3.486978660677	0.523263560655	2.954527708061
C	2.254621688275	-3.038915291771	2.127279049249
H	2.304592892939	-2.452677449818	0.073696312380
C	2.452301281783	-2.680705616864	3.466406849530
H	3.088634348616	-1.069848303875	4.758132940043
H	1.931989322908	-4.049957771551	1.878908109504
H	2.308183931152	-3.399586445195	4.268970505374

C_α-Li distance = 5.8 Å

C	3.176500478901	0.148295890051	0.236145468604
Li	-2.597445952568	-0.026525527749	-0.284402280176
O	-2.286484732399	1.898050070574	-0.566554899670
C	-1.036745428845	2.487042057137	-1.054647878207
C	-3.124714683822	2.932754699425	-0.006306829584
C	-1.175390063014	3.998709917981	-0.860485103814
H	-0.212845794557	2.079597337552	-0.461939508534
H	-0.912580648461	2.197194932209	-2.101565668528
C	-2.183313056426	4.096979610488	0.294596236207
H	-3.890355620153	3.215238511847	-0.742813719113
H	-3.623624210515	2.522017756979	0.877107759623
H	-1.580021039509	4.473464604736	-1.762053256008
H	-0.210733591610	4.455601563945	-0.624662778494
H	-2.706458674024	5.057069606567	0.334726476218
H	-1.676138819516	3.940972592746	1.253412291905
O	-2.123925431260	-0.505865257530	1.570543524884
C	-1.486983949822	-1.765670160271	1.920573504445
C	-1.840989211183	0.478188108607	2.603485258090
C	-1.334430720181	-1.723050127438	3.435973805196
H	-2.135717942908	-2.569472207171	1.559085999955
H	-0.510359326228	-1.831990956950	1.427994218969
C	-1.002592890394	-0.240560734806	3.669756973958
H	-1.314275534666	1.321227967082	2.146596054719
H	-2.803815583676	0.828012162865	2.996633549201
H	-0.536617341570	-2.384669239431	3.782305566473
H	-2.274728394768	-2.001742384754	3.927537972039
H	0.066224432767	-0.073618763833	3.503763541428
H	-1.247263822510	0.100357153602	4.680094926810
O	-4.487059113357	-0.411803891078	-0.619636589665
C	-5.074223674072	-0.195320969744	-1.927681788764
C	-5.408549768422	-1.133737215816	0.233304240605
C	-6.319613024631	-1.081779987495	-1.968985383129
H	-5.326459946043	0.867934815474	-2.022859445447
H	-4.323425520742	-0.448285955113	-2.681503530686
C	-6.753064285452	-1.096335940297	-0.494409241427
H	-5.043144920048	-2.161523717220	0.354686310894
H	-5.418688329590	-0.647944535697	1.212462857424
H	-6.059734306250	-2.093388041169	-2.301530707456
H	-7.087108936869	-0.689808051528	-2.642221393992
H	-7.388584172018	-1.948673370177	-0.238218795506
H	-7.297871720681	-0.178220009388	-0.245982151208
O	-1.499472247914	-1.151781029370	-1.481911260285
C	-1.801288785947	-2.541633948003	-1.738987250082
C	-0.114513871664	-0.868991451218	-1.883219459105

