NOVEL NITROGEN CONTAINING POLYMERS
VIA RESSERT CHEMISTRY

by

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(ABSTRACT)

Novel A-A and A-B difunctional monomers were synthesized by utilizing Reissert compound chemistry and via the use of bis(α-aminonitrile)s. These monomers were produced in high yields with preformed heterocyclic nuclei which included benzothiazole, isoquinoline and quinoline. Acylated linear polyamine derivatives were obtained by the step growth condensation polymerization of open chain bis(Reissert compound)s with suitable dihaloalkanes; intrinsic viscosities of up to 0.48 dl/g were obtained in unoptimized runs. The constitutional repeat unit of these polymers consists of four independent structural variables and thus provides versatility for tailor made macromolecular syntheses.

Novel bis(Schiff base) monomers based on 1,4-trans-diamino cyclohexane were synthesized and these could be used either directly in the production of poly(azomethine aryl ether)s or synthesis of diamines and dicarboxylic acids containing the trans cyclohexyl moiety.

Novel aromatic diamine based bis(α-aminonitrile)s were synthesized from commercially available diamines and are
currently being used in the syntheses of post-reaction modifiable co-polyamides.

A novel and unique product of rearrangement of benzothiazole Reissert compounds was isolated and characterized. It was postulated that the reaction proceeds via a bimolecular reaction between 2-cyanobenzothiazole and the ring opened azomethinethiophenoxide followed by an intramolecular acyl transfer and eventual reaction with methyl iodide leading to a novel benzothiazine.

A novel nucleophilic aromatic substitution reaction was discovered which involved the reaction of a masked carbonyl carbanion synthon with activated aromatic fluorides. Hitherto unknown poly(aryl ketone sulfone)s were synthesized when this chemistry was extended with the use of bis(α-aryl aminonitrile)s.

A novel quinodimethane was synthesized in quantitative yield by an intramolecular dehydrocyanation. Its structural features are unique in that one end is substituted by a donor moiety while the other end is captodative; this makes it attractive in the fields where electrical conductance and non linear optical (NLO) applications are important.
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My parents and my sister have provided me with lots of encouragement, love and support throughout my life. My wife, Lavanya, provided me a lot of strength and my time spent with her continues to be filled with fun and understanding. They are thanked from the bottom of my heart.
dedication

to those human minds that strive on questioning

and

to an incisive thinker and a brilliant teacher, J. Krishnamurti.
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CHAPTER 1
INTRODUCTION

A) RATIONALE FOR CURRENT RESEARCH

1) Historical

Although natural polymers (like wool, leather, cotton, rubber, shellac and wood) have contributed to the development of structural items for the comfort and use of mankind for at least five millenia, chemists were largely unaware of the structure and mechanism of formation of polymers until the last few decades. The first commercial vinyl polymer (polyvinylchloride) in the USA was introduced at the end of the third decade of this century\(^1\) and the growth of these synthetic polymers has continued to proliferate and a slow but gradual displacement of conventional building materials (like wood, steel, titanium, aluminum and silica) by synthetic polymers has been seen.

One of the most attractive features of the polymers is their low density. The vinyl polymers (accounting for most of the consumer market for common items) have densities in the range of 0.90 - 1.45 g/cc with the halogen containing polymers lying towards the high end; perhalo polyvinyl polymers and glass filled polymeric systems exhibit densities of up to 2.50 g/cc. Metals on the other hand show densities of 2.7 g/cc (aluminum) to 8.8 g/cc (copper).
The specific strengths and moduli (i.e., density normalized) of some polymers are comparable to metals and in some cases even higher\textsuperscript{2} (highly oriented crystalline polyethylene for example).

2) Motivation for the research project

Certainly then it remains a challenge to polymer chemists to develop novel materials which are able to perform multiple high performance functions. Nitrogen containing polymers are one of the most versatile classes of polymers. The utilitarian importance of nitrogen containing polymers is covered in the next section. Outstanding textbook reviews,\textsuperscript{3, 4} symposia proceedings\textsuperscript{5} and a recently authored book\textsuperscript{6} give a good perspective on currently available nitrogen containing polymers.

Our research group's interests are in the syntheses of novel polymers which by design have versatility in the end structure and in some cases can be modified later. One approach is by the synthesis of polyrotaxanes\textsuperscript{7} and the other is via the use of Reissert compound chemistry.\textsuperscript{8} The latter utilizes the principles of step growth condensation polymerization for polymer synthesis. The motivation behind this work was thus basic research into the development of novel polymers by using well known procedures of polymer chemistry and their application to some quantitative reactions of Reissert chemistry hitherto unattempted toward polymer synthesis.
B) NITROGEN CONTAINING POLYMERS

This class of polymers has been known for their high utilitarian value (Kevlar™,nylons,cyano-acrylates,soft and rigid polyurethane for foams,undergarments and sportswear,melamine,two part epoxy adhesives,acrylic fibers to mention a few) and high performance qualities. The polarity of the C-N bond contributes much to the mechanical integrity of these polymers. The nitrogen imparts basicity to the resulting polymer and this has been known to increase adhesion,which is the critical property at an interface. Quaternized salt forms of certain polymers have lent usage in water treatment and coagulation. The polyurethanes are unique in being used as biomaterials. The first artificial human heart, the Jarvik-7, was made of polyurethanes. Another widespread use of the polyurethanes is in the undergarments,sportswear and recreation wear industry where the thermoplastic elastomer Lycra™ has captured a multi-million dollar market.

The hydrogen bond is the basis of the structural existence of the DNA in a helical form and is manifested in the strength of polyamides like nylon-6,6 and Kevlar™. The production of nylon in 1990 (in the USA) was 3.22 billion lbs.;9 about 83% of this was in the synthetic fiber form and the rest as moldable thermoplastic. This does not compare too well with the largest volume vinyl polymer,polyethene (both HDPE and LDPE) the production of which was 19.5 billion lbs. for the same year (the highest for any polymer). But when one takes into account that the price of nylon
is approximately five times that of polyethene, then on a total dollar value basis nylon is about equivalent to the highest used thermoplastic commodity resin, polyethylene.

Other noteworthy classes of heterocyclic nitrogen containing polymers are polyquinolines, polyquinoxalines, polybenzimidazoles, polybenzoxazoles, polyoxadiazoles, polyimidazoles, polybenzothiazoles, polyimides and polyamide-imides. These polymers are known to retain key performance properties at elevated temperatures for long periods of time and specialty mineral filled materials could easily withstand 150° C for 500 h (N.B. polyethylene melts at ca. 140° C). Polyacrylonitrile, a vinylic nitrogen containing polymer, when pyrolyzed, can be rolled into a high strength, high modulus fiber which is used in the manufacture of composite materials. The advantage of polymeric fibers with respect to conventional inorganic or metallic fibers is the weight saving at the same level of performance without corrosion. Although these polymers are low volume specialty resins, their prices are up to 35 times higher\textsuperscript{10, 11} than the routine commodity polymers. Cyanoacrylate resins are yet another example of how the presence of nitrogen (as a nitrile) in the polymer has given outstanding adhesive properties\textsuperscript{12} to 'crazy glue\textsuperscript{TM}'.

C) BRIEF OVERVIEW OF STEP GROWTH POLYMERIZATION

Polymers can be made either by polyaddition (chain growth mechanism) or polycondensation (step growth mechanism). In this section, we restrict our discussion to understanding the mechanism of step growth (condensation) polymerization of difunctional reactants, since these will give linear (uncrosslinked) polymers. Some industrially important high volume polymers like the polyamides and the polyesters are synthesized using polycondensation techniques. Very stringent conditions have to be maintained when employing this mode of polymerization to obtain high molecular weight polymers. The reason will be apparent when we continue our discussion after a brief mathematical treatment of the polycondensation.

The following requirements need to be met rigorously if a high molecular weight is to be obtained for a polymer via polycondensation.

1) Difunctional starting materials
2) Stoichiometric balance of reactants (can be inbuilt)
3) High purity starting materials
4) Yields of reaction approaching 100% (at least 98.5%)
5) Absence of side reactions
6) Mutual accessability of reactive groups

Such a polymer could be either monadic (1-1) or dyadic (1-2).
\[ n \ A-R-B \longrightarrow -(RX)_n^- + \text{small molecule} \quad (1-1) \]
\[ n \ A-R_1-A + n \ B-R_2-B \longrightarrow -(XR_1R_2X)_n^- \quad (1-2) \]

where \( A + B \longrightarrow X \)

For the monadic system (originating from A-B type difunctional monomer) the repeating unit consists of one structural unit, but for the dyadic system (originating from the reaction between A-A and B-B difunctional monomers) the repeating unit consists of two structural units. This is the basis of difference between \( X_n \) (the average number of structural units per polymer molecule) and \( DP_n \) (the average number of repeating units per polymer molecule). \( X_n \) is defined as the ratio of total number of molecules initially present to the total number of molecules present at a given time \( t \).

\[ X_n = \frac{N_0}{N} = \frac{[M]_0}{[M]} \quad (1-3) \]

\([M]_0\) is the initial concentration of the reactive groups and this depletes with time and extent of reaction. At a given extent of conversion, \( p \) (a number between 0 and 1 signifying 0% and 100% reaction) and time \( t \), the monomer concentration is given by:

\[ [M] = [M]_0 - [M]_0p = [M]_0 (1 - p) \quad (1-4) \]
Combining (1-3) and (1-4), we get:

$$X_n = 1 / (1 - p) \quad (1-5)$$

This is the simplest case of the equation known as the Carothers equation. Here an exact stoichiometry of the reacting species was assumed. This means that in the monadic case (1-1), no other impurities were present and that in the dyadic case (1-2), equivalent amounts of the difunctional reactants were present. A more general treatment which includes non-stoichiometric proportions of the reactants gives rise to the following equation

$$X_n = (1 + r) / (1 + r - 2r p) \quad (1-6)$$

where $r$ is the ratio of the smaller concentration difunctional monomer to the larger concentration difunctional monomer (either 1 or less than 1); $r$ is also called the stoichiometric imbalance. For $r = 1$, (1-6) becomes identical to (1-5). The following table shows the variation of $X_n$ with respect to $p$ for (1-5) and the resulting molecular weight for a hypothetical polymer with a repeat unit molecular weight ($M_0$) of 200 g/mole.

<table>
<thead>
<tr>
<th>$p$</th>
<th>0.900</th>
<th>0.950</th>
<th>0.960</th>
<th>0.970</th>
<th>0.980</th>
<th>0.990</th>
<th>0.995</th>
<th>0.999</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP$n$</td>
<td>5</td>
<td>10</td>
<td>12.5</td>
<td>16.5</td>
<td>25</td>
<td>50</td>
<td>100</td>
<td>500</td>
</tr>
<tr>
<td>$M_n$</td>
<td>1K</td>
<td>2K</td>
<td>2.5K</td>
<td>3.3K</td>
<td>5K</td>
<td>10K</td>
<td>20K</td>
<td>100K</td>
</tr>
</tbody>
</table>
The following table shows how the stoichiometry (or the imbalance of it) affects the molecular weight for the same hypothetical polymer \( M_0 = 200 \) at full conversion, i.e., \( p = 1 \) in (1-6).

<table>
<thead>
<tr>
<th>r</th>
<th>0.970</th>
<th>0.975</th>
<th>0.980</th>
<th>0.985</th>
<th>0.990</th>
<th>0.995</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPn</td>
<td>33</td>
<td>40</td>
<td>49.5</td>
<td>66</td>
<td>99.5</td>
<td>199.5</td>
</tr>
<tr>
<td>( M_n )</td>
<td>6.6K</td>
<td>8K</td>
<td>9.9K</td>
<td>13.2K</td>
<td>19.9K</td>
<td>39.9K</td>
</tr>
</tbody>
</table>

Thus it is evident from the perusal of both tables that to obtain a high molecular weight polymer by a step growth mechanism, various 'bases should be covered simultaneously', i.e., the six requirements laid down previously should be satisfied at the same time. A significant number of the commercially important polymers like the polyesters, polycarbonates, poly(arylene ether ketone)s, polyimides and the polysulfones are synthesized by the polycondensation technique. A more thorough treatment with calculated examples, rate equations and kinetics of non-stoichiometric polymerizations has been given in recent textbooks\(^{15, 16}\) and provide ample coverage of the phenomenon.

**D) INTRODUCTION TO REISSELT COMPOUNDS**

Reissert compounds are a generic class of compounds which possess an \( \alpha \)-amido-nitrile moiety. The first Reissert compound was synthesized\(^{17}\) at the turn of this century by Arnold Reissert.
when he shook a mixture of aqueous potassium cyanide, quinoline and benzoyl chloride. The Reissert compounds are obtained by the addition of the elements of the acyl cyanide group across an imine linkage (C=N) which is often a part of a heterocyclic ring system. A typical Reissert compound 1 from isoquinoline and benzoyl chloride, essentially a functionalized derivative of isoquinoline, is systematically known as 2-benzoyl-1-cyano-1,2-dihydro-isoquinoline.

![Chemical Structure](image)

Since then a variety of heterocyclic bases and acid chlorides (aliphatic and aromatic) have been used in the synthesis of Reissert compounds by many workers and voluminous work in classical organic chemical applications has been aptly covered in comprehensive reviews.\(^{18, 19}\)

There are many reported procedures for the formation of Reissert compounds. These include the historical aqueous method,\(^ {17}\) liquid HCN-benzene,\(^ {20}\) and some modern methods which use organometallic reagents like Bu\(_3\)SnCN\(^ {21}\) and Et\(_2\)AlCN.\(^ {22}\) In the aqueous method, the heterocycle and the acid chloride are mixed with an aqueous solution of KCN. This method is of little
use when aliphatic acid chlorides are used. A slightly better method is to use anhydrous benzene and HCN as the nitrile source; but the health hazard that it poses is unacceptable. Nonetheless, the most successful is the very convenient two-phase method.\textsuperscript{23} This procedure involves the use of methylene chloride and water with or without a phase transfer catalyst and agitation for a successful reaction between the acylium complex and potassium cyanide.

This technique fails in the case of aliphatic or other easily hydrolyzed acid chlorides and with five membered fused heterocycles, e.g., benzothiazole and benzimidazole, partly because of pseudo-base formation and the subsequent ring opening. A Thai research group reported\textsuperscript{24} the use of trimethylsilyl cyanide (TMSCN) as the nitrile source in a homogeneous organic medium and achieved excellent yields for Reissert compounds from isoquinoline and quinoline. The lability of the nitrile in the TMSCN method is comparable to that of other organometallic nitrile sources i.e., Bu\textsubscript{3}SnCN and Al\textsubscript{2}EtCN. Recently, a patent\textsuperscript{25} described the synthesis of the first bis(Reissert compound) from benzimidazole and the first successful synthesis of a benzimidazole Reissert compound from an acid chloride has been reported by Jois and Gibson\textsuperscript{26} via the TMSCN method.

Table 1 shows a few select examples of the diversity of heterocycles and acid chlorides used over the years.
Table 1: Reissert compounds from various Heterocycles

<table>
<thead>
<tr>
<th>Heterocycle</th>
<th>Acid chloride</th>
<th>Yld.(%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quinoline</td>
<td>Benzoyl</td>
<td>70\textsuperscript{a}, 89\textsuperscript{b}</td>
<td>27</td>
</tr>
<tr>
<td>Isoquinoline</td>
<td>Acetyl</td>
<td>70\textsuperscript{a}, 84\textsuperscript{b}</td>
<td>27</td>
</tr>
<tr>
<td>Phenanthridine</td>
<td>Benzoyl</td>
<td>71\textsuperscript{a}</td>
<td>27</td>
</tr>
<tr>
<td>Phthalazine</td>
<td>Benzoyl</td>
<td>55\textsuperscript{a}</td>
<td>28</td>
</tr>
<tr>
<td>Ellipticine</td>
<td>2-Chloromethyl-benzoyl</td>
<td>82\textsuperscript{b}</td>
<td>29</td>
</tr>
<tr>
<td>Quinazoline</td>
<td>4-Chlorobutyryl</td>
<td>49\textsuperscript{b}</td>
<td>30</td>
</tr>
<tr>
<td>Quinine</td>
<td>Benzoyl</td>
<td>28\textsuperscript{b}</td>
<td>31</td>
</tr>
<tr>
<td>Benzothiazole</td>
<td>2-Chlorobenzoyl</td>
<td>0\textsuperscript{a}, 100\textsuperscript{b}</td>
<td>32</td>
</tr>
<tr>
<td>Benzimidazole</td>
<td>Benzoyl</td>
<td>0\textsuperscript{a}, 96\textsuperscript{b}</td>
<td>26</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Two phase method involving CH\textsubscript{2}Cl\textsubscript{2}-H\textsubscript{2}O; typically, molar ratio of heterocycle : acid chloride : KCN = 1 : 2 : 3.