C	-0.447124695413	-3.234128294910	-1.872540647495
H	-2.414123938254	-2.915893451774	-0.912271048643
H	-2.383045960075	-2.618000435409	-2.669040008613
C	0.395032726108	-2.145302511646	-2.553086001716
H	-0.126491498995	-0.007582541166	-2.554278717003
H	0.460989293802	-0.616574519905	-0.987580384478
H	-0.507964584667	-4.162186630600	-2.448892157244
H	-0.039900083113	-3.467739689317	-0.882284436113
H	0.191411677091	-2.123929036878	-3.630161854274
H	1.471391058081	-2.267279087185	-2.415581760313
C	3.581457044186	-0.324316934327	-1.089299371102
C	4.385073768161	-1.485349473564	-1.270265814960
C	3.188669315996	0.325908137741	-2.294722501878
C	4.740916651328	-1.959468944679	-2.529095530970
H	4.746125712399	-2.009452645606	-0.390340884046
C	3.559933401543	-0.141055358722	-3.552783502920
H	2.576884266935	1.221460132395	-2.229460548620
C	4.334804608006	-1.296989796690	-3.693526214635
H	5.365273331221	-2.848724785557	-2.601447005366
H	3.229375517135	0.401387698382	-4.437902374837
H	4.624538054265	-1.661626673621	-4.675614207048
C	2.925777960805	1.568623963891	0.453792427673
C	1.961033495155	2.056662414145	1.386748007999
C	3.619552238495	2.587303284193	-0.265510085649
C	1.720621638068	3.415056724358	1.579746091939
H	1.399719446159	1.338954451804	1.978107059986
C	3.364339906095	3.940629828346	-0.083668591436
H	4.391165679838	2.290180593838	-0.968953338077
C	2.408806653687	4.384970041871	0.841123650063
H	0.984410779065	3.721435386271	2.323708275493
H	3.940061045245	4.666508456662	-0.655982125611
H	2.233862187597	5.445534165413	1.003333441427
C	2.923371335502	-0.811724507232	1.303982524852
C	3.084071280510	-0.483047324709	2.684133117175
C	2.491029864703	-2.152015398836	1.062536088498
C	2.826760385644	-1.388944892494	3.707074209199
H	3.452129106873	0.505531973347	2.941413579297
C	2.245472905815	-3.059973206928	2.089194260761
H	2.367372665486	-2.483896062361	0.035689630642
C	2.398153190624	-2.695618933689	3.432697932250
H	2.993345917350	-1.079906814160	4.738246395682
H	1.930857456200	-4.072092600253	1.835039442491
H	2.227768251381	-3.411333603347	4.233021489174

C_α-Li distance = 5.9 Å

C	3.227306686985	0.162947543502	0.226635523756
Li	-2.648529213925	-0.043589459477	-0.265190232645
O	-2.315543564957	1.880727696652	-0.536157816950
C	-1.052432731098	2.466186368166	-0.992810695027
C	-3.160292813096	2.916471998771	0.012660673210
C	-1.180039549086	3.976095205452	-0.777020112208
H	-0.242150210879	2.040163104609	-0.394091951006
H	-0.912075646189	2.192695663259	-2.042032895265
C	-2.217071547750	4.068257355993	0.352826875921
H	-3.902841918670	3.214219163563	-0.741168048849
H	-3.686869203554	2.499887092831	0.877056094289
H	-1.556042392126	4.469282097254	-1.680949685425
H	-0.216516638084	4.418687121038	-0.510964669505
H	-2.732557336915	5.032487440090	0.391919248876
H	-1.737743758668	3.895930580722	1.323290971155
O	-2.188828736349	-0.526829427714	1.596513193744
C	-1.539721043549	-1.782421739133	1.943472345572
C	-1.909222246801	0.461072775026	2.626678312613
C	-1.325864340748	-1.719065808661	3.451059742923
H	-2.201924157248	-2.592056320383	1.621191911705
H	-0.584304536800	-1.856784805539	1.412140253049
C	-1.005315731930	-0.230206284202	3.654537823279
H	-1.435497294387	1.327361274390	2.156057570656
H	-2.869472239919	0.769511847986	3.059509989038
H	-0.505002795097	-2.365373466908	3.771570742429
H	-2.240939952678	-2.004190414375	3.984760413991
H	0.050903063043	-0.048500681585	3.432505137689
H	-1.203694922469	0.117385423746	4.672689706837
O	-4.534097411215	-0.410368412670	-0.632624793462
C	-5.090546031755	-0.190729278564	-1.953611951672
C	-5.466841273131	-1.152617561118	0.190417992149
C	-6.318912469358	-1.097759729711	-2.036228571280
H	-5.358775424243	0.868925481101	-2.044981348063
H	-4.315834603515	-0.423512664652	-2.689518061073
C	-6.791317213041	-1.133657893061	-0.573862259512
H	-5.087040856094	-2.174412255471	0.317082813850
H	-5.512804125081	-0.672113070610	1.171189065102
H	-6.033174328619	-2.101488733481	-2.371386146622
H	-7.074896360413	-0.712132502024	-2.725945930437
H	-7.417375232640	-1.999931585177	-0.342373844435
H	-7.359995771149	-0.228245409402	-0.332517467507
O	-1.520896509580	-1.170460127083	-1.443290835258
C	-1.811132619928	-2.565686522090	-1.688959214564
C	-0.137985128255	-0.879284204995	-1.845338609900