\textsuperscript{b} Single phase method involving Me\textsubscript{3}SiCN; typically, molar ratio of heterocycle : acid chloride : Me\textsubscript{3}SiCN = 1 : 1 : 1.

Comparison of yields for the Reissert compound from quinoline and benzoyl chloride \textsuperscript{2} from the various synthetic methods with comments regarding limitations, cost, toxicity etc. is given in Table 2.
Table 2: Comparison of performance of various synthetic methods for Quinoline Reissert compound (2) formation.

<table>
<thead>
<tr>
<th>Method</th>
<th>Yield(%)</th>
<th>Ref.</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous</td>
<td>94</td>
<td>17</td>
<td>a, b, c</td>
</tr>
<tr>
<td>HCN-Benzene</td>
<td>96</td>
<td>20</td>
<td>d</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$-H$_2$O</td>
<td>70</td>
<td>23</td>
<td>a,c</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$-Me$_3$SiCN</td>
<td>89</td>
<td>24</td>
<td>a, d, e, f</td>
</tr>
<tr>
<td>Bu$_3$SnCN</td>
<td>96</td>
<td>21</td>
<td>d, f</td>
</tr>
<tr>
<td>KCN on Amberlite</td>
<td>10</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>Et$_2$AlCN</td>
<td>85</td>
<td>22</td>
<td>d, f</td>
</tr>
<tr>
<td>DMF-KCN</td>
<td>100</td>
<td>34</td>
<td>a, b, c</td>
</tr>
</tbody>
</table>

a) convenient         b) not general c) inexpensive  
d) toxic/carcinogenic compounds involved e) versatile  
f) expensive
The Reissert moiety consists of an α-amido nitrile which renders the proton on the α-carbon acidic. Deprotonation by various bases such as PhLi, NaH, NaOH or LDA results in the conjugate base which undergoes a substitution in the presence of an electrophile. A few substitutions, particularly the alkylations, involving the nucleophilic attack of the Reissert anion, result in quantitative yields of the substituted product. For example alkylations of the anion of 1 produce derivatives 3 in excellent yields. These and other reactions have been widely used in classical organic synthesis. Scheme 1 shows the reaction of the conjugate base of 1 with an alkyl halide.

\[ \text{Scheme 1: Reaction of 1 with an alkyl halide in the presence of a base.} \]
Popp and Wefer\textsuperscript{35} demonstrated the facile reaction of 1 and 2 in DMF with NaH as the base with various alkyl halides. PhLi was the base of choice previous to that work, but lower temperatures had to be employed due to undesirable side reactions in that system. Table 3 shows substitutions of 1 with various alkyl and aromatic halides. It is noteworthy that quantitative yield was obtained when 4-nitrofluorobenzene was used.\textsuperscript{37} The yield with 2-bromo-3-nitropyridine was 56%.\textsuperscript{37}

Other Reissert compounds involving heterocycles like benzothiazole\textsuperscript{32} and phthalazine\textsuperscript{28} and 3,4-dihydro-β-carboline\textsuperscript{38}
also give near quantitative yields of methylation. This reaction is not an exhaustively studied one but holds a lot of promise for application towards polymeric systems by the condensation route if suitable bis(Reissert compound)s are designed.

The quinoline Reissert compound 2 upon deprotonation yields an anion that is ambident, since it can be delocalized to the 4-position. Methylation was reported by Boekelheide and Weinstock but the mass balance was not accounted adequately.39 Gibson and Guilani40 reinvestigated the methylation of 2 and conclusively proved that the ratio of monomethylation at the 4-position to that at the 2-position is 84 : 16 and that if the 4-methylated Reissert compounds is further methylated, then the methyl group has approximately the same preference for the two positions.

**Table 3:** Reaction of 1 with various alkyl and aromatic halides (NaH / DMF)

<table>
<thead>
<tr>
<th>R</th>
<th>isopropyl</th>
<th>butyl</th>
<th>4-nitrophenyl</th>
<th>2-methyl-benzyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (%)</td>
<td>10036</td>
<td>9835</td>
<td>9737</td>
<td>9935</td>
</tr>
</tbody>
</table>

Alkylation have also been used toward the synthesis of alkaloids containing diazaheteroaromatic systems. Specifically, the Reissert compound from 6,7-dimethoxyphthalazine and benzoyl chloride was condensed with 3,4-dimethoxybenzyl chloride to yield
95% of the alkylated product which was eventually hydrolyzed to 3-azapapaverine.\textsuperscript{41} This represents \textit{diversification} onto Reissert compounds from heterocycles \textit{other than isoquinoline}.

\begin{center}
\includegraphics[width=0.8\textwidth]{scheme2.png}
\end{center}

3-azapapaverine

Another popular class of electrophiles used in reaction with 1 are aldehydes. The initial addition product, an alkoxide, further reacts with the amide carbonyl yielding eventually the ester 4 as shown in \textbf{Scheme 2}. PhLi was again the base of choice before the ease of use of NaH was proven. Popp and Gibson\textsuperscript{42} reported the reaction of various substituted benzaldehydes with the conjugate base of 1 and representative examples are shown in \textbf{Table 4}. Walters and coworkers condensed 1 and 2 with various aldehydes and ketones\textsuperscript{43} by using PhLi as the base and the yield of the benzoate esters are shown in \textbf{Table 4}. The notably high yields in some cases coupled with the fact that this reaction is not thoroughly studied using the DMF/NaH route gave us the impetus to
study it in detail and apply it to other heterocycles with a long range view to apply it toward the syntheses of novel polymers; this was certainly realized before the completion of this dissertation.

Scheme 2: Reaction of 1 with aldehydes in presence of a base.
Table 4: Reaction of 1 and 2 with substituted benzaldehydes\textsuperscript{42, 43} (PhLi / ether-dioxane)

<table>
<thead>
<tr>
<th>Reissert cmpd.</th>
<th>aldehyde</th>
<th>yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-bromobenzaldehyde</td>
<td>89</td>
</tr>
<tr>
<td>1</td>
<td>3-bromo-4-methoxy benzaldehyde</td>
<td>91</td>
</tr>
<tr>
<td>1</td>
<td>benzaldehyde</td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td>benzaldehyde</td>
<td>89</td>
</tr>
<tr>
<td>2</td>
<td>butyraldehyde</td>
<td>89</td>
</tr>
<tr>
<td>2</td>
<td>2,6-dichlorobenzaldehyde</td>
<td>82</td>
</tr>
</tbody>
</table>

Besides 1 and 2, various other Reissert compounds involving different heterocyclic nuclei have also been used in the aldehyde reaction. Gibson\textsuperscript{44, 45} has reported the synthesis of calycotomine and armepavine alkaloids involving the use of the Reissert compound from 6,7-dimethoxyisoquinoline and benzaldehyde \textsuperscript{5}. The yield of the benzoate was 77% when formaldehyde\textsuperscript{44} was used and 82% when p-benzylxybenzaldehyde was used.\textsuperscript{45}
Popp has also reported the condensation of the phthalazine (3-azaisoquinoline) Reissert compound with benzaldehyde resulting in a quantitative yield of the benzoate.\textsuperscript{28} Kant and Popp reported the reaction of the phenanthridine/benzoyl Reissert compound with benzaldehyde resulting in 80% of the alcohol\textsuperscript{46} and Bass condensed the Reissert compound from thieno[2,3-c]pyridine and benzoyl chloride with benzaldehyde to yield 67% of the benzoate.\textsuperscript{47} The above were done using NaH/DMF system. Thus the aldehyde reaction is applicable to a variety of Reissert compounds and holds a lot of promise if it is optimized.

In the absence of an electrophile, the anion undergoes a rearrangement to yield 1-acylisoquinoline \textsuperscript{6} via a tricyclic aziridine intermediate,\textsuperscript{48} this is outlined in Scheme \textsuperscript{3}.
Scheme 3: Rearrangement of the conjugate base of 1 in the absence of an electrophile.

Open chain Reissert compounds are also known\textsuperscript{49, 50} and are obtained by the condensation of $\alpha$-aminonitriles \textbf{7} with acid chlorides. A generic open chain Reissert compound (\textbf{8}) is shown below.
$R_1$, $R_2$ and $R_3$ could be all aliphatic or all aromatic or mixed aliphatic-aromatic. If $R_1$ is aromatic, then the $\alpha$-proton is acidic enough to be deprotonated by NaH in N,N-dimethylformamide (DMF) at ambient temperature. The anion of the open chain Reissert compound reacts with an alkyl halide in the same fashion as the aromatic heterocyclic Reissert compound in that yields of substitution products 9 are quantitative in a few cases. 4 9 Alkaline hydrolysis of these products (9) yields ketones 10 as shown in Scheme 4. Thus the open chain Reissert compounds can be used as masked carbonyl equivalents. For the scheme shown below, the yields of alkylations are listed in Table 5.

Scheme 4: Alkylation of open chain Reissert compound and subsequent hydrolysis to ketones.
Table 5: Reaction of 8 with benzyl halides to yield 9

(R2 = R3 = Phenyl, R4 = benzyl)

<table>
<thead>
<tr>
<th>R1</th>
<th>phenyl</th>
<th>n-butyl</th>
<th>p-chlorophenyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield</td>
<td>91</td>
<td>95</td>
<td>100</td>
</tr>
</tbody>
</table>

Reactions with aldehydes yield α-anilinoketones (11) (Scheme 5) and the rearrangement of the anion in the absence of an electrophile is complex and yields desoxybenzoins (12); this happens only when benzylamines are used (Scheme 6).
Scheme 5: Reaction of 8 with aldehydes.
Scheme 6: Rearrangement of 8 to desoxybenzoins 12
Thus, Reissert compounds offer novel C-C bond forming methods. These syntheses have been applied to isoquinoline natural products. In some cases, the reactions with aldehydes are quantitative and have been used to synthesize polymers. Our goal is to extend this methodology to polymerizations involving novel A-A monomers of the bis(Reissert compound) category and suitable dihalo electrophilic B-B monomers by the polycondensation route to yield novel polymers. Another approach is to synthesize Reissert compounds with an electrophilic end built into the skeleton to yield an A-B monomer which can be self condensed to obtain polymers.

E) INTRODUCTION TO α-AMINONITRILES

1) Background

An aminonitrile is a molecule which contains the amine and nitrile functional groups. When these two groups are present on the same carbon, then the molecule bears a special name, i.e., α-aminonitrile. A brief overview of the diverse chemistry of α-aminonitriles is presented. Structurally this class is represented by 10.

\[
\begin{align*}
R_1 \\
R_2 & \quad C \quad \text{CN} \\
\quad \downarrow & \\
\text{NR}_3R_4 & \\
\text{10}
\end{align*}
\]
2) **Synthesis**

There are many ways to synthesize α-aminonitriles. The addition of HCN to the imino linkage of benzylideneaniline was probably the earliest description of the synthesis of α-aminonitriles in 1880 by Plochl.\(^{51}\)

\[
\begin{align*}
\text{Ph} & \quad \text{N=CH} & \quad \text{HCN} & \quad \text{Ph} \\
& & \rightarrow & \\
\text{Ph} & \quad \text{NH} & \quad \text{CH} & \quad \text{CN} \\
\end{align*}
\]

Another analogous method avoids the direct use of HCN by producing it *in situ* by the addition of equal amounts of KCN and conc. HCl.\(^{52}\) One very convenient way is from aldehydes by the Strecker synthesis\(^{53}\) which involves the use of sodium cyanide and ammonium chloride with the carbonyl compound. There are two possible pathways for the reaction. The cyanohydrin may be formed initially followed by a nucleophilic substitution by the amine or the Schiff base (imine) may be formed and by the subsequent addition of NaCN gives the α-aminonitrile. Mechanistic details have been proposed for both pathways.\(^{54, 55}\)

\[
\begin{align*}
\text{R}_1 & \quad \text{C} & \quad \text{O} & \quad \text{NaCN} & \quad + & \quad \text{NH}_4\text{Cl} & \quad \rightarrow & \quad \text{R}_1 & \quad \text{NH}_2 \\
& \quad \text{R}_2 & \quad & & & \quad & \quad & \quad & \quad \text{R}_1 & \quad \text{CN} \\
\end{align*}
\]
Other synthetic methods include reaction of the aldehyde with the amine and NaCN (or KCN) in presence of NaHSO₃ with or without acetic acid shown in Scheme 7.

$$\text{R}_1\text{CHO} + \text{NaHSO}_3 + \text{R}_3\text{NH}_2 + \text{NaCN}$$

$$\downarrow$$

$$\text{R}_1\text{CH-NHR}_3\text{CN} \downarrow$$

**Scheme 7**: Aqueous synthetic route for α-aminonitriles.

In the aqueous route, which is a convenient one pot, multistep procedure for α-aminonitrile synthesis, if the amine or aldehyde are both aromatic, then Schiff base formation is predominant. In such a case refluxing the cyanohydrin with the amine in ethanol gives the α-aminonitriles selectively. Sandhu and associates have synthesized aromatic α-aminonitriles in the presence of glacial acetic acid without the formation of Schiff base. Ojima et al. have prepared α-aminonitriles by cyanosilylation of Schiff bases by trimethylsilyl cyanide (TMSCN) in presence of catalytic amounts of Lewis acids as shown in Scheme 8.
Scheme 8: Synthesis of α-aminonitriles by cyanosilylation of the Schiff base.

Table 6: Representative yields of aminonitriles 10, R4 = H by Ojima's method.59

<table>
<thead>
<tr>
<th>R^1</th>
<th>R^2</th>
<th>R^3</th>
<th>Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenyl</td>
<td>H</td>
<td>benzyl</td>
<td>98</td>
</tr>
<tr>
<td>phenyl</td>
<td>H</td>
<td>phenyl</td>
<td>81</td>
</tr>
<tr>
<td>phenyl</td>
<td>methyl</td>
<td>benzyl</td>
<td>87</td>
</tr>
<tr>
<td>——(CH2)_5——</td>
<td></td>
<td>benzyl</td>
<td>82</td>
</tr>
</tbody>
</table>
Another approach is to cyanosilylate the carbonyl compound initially and then react the trimethylsilyl ether of the cyanoxydrin with amines to yield the desired α-aminonitriles as shown in Scheme 9.

\[
R_1\text{CHO} + \text{Me}_3\text{SiCN} \rightarrow R_1\text{CH-OSiMe}_3\text{CN}
\]

\[
R_3R_4\text{NH} \rightarrow R_1\text{CH-NR}_3\text{R}_4\text{CN}
\]

10, \(R_2 = \text{H}\)

**Scheme 9**: Synthesis of α-aminonitriles by initial cyanosilylation of the aldehyde.

**Table 7**: Representative yields of aminonitriles 10, \(R_2 = \text{H}\) by Mai and Patil's method.

<table>
<thead>
<tr>
<th>R</th>
<th>R1</th>
<th>R2</th>
<th>Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethyl</td>
<td>H</td>
<td>H</td>
<td>91</td>
</tr>
<tr>
<td>benzyl</td>
<td>H</td>
<td>H</td>
<td>99</td>
</tr>
<tr>
<td>2,6-dichloro-phenyl</td>
<td>H</td>
<td>H</td>
<td>90</td>
</tr>
<tr>
<td>4-carbomethoxy-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
phenyl \ H \ H \ 77
3-nitrophenyl \ -(CH_2)_4-- \ 95

Recently, Harusawa et al. reacted diethyl phosphorocyanidate, (EtO)_2P(O)CN, with carbonyl compounds (mostly ketones) in the presence of amines (NH_3, 1^0 and 2^0) to obtain good yields of the corresponding \(\alpha\)-aminonitriles.\(^{63}\)

3) Synthetic utility of the \(\alpha\)-aminonitriles

\(\alpha\)-Aminonitriles have proven to be extremely versatile synthetic reagents; the central carbon can be made either electrophilic or nucleophilic, by altering the reaction conditions, providing in the former case, an iminium salt through the loss of the cyanide and in the latter case a masked carbonyl equivalent. \(\alpha\)-Aminonitriles can also be dehydrocyanated to the corresponding enamine (or a diename in case of \(\alpha,\beta\)-unsaturated carbonyl compound as the starting material) or decyanated reductively to the amine which is arguably the most useful synthetic moiety in organic chemistry.

The concept of reversing the polarity of a functional group for the purposes of carrying out a synthetic sequence which may not be amenable otherwise is certainly a well known one. Examples include the Grignard reagent (RMgX) in which the R group is nucleophilic but in the starting material, i.e., RX, it was electrophilic and the use of the nucleophilic cyanide anion as a
masked carboxylic acid (HCOOH), which certainly could not be used for carboxylic acid homologation type sequence.

Seebach\textsuperscript{64} has used the German word \textit{umpolung} for such a reaction sequence where traditional polarity is reversed. In fact, the meaning of the word \textit{umpolung} is reversal of dipoles. Conversion of the carbonyl to the α-aminonitrile group is an example of \textit{umpolung}. Another very popular method is the conversion of the carbonyl group to a dithiane derivative\textsuperscript{65} (Scheme 10), which achieves the same purpose and the chemistry is analogous to that of α-aminonitriles.

\begin{equation*}
\text{RCHO} + \text{HS(CH}_2\text{)}_2\text{SH} \quad \rightarrow \quad \text{RCH_2SCH}_2\text{R} \\
\begin{array}{c}
\text{R}_1\text{X} \\
\text{B}^- \\
\end{array} \\
\text{RCH}_2\text{COR}_1
\end{equation*}

\textbf{Scheme 10} : Synthetic utility of the dithiane derivative.
However, Stork\textsuperscript{66} has pointed out the advantages of $\alpha$-aminonitriles over the dithiane derivatives: namely the lower cost and better selectivity in Michael type reactions. Martin\textsuperscript{67}, Albright\textsuperscript{68}, Lever\textsuperscript{69} and Seebach\textsuperscript{64, 70} have written comprehensive reviews on the subject matter which cover a broad range of synthesis, application to various reaction types and deprotection of $\alpha$-aminonitriles amongst other umpolung reagents.

$\alpha$-Aminonitriles have also found use as substances with pharmacological activity. Metabolism of organic nitriles is believed to occur in part by the loss of cyanide which is eventually metabolized to a thiocyanate.\textsuperscript{71} Many such compounds are used in cancer chemotherapy as antineoplastic agents.\textsuperscript{72} This is presumably due to the liberation of cyanide \textit{in vivo}.\textsuperscript{73} Some $\alpha$-N-alkylaminonitriles are unstable as hydrochloride salts and readily dissociate releasing cyanide in aqueous solution.

If in 9 either $R_1$ or $R_2$ is H and $R_3$ and $R_4$ other than H, then the $\alpha$-proton ($R_1$ or $R_2$) is quite acidic and is deprotonated by a variety of bases. These include LDA, NaH, MeONa, BuLi and NaNH$_2$. A few select examples of the synthetic utility of $\alpha$-aminonitriles are discussed below.

Stork has very elegantly shown the synthetic utility of these masked carbonyl compounds by the use of N,N-diethylaminoacetonitrile (9, $R_1 = R_2 = H$, $R_3 = R_4 =$ ethyl) for the homologation of an aldehyde by the use of an alkyl halide.\textsuperscript{66} Ketones (symmetrical or unsymmetrical) can be produced by
carrying out the same chemistry one more time as shown in Scheme 11. Thus the overall transformation is that of introducing a carbonyl moiety linking two alkyl groups (from the starting alkyl halides).

\[
\begin{align*}
R_2NCH_2CN & \xrightarrow{\text{1) base / } R_1X} R_2N\text{-CH-CN} \\
R_2N \begin{array}{c}
\text{O} \\
R_1 \quad R_3
\end{array} & \xrightarrow{\text{base / } \Delta} R_3X \\
R_2N \begin{array}{c}
\text{O} \\
R_1 \quad R_3
\end{array} & \xrightarrow{\text{base / } \Delta} R_3X
\end{align*}
\]

Scheme 11: Synthesis of symmetrical or unsymmetrical ketones by Stork's method.\textsuperscript{66}

A case in point is the synthesis of ketoaldehyde \textsuperscript{13} shown below.\textsuperscript{66}
Stork has also synthesized β-aminoalcohols by an analogous sequence but by the use of heteroaliphatic Reissert compounds\textsuperscript{74} and open chain Reissert compounds although no mention was made of the term "Reissert compounds".

Delgado and Mauleón\textsuperscript{75} have carried out an asymmetric synthesis of some aryl 2-piperidylmethanols from chiral α-aminonitriles. α-Aminonitriles were key intermediates in the
intramolecular ring contraction approach to the synthesis of indolizidine alkaloids. Takahashi has synthesized some symmetrical diketones (Scheme 12) by reacting the \( \alpha \)-aminonitriles with alkyl dibromides.

\[ \text{Me} \text{N} = \text{CH-CN} \xrightarrow{1) \text{DMF} / \text{NaH}} \xrightarrow{2) \text{Br(CH}_2\text{)}_n\text{Br}} \text{Me} \text{N} = \text{C-(CH}_2\text{)}_n\text{C-N} \text{Me} \]

\[ \text{Ph} \xrightarrow{\text{H}^+ / \Delta} \text{Ph} \text{(CH}_2\text{)}_n\text{Ph} \]

Scheme 12: \( \alpha,\omega \)-dicarbonyl compounds via \( \alpha \)-aminonitriles.

Albright and McEvoy did some very elegant work with aryl \( \alpha \)-aminonitriles (Scheme 13) and their reactions with activated aromatic halides (giving unsymmetrical aryl ketones), chloroformates, acid chloride (giving unsymmetrical benzils) amongst others. The initial reaction product was a substituted aminonitrile; stripping off the aminonitrile linkage in refluxing 70% acetic acid afforded the carbonyl compounds in high yields. The reaction conditions are quite mild and the nucleophilic aromatic substitution occurs with ease. When acid chlorides are used, benzils are the final reaction products; these can be
symmetric or unsymmetric. The same is true for the carbonyl compounds.

\[
\begin{array}{cc}
\text{CH-CN} & \text{NaH/DMF} \\
\text{1)} & \text{p-Fluoro-nitrobenzene} \\
\text{2)} & \text{70\% AcOH} \\
\text{3)} & \text{89\%}
\end{array}
\]

\[
\begin{array}{cc}
\text{O} & \text{CN} \\
\text{1)} & \text{NaH/DMF} \\
\text{2)} & \text{p-Fluoro-cyanobenzene} \\
\text{3)} & \text{70\% AcOH} \\
\text{88\%}
\end{array}
\]

Scheme 13: Nucleophilic aromatic substitution with \(\alpha\)-aryl-aminonitriles.

This provided a good nucleus of ideas for us; the \(\alpha\)-arylaminonitriles are precursors of open chain Reissert compounds and we had to synthesize them before the amidification step. The same chemistry could be applied to open chain Reissert compounds and we did achieve near quantitative yields in model reactions with activated aromatic halides. The \(\alpha\)-arylaminonitrile chemistry was extended to make difunctional aminonitriles and diversification into novel polymeric systems has resulted.
REFERENCES


51) Plochl, A. Ber. 1880, 1281.


CHAPTER 2

RESULTS AND DISCUSSIONS

A) POLYMERS FROM AROMATIC HETEROCYCLIC REISSERT COMPOUNDS

1) Reissert compounds from diacid chlorides: A-A monomers

The use of diacid chlorides in the syntheses of aromatic heterocyclic bis(Reissert compound)s has been limited. Earlier attempts towards the synthesis of bis(Reissert compound)s, 14a, gave poor yields with 22% as the best yield when R = p,p'-diphenyl ether. 79, 80 14c, 15b and 15c have also been synthesized before in trace yields. 80

![Chemical Structure](image)

14a. \( R = \text{Ph} \quad 14b. \quad R = -(\text{CH}_2)_6^+ \)

14c. \( R = \text{O} \quad 14d. \quad R = \text{Ph} \)

The reason, in part, for the low yields is the hydrolysis of the diacid chloride by the H₂O in the H₂O / CH₂Cl₂ method of synthesis.
that was the most popular method until the use of the single phase method was proven superior.

We needed to synthesize bis(Reissert compound)s, involving the use of various heterocycles and bisacid chlorides, as novel A-A monomers. Toward this end, we chose to employ the single phase method which utilizes CH₂Cl₂ and trimethylsilyl cyanide as the organic soluble cyanide source. The heterocycles included were isoquinoline, quinoline, benzothiazole and benzoxazole. The diacid chlorides were terephthaloyl chloride, isophthaloyl chloride, oxybisbenzoyl chloride and adipoyl chloride. These attempts culminated successfully in the syntheses of 14 - 17.81

\[
\begin{align*}
15a, & \quad R = \begin{array}{c} \text{phenyl} \end{array} & 15b, & \quad R = -(\text{CH}_2)_6- \\
15c, & \quad R = \begin{array}{c} \text{bicyclo[2.2.2]octyl} \end{array} & 15d, & \quad R = \begin{array}{c} \text{benzyl} \end{array} \\
15e, & \quad R = \begin{array}{c} \text{phenyl} \end{array}
\end{align*}
\]
\[
\begin{align*}
16, \ X = S, \ R &= -\text{phenyl} \quad 17, \ X = O, \ R &= -(\text{CH}_2)_6^-
\end{align*}
\]

**Table 8**: Novel bis(Reissert compound)s synthesized by the single phase technique (Trimethylsilyl cyanide / CH\textsubscript{2}Cl\textsubscript{2}).

<table>
<thead>
<tr>
<th>Heterocycle</th>
<th>Product</th>
<th>Yield (%)</th>
<th>mp (°C)</th>
<th>Prev best (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>isoquinoline</td>
<td>14\textit{a}</td>
<td>50</td>
<td>209.6 - 210.3\textsuperscript{a}</td>
<td>22\textsuperscript{a}</td>
</tr>
<tr>
<td>isoquinoline</td>
<td>14\textit{b}</td>
<td>100</td>
<td>184 - 185\textsuperscript{b}</td>
<td>8\textsuperscript{b}</td>
</tr>
<tr>
<td>isoquinoline</td>
<td>14\textit{d}*</td>
<td>95</td>
<td>151 - 158</td>
<td>- -</td>
</tr>
<tr>
<td>quinoline</td>
<td>15\textit{a}*</td>
<td>80</td>
<td>188 - 191</td>
<td>- -</td>
</tr>
<tr>
<td>quinoline</td>
<td>15\textit{d}*</td>
<td>100</td>
<td>206 - 207</td>
<td>- -</td>
</tr>
<tr>
<td>quinoline</td>
<td>15\textit{e}*</td>
<td>95</td>
<td>238 - 241</td>
<td>- -</td>
</tr>
<tr>
<td>benzothiazole</td>
<td>16\textit{*}</td>
<td>100</td>
<td>250 - 253</td>
<td>- -</td>
</tr>
<tr>
<td>benzoazole</td>
<td>17\textit{*}</td>
<td>96</td>
<td>195 - 196</td>
<td>- -</td>
</tr>
</tbody>
</table>

\textsuperscript{a} lit.\textsuperscript{79} mp = 140 - 163\textdegree C.

\textsuperscript{b} lit.\textsuperscript{80} mp = 189 - 190\textdegree C.

\textsuperscript{*} these are new compounds.
14a, 15a, and 15d were made by Mr. Bardia Guilani (who graduated with a M. S.; experimental details can be found in his M. S. thesis). 14b and 17 were made by Dr. Jois in our research group. 14d, 15e and 16 were synthesized by the author. The single phase technique thus gives very good yields and although the lowest yield is 50%, it is more than a twofold improvement over yields reported to date for bis(Reissert compound)s from diacid chlorides.

The isoquinoline-terephthaloyl bis(Reissert compound) 14d, a pale yellow solid, was very soluble in a variety of solvents; its crystallization was difficult because of the presence of diastereomers. It was repeatedly recrystallized from ethanol and exhibited a mp of 151 - 158°C with part of it shrinking at 140 - 143°C. Its FTIR spectrum showed peaks at 1672, 1628 cm⁻¹ for the two conformers of the amide carbonyl, 1572 cm⁻¹ for the phenyl ring and 720, 752 cm⁻¹ for m-disubstituted benzene. The ¹H NMR showed signals that well matched the structure but some peaks were broad indicating conformational isomerization at ambient temperature (this will be dealt with in depth for model compounds in a later section).

The solubility of the quinoline-terephthaloyl Reissert compound 15e was in sharp contrast to 14d; it was soluble only in hot dimethylformamide-ethanol mixture from which it was recrystallized. This shows the effect of the para-orientation with respect to meta-orientation (15e versus 14d) where the molecule is less symmetric, packs loosely and melts lower in general. The
amide carbonyl conformers showed at 1685 and 1647 cm\(^{-1}\) in the FTIR spectrum. The \(^1\)H NMR spectrum for 15\(\text{e}\) is much sharper than for 14\(\text{d}\) because it is diastereomERICally pure as evidenced by a smaller melting range (mp = 238 - 241°C, dec.).

The effect of \textit{para}-orientation is evident on the solubility of the benzothiazole-terephthaloyl bis(Reissert compound) 16 which is insoluble in common solvents and was purified by Soxhlet extraction. Its FTIR spectrum shows a single carbonyl peak at 1665 cm\(^{-1}\) and the absence of cyano peak just as for 14\(\text{d}\) and 15\(\text{e}\). The \(^1\)H NMR spectrum shows broad peaks; in fact H\(\text{d}\) centered at 6.6 ppm was broad enough (ca. 0.22 ppm) to be mistaken as an acidic proton. \(\text{D}_2\text{O}\) exchange, which did not occur, showed it to be a nonexchanging proton and selective homonuclear decoupling proved it to be H\(\text{d}\). In fact, the curious \(^1\)H NMR spectrum prompted us to an in depth conformational analysis of model mono-Reissert compounds based on benzothiazole; this is reported in a following section.

15\(\text{d}\) and 16 showed unusual thermograms (dynamic runs at a heating rate of 10°C/min in air) in that up to 30% by weight of the material was retained at ca. 550°C; in contrast, a total weight loss for 52, an acyclic aliphatic diamine based bis(Reissert compound, see Scheme 20), was attained at ca. 450°C under the same conditions.
2) DMF / KCN route

As can be seen from Table 8, the yields of bis(Reissert compound)s obtained by the single phase technique are considerably better than any other previously reported. Therefore our attempt toward the synthesis of novel A-A bis(Reissert compound) monomers, with the heterocyclic moiety preformed, was very successful. Nonetheless, the drawbacks of this synthetic method are the cost, toxicity and lability of the trimethylsilyl cyanide. Therefore we sought a method which would not have those shortcomings. We embarked upon the DMF / KCN method and obtained partial success. The method consisted of mixing the heterocycle with twice the molar amount of acid chloride and thrice the molar amount of dry powdered KCN in dimethylformamide (DMF) solvent. The heterogeneous mixture was stirred for 48 hours and then quenched into ten fold excess H2O and the resulting gum was crystallized by trituration with EtOH. Quantitative yields of Reissert compounds 1 and 2 were obtained when the acid chloride used was benzoyl chloride and the heterocycles were isoquinoline and quinoline. The yield of the Reissert compound was zero when benzothiazole was the heterocycle partly due to the lower basicity of benzothiazole (ca. 3 orders of magnitude).
**Table 9**: Novel route to Reissert compound synthesis

<table>
<thead>
<tr>
<th>Heterocycle</th>
<th>acid</th>
<th>chloride</th>
<th>product</th>
<th>yield (%)</th>
<th>prev. best (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>quinoline</td>
<td>benzoyl</td>
<td></td>
<td>18</td>
<td>100</td>
<td>8424</td>
</tr>
<tr>
<td>isoquinoline</td>
<td>benzoyl</td>
<td></td>
<td>1</td>
<td>100</td>
<td>8924</td>
</tr>
<tr>
<td>benzothiazole</td>
<td>benzoyl</td>
<td></td>
<td>19</td>
<td>0</td>
<td>10084</td>
</tr>
</tbody>
</table>

![Chemical structures](image)

**18**

**19**

The motive of the above synthetic modification was

a) to invent a *novel economical route* to Reissert compounds

b) *extend* it to the bis(Reissert compound) synthesis that we had undertaken in this project. Melvin Rasco, a graduate student in the group, undertook the bis(Reissert compound) synthesis via this method and pertinent data may be found in his thesis.
3) Reissert compounds from halomethylbenzoyl chlorides: A-B monomers

a) Monomer synthesis

The A-B type of Reissert compounds have an electrophilic moiety inbuilt in the acid chloride; the anion formed by deprotonation provides the nucleophilic portion. Prior to the work we undertook, there were not many reports in the literature regarding such an approach. All of the reported few were attempts toward heterocyclic alkaloid syntheses of pharmaceutical significance. Some details have already been covered in the first chapter.