C	-0.453472752376	-3.243180181650	-1.864343394487
H	-2.391342687475	-2.948372997678	-0.842661750236
H	-2.421856677342	-2.649520276169	-2.599272719599
C	0.363314742470	-2.138612184079	-2.550047161309
H	-0.153355161645	-0.000406848086	-2.492960415152
H	0.446404488149	-0.652831013720	-0.948307816206
H	-0.520473016714	-4.164284888529	-2.451038035191
H	-0.019941187531	-3.486616257946	-0.887727104226
H	0.130171912020	-2.100834061515	-3.620764853111
H	1.443840196303	-2.255229890000	-2.442858670837
C	3.606091375173	-0.321177256843	-1.102052287825
C	4.384267374139	-1.498201339001	-1.291209711518
C	3.208202963571	0.333527087186	-2.303533760855
C	4.712719524995	-1.982171605510	-2.553780850035
H	4.747498929434	-2.026838844389	-0.414858217200
C	3.551527832280	-0.144086748976	-3.565392118288
H	2.615119859699	1.241049107936	-2.231564625274
C	4.302209765471	-1.315057518189	-3.714150346245
H	5.319006824942	-2.883326353779	-2.632739808061
H	3.218666683938	0.402313005341	-4.447240754605
H	4.570519999151	-1.687761423180	-4.699310035360
C	3.000453722471	1.589065713412	0.437355442402
C	2.034090012788	2.097434491498	1.356727298857
C	3.719467952381	2.590910106433	-0.279530080970
C	1.815605128769	3.460905933012	1.541071138601
H	1.452602313921	1.392192689140	1.944058422783
C	3.487128021673	3.949550760836	-0.106115908788
H	4.490686658168	2.275742590943	-0.975831659494
C	2.530035941750	4.414618594787	0.806636509274
H	1.075634072324	3.783900188870	2.274180779379
H	4.081030895044	4.662527649012	-0.676018198797
H	2.371521035782	5.478872492265	0.961342167681
C	2.954766127508	-0.787049268754	1.297496729253
C	3.111990868891	-0.453037723720	2.677140504683
C	2.503063322887	-2.122352499445	1.061648596851
C	2.836325813485	-1.349502153303	3.703371336693
H	3.491577065976	0.531957460464	2.931454143882
C	2.238964296640	-3.020785163361	2.091894245331
H	2.378743007910	-2.457760362702	0.036059273221
C	2.390916595566	-2.651836978933	3.434414473602
H	3.001608716968	-1.036755341522	4.733667289771
H	1.911416662877	-4.029787388123	1.841297101133
H	2.208380001139	-3.361198817314	4.237763145439

C_α-Li distance = 6.0 Å

C	3.285646491792	0.120286928810	0.204871358980
Li	-2.693790418621	-0.005455173430	-0.275250981618
O	-2.417968532019	1.928175684626	-0.544779823773
C	-1.168202525052	2.525061446487	-1.022264788981
C	-3.259713220521	2.955603029492	0.022161326505
C	-1.292427050179	4.031249265533	-0.776414777671
H	-0.343730629306	2.089434108196	-0.450523856560
H	-1.052954907405	2.270854284891	-2.079596880575
C	-2.314741795811	4.103994037531	0.368553772975
H	-4.008454977852	3.262268336149	-0.721991670736
H	-3.778490780631	2.527119519939	0.885455302812
H	-1.679739735395	4.541561027906	-1.665859130886
H	-0.324414956286	4.467569228544	-0.516281284761
H	-2.831138718324	5.066647908348	0.428812939952
H	-1.823844400698	3.917262846153	1.330522160208
O	-2.212249347169	-0.480669147774	1.582908624344
C	-1.576755442310	-1.741720459629	1.934256085199
C	-1.934306731037	0.504092711387	2.615862587081
C	-1.382070712332	-1.682768145227	3.444706543126
H	-2.240758987164	-2.545265733376	1.600626642321
H	-0.614932545517	-1.822785456592	1.415684068438
C	-1.050060284658	-0.197107667843	3.654188442382
H	-1.446388605563	1.365832721502	2.151185761969
H	-2.896245015025	0.822561106258	3.037767063082
H	-0.571569405205	-2.337655335898	3.773859329483
H	-2.306750348465	-1.959953731224	3.965882811889
H	0.010556239637	-0.025493369936	3.445042771175
H	-1.257687515198	0.151425022261	4.670217364624
O	-4.567560749365	-0.455116478235	-0.603669247201
C	-5.205217226337	-0.245837084569	-1.888877965164
C	-5.464902146284	-1.150114561934	0.297246487211
C	-6.458682530660	-1.121283961635	-1.869893852575
H	-5.452577383070	0.818569742306	-1.985037905550
H	-4.488140176287	-0.512665664921	-2.670285712418
C	-6.835543514105	-1.109596819167	-0.379883269764
H	-5.106018502231	-2.179357807048	0.423807356835
H	-5.431881128462	-0.646294980891	1.266701572263
H	-6.220121692731	-2.140017820666	-2.196512655389
H	-7.247792423062	-0.732220467120	-2.519388294358
H	-7.468982565362	-1.951513796777	-0.086846118713
H	-7.361823732313	-0.182464036686	-0.125072156461
O	-1.518405087199	-1.088120045360	-1.448783656154
C	-1.808051763978	-2.473494935110	-1.750902097300
C	-0.116443665382	-0.798303131174	-1.775496958096

C	-0.449751558400	-3.150584862198	-1.929093776629
H	-2.404469249806	-2.886265787969	-0.930324155901
H	-2.403274593520	-2.519123583371	-2.673823247403
C	0.388147867093	-2.019052981933	-2.540893593624
H	-0.091542089086	0.121309336144	-2.362807794471
H	0.437228113588	-0.645648209100	-0.843831862287
H	-0.509292551999	-4.041692430883	-2.561108024115
H	-0.038102086979	-3.443274334629	-0.956498713134
H	0.173492422453	-1.919968975709	-3.611651853892
H	1.465837773171	-2.149522030157	-2.421838499729
C	3.762160899655	-0.365752609958	-1.093169726828
C	4.594186393723	-1.513421254695	-1.213439995656
C	3.413690830757	0.256609091795	-2.325296147570
C	5.019014846813	-2.001581924039	-2.445100096622
H	4.919068156557	-2.016254449278	-0.307195738483
C	3.852316520156	-0.224808891025	-3.556207050798
H	2.783099656593	1.141336474167	-2.303176812363
C	4.655792428910	-1.366543881864	-3.638308143953
H	5.661616264095	-2.880266192032	-2.472789209811
H	3.552842189074	0.294409296321	-4.465895028169
H	4.998162482385	-1.742427135110	-4.599057012254
C	3.018850640126	1.541061529651	0.392146144191
C	2.004623948017	2.036566320633	1.267211286363
C	3.743934139333	2.554115383219	-0.304500674628
C	1.751375715153	3.396455863688	1.432166966991
H	1.415716620312	1.323558902314	1.837063140474
C	3.475979333845	3.908312357120	-0.151272421576
H	4.549377617980	2.251456473315	-0.966539047953
C	2.473970580337	4.360288767285	0.719361249387
H	0.978828747655	3.709292855370	2.135846047234
H	4.077060256839	4.629579911022	-0.703006117353
H	2.289214456604	5.422158988288	0.861067272977
C	2.959610869495	-0.833558789834	1.256512945991
C	3.026397014270	-0.502607646632	2.644395369262
C	2.542306877063	-2.174838730201	0.989491829135
C	2.702523572562	-1.407392685381	3.649040738884
H	3.377849280384	0.485915177960	2.924319950149
C	2.226688394853	-3.080227367500	1.998659536021
H	2.488883663699	-2.508817309954	-0.042700781388
C	2.291377480735	-2.714610926936	3.349259472482
H	2.802862567791	-1.097621128664	4.688666448987
H	1.928582451448	-4.092358735692	1.725133508832
H	2.071333658711	-3.429913834313	4.137862990152