Chloromethylbenzoyl chlorides are commercially available and thus we chose the haloalkyl group to be the electrophilic functionality. The o-derivative was rejected as a possibility due to the internal cyclization that it undergoes as shown in Scheme 14. The o-(chloromethyl)benzoyl isoquinoline Reissert compound 20 was cyclized to yield the lactam 21 by Tyrrell and McEwen\textsuperscript{85} and this intramolecular reaction can seriously compete with polymerization. This possibility is precluded in the para and meta derivatives 20 and 21 by geometric considerations.
Scheme 14: Intramolecular cyclization of \( \textbf{20} \) to a tetracyclic lactam \( \textbf{21}^{85} \)

\[
\begin{align*}
\text{22.} & \quad R = H, \quad R_1 = \text{CH}_2\text{Cl} \\
\text{23.} & \quad R = \text{CH}_2\text{Cl}, \quad R_1 = H \\
\text{24.} & \quad R = H, \quad R_1 = \text{CH}_2\text{I} \\
\text{25.} & \quad R_2 = \text{CH}_2\text{Cl} \\
\text{26.} & \quad R_2 = \text{CH}_2\text{I}
\end{align*}
\]

Thus, five novel difunctional Reissert compounds of the A-B category were synthesized.\(^86\) The heterocycles involved were isoquinoline (\(\textbf{22} - \textbf{24}\)) and benzothiazole (\(\textbf{25}, \textbf{26}\)). Synthesis of
22 and 23 involved the classical two phase method involving CH₂Cl₂, H₂O and potassium cyanide as the nitrile source. 25 was synthesized from benzothiazole by the single phase method using trimethylsilyl cyanide as the nitrile source. 22 and 25 were converted quantitatively to their iodomethyl derivatives 24 and 26 using sodium iodide in acetone. This was done because iodide is a better leaving group than chloride and renders the halomethyl moiety more electrophilic and more susceptible to attack by the nucleophilic conjugate base of the Reissert compound. 22 - 26 displayed the carbonyl stretch from 1670 - 1645 cm⁻¹ in their FTIR spectrum. The nitrile stretch was only weakly present in 24 and 25 but this is not entirely unexpected because the nitrile stretch resonance is usually very weak for the Reissert compounds.48

The ¹H NMR spectra of the iodides 24 and 26 exhibited an upfield shift of 0.17 ppm for the benzylic protons relative to the respective chlorides, while all other resonances stayed practically unchanged. The iodomethyl Reissert compounds were unstable in common solvents at elevated temperatures and the purple coloration characteristic of iodine was seen. In the solid state, the Reissert compounds were quite stable and can be stored for long periods of time without any apparent decomposition. These novel A-B Reissert compound monomers are summarized in Table 10.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Method&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Yield (%)</th>
<th>mp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22&lt;sup&gt;*&lt;/sup&gt;</td>
<td>T</td>
<td>63</td>
<td>135.0 - 136.0</td>
</tr>
<tr>
<td>23&lt;sup&gt;*&lt;/sup&gt;</td>
<td>T</td>
<td>33</td>
<td>179.0 - 180.5</td>
</tr>
<tr>
<td>24&lt;sup&gt;*&lt;/sup&gt;</td>
<td>E</td>
<td>100</td>
<td>168.0 - 170.0</td>
</tr>
<tr>
<td>25&lt;sup&gt;*&lt;/sup&gt;</td>
<td>S</td>
<td>100</td>
<td>143.5 - 145.0</td>
</tr>
<tr>
<td>26&lt;sup&gt;*&lt;/sup&gt;</td>
<td>E</td>
<td>100</td>
<td>149.0 - 150.0</td>
</tr>
</tbody>
</table>

*) all are new compounds.

<sup>a</sup> T = two phase method (CH₂Cl₂/H₂O, KCN, ArCOCl); E = exchange of chloride by treatment with NaI in refluxing acetone; S = single phase method [CH₂Cl₂/(CH₃)₃SiCN, ArCOCl]. It is known that the single phase method provides better yields than the two phase method, particularly with easily hydrolyzable acid chlorides such as these. Undoubtedly, 22 and 23 can be made quantitatively by the single phase technique.

When we attempted to convert the p-chloromethylbenzoyl Reissert compound from isoquinoline 22 to its 4-formyl derivative 22a (another novel A-B monomer) via the alcohol 22b, the reaction did not work (Scheme 15). 22 was initially reacted with tetramethylammonium hydroxide in the hope to convert it to 22b.
and eventually oxidize 22b to the aldehyde 22a; instead 22 (an amide) was hydrolyzed to isoquinoline. This sequence was undertaken because the aldehyde group of 4-formylbenzoyl chloride, reacts with trimethylsilyl cyanide to give the trimethylsilyl cyanoxydrin ether and the expected product 22b was never isolated by the direct reaction (experimental details can be found in Mr. Bardia Guilani's M. S. thesis).
Scheme 15: Hydrolysis of 22 by Bu₄NOH
Another route to obtaining the formyl linkage from halomethyl group is via dimethylsulfoxide oxidation.\textsuperscript{87} Gibson used it effectively to obtain poly(vinylbenzaldehyde) from poly(vinylbenzyl chloride).\textsuperscript{87} The use of protected aldehyde (as an acetal) is also possible except that the reaction should be carried out under neutral or basic conditions. This precludes the use of the two-phase technique where inevitably some hydrolysis of the acid chloride liberates HCl; the single phase technique could be used with advantage here (trimethylsilyl cyanide / CH\textsubscript{2}Cl\textsubscript{2}).

b) Polymer synthesis

Although neither of \textsuperscript{14} - \textsuperscript{17} were directly used by the author for polymerizations, they were used by other members of the group to synthesize polymers. Details can be found in Mr. Bardia Guilani's M. S. thesis as well as in a publication and references therein.\textsuperscript{8}

When the p-chloromethylbenzoyl Reissert compound from isoquinoline \textsuperscript{22} was polymerized in THF at -78\textdegree C under N\textsubscript{2} atmosphere with nBuLi, and the resulting polyamide \textsuperscript{27} (Scheme \textsuperscript{18}) was purified by three precipitations from THF into water and dried, a number average molecular weight of 2400 g/mol was obtained from GPC data (polystyrene standards, polydispersity index = 2.1) and the NMR spectrum of the polymer showed peaks that well matched the repeat unit. An interesting part of the \textsuperscript{1}H NMR spectrum (\textbf{Figure 1}) of \textsuperscript{27} was the region of absorption of H\textsubscript{3}, H\textsubscript{4} and the benzylic methylene protons. In the \textsuperscript{1}H NMR spectrum
(Figure 2) of the monomer 22, H₃ appears as a doublet, H₄ is overlapped by H₁ and appears as a broad partially resolved doublet; the benzylic methylene protons appear as a sharp singlet. In the NMR spectrum of the polymer 27, both H₃ and H₄ appear as multiplets; this is an effect of the chirality at C₁ and hence the presence of stereoisomers resulting from the R or S absolute configuration at C₁, i.e., tacticity. The benzylic methylene protons appear as two broad multiplets, each of which integrates for one proton, since they are rendered diastereotopic by the vicinal stereogenic center.

Scheme 16: Polymerization of 22 with nBuLi
The polymer 27 was thermally stable up to 220° C, exhibiting a 15% weight loss \textit{(in air)} at 275° C, and showed a $T_g$ of 119° C. The plateau that followed after the 15% weight loss is consistent with the initial loss of HCN, presumably forming the more stable conjugated polymer 28. The reason for low molecular weight is that the base employed, $n$BuLi, is a very strong base and certainly has strong nucleophilic character. The Reissert compound 22 has sensitive electrophilic sites besides the chloromethyl, namely the amide carbonyl and the nitrile. Further, there is a possibility of proton abstraction from the chloromethyl group and further dechloridation to yield a benzylic carbene; any of the aforementioned detours flattens any hope of getting a high molecular weight polymer via step growth polymerization process.

When the base was changed to NaH for the attempted polymerization of 24 (the iodomethyl derivative of 22) and the product worked up, an off-white polymer was obtained with $^1$H NMR spectrum similar to that of the polymer obtained by the $n$BuLi trial. Its FTIR spectrum was identical in the fingerprint region to
that of the nBuLi trial. Once again the molecular weight was not high ([η] = 0.06 dl/g in CHCl₃ at 25°C) and presumably carbene type intermediates are responsible for unattainability of high molecular weights. Rearrangement also may be possible and contributes in limiting the molecular weight (Scheme 3, chapter one).

When we attempted to polymerize the m-chloromethylbenzoyl Reissert compound from benzothiazole (25) to polyamide 29 at ambient temperature (in dimethylformamide using NaH), an orange red solid was isolated.

\[
\begin{align*}
\text{25} & \quad \text{DMF/N₂} & \quad \text{29} \\
\begin{array}{c}
\text{N} \\
\text{C} \\
\text{O} \\
\end{array} & \quad \begin{array}{c}
\text{CH₂} \\
\text{CN} \\
\text{O} \\
\end{array} & \quad \begin{array}{c}
\text{S} \\
\text{N} \\
\end{array} \\
\text{Cl} & \quad \text{phenyl} & \quad \text{n}
\end{align*}
\]

An Mₙ value of 2740 g/mol (vis a vis polystyrene standards) was obtained, indicating an average of 10 repeat units per oligomer. Hence there was a side reaction occurring which was curtailing the molecular weight to large extent.
When a small portion of the product oligomer was dissolved in dimethylformamide and a drop of HCl was added, the color immediately changed to pale yellow. Scheme 17 is a proposal to explain the occurrence of color and the subsequent decoloration upon treatment with acid. The rearrangement product 30 would contribute to curtailment of the molecular weight since it is a monofunctional entity. If there is any 31 or 31a (the cyclic product), then we can expect color on the basis of the conjugated donor (the o-thioaniline residue) - acceptor (the cyanobenzoyl ketone residue) structure. Acid hydrolysis of 31 or 31a yields 32 and the loss of conjugation explains the decoloration from orangish red to pale yellow. When a small part of purified decolorized product was analyzed by GPC, a loss in molecular weight was also noted. This suggests presence of oligomeric 31; acid hydrolysis results in chain scission and loss of color.

To understand the overall process, it was decided to undertake a model reaction study based on benzothiazole Reissert compounds without any haloalkyl substituents and study their reactions in order to optimize the molecular structure and reaction conditions.
(continued on next page)
Scheme 17: Potential side reactions in attempted polymerization of benzothiazole based A-B monomer 25.
4) Synthesis and stereochemistry of benzothiazole Reissert compounds

a) Synthesis of model compounds

For this purpose, we synthesized the benzothiazole Reissert compounds 19 and 33-36 and their alkylation products 37-40. Uff88 has previously reported the synthesis of a few Reissert compounds by the use of benzothiazole and p-substituted benzoyl chlorides. The Reissert compounds 19 and 33-36 were synthesized in quantitative yields utilizing o-chlorobenzoyl chloride, o-toluyl chloride, p-toluyl chloride, p-t-butylbenzoyl chloride and benzoyl chloride by the use of trimethylsilyl cyanide as the nitrile source in methylene chloride (Table 11). Some of these Reissert compounds were alkylated 37-40 via the corresponding carbanions (NaH / dimethylformamide) in very high yields (Table 11).
33: \( R_1 = \text{Cl}, \ R_2 = \text{H} \)
34: \( R_1 = \text{Me}, \ R_2 = \text{H} \)
19: \( R_1 = R_2 = \text{H} \)
35: \( R_1 = \text{H}, \ R_2 = \text{Me} \)
36: \( R_1 = \text{H}, \ R_2 = \text{t-Bu} \)
37: \( R = \text{Me}, \ R_1 = \text{Cl}, \ R_2 = \text{H} \)
38: \( R = \text{Me}, \ R_1 = \text{Me}, \ R_2 = \text{H} \)
39: \( R = \text{Me}, \ R_1 = R_2 = \text{H} \)
40: \( R = \text{p-ClC}_6\text{H}_4\text{CH}_2, \ R_1 = R_2 = \text{H} \)
<table>
<thead>
<tr>
<th>Cmpd</th>
<th>Yield (%)</th>
<th>Melting point (°C)</th>
<th>Recrystallization solvents (v:v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>33*</td>
<td>100</td>
<td>183.5 - 185.0</td>
<td>3:7 DMF&lt;sub&gt;a&lt;/sub&gt;:EtOH</td>
</tr>
<tr>
<td>34*</td>
<td>100</td>
<td>152.5 - 154.0</td>
<td>1:18 DMF:EtOH</td>
</tr>
<tr>
<td>19</td>
<td>100</td>
<td>127.0 - 128.5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>95% EtOH</td>
</tr>
<tr>
<td>35</td>
<td>100</td>
<td>153.4 - 154.2&lt;sup&gt;c&lt;/sup&gt;</td>
<td>95% EtOH</td>
</tr>
<tr>
<td>36*</td>
<td>100</td>
<td>131 - 132</td>
<td>95% EtOH</td>
</tr>
<tr>
<td>37*</td>
<td>85</td>
<td>163.8 - 164.8</td>
<td>95% EtOH</td>
</tr>
<tr>
<td>38*</td>
<td>85</td>
<td>110.8 - 111.8</td>
<td>95% EtOH</td>
</tr>
<tr>
<td>39*</td>
<td>100</td>
<td>112 - 115</td>
<td>95% EtOH</td>
</tr>
<tr>
<td>40*</td>
<td>100</td>
<td>172 - 174</td>
<td>100% EtOH</td>
</tr>
<tr>
<td>41*</td>
<td>100</td>
<td>131 - 132</td>
<td>95% EtOH</td>
</tr>
</tbody>
</table>

*) these are new compounds.

<sup>a</sup> N,N-Dimethylformamide.

<sup>b</sup> lit.88 139 - 141° C.

<sup>c</sup> lit.88 158 - 160° C.
b) Conformational analysis of benzothiazole Reissert compounds

The investigation into benzothiazole Reissert compounds from ortho substituted benzoyl chlorides was motivated by a very peculiar $^1$H NMR spectrum (Figure 3) obtained for a solution of 19 in CDCl$_3$. The 4-proton signal, located at 6.75 ppm, was unusually broad (ca. 0.26 ppm at ambient temperature) and did not exchange with D$_2$O. Selective proton decoupling yielded confirmation of its assignment as the 4-proton. The broadness of the 4-proton in the NMR spectrum of 19 is attributed to the slow interconversion of rotamers relative to the NMR time scale. This phenomenon was also seen in the case of the benzothiazole-terephthaloyl bis(Reissert compound) 16. When the solution $^1$H NMR spectrum of methylated derivative 39 was taken, all the peaks were sharp (over a broad temperature range; discussed later) and assignable with the use of selective homonuclear decoupling.

A rotamer is a conformational (not configurational) isomer obtained by rotation about a bond, in this case the nitrogen-carbonyl bond which through resonance has double bond character. At low temperatures, the two isomers are separately detected since the interconversion rate is slow. Conformational analysis of Reissert compounds has been dealt with in depth by Gibson$^{89 - 91}$ in the isoquinoline series (with and without substitution at the 3 position). This phenomenon is a classic one and has been discussed thoroughly in a treatise.$^{92}$ The general figure below portrays the
conformational isomerism about the amide C-N bond for 19 in particular.

19 : \( R_1 = R_2 = H \)

The 4-proton experiences a different magnetic environment in the two conformations E and Z. E is the conformation where the carbonyl C=O bond is trans to the nitrile and Z is the conformation where the C=O is cis to the CN moiety. At low temperatures, the interconversion is slow and there are two distinct signals for the 4-proton in the NMR. At intermediate temperatures, the interconversion is more rapid and the two peaks broaden and a smeared resonance is seen. At high temperatures, the rate of interconversion is fast and only one peak is observed, corresponding to the time averaged contributions of E and Z.

This effect should also manifest in the case of 2-cyano-1-(o-tolyl)-1,2-dihydroquinoline 41 which is the Reissert compound...
derived from quinoline and o-toluyl chloride. The 8-proton contributes to the steric hindrance in the following interconversion from conformation 41E to 41Z.

![Chemical structures](image)

**41E**  \(\rightarrow\)  **41Z**

To prove this, 41 was synthesized and its \(^1\text{H}\) NMR spectrum (CDCl\(_3\), 270 MHz, ambient temperature, Figure 4) showed the analogous effect. The resolution of the peaks in the aromatic region was not good but the methyl group signal, 3.4 - 1.2 ppm, was a very broad (ca. 590 Hz) double hump, apparently close to coalescence.

Further, when the *low temperature* (typically at 213K) NMR spectrum of 34 was obtained in either CDCl\(_3\) or C\(_6\)D\(_5\)CD\(_3\) (Figures 5 - 8), *four* signals were obtained in the methyl region of the NMR spectrum. These arise surely due to the freezing out of the four possible conformational isomers as shown in Scheme 18.
Scheme 18: Conformational isomers of 34
These conformational isomers (also known as rotational isomers or rotamers) arise due to the restricted rotation around a) the N-C=O bond and b) the aryl-C=O bond. The restricted rotation due to a) gives rise to E and Z isomer pairs and due to b) gives rise to syn and anti isomer pairs. When the methyl and nitrile groups are in opposite spatial directions, i.e. the dihedral angle is greater than 90° and less than 180°, then that conformation is known as the anti. When the dihedral angle is between 90° and 0°, then that is the syn conformation. At low temperatures, the rates of interconversion are slow relative to the NMR frequency. It is then possible to view the protonic shifts of each conformer in the NMR spectrum.