C_α-Li distance = 6.4 Å

C	3.485737967258	-0.098295603845	0.080818385074
Li	-2.904536892289	0.179613647753	-0.136325175091
O	-2.736876820823	2.131335263791	-0.380905581364
C	-1.559165998832	2.800809751444	-0.935027630941
C	-3.615345128892	3.113250426725	0.207980039623
C	-1.726242115554	4.293223964560	-0.625162743449
H	-0.673849611174	2.381285129593	-0.449810201956
H	-1.518893146072	2.591616544386	-2.008039965158
C	-2.711561117055	4.293594559372	0.554928386415
H	-4.386452989747	3.398751330615	-0.521663532449
H	-4.102883866840	2.650879642352	1.071570729710
H	-2.158042840457	4.824434472326	-1.480843846974
H	-0.763825758124	4.752902362842	-0.386011139368
H	-3.265710859242	5.231371128900	0.656292239228
H	-2.184883722184	4.103078144452	1.497196242780
O	-2.393762615555	-0.319370950857	1.712943048785
C	-1.629479551211	-1.524192751964	2.014938620727
C	-2.208045984567	0.651765836223	2.776935294013
C	-1.304055297907	-1.441367536667	3.502266877413
H	-2.248781768616	-2.384956960207	1.744693234035
H	-0.717339586024	-1.528774411808	1.409263837993
C	-1.132083821201	0.072157683583	3.698605550281
H	-1.923044044558	1.605134809691	2.322848142303
H	-3.168017270040	0.775914324482	3.295659208668
H	-0.398492969566	-2.003559335658	3.744413018873
H	-2.138028731582	-1.822317204199	4.104460277353
H	-0.132938033105	0.377011296330	3.370842677902
H	-1.263753469023	0.392343118127	4.736324168992
O	-4.741163350677	-0.371585813239	-0.510079545110
C	-5.335159143829	-0.219035004413	-1.825142919909
C	-5.589722175613	-1.188637617179	0.333305856178
C	-6.511330055340	-1.197296090916	-1.862844132487
H	-5.665050305688	0.821016348386	-1.934764761968
H	-4.564127375578	-0.425706999484	-2.572795013157
C	-6.936279025081	-1.251229435190	-0.386720581636
H	-5.137583705970	-2.184036219101	0.430561109515
H	-5.632437607947	-0.724352251767	1.321779558030
H	-6.178842365236	-2.185326421853	-2.201272454430
H	-7.308987061910	-0.861153579745	-2.531123758855
H	-7.503019847247	-2.151382012494	-0.132683289133
H	-7.548658492266	-0.378878412102	-0.130763027570
O	-1.641749716979	-0.815399799467	-1.316894252955
C	-1.788921493696	-2.233404434793	-1.578009092837
C	-0.290150864337	-0.389320256947	-1.698341677103