A useful technique to determine which group is E or Z relative to the amide carbonyl oxygen is to determine ASIS (Aromatic Solvent Induced Shifts). This consists of determining the NMR spectrum of the compound of interest in CCl₄ or CDCl₃ and then in an aromatic solvent such as C₆D₅CD₃. If the subtraction of the shift of a protonic moiety in the C₆D₅CD₃ NMR spectrum from the corresponding one in CDCl₃ gives a large positive value, i.e., an upfield shift in the aromatic solvent, then that moiety is deemed trans (more correctly E as defined earlier) to the amide carbonyl oxygen; the cis (more correctly Z as defined earlier) substituent also gives upfield shifts but only up to half the magnitude of the trans group.
Table 12 lists the shifts and percentages pertaining to the various rotamers for the NMR spectrum of 34 (AP-2-75-28 at 213 K in CDCl₃) based on the H₂, H₄ and the methyl protons.

<table>
<thead>
<tr>
<th>Proton</th>
<th>Z-anti δ</th>
<th>Z-syn δ</th>
<th>E-anti δ</th>
<th>E-syn δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>(%)</td>
<td>(%)</td>
<td>(%)</td>
<td>(%)</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>6.87</td>
<td>6.74</td>
<td>5.84</td>
<td>6.02</td>
</tr>
<tr>
<td>(42.9%)</td>
<td>(34.7%)</td>
<td>(15.8%)</td>
<td>(6.7%)</td>
<td></td>
</tr>
<tr>
<td>H₄</td>
<td>5.96</td>
<td>5.90</td>
<td>8.03</td>
<td>8.24</td>
</tr>
<tr>
<td>(43.9%)</td>
<td>(37.3%)</td>
<td>(14.3%)</td>
<td>(4.4%)</td>
<td></td>
</tr>
</tbody>
</table>

Table 12: NMR data for 34 in CDCl₃ at 213 K

Table 13 lists the shifts and percentages pertaining to the various rotamers for the NMR spectrum of 34 (AP-3-73-2) at 213 K.

<table>
<thead>
<tr>
<th>Proton</th>
<th>Z-anti</th>
<th>(Z+E)-syn</th>
<th>E-anti</th>
</tr>
</thead>
<tbody>
<tr>
<td>(%)</td>
<td>(%)</td>
<td>(%)</td>
<td>(%)</td>
</tr>
<tr>
<td>CH₃</td>
<td>1.87</td>
<td>2.53</td>
<td>2.40</td>
</tr>
<tr>
<td>(42.0%)</td>
<td>(41.9%)</td>
<td>(16.1%)</td>
<td></td>
</tr>
</tbody>
</table>
Table 13: NMR data for 34 in C₆D₅CD₃ at 213 K

<table>
<thead>
<tr>
<th></th>
<th>Z_anti</th>
<th>Z_syn</th>
<th>E_anti</th>
<th>E_syn</th>
</tr>
</thead>
<tbody>
<tr>
<td>proton</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
</tr>
<tr>
<td>(%)</td>
<td>(%)</td>
<td>(%)</td>
<td>(%)</td>
<td>(%)</td>
</tr>
<tr>
<td>H₂</td>
<td>5.64</td>
<td>5.50</td>
<td>4.05</td>
<td>4.60</td>
</tr>
<tr>
<td>(28.6%)</td>
<td>(28.6%)</td>
<td>(35.7%)</td>
<td>(7.1%)</td>
<td></td>
</tr>
<tr>
<td>CH₃</td>
<td>1.52</td>
<td>2.22</td>
<td>2.03</td>
<td>2.38</td>
</tr>
<tr>
<td>(27.2%)</td>
<td>(30.0%)</td>
<td>(34.7%)</td>
<td>(8.1%)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Z_{(syn+ anti)}</th>
<th>E_anti</th>
<th>E_syn</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₄</td>
<td>5.70</td>
<td>8.11</td>
<td>8.51</td>
</tr>
<tr>
<td>(58.1%)</td>
<td>(35.8%)</td>
<td>(6.2%)</td>
<td></td>
</tr>
</tbody>
</table>

Before interpreting the data, certain hypotheses should be made clear. The aroyl group in 34 has a local asymmetry in that there is a methyl group at the 2 position and a proton in the 6 position. This would give rise to four possible amide conformers when all rotameric interconversion is frozen at low enough temperatures and unequal proportions of conformers would be obtained. \( Z_{anti} \) and \( Z_{syn} \) are the rotamers in which the amide
carbonyl oxygen atom is Z to CN. \( \text{E}_{\text{anti}} \) and \( \text{E}_{\text{syn}} \) are the rotamers in which the amide carbonyl oxygen atom is E to the CN. Apart from the amide conformers, we can expect additional rotamers from conformational changes at other junctures in the molecule, namely the nitrogen inversion\(^96\) and the ring inversion involving C2, N and S in a concerted movement.\(^97\) The energy barrier for the interconversion for the latter two modes is known to be quite low (both being ca. 1-2 kcal/mol) and we can expect the amide isomerism to be the dominant one observed near 25°C. Yet if more peaks than expected appear at lower temperature, then the additional isomerism due to inversion can be invoked and the phenomenon adequately rationalized. The absence of more peaks than expected for the amide/aryl conformers certainly does not rule out these isomers; rather the interconversion rate is rapid at the temperature of the experiment.

Analysis of spatial representations of the four conformers (Scheme 18) on the basis of magnetic and electronic environments of the different protonic moieties in the various rotamers points to the following situation. For the E form, assuming the N-C=O group and attached atoms are planar or nearly so, H4 lies in the nodal plane of the \( \pi \) system of the amide carbonyl linkage and thus is deshielded. The H2 proton, on the other hand, is so situated spatially that it lies in the shielding region (\( \pi \)-cloud) of the phenyl ring. The reverse is true for the Z form. Within either the E or the Z amide isomer, the \textit{syn} rotamer has the methyl group placed
within the deshielding region of the cyano group. This tends to make the methyl group appear at lower field; this was used as diagnostic in assigning the observed signal to that rotamer. Aryl methyl protons typically resonate at ca. 2.27 ppm. A downfield shift (relative to δ 2.27) can therefore be ascribed to the syn form. Conversely, for the E anti and the Z anti conformers, the methyl group is expected to be shielded more so than for the remaining rotamers; this is because the protons would be buried in the π-cloud of the aromatic ring of the benzothiazole moiety. These effects are understood better with figures which appear in standard textbooks.

If these arguments are correct, then in Z anti and Z syn H4 should be shielded, since it is in the π-cloud of the phenyl ring. Also, H4 has only one vicinal proton and therefore will appear as a doublet with a coupling of ca. 6.5 - 8 Hz (typical range for 3 bond ortho coupling for aromatic systems). H2 on the other hand can appear only as a singlet. Further, each signal corresponding to H2 and H4 at ambient temperature is expected to split into a maximum of 4 signals (barring accidental overlap) at a lower temperature, the relative integrations being an indicator of the amounts of conformers frozen out. Homonuclear decoupling at low temperature would lend strong credence to the assignments.

Based on the above logic, we assigned the two downfield signals for H2 (6.87 and 6.74 ppm) to the Z form and the upfield signals, 5.84 and 6.02 ppm, to the E form (Table 12). Steric
hindrance by the methyl group dictates that the peak with a larger integration (and hence the larger relative conformer amount) within the Z form be Zanti; therefore the H2 peak at 6.87 ppm with an overall integration of 42.9% was ascribed to Zanti. The Zsyn population is 34.7%, Eanti, 15.8% and Esyn, 6.7% in CDCl3. The Eanti and the Zanti conformer resonances for H2 occur 1.03 ppm apart. For H4, the E form is more deshielded than the Z form and therefore the two H4 doublets at 8.24 ppm (J = 8.08 Hz) and 8.03 ppm (J = 8.24 Hz) are representative of the E form. Steric hindrance by the methyl group dictates that the peak with a larger integration (and hence the larger relative conformer amount) within the E form be Eanti; therefore the H4 peak at 8.03 ppm with an overall integration of 14.3% was ascribed to Eanti and the H4 peak at 8.24 ppm with an integration indicative of 4.4% conformer content was assigned to Esyn. The H4 peaks at 5.96 ppm (J = 8.08 Hz) and 5.90 (J = 8.24 Hz) are of the Z form. The integration ratios help in consolidating the assignments. Thus the H4 peak at 5.96 ppm with an integration of 43.9% belongs to the Zanti conformer. Similarly, the H4 peak at 5.90 ppm, integration 37.3%, is indicative of the Zsyn conformer. The Zsyn and the Esyn conformer resonances for H4 occur 2.34 ppm apart; this implies the close proximity of the H4 to the deshielding carbonyl moiety in Esyn and the shielding aromatic ring of the aroyl moiety in Zsyn. One of the methyl resonances occurs at 1.87 ppm. This peak is shielded ca. 0.4 ppm compared to a normal aryl methyl and represents the Zanti
form for that is the rotamer in which the aryl methyl is expected to be most shielded by the fused aromatic ring π-cloud. The methyl peak at 2.53 ppm is ascribed to the $E_{\text{syn}}$ and $Z_{\text{syn}}$ conformers since the methyl is deshielded by the nitrile; integration analysis indicates that there is an accidental overlap of both the resonances and therefore the combined conformer population is 41.9%. The remaining methyl peak at 2.40 ppm represents the $E_{\text{anti}}$ conformer and its relative integration is in close agreement with that of analogous assignments for H$_2$ and H$_4$. This gives a relative ratio of 79 : 21 (±3%) of Z : E, as an average ratio of conformer population.

When the solvent is changed to C$_6$D$_5$CD$_3$ (Table 13), there is a change in the ratio of the conformer populations of 34. The H$_2$ resonances have moved *upfield* to a considerable extent. This means that the solvation of the different conformers by the deuterotoluene has a shielding effect and is manifested in the resonances. This is *not entirely unexpected* and in fact has been reported in the literature by Hatton and Richards$^{94}$ and Moriarty$^{95}$ for amides and lactams respectively. The same is not true for H$_4$. In fact both the conformers of the E form, which are still expected to exhibit resonances at lower fields, are more deshielded than in deuterochloroform. For H$_2$, the two *upfield* resonances are 4.05 ppm and 4.60 ppm and the *downfield* resonances are at 5.50 and 5.64 ppm. Compared to the shifts of H$_2$ in deuterochloroform, where the two *most upfield* H$_2$ resonances are at 5.84 and 6.02 ppm, there is certainly a shielding effect of the solvent evident.
The H₂ peak at 4.05 ppm with a relative integration of 35.7% is assigned as the E\textit{anti} conformer and the H₂ peak at 4.60 ppm to the E\textit{syn} conformer with a relative integration of 7.1%. For H₂, the Z\textit{syn} and the Z\textit{anti} conformers are again expected to be deshielded, although not as much as in the deuterochloroform, and the H₂ peaks at 5.50 and 5.64 with equal relative integrations of 28.6% are assigned to those conformers. For H₄, the E\textit{anti} and the E\textit{syn} conformers are expected to be the most deshielded ones. The H₄ peaks at 8.11 and 8.51 ppm with relative integrations of 35.8% and 6.2% are assigned to E\textit{anti} and E\textit{syn} respectively and a comparison with the integrations of the various conformer assignments based on H₂ corroborates it. The two upfield methyl resonances at 1.52 (27.2%) and 2.03 (34.7%) ppm are assigned to the E\textit{anti} and the Z\textit{anti} conformers since the methyl group is \textit{anti} to the nitrile and, as explained earlier, is shielded by the aromatic ring of the benzothiazole moiety; Z\textit{anti} is more upfield than E\textit{anti} due to the closer proximity of the methyl protons to the shielding region of the aromatic ring. Both of these methyl signals are shielded, by 0.35 and 0.37 ppm, respectively in deuterochloroform, relative to deuterochloroform. The remaining methyl peaks at 2.22 ppm (30.0%) and 2.38 ppm (8.1%) are indicative of the Z\textit{syn} and the E\textit{syn} conformers; these too are shielded relative to deuterochloroform by 0.31 and 0.15 ppm respectively. The Z : E conformer population ratio for 34 turns out to be 57 : 43 (±3%) in deuterochloroform. This lowering in Z : E conformer ratio when the
solvent is changed to deuterotoluene is rationalized on the basis of the following. The overall dipole moment of the molecule is highest in the Z form when the dihedral angle between the CN and the C=O approaches zero. This is also very sterically hindered and lies on the energy maxima when converting from $Z_{syn}$ to $Z_{anti}$. The E form has the lower dipole moment and thus is more stabilized in a nonpolar solvent like toluene while the Z form is more stabilized in a polar solvent like chloroform.

Table 14 lists the ASIS values for each conformer. $\Delta(E_{anti})$ means the difference of shifts for the $E_{anti}$ conformer when the solvent is changed form CDCl$_3$ to C$_6$D$_5$CD$_3$.

Table 14: ASIS values for different conformers of 34 at 213 K.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta(E_{anti})$</th>
<th>$\Delta(E_{syn})$</th>
<th>$\Delta(Z_{anti})$</th>
<th>$\Delta(Z_{syn})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>+1.79 ppm</td>
<td>+1.42 ppm</td>
<td>+1.23 ppm</td>
<td>+1.24 ppm</td>
</tr>
<tr>
<td>H$_4$</td>
<td>-0.08 ppm</td>
<td>-0.27 ppm</td>
<td>+0.26 ppm</td>
<td>+0.20 ppm</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>+0.37 ppm</td>
<td>+0.15 ppm</td>
<td>+0.35 ppm</td>
<td>+0.31 ppm</td>
</tr>
</tbody>
</table>

It is evident from Table 14 that H$_2$ is much more sensitive to a change in solvent than H$_4$. In all the conformations, H$_2$ is shielded to large extents; particularly both the conformers of the E form. Hatton and Richards$^{94}$ have reported analogous upfield shifts for
both the cis (more correctly Z as defined earlier) and trans (more correctly E as defined earlier) forms of the amides that they studied (a $\Delta \delta$ of 2.16 ppm for the trans form and ca. 1 ppm for the cis form was reported when the solvent was changed to $\alpha$-naphthylamine!). The reason for these upfield shifts in aromatic solvents is thought to be due to selective shielding of the proton (or alkyl group) E to the amide carbonyl group by the aromatic solvent; donor groups on the aromatic ring contribute in increasing the shielding. This is shown below.

![Chemical Structure](image)

Preferential complexation of an aromatic solvent in the Eanti form.

Moriarty in his study of lactams of different sizes has reported a maximum upfield shift of 1.18 ppm for the trans isomer and 0.84
for the cis isomer. Hence, the observed shifts corroborate well with the literature and ASIS hypothesis.

When 19 was converted to 39 via methylation, both its solution 1H NMR spectra at ambient temperature and 213 K showed only one signal in the methyl region in both CDCl3 and C6D5CD3 (Figures 9 - 12). A tabulation (Table 15) of shifts in those two solvents and differences in shifts at ambient temperature and 213K is shown below.

| Table 15: ASIS results for 39 at 294 K and 213 K |
|----------------|----------------|----------------|----------------|
|                | CH3            | H4             |                |
|                | 294 K          | 213 K          | 294 K          | 213 K          |
| δ (CDCl3)     | 2.33           | 2.39           | 6.12           | 6.15           |
| δ(C6D5CD3)    | 1.95           | 1.84           | 5.87           | 5.80           |
| Δδ (ppm)      | +0.38          | +0.55          | +0.25          | +0.35          |

Perusal of Table 15 indicates that the amide carbonyl oxygen is Z to the CH3 as indicated by H4 shift values. A comparison to H4 shift values in Tables 12 and 13 for the Z form indicates comparable numbers, i.e. ca. +0.2 ppm. ASIS value for H4 are the
same as for the Z form of H₄ in Table 14, thus lending more support to the existence of the alkylation product in the Z form. If the E form had been present, then the protons' shifts would have been far downfield due to the influence of the C=O linkage. Signal doubling does not occur as the temperature is changed from ambient to 213 K (-60°C). This means that either there is only one conformer present or that interconversion of the two rotamers is occurring still rapidly at 213 K. In fact, upon methylation we expect to increase the steric bulk around C-2 which in turn would increase the interconversion barrier from the E to the Z form. The possibility of lowering the barrier to interconversion upon increasing the steric bulk is very small. Of course, it does not rule out the fast rotation of the aryl ring (around the aryl C=O bond). This is in contrast to 34, where the bulky 2-methyl group dictates the aryl-C=O motion and in fact all four conformers are identifiable on the basis of distinct resonances in their NMR spectrum. Therefore, the methyl group restricts the rotation around the N-C=O completely, yielding only one rotamer as shown below.
5) Rearrangement of benzothiazole Reissert compounds

The model benzothiazole Reissert compound 19 was chosen to investigate the rearrangement study (Scheme 19). When it was reacted with 1.1 equivalents of NaH in dry dimethylformamide (under N₂), a vigorous bubbling (release of H₂) and an immediate change to blood red color were noted. The color stayed so until the end of the reaction (3 h) and when quenched (into ten fold excess cold water), an orange red solid was obtained.
Scheme 19: Proposed potential rearrangement pathways for 19
When the crude product was chromatographed over silica gel with ethyl acetate-hexane eluant, ca. 10% yield of the 'normal' rearrangement product 42 was obtained as confirmed spectroscopically and by elemental analysis. The rest of the material remained an oil which never crystallized and showed multiple spots on TLC plates. For a structure like 43, we expect the product to be colored and highly sensitive to basic and acidic media since it is a donor-acceptor Schiff base. Uff et al. 88 have also faced the same problems when they attempted to rearrange 45; they reported isolation of a 'gum' which did not crystallize and was not characterized any further. They also reported isolation of the 'normal' rearrangement product 46 analogous to 42 in about 10% yield.

![Chemical Structures](image)

After numerous futile trials to isolate pure material out of the rearrangement of 19, it was decided to try another approach like quenching the reaction with methyl iodide before workup. 35 was chosen to be the suitable substrate for this purpose because the p-
methyl is a good tag in the aliphatic region in the $^1$H NMR spectrum. 35 was dissolved in dry dimethylformamide, under N$_2$, reacted with 1.1 equivalents of NaH and the reaction quenched with excess methyl iodide before pouring the reaction mixture over ice-cold water. The gummy red product that was isolated was dissolved in ethyl acetate and when allowed to stand overnight, a light orange solid crystallized out. This was crystallized from ethyl acetate and elemental analyses and high resolution mass spectroscopy yielded a molecular formula of C$_{25}$H$_{18}$N$_4$O$_2$S$_2$. Details of the structure elucidation will be included in the appendix (Appendix 1).

B) POLYMERS FROM ACYCLIC REISSERT COMPOUNDS

1) Monomer synthesis

a) Acyclic Bis(Reissert Compound)s Based on Aliphatic Diamines

As discussed in chapter 1, open chain Reissert compounds 8 (Scheme 4) can be synthesized easily and exhibit reactions analogous to the 'routine' Reissert compounds. Precursors of these Reissert compounds are $\alpha$-aminonitriles which are very easily synthesized, too. Bis(aminonitrile)s would be the natural precursors to open chain bis(Reissert compound)s which were hitherto unknown. A variety of bis(aminonitrile)s are reported in the literature$^{101, 102}$; the chief use has been in the pharmaceutical industry or related areas. Simple acylation of the amino functionality of the bis(aminonitrile)s would lead to the
open chain bis(Reissert compound)s. We decided to use the readily available and economical alkane diamines in the synthesis of bis(amino nitrile)s which were subsequently acylated to open chain bis(Reissert compound)s as novel A-A monomers; this is depicted in Scheme 20.
2 ArCHO + 2 NaHSO₃ + H₂N-(CH₂)ₓ-NH₂ + 2 NaCN

\[ \text{H₂O} \xrightarrow{\text{stir}} \]

\[
\begin{array}{c}
\text{Ar} \\
\text{NC} \text{---CH---NH---(CH₂)ₓ---NH---CH---CN}
\end{array}
\]

47. Ar = C₆H₅, x = 2; 48. Ar = C₆H₅, x = 4;
49. Ar = C₆H₅, x = 6; 50. Ar = p-CH₃OC₆H₄, x = 2;
51. Ar = p-FC₆H₄, x = 2.

\[
\begin{array}{c}
\text{PhCOCl / pyridine}
\end{array}
\]

\[
\begin{array}{c}
\text{Ar} \\
\text{NC} \text{---CH---N---(CH₂)ₓ---N---CH---CN}
\end{array}
\]

COR

52. Ar = R = C₆H₅, x = 2; 53. Ar = R = C₆H₅, x = 4;
54. Ar = R = C₆H₅, x = 6; 55. Ar = C₆H₅, R = t-Bu, x = 6;
56. Ar = C₆H₅, R = p-t-BuC₆H₄, x = 6;
57. Ar = p-CH₃OC₆H₄, R = p-t-BuC₆H₄, x = 2.

Scheme 20: Synthesis of open chain bis(Reissert compound)s
The bis(aminonitrile)s 47 - 51 were synthesized via a multi-step one-pot efficient, economical, convenient and mild method. The aldehyde was first converted to the bisulfite addition product, then the amine was added in one aliquot and after 2 h of stirring the NaCN was added in one aliquot and stirred for 8 h to obtain near quantitative yields of the bis(aminonitrile)s. Acylations were carried out in dry pyridine with 2.2 equivalents of the acid chloride (benzoyl chloride, pivaloyl chloride and 4-t-butylbenzoyl chloride) to obtain the open chain bis(Reissert compound)s 52 - 57 (Table 16).

52 is a good choice for a monomer with only two carbons in the initial diamine; the problem is its insolubility in various solvents including dimethylformamide. The melting points decrease from 225 - 227°C (52) to 202.5 - 203.5°C (53) to 169 - 170.5°C (54) and the solubility increases in the order 52, 53, 54. Even then a 10% solution by weight of 54 in dimethylformamide can be made only by heating. 53 and 54 were purified by recrystallization from ethanol-dimethylformamide mixtures. 52 is more insoluble and was purified by Soxhlet extraction with ethanol which stripped off all other impurities. 52 purified by such a technique and dried gave a very favorable elemental analysis. Although 57 had a higher melting point (251 - 252°C) than 52 (225 - 227°C), it was more soluble in common solvents.

The FTIR spectra of 52 - 57 display the usual amide carbonyl stretch between 1659 and 1636 cm⁻¹ and practically no absorption
in the 2200 cm\(^{-1}\) region (expected for nitrile stretch). The FTIR spectrum of 57 showed peaks at 1651 cm\(^{-1}\) for carbonyl, 1253 cm\(^{-1}\) for aryl alkyl ether and 852 cm\(^{-1}\) for p-disubstituted benzene. The \(^1\)H NMR spectra of 52 - 57 were in agreement with the structural features and all displayed a very broad absorption (ca. 7.1 - 5.8 ppm) for the acidic proton alpha to CN, due to conformational (amide) isomerism or diastereomerism in CDCl\(_3\) solution. The acidic proton is deshielded much more (broad, ca. 6.5 ppm) in the compounds 52 - 57 relative to the bis(aminonitrile)s 47 - 51 (ca. 4.8 ppm).
Table 16: Bis(aminonitrile)s and Corresponding Acyclic Bis(Reissert compound)s

<table>
<thead>
<tr>
<th>Compound</th>
<th>yield (%)</th>
<th>m.p [°C, corrected]</th>
</tr>
</thead>
<tbody>
<tr>
<td>47</td>
<td>100</td>
<td>118 - 120&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>48</td>
<td>100</td>
<td>89.0 - 90.5&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>49</td>
<td>100</td>
<td>oil&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>50</td>
<td>99</td>
<td>107 -109&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>51&lt;sup&gt;*&lt;/sup&gt;</td>
<td>100</td>
<td>124.8 - 126.3</td>
</tr>
<tr>
<td>52&lt;sup&gt;*&lt;/sup&gt;</td>
<td>100</td>
<td>225 - 227</td>
</tr>
<tr>
<td>53&lt;sup&gt;*&lt;/sup&gt;</td>
<td>100</td>
<td>202.5 - 203.5</td>
</tr>
<tr>
<td>54&lt;sup&gt;*&lt;/sup&gt;</td>
<td>100</td>
<td>169.0 - 170.5</td>
</tr>
<tr>
<td>55&lt;sup&gt;*&lt;/sup&gt;</td>
<td>77</td>
<td>162 - 163</td>
</tr>
<tr>
<td>56&lt;sup&gt;*&lt;/sup&gt;</td>
<td>42</td>
<td>174.5 - 175.5</td>
</tr>
<tr>
<td>57&lt;sup&gt;*&lt;/sup&gt;</td>
<td>95</td>
<td>251 - 252</td>
</tr>
</tbody>
</table>

<sup>a</sup> lit. 102 118 - 123°C (decomposition).
<sup>b</sup> lit. 101 88°C.
<sup>c</sup> lit. 101 68°C.
<sup>d</sup> lit. 102 95 - 97°C (decomposition).

* These are new compounds.
b) Cycloaliphatic diamine: trans-1,4-diaminocyclohexane

In our quest for variation in structural parameters in the diamine component of the open chain bis(Reissert compound)s, we decided to use trans-1,4-diaminocyclohexane. We expected the cyclohexyl moiety to contribute to increasing the thermal transitions of the resulting polymer and the cyclohexyl group has been known to have properties between a completely aliphatic system and an aromatic system in certain thermotropic polyesters. When we attempted to be condense trans-1,4-diaminocyclohexane with benzaldehyde and sodium cyanide in the routine multi-step one-pot aqueous route of bis(aminonitrile) synthesis, a mixture of products was obtained, the major being the bisSchiff base as indicated by the peak at 8.4 ppm in the NMR spectrum. Next, it was decided to condense the trans-1,4-diaminocyclohexane with the bisulfite addition product of the aldehyde in an aqueous solution. To our surprise, a 35% yield of N,N'-bisbenzylidene-trans-1,4-diaminocyclohexane 58 was obtained. Schiff base formation, an equilibrium reaction, is normally very facile but generally requires the azeotropic removal of water. 103 4-fluorobenzaldehyde gave the bisSchiff base 59 in 17% yield by an analogous procedure. Both of these are new compounds and the 1H NMR spectra showed the characteristic imino proton absorption at ca. 8.4 ppm and the FTIR spectrum exhibited the C=N stretch at 1643 and 1645 cm⁻¹ respectively. Scheme 21 outlines the syntheses of these novel bis(Schiff base)s. These bis(Schiff base)s can be easily converted
to bis(aminonitrile)s in high yields by Ojima's method \(^{59}\) by the reaction of imines with trimethylsilyl cyanide in presence of catalytic amounts of Lewis acids (Scheme 8 and Table 6, chapter 1). Acylation of the bis(aminonitrile)s should result in the formation of novel cycloaliphatic bis(Reissert compound)s.

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{NH}_2 \\
\text{R} & \text{-CHO} \quad \text{NaHSO}_3 / \text{H}_2\text{O} \\
\text{R} & \quad \text{R} \\
\text{58}, \quad \text{R} = \text{H}; & \quad \text{59}, \quad \text{R} = \text{F}
\end{align*}
\]

**Scheme 21:** Novel bis(Schiff base)s from trans-1,4-diaminocyclohexane: Potential monomers.

Certainly \(58\) and \(59\) can be efficiently made by the usual azeotropic method using toluene as the solvent but the fact that these can be synthesized from an aqueous medium was a little surprising. The importance of \(59\) is that the fluoro is activated by the *para* imino linkage in just about the same manner that a *para* carbonyl group activates fluorine.\(^{104}\) \(59\) can perhaps be
condensed with commercially available bisphenols and novel ether containing poly(azomethine)s 60 can be synthesized (Scheme 22).

\[
\begin{align*}
\text{HO} & \quad \text{Ar} \quad \text{OH} \\
59 + & \\
\text{dipolar aprotic solvent} \quad K_2CO_3 & \\
\rightarrow \\
\begin{array}{c}
\text{(} \\
\text{O} \\
\text{O} \\
\text{N} \quad \text{N} \quad \text{N} \quad \text{N} \\
\text{O} \\
\text{O} \text{)} \\
\text{Ar} \\
\end{array}
\end{align*}
\]

60. \( \text{Ar} = \text{p-phenylene, p,p'-biphenyl, p,p'-isopropylidenebiphenyl, etc.} \)

**Scheme 22**: Novel poly(azomethine)s based on 59.
Poly(azomethine)s have been useful as heat stable polymers but their lack of solubility and poor acid resistance are problems that need to be addressed.\textsuperscript{105 50} can perhaps contribute to solving part of the problem because the cyclohexyl group has properties \textit{intermediate between} aliphatic and aromatic moieties.
c) Acyclic Bis(Reissert Compound)s Based on Aromatic Diamines

Our next choice was to incorporate aromatic diamines into the bis(aminonitrile)s since it is well documented in the literature that aromatic groups improve thermal stability to a considerable extent. The diamines chosen were p-phenylenediamine, 4,4'-diaminodiphenyl ether and 4,4'-diaminodiphenylmethane. When the aqueous method was employed with 4,4'-diaminodiphenyl ether and benzaldehyde in presence of sodium cyanide and sodium bisulfite, a yellow sticky mass was obtained in 78% yield; this was shown to be a mixture of the bis(Schiff base) (50%), 13% of the expected product and 37% starting material. The propensity for Schiff base formation is very high for aromatic diamines and aromatic aldehydes due to the resultant conjugation.

McEwen and coworkers49 had solved this problem by using a different route which completely eliminated the Schiff base formation. They employed the cyanohydrin derivative of the aldehyde which was refluxed with an equivalent amount of the amine; this resulted in high yields of the expected aminonitrile. We extended the concept by using diamines and this resulted in moderate to high yields of the aromatic bis(aminonitrile)s 61 - 66 depicted in Scheme 23. The cyanohydrins used were lactononitrile (R = CH₃) and mandelonitrile (R = C₆H₅).
Scheme 23: Aromatic bis(aminonitrile) synthesis
62 is known in the literature106 but has been reported only once. 61 and 63 - 66 are new compounds and are potential monomers.107 All of these show characteristic bands in the FTIR at ca. 3350 cm⁻¹ corresponding to the NH stretch and between 2239 cm⁻¹ and 2221 cm⁻¹ for the nitrile stretch. The yields range from 55 - 75%; four of the six aromatic bis(aminonitrile)s, i.e. 61 - 63 and 65, yielded more than 75% of the diastereomeric products. The 1H NMR spectra for the aromatic bis(aminonitrile)s corroborate the structures. The acidic proton appears as a multiplet from 4.55 - 4.40 for 61 and as a multiplet at 4.25 ppm for 63 and 65. The acidic proton is deshielded more in 62, 64 and 66 and appears as a singlet at 5.4 ppm. The rest of the peaks display the expected pattern i.e. AA'BB' for p-disubstituted benzene nucleus and the diastereotopic multiplet for the benzylic methylene in 64 and 67 and the integrations are in good agreement.

Except for 61 and 62, these aromatic bis(aminonitrile)s are readily soluble in a variety of common solvents. The para linkage in 61 and 62 is known to decrease solubility due to better packing of crystals. 64 and 66 could not be recrystallized because they invariably formed gums. This is in contrast to 63 and 65 which gave good crystals perhaps because the methyl group (from the lactononitrile) renders the crystals more compact than in 64 and 66 where the bulky phenyl (from the mandelonitrile) decreases the intermolecular forces resulting in a lower melting point. The
presence of diastereomers further complicates the issue and contributes to gum formation.

62 was acylated using p-toluoyl chloride to obtain the novel aromatic open chain bis(Reissert compound) 67.\textsuperscript{107}

\begin{center}
\includegraphics[width=0.5\textwidth]{67.png}
\end{center}

\textbf{67, a new compound}, is obtained as shiny, colorless crystalline needles when purified by recrystallization from ethanol-dimethylformamide mixture (3:1 v/v), mp = 231.5 - 232.5\degree C. The sharpness of the melting point suggests that a pure diastereomer was obtained. The FTIR spectrum displays an amide carbonyl stretch at 1664 cm\(^{-1}\), 1311 cm\(^{-1}\) for methyl attached to a phenyl ring and 829 cm\(^{-1}\) for p-disubstituted benzene. The \textsuperscript{1}H NMR spectrum (Figure 13) is in agreement with the structure.
d) Model reactions: Novel aromatic nucleophilic substitutions via open chain Reissert compounds.

It was then decided to investigate whether it was possible to displace an activated fluoride from bis(p-fluorophenyl) sulfone by the conjugate base of an open chain Reissert compound. If this works, then it becomes possible to extend the polycondensation to activated aromatic halides; the resulting polymers would have better thermal properties and higher softening temperatures than polymers that have more aliphatic bulk. The model chosen for this novel nucleophilic aromatic substitution was 68, which was obtained from 68a. This is shown in Scheme 24.