C	-0.373275872479	-2.763832908335	-1.803180397785
H	-2.300126410563	-2.687601543537	-0.722821152297
H	-2.415500627215	-2.364340288326	-2.471333869834
C	0.312263596802	-1.561483687224	-2.467289834935
H	-0.383214576137	0.520559226242	-2.294836835911
H	0.278177692516	-0.167283531787	-0.789582502896
H	-0.363030983009	-3.666727816025	-2.420945157672
H	0.112404881174	-2.992452332746	-0.847765473259
H	0.044633366950	-1.505830073397	-3.529560486428
H	1.402308835423	-1.576780103773	-2.387513020902
C	4.164683867549	-0.594564930417	-1.121287125786
C	5.104853523385	-1.658983520287	-1.064024789177
C	3.923008822350	-0.067889103772	-2.419637322970
C	5.737264342388	-2.155136040119	-2.199045443292
H	5.343628763913	-2.087551541463	-0.094718601954
C	4.567294144304	-0.557045206096	-3.553964555184
H	3.212065629384	0.746894455185	-2.528636296489
C	5.481011905327	-1.610794020637	-3.462691291590
H	6.455997039918	-2.966346663904	-2.094050186237
H	4.343429263262	-0.115154617775	-4.524084445016
H	5.983740753279	-1.992593279853	-4.347698289577
C	3.106826257458	1.300416025612	0.187471348314
C	1.993059774689	1.752147937186	0.964306993929
C	3.808909268273	2.345304652571	-0.490021209047
C	1.640830927220	3.095525012881	1.068306881824
H	1.407222264702	1.017658547249	1.509613806098
C	3.439954749588	3.680792826669	-0.398966335903
H	4.680969568968	2.084365946066	-1.081519125927
C	2.349752505410	4.089322625808	0.383415429507
H	0.799919563211	3.371638370491	1.707253763943
H	4.031606189316	4.425623960715	-0.929505905700
H	2.089097759018	5.140328105451	0.481280406827
C	3.077838099567	-1.050774816636	1.106712842667
C	2.987968168777	-0.707841447651	2.489091020968
C	2.728427196627	-2.402863985095	0.805613132935
C	2.580365503154	-1.615152479173	3.461258104712
H	3.283667752794	0.291405824389	2.795172657439
C	2.323415528398	-3.308927639584	1.781364594201
H	2.796603057497	-2.739310757535	-0.225301864454
C	2.233219991317	-2.932602665139	3.128160325318
H	2.564769040465	-1.298909743426	4.503941160115
H	2.078079448192	-4.328903082790	1.486432216990
H	1.944016898803	-3.648495171923	3.893776318808

C_α-Li distance = 6.8 Å

C	3.655995984108	-0.433475974458	0.047646808159
Li	-3.078895437215	0.494293602410	-0.095462516309
O	-3.023254567923	2.451283590359	-0.324347564690
C	-1.923169232345	3.222734051115	-0.901755749558
C	-4.018702072931	3.352081981519	0.204533920878
C	-2.252732785842	4.699314924843	-0.638846626945
H	-0.997123614383	2.908978855147	-0.412068199113
H	-1.859746631681	2.987207534769	-1.968170191873
C	-3.254436193355	4.633102351770	0.525803760652
H	-4.796169802791	3.527208695457	-0.552653246092
H	-4.476570426226	2.870331260254	1.073322138149
H	-2.722630010305	5.155234108380	-1.517384375469
H	-1.354532686020	5.274832564003	-0.400486672121
H	-3.907065481130	5.508990526824	0.584885703133
H	-2.729817921360	4.530941067452	1.482787701120
O	-2.486546560866	0.001959648123	1.736704642755
C	-1.547078873445	-1.091997630461	1.961880113094
C	-2.410982365764	0.941740287179	2.840131029050
C	-1.133918154948	-0.990730765007	3.426379018945
H	-2.056260224577	-2.027288438294	1.711043343197
H	-0.690051061241	-0.957327452711	1.295347330237
C	-1.192017823442	0.525913240026	3.666558823349
H	-2.332087130984	1.949110340829	2.421029840696
H	-3.341081916271	0.867621078315	3.419398007432
H	-0.140643366975	-1.416844076175	3.591949611845
H	-1.853302778133	-1.512294027679	4.069181107268
H	-0.284596094943	1.005276553697	3.284358229547
H	-1.299687770047	0.792749330979	4.721936987982
O	-4.886373643540	-0.175840245438	-0.419406041638
C	-5.453226661943	-0.158566383464	-1.754593783413
C	-5.584955898368	-1.139092634209	0.410434788179
C	-6.323682494889	-1.411742607199	-1.843387366735
H	-6.046344264770	0.757231707918	-1.869825684215
H	-4.626336173989	-0.139111575400	-2.469819848732
C	-6.815211659936	-1.562297688747	-0.394921788363
H	-4.913392639742	-1.985013905443	0.601859308784
H	-5.824830306539	-0.659992459978	1.363388042724
H	-5.719073907939	-2.277895484535	-2.136041821763
H	-7.136345030701	-1.304069776642	-2.567195708606
H	-7.140382477754	-2.577703367212	-0.151890890009
H	-7.652827706467	-0.882102328589	-0.202430797563
O	-1.812754485694	-0.439342842513	-1.326582603473
C	-1.860822688038	-1.864383072361	-1.572863309972
C	-0.500962854300	0.078020312204	-1.738983482089