![Chemical structure](image)

68a

68 did not rearrange at all when subjected to sodium hydride in dry dimethylformamide at 80°C. This means that no unwanted side reaction would curtail the polymer molecular weight when the optimized reaction is extended to polymerization.
Scheme 24: Novel nucleophilic aromatic substitution: Reaction of 68 with bis(p-fluorophenyl) sulfone.

When 68 was reacted with bis(p-chlorophenyl) sulfone or bis(p-fluorophenyl) sulfone in a 2:1 stoichiometry at ambient
temperature in dimethylformamide, the reaction did not go to completion in 48 h. But when the temperature was raised to 80°C in presence of bis(p-fluorophenyl) sulfone, the reaction was complete in 16 h, as evidenced by the presence of a sharp single product spot when monitored by TLC, and was worked up by quenching the reaction in excess water; a quantitative yield of \(69\), a novel nucleophilic substitution product, was obtained. \(69\) was purified by column chromatography; the pale yellow solid melts at 170 - 225°C indicating a mixture of diastereomers. The FTIR spectrum showed amide carbonyl stretches at 1662 and 1654 cm\(^{-1}\), an aryl alkyl ether stretch at 1258 cm\(^{-1}\) and a sulfone stertch at 1327 cm\(^{-1}\). The \(^1\)H NMR spectrum (Figure 14) showed peaks that included tell tale patterns for AA'BB' para-disubstituted benzene rings and the aliphatic protons typical of methoxy and t-butyl groups. This reaction ought to work when 4,4'-difluorobenzophenone is used. There are not many carbanionic aromatic nucleophilic substitutions known in the literature besides the important Grignard or lithio based substitutions. Hence this reaction is significant and can perhaps contribute towards the development of novel polymeric systems.
2) Polymer synthesis from Acyclic Bis(Reissert Compound)s

a) Attempted Rearrangement

Before any serious attempt towards polymerization was made, it was necessary to eliminate any side reaction. This is important in the case when novel systems are being optimized for polymer synthesis via step growth mechanism. Rearrangement is an important side reaction in the case of Reissert compounds from aromatic heterocycles and is driven by the force to regain aromaticity and the facile loss of the good leaving group, nitrile (please refer to Scheme 3, chapter 1).

To ascertain the noninterference of the rearrangement in open chain bis(Reissert compound)s, 54 was dissolved in dimethylformamide and 2.2 equivalents of sodium hydride were added and the reaction mixture stirred for 2 d. When the reaction was quenched and worked up, the off-white solid product after two recrystallizations yielded a white solid mp 169 - 171°C with FTIR and 1HNMR spectra identical to 54. Elemental analysis also unequivocally supported its structure as the starting material 54. This is an advantage of the acyclic systems. In some bis(isoquinoline) Reissert compounds a rearrangement analogous to conversion of 1 to 6 (Scheme 3, chapter 1) is a side reaction which decreases molecular weight and increases molecular weight distribution.108
Next, polymerizations of these novel A-A monomers with dihaloalkanes were attempted as outlined in Scheme 25.

**b) Acylated Polyamines via Acyclic Bis(Reissert Compound)s**

\[ \text{Scheme 25 : Polymer synthesis from 54.} \]

Condensation of acyclic bis(Reissert compound) 54 via its dianion with suitable dihalo aliphatics gave novel polymers with flexible spacers. When diiododecane was used with the conjugate (di)base of 54 (37% solids initially), a gel 70 was obtained; no overhead stirrer was employed and no salt (alkali metal halide) was used to help solubilize the polyamide. The gel was dissolved in DMF with the application of heat and precipitated into ice-
water. An absolute GPC determination of molecular weights gave \( M_n = 14.5K \) and \( M_w = 162K \). The high polydispersity is attributed to the presence of low molecular mass species trapped when gelation occurred.

In a separate trial, when the dianion of 54 was condensed with diiododecane in DMF (ca. 38% solids initially), a gel resulted in ca. 18 h indicating the success of the proposed polymerization. The gel was dissolved by addition of solvent and application of heat and after the reaction mixture was stirred for ca. 12 h, it gelled again. The gelling is due to the polyelectrolyte effect and can be explained as follows. As time progresses and the molecular weight of the polymer increases, the viscosity of the solution increases. The counterion of the (di)carbanion of the bis(Reissert compound) is sodium and at some critical conversion, the combined effect of molecular weight and coulombic interaction results into a (thermoreversible) gelation. Addition of more solvent and heating solubilized the gel and the (average) molecular weight increased further till a critical conversion which resulted into a gelled species due to the previously mentioned factors. The reaction thus exhibited (some) characteristics of a living polymerization; sequential addition can lead to block copolymers. When the concentration was halved (18% solids initially), the solution still gelled, indicating the effect of secondary interactions causing the gelation. This gelation is thermo-reversible as opposed to any crosslinking type process.
When the same reaction (37% solids initially) was repeated after ca. 2 yrs, identical observations were made and the polymers (two batches, 5 g and 10 g scale) that were isolated were purified and exhibited an inherent viscosity of 0.21 and 0.27 dL/g respectively.

Next, NaI was added to dibromodecane in order to generate the diiododecane in situ. This avoided the handling of the air-sensitive diiododecane. In the presence of NaI no gelling of 70 was observed, presumably due to increased ionic strength. The resulting polymer showed an intrinsic viscosity of 0.35dL/g. The same procedure using dibromobutane resulted in a polymer 71 with an inherent viscosity of 0.07dL/g and 72 resulted when m-xylene dibromide was used.

Polyamides 70 - 72 were pale yellow or pale brown, thermally stable (<1% weight loss) up to 225°C (in air) and showed a 10% weight loss above 300°C (specifically between 300 and 315°C). The *intrinsic* viscosities (NMP, 25°C) were between 0.07 and 0.48dL/g. Glass transition temperatures were found to be 72°C (for 70) to 116°C (for 72). The decamethylene spacer being the most flexible gave the lowest Tg of 72°C. With the incorporation of the m-xylene moiety, the Tg rose to 116°C, while the Tg was 84°C in the case of the tetramethylene spacer (71). No evidence of crystallinity was obtained from the DSC (2nd heat). Table 17 summarizes the results.
Table 17: Thermoplastic polyamides from acyclic bis(Reissert compound)s derived from 54.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Viscosity( ^a )</th>
<th>TPWL( ^{\circ} C )^b,c</th>
<th>Tg( ^{\circ} C )^c</th>
</tr>
</thead>
<tbody>
<tr>
<td>70( ^d,e )</td>
<td>0.48dL/g</td>
<td>305</td>
<td>72</td>
</tr>
<tr>
<td>70( ^f )</td>
<td>0.15dL/g</td>
<td>305</td>
<td>72</td>
</tr>
<tr>
<td>70( ^g )</td>
<td>0.35dL/g</td>
<td>305</td>
<td>71</td>
</tr>
<tr>
<td>71( ^g )</td>
<td>0.07dL/g</td>
<td>307</td>
<td>84</td>
</tr>
<tr>
<td>72( ^h )</td>
<td>0.09dL/g</td>
<td>300</td>
<td>108</td>
</tr>
<tr>
<td>72( ^g )</td>
<td>0.08dL/g</td>
<td>312</td>
<td>116</td>
</tr>
</tbody>
</table>

\( ^a \) intrinsic viscosities in NMP at 25\( ^\circ \)C.

\( ^b \) ten percent weight loss in air, TGA, 10\( ^\circ \)C/min.

\( ^c \) DSC at a heating rate of 10\( ^\circ \)C/min.

\( ^d \) without NaI, 37.5% solids initially, gel obtained and worked up upon dissolution.

\( ^e \) Absolute M\( _n \) = 14K, M\( _w \) = 162K.

\( ^f \) without NaI, 19% solids initially, gel obtained.

\( ^g \) with NaI.

\( ^h \) without NaI, M\( _n \) = 8.8K, M\( _w \) = 33K.

The polymer 70 can be viewed as having a constitutional repeat unit (CRU) of decamethylene and hexamethylene separated by an \( \alpha \)-amido nitrile moiety. While the Tg of Nylon-6,12 is
the T$_g$ of 70 is 72$^\circ$C. This 26$^\circ$ rise in the T$_g$ for 70 is attributed to the bulkiness of the phenyl groups and the secondary interactions of the polar nitrile group, despite the absence of H-bonding due to the primary amide linkages characteristic of the Nylon-6,12. Polyamides 70 - 72 are derivatized linear polyamines. Selective hydrolysis of the benzoyl group of the amides 70 - 72 should lead to linear polyamine derivatives. This would be unique since there are very few linear aliphatic polyamines known due to the problems of branching. Exceptions are the polyethyleneamines derived by hydrolysis of polyoxazolines, made by the "no catalyst polymerization via zwitterionic intermediates"; these, however, usually have low molecular masses.

Proton NMR spectra of these polymers showed the usual broadness of the peaks associated with polymeric materials due to the presence of tacticity. The Reissert compound derived polymers have two stereogenic centers per constitutional repeat unit, each of which is capable of existing in the R or S configuration. All showed peaks in the appropriate aromatic and aliphatic regions (Figure 15), the integration ratio of which matched exactly with the theoretical expectations. The FTIR spectra lend proof of structure and show broad absorptions of the amide carbonyl and a very, very weak nitrile peak.

In the case of m-xylylene dibromide side reactions are possible at the benzylic carbon leading to a carbene type intermediate which would certainly curtail the molecular weight.
of the resulting polymer. Overall, however, these preliminary results were quite encouraging and next we sought to increase the molecular weight and the thermal transition temperatures of these novel polymers. We had to choose from either reducing the length of the flexible spacer derived from the dihaloalkane or decreasing the number of methylenes from the initial diamine. We chose the latter option and decided to work with 52 and 57 as shown in Scheme 26.

Scheme 26: Use of ethylene diamine based open chain bis(Reissert compound)s in the polymerizations.

When 52 was condensed with dibromomethane at ca. 100°C in dimethylformamide, no high polymer was obtained; the intrinsic
viscosity of the resultant pale yellow powder was 0.047 dl/g. When 57 was condensed with dibromohexane, the resultant product had an intrinsic viscosity of 0.045 dl/g; when dibromodecane was used, the intrinsic viscosity was 0.05 dl/g. The data is tabulated in Table 18. The failure of ethylenediamine based systems to result in high molecular weight polymers is probably due mainly to the steric hindrance. This is supported by study of space filling models. In 57 there may be some additional factors like the electronic effect of the p-methoxy group responsible in curtailing polymer growth. Due to this, the conjugate base is more nucleophilic and less easy to form. Additionally, ease of six-membered ring formation can lead to products like 76 thus upsetting the stoichiometry as shown in Scheme 27.
Scheme 27: Possible detour resulting in the disruption of intended polymerization.
When 57 was attempted to be rearranged in DMF at 60°C for 2 d, there seemed to be no rearrangement as indicated by FTIR and 1H NMR spectra; thus steric hindrance seems to be the main cause of incomplete polymerization.

c) Acylated Poly(amine sulfone)s via Acylc Bis(Reissert Compound)s

Encouraged by the successful reaction of 68 with bis(p-fluorophenyl) sulfone, we decided to extend it to polymerization, since 52 - 57 can be substituted in place of 68 to produce polymers. However, when 54 was condensed with bis(p-fluorophenyl) sulfone in a 1:1 stoichiometry in dimethylformamide, the resultant pale brown solid 77 exhibited an inherent viscosity of 0.04 dL/g. The higher reaction temperature seems to be the culprit and the reaction could be optimized at lower temperatures. This reaction was tried only once and certainly deserves much more attention because if successful, it could be extended to 4,4'-difluorobenzophenone and the resulting polymer would the first system to have a backbone composed of aryl ketone and aliphatic moieties.
Table 18: Attempted polymerization products from the use of open chain bis(Reissert compounds) 52 - 57.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Polymer</th>
<th>Viscosity&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>52</td>
<td>72</td>
<td>0.047 dL/g</td>
</tr>
<tr>
<td>54</td>
<td>75</td>
<td>0.04 dL/g</td>
</tr>
<tr>
<td>57</td>
<td>73</td>
<td>0.045 dL/g</td>
</tr>
<tr>
<td>57</td>
<td>74</td>
<td>0.05 dL/g</td>
</tr>
</tbody>
</table>

<sup>a</sup> inherent viscosity at 1.5 % by weight solution of the polymers in NMP at 25°C.
C) POLYMERS FROM AMINONITRILES

1) Background

α-Aminonitriles and bis(aminonitrile)s were used by us as precursors to the Reissert compounds. α-Aminonitriles themselves show interesting chemistry which has been discussed (chapter 1). The conjugate bases of the α-aminonitriles are selective and powerful nucleophiles which can displace activated halides$^{78}$, resulting in products otherwise difficult to synthesize. We decided to investigate this reaction and try activated aromatic halides like 4,4'-difluorobenzophenone and bis(p-fluorophenyl) sulfone for polymer synthesis. These are the monomers which have been used in the synthesis of high performance commodity polymers. Johnson$^{111}$ used various bisphenols in his classic study which formed the basis for the commercial production of poly(ether sulfone)s and poly(ether ketone)s. The nucleophile for this aromatic substitution is the phenoxide; the polymer reaction is shown in Scheme 28. ICI's PEEK$^{TM}$ (poly(ether ether ketone)) (78, Ar = p-phenylene, Y = CO) is an industrially important high performance semi-crystalline resin. It is also among the highest priced engineering polymers and among the top two polymers to exhibit thermal stability vis a vis engineering property retention. One of the problems with PEEK$^{TM}$ is its insolubility and the problems associated with processing it; albeit composite engineers would still like to see a higher melting transition ($T_m$ = ca. 345°C) to improve the thermal sustenance even further.
It has also been recognized that fewer ether oxygen atoms and more carbonyl groups in the backbone lead to higher melting point and greater propensity to crystallize.

\[
n \text{HO-Ar-OH} + n \text{X-Y-X} \xrightarrow{\text{DMAc / toluene}} \text{K}_2\text{CO}_3 / \Delta \xrightarrow{\text{Y = CO, SO}_2} (\text{O-Ar-O-Y})_n
\]

**Scheme 28**: Classical poly(aryl ether) syntheses

The ideal system then is the poly(aryl ketone) polymer **79** which has no oxygen atoms in the backbone.

\[-(\text{Ar-CO})_n-\]

**79.** \(\text{Ar} = \text{p,p'-biphenyl, 2,6-naphthoyl, etc.}\)

113
The obvious synthetic pathway toward such systems is the Friedel-Crafts acylation (electrophilic aromatic substitution) with the use of AlCl₃ and a common solvent such as CH₂Cl₂. Such attempts¹¹² have been made and only oligomeric species were obtained, since the insolubility of the propagating chain above a certain number of units in the backbone resulted in the precipitation from the (poor) solvent. The Friedel-Crafts method, unfortunately, does not tolerate the use of polar aprotic solvents which are very useful solvents for the semi-crystalline engineering polymers. Thus not much advance was achieved in the synthesis of poly(aryl ketone) type polymers by the use of electrophilic aromatic substitution. Also to date, nucleophilic aromatic substitution was applied toward the synthesis of high performance polymers by the use of bisphenoxide nucleophiles which precludes the absence of ether oxygen atoms from the backbone. In the subsequent sections, we report and discuss the initial stages of development of a polymer based on nucleophilic aromatic (poly)substitution, the backbone of which is devoid of ether oxygen atoms.

2) Model reactions

When (α-morpholino)benzyl cyanide 80 was condensed with bis(fluorophenyl) sulfone in a 2:1 stoichiometric ratio in dry dimethylformamide, the resultant product (diastereomeric) 81 was
obtained in 100% crude yield. The FTIR spectrum of the product showed no absorbance in the carbonyl region, strong peaks corresponding to SO$_2$ (1324, 1161 cm$^{-1}$) and characteristic peaks matching the general structural features (1117 cm$^{-1}$ for C-O-C, 747 cm$^{-1}$ for benzene) of the molecule were observed. The $^1$H NMR spectrum (Figure 16) lent strong credence to the structure 81 and the integration of the aromatic protons with respect to aliphatic protons was very satisfactory. The product showed a broad melting range and was purified by recrystallization from benzene-hexane; some benzene persisted as solvent of crystallization and could not be removed by drying under vacuum at 110°C. The confirmation of relative atomic proportions based on elemental analysis was done by including a molecule of benzene in the molecular formula of 81.
The elements of nitrile and morpholine can be stripped off in the presence of an acid and the carbonyl can be regenerated, the reverse of aminonitrile formation. 82 was obtained when 81 was suspended in 70% aqueous acetic acid and refluxed for 1.5 h. The FTIR spectrum (Figure 17) of 82 showed a sharp intense carbonyl stretching absorption at 1668 cm\(^{-1}\), with a shoulder at 1654 cm\(^{-1}\) corresponding to benzophenone derivatives, sulfone stretching absorptions at 1331 and 1165 cm\(^{-1}\) and aromatic phenyl bending modes at 704 cm\(^{-1}\). The \(^1\)H NMR spectrum is devoid of any aliphatic protons and the pattern obtained is in agreement with the structural features of 82.
82 was purified by recrystallization from toluene-ethanol. The literature shows only one reported synthesis (patented)\textsuperscript{113} from diphenyl sulfide and benzoyl chloride via the Friedel-Crafts method and eventual oxidation of the sulfide to the sulfone; our's is the first synthesis via nucleophilic aromatic substitution.