C	-0.404957587022	-2.318318850853	-1.637174407125
H	-2.439655841067	-2.324490185358	-0.765377325856
H	-2.380255436779	-2.047708620691	-2.524773498564
C	0.275783452315	-1.113917636074	-2.307004526018
H	-0.667242493182	0.869497698328	-2.475654858460
H	-0.010559750818	0.503850614832	-0.858718527409
H	-0.285195171454	-3.246422913135	-2.203819948906
H	0.004776095843	-2.479082096236	-0.634208821322
H	0.162527396814	-1.167564911573	-3.395965312352
H	1.341673174025	-1.047683492185	-2.073682268706
C	4.489958236153	-0.827391055446	-1.093557279793
C	5.501399339252	-1.817214603100	-0.964673746760
C	4.339326159449	-0.279831171228	-2.396231994955
C	6.283791502193	-2.226406181685	-2.039312371561
H	5.671021310640	-2.259781045073	0.012895068305
C	5.132070733054	-0.681214803648	-3.468508193294
H	3.574943923164	0.474314811081	-2.563141779273
C	6.114654946659	-1.662322600873	-3.308675854710
H	7.049179968033	-2.984414997706	-1.880199968512
H	4.970287015468	-0.229599469094	-4.446491709245
H	6.733225122100	-1.975239309525	-4.146115220378
C	3.131901005673	0.909779781978	0.167469580084
C	1.947280817668	1.227350101187	0.912794312807
C	3.741712269687	2.045618102456	-0.458606691922
C	1.445102458329	2.521795305686	1.019367645866
H	1.430229400089	0.425988764781	1.432068099021
C	3.225196900732	3.329501468985	-0.359975902194
H	4.662930772859	1.897962647200	-1.012882841069
C	2.062721469270	3.602599029693	0.378173818727
H	0.556214768738	2.692636965577	1.631094167383
H	3.755080484166	4.145034751371	-0.850753115179
H	1.683246727162	4.616521299388	0.479634900737
C	3.250632919309	-1.462538827228	1.007618715511
C	3.084248161957	-1.195469697583	2.396033468138
C	2.978279574507	-2.805506101277	0.617235745625
C	2.661726944368	-2.167332809403	3.299229512086
H	3.321349404135	-0.201116109447	2.763833432534
C	2.561577345309	-3.777607762455	1.522565526797
H	3.105038792056	-3.077107487359	-0.427365138076
C	2.385537923671	-3.474671233014	2.878114399969
H	2.581464246709	-1.909874211800	4.355269075210
H	2.366402877191	-4.787443923775	1.163509281550
H	2.070092232338	-4.236836615656	3.586379002251