Next, 4,4'-difluorobenzophenone was used as the activated aromatic dihalide and the condensation with 80 was done in an analogous manner. The resultant product 83 (diastereomeric) was obtained in quantitative yield. It exhibited a typical broad melting point, 80 - 125°C and was soluble in all common solvents in high proportions. The FTIR spectrum showed peaks at 2227 cm\(^{-1}\) (very weak) corresponding to the nitrile stretch, carbonyl stretch at 1734 cm\(^{-1}\) and 1117 cm\(^{-1}\) for the C-O-C of the morpholine ring.
The \(^1\)H NMR spectrum (Figure 18) lent strong credence to the structure 83 and the integration of the aromatic protons with respect to aliphatic protons was satisfactory.

Upon refluxing a suspension of 83 in 70% aqueous acetic acid, the aminonitrile linkage was stripped off, yielding 84 in nearly quantitative yield. The FTIR spectrum of 84 showed peaks at 1648 cm\(^{-1}\) for carbonyl stretch and at 793 cm\(^{-1}\) for \(p\)-disubstituted benzene. The \(^1\)H NMR spectrum is in agreement with the structure.
The solubility of 84 is in sharp contrast to that of 83. It is highly insoluble in most of the common solvents and was purified by recrystallization from dimethylformamide. 84 is also much less soluble than 82 and higher melting (231 - 232°C versus 203 - 204°C), too; this directly compares the effect of the carbonyl group with respect to the sulfone group. The intermolecular forces in 84 are stronger than in 82 partly due to the larger dipole
moment and more planar structure, resulting in tighter packing of crystals. The same effect is manifested in polymers and the result is that the poly(ether sulfone)s are generally amorphous but quite a few poly(ether ketone)s are semi-crystalline (depending on the rest of the structural features of the repeat unit).

3) A-B type Monomeric Aminonitrile from Functionalized Aldehyde

Based on the successful results of the modeling reactions, it was decided to synthesize the (α-aryl)aminonitrile 85 using 4-fluorobenzaldehyde; subsequent treatment of this A-B monomer with sodium hydride should lead to a poly(aryl aminonitrile) 86 which is a precursor to poly(carbonyl-p-phenylene) 87. This is shown in Scheme 29.
Scheme 29: Proposed synthesis of poly(carbonyl-p-phenylene)

When this polymerization reaction was attempted in dimethylformamide with sodium hydride, a vigorous bubbling was seen with a color change to green and eventually to brownish red. However, at the end of 3 days, not much increase in viscosity was seen and when the reaction was quenched in water, starting material was obtained. The reason for this non-reactivity apparently is that the halide is not activated enough for aromatic displacement by a nucleophile, in this case the benzylic carbanion situated para to it. Literature\textsuperscript{111, 112} has shown that only those aromatic halides that have a carbonyl or sulfonyl or such strongly
electron withdrawing groups situated \textit{para} to them are activated for a nucleophilic displacement. Nonetheless, \textbf{85} can be used toward the syntheses of novel activated bis(fluoroaryl) ketones or bis(fluoroaryl) keto-sulfones by progressively \textit{adding} the p-fluorocarbonyl moiety. \textbf{85} can be viewed as a \textit{masked synthon} for p-fluorocarbonyl group, more about this in the \textbf{CONCLUSIONS AND FUTURE WORK} chapter.

\textbf{4) A-A Monomeric Bis(aminonitrile)s Based on Dialdehydes}

a) Monomer synthesis

Next, we focused on novel A-A type monomers from dialdehydes. We decided to use terephthalaldehyde and isophthalaldehyde in the aqueous one-pot method. The result was two novel aromatic bis(aminonitrile)s \textbf{88} and \textbf{89}. 

122
CHO

+ 2 NaHSO₃ + 2 Morpholine + 2 NaCN

H₂O / stir / 12 hrs

88, p-isomer; 89, m-isomer

88 (mp = 230 - 232ºC) is much less soluble than 89 (mp = 118.5 - 135.5ºC) and ca. 100ºC higher melting. Both were obtained in near quantitative yields. The FTIR spectra exhibited peaks for nitrile stretch, C-O-C stretch and aromatic bends. The ¹H NMR spectrum (Figure 19) of 89 shows peaks (in the aromatic region) at δ 7.73 and 7.69 (total of 1H,), 7.59 (d, 2H, J = 7.5 Hz), 7.50 - 7.44 (m, 1H). The separation of the 7.73 and 7.69 ppm peaks (12 Hz) is
too large for ortho coupling. When selective decoupling was done, it became clear that the two peaks at 7.73 and 7.69 are due to different diastereomers of \textbf{89}. These peaks are due to the 2-proton of \textbf{89} because that is the only uncoupled proton in either diastereomer (the meta coupling being too small to be observed). The peak at 7.59 ppm is due to the 4-proton and the coupling it displays is typical of 3 bond ortho coupling in aromatic systems; it integrates for two protons because the symmetry of \textbf{89} makes it \textit{magnetically equivalent} to the 6-proton. The 5-proton is a multiplet split by the vicinal ortho protons. This was not observed in either \textbf{88} or other open chain bis(Reissert compound)s \textbf{52} - \textbf{57}, although it is theoretically possible.

\textbf{b) Polymer synthesis : Novel poly(aryl ketone ketone sulfone)s}

When \textbf{88} was condensed with bis(p-fluorophenyl) sulfone (Scheme 30) at 105°C in dimethylformamide with sodium hydride (6 g of product scale) for ca. 3 days and eventually quenched into water, a pale yellow solid \textbf{90} was obtained in 99% yield. The \textsuperscript{1}H NMR spectrum (Figure 20) of \textbf{90} showed a nice AA'BB' pattern and a singlet in the aromatic region and two multiplets in the aliphatic region corresponding to the morpholine ring. The symmetry and the integration ratios suggested either an oligomer or a polymer or a cyclic structure. A 10% weight loss occurred at 252°C (in air) followed by approximately 60% retention of weight up to 500°C and
a complete loss of weight at 600°C as detected by TGA. The FTIR spectrum (Figure 21) shows peaks at 1676 cm⁻¹ (weak, carbonyl, probably some hydrolysis during workup), 1327, 1160 cm⁻¹ (SO₂) and 1117 cm⁻¹ (C-O-C). An absolute molecular weight determination by GPC (NMP, 60°C) indicated an Mₙ of 345 (!) and Mₜ of 3400. There was no evidence of identifiable end groups by either FTIR spectroscopy or ¹H NMR spectroscopy which shows a very symmetric pattern (in the aromatic region) and displays peaks at 8.12 - 7.48 ppm (m), 3.97 - 3.63 (br. m) and 2.72 - 2.38 (m); the integrations in the aromatic and aliphatic region are approximately equal. Certainly some side reaction occurred that seriously affected the yield of the expected poly(aminonitrile sulfone) 90.

When a small portion of 90 was suspended in 30% acetic acid and refluxed 1.5 h, the resulting pale brown solid 91 was insoluble in all common solvents including dimethylformamide. The FTIR spectrum (Figure 22) of 91 shows intense carbonyl absorption at 1668 cm⁻¹ and loss of the peak at 1117 cm⁻¹ characteristic of C-O-C stretch of the morpholine ring. 91 exhibited a 10% weight loss at 490°C (in air) (Figure 21). This means that removal of the aminonitrile linkage by hydrolysis yielded 91 which displays a much higher stability to elevated temperatures than 90.
Next, the same reaction (Scheme 30) was tried on a smaller scale (1 g of polymer 90) at ambient temperature. 88 was insoluble in dimethylformamide under the reaction conditions. The reaction was carried out under initially heterogeneous conditions but as time progressed, the reaction became homogeneous presumably due to the solubility of the dianion and the resultant displacement product. The product was a pale yellow powder with FTIR and $^1$H NMR spectra identical to the previous trial (at 105°C); so were the TGA results. The intrinsic viscosity of the product was 0.1 dl/g (dimethylformamide, 23°C).

The reaction was repeated twice more in an earnest attempt to increase the molecular weight of the polymer, since the thermal data was very promising (in that the 10% weight loss temperature jumped by 232°C when 90 was converted to 91). When the reaction was done on a 6 g (expected for 90) scale, $M_n$ was 5,000 and $M_W$ was 15,400. When done on a 3 g scale (expected for 90), $M_n$ was 8600 and $M_W$ was 17,200. The data is tabulated in Table 19.
Table 19: Attempts to optimize the molecular weight for 90.

<table>
<thead>
<tr>
<th>Notebook #</th>
<th>Temp. (°C)</th>
<th>Scale ( <em>a</em> )</th>
<th>( M_n^b )</th>
<th>( M_w^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP-3-12</td>
<td>105/69</td>
<td>5</td>
<td>345</td>
<td>3,400</td>
</tr>
<tr>
<td>AP-3-17</td>
<td>ambient/168</td>
<td>1</td>
<td>([\eta]^c = 0.1 \text{ dl/g})</td>
<td></td>
</tr>
<tr>
<td>AP-3-59</td>
<td>ambient/120</td>
<td>6</td>
<td>5,000</td>
<td>15,400</td>
</tr>
<tr>
<td>AP-3-62</td>
<td>ambient/120</td>
<td>3</td>
<td>8,600</td>
<td>17,200</td>
</tr>
</tbody>
</table>

a) theoretical grams of polymer 90.
b) Absolute molecular weights by GPC in NMP/0.5% LiCl at 60°C.
c) in dimethylformamide at 23°C.

Thus although reasonable molecular weights are attained, it is evident that there is a side reaction which is curtailing the growth of the polymer chain. Looking carefully at the structure of the monomer \( 88 \), we realize that the anion formed by the initial deprotonation of \( 88 \) is a \((\alpha\text{-cyano})\text{benzylic carbanion}\) and such a system could undergo an intramolecular elimination by ejecting the remote nitrile which is a good leaving group. This would lead to loss of reactivity at the chain ends, causing cessation of the step growth process and limiting the molecular weight. This is even more likely to happen at the end of the polymerization since the
propagation is a bimolecular reaction and the concentration of the nucleophilic and electrophilic ends is low. However, the intramolecular expulsion of the nitrile is a unimolecular reaction and independent of conversion. Thus the elimination reaction may predominate towards the end of the polymerization. This is shown in Scheme 31. Other possibilities are formation of cyclics as has been very elaborately shown recently.114 The purification procedure (3 times precipitation into a non-solvent from a good solvent) should fractionate out most of the cyclics, though; GPC would be a good technique to detect these since they have a lower hydrodynamic volume and molecular mass. That the nitrile elimination was indeed the cause of molecular weight curtailment was proved by conducting a model reaction; this is discussed in a later section.
Scheme 31: Proposed intramolecular decyanation side reaction leading to low molecular weights.

The TGA of sample AP-3-17 poly(aminonitrile) 90 showed a 10% weight loss (in air) at 252°C. When a part of it was suspended in acetic acid and hydrolyzed, the product 91 was insoluble in all
solvents and exhibited a 10% weight loss at 493°C; this represents a gain of ca. 240°C in the 10% weight loss temperature. DSC of the hydrolyzed sample (91, AP-3-30-28) showed a T\textsubscript{g} of 193°C and a melting endotherm peaked at 331°C (Figure 23).

The TGA of sample AP-3-59 of 90 and its hydrolyzed product 91 showed analogous results to those of AP-3-17. The DSC results for the precursor poly(aminonitrile) did not show any transitions up to 250°C (both first and second heats, Figures 24, 25) beyond which it started degrading. When the hydrolyzed sample 91 was analyzed by DSC, it showed a T\textsubscript{g} of 199°C, a crystallization exotherm peak at 266°C and a melting endotherm peak at 415°C (first heat, Figure 26). The second heat (Figure 27), after cooling at 10°C / minute, showed a T\textsubscript{g} at 228°C and a (smaller) melting endotherm peak at 414°C. When the sample was quenched rapidly from 460°C and then heated (Figure 28), a T\textsubscript{g} of 225°C was detected and a small crystallization exotherm peak at 290°C. These results indicate that the polymer has a low rate of crystallization. The increase in T\textsubscript{g} in the second heat indicates the presence of residual solvent which plasticized the polymer, resulting in a low T\textsubscript{g} during the first heat. The lower value of the endothermic melting transition during the second heat coupled with the non-existence of a melting transition when the polymer was quenched rapidly strongly indicates a low rate of crystallization; this is understandable because of the presence of the sulfone group. Wide angle x-ray crystal structure analysis was
indicative of semicrystalline nature of \textbf{91} as isolated from the reaction mixture (appendix 2, pg. 212). That there was a melting transition was a pleasant surprise, since the commercial poly(sulfone)s are predominantly amorphous and poly(sulfone)s generally exhibit a lack of crystallinity.\textsuperscript{115} The melting point, 414\,\degree C, is the highest reported to date in the literature of poly(aryl ketone)s.\textsuperscript{112}

This is the \textbf{first synthesis} of a poly(aryl ketone ketone sulphone). Due to the carbanionic aromatic nucleophilic displacement reaction employed for the polycondensation, it was possible to eliminate the presence of oxygen connecting atoms in the backbone. This route also successfully incorporates carbonyl and sulfonyle groups in a \textit{para} fashion which is \textbf{impossible} when electrophilic aromatic substitution is attempted, as was the earlier reported literature case\textsuperscript{112}; the presence of oxygen atoms connecting the aromatic rings was necessary though.

The unattainability of higher molecular weight despite repeated attempts was thus attributed to the intramolecular decyanation. This side reaction that curtailed polymer molecular weights can be used fruitfully toward the synthesis of novel monomers. This is discussed more in detail in the next section in this chapter.

The intramolecular decyanation can be eliminated if a \textit{meta} linked system is used for the bis(aminonitrile). \textbf{89} was thus synthesized for such a purpose. When \textbf{89} was condensed with
bis(p-fluorophenyl)sulfone in dimethylformamide under N₂ (Scheme 32), polymer 93 was obtained with an $M_n$ of 32.3 kg/mol and an $M_w$ of 44.0 kg/mol (absolute GPC, NMP, 60°C). 94, the hydrolysis product of 93, had an $M_n$ of 16.4 kg/mol and $M_w$ of 30.6 kg/mol.

Scheme 32: Synthesis of a novel poly(ketone ketone sulfone) from 89.
When 93 was analyzed thermogravimetrically, the 10% weight loss (in air) was detected at 298°C and that increased by 180°C when 93 was hydrolyzed to 94 to 478°C (Figure 29). The DSC of 93 during the first heat (Figure 30) showed a huge exotherm peak at ca. 278°C. In its second heat (Figure 31), the exotherm (smaller in magnitude than the first heat) shifted to beyond ca. 370°C. The TGA of 93 had shown incipient degradation at ca. 260°C. Correlating the DSC and the TGA data, we concluded that a crosslinking reaction occurs and that this happens either by a initial cleavage of the C-CN bond or the C-morpholine bond, resulting in a highly stabilized benzylic radical, followed by recombination of radicals. The shift of the exothermic maximum to a higher temperature during the second heat along with the decreased caloric content of the transition lends a strong support to the crosslinking mechanism; the higher temperature is required for the cure during the second heat due to the increased Tg of the partial network formed during the first heat.

When 94 was analyzed calorimetrically (Figure 32), a Tg of 192°C was detected with an exothermic transition peak at 242°C and an endothermic transition peak at 257°C. During the slow cool (Figure 33), a Tg of 193°C was detected and at the end of the second heat (Figure 34), a Tg of 195°C was obtained and no other transitions were seen. This means that the polymer crystallizes slowly and that the crystallinity (as seen in the first heat) developed as the polymer was being formed in solution. The Tg -
$T_m$ window is narrow and this is one of the reasons for slow development of crystallinity. The other reason is that not all the aminonitrile linkages are hydrolyzed and the partial hydrolysis resulted in only a limited number of carbonyl groups; this is supported by absorbance at 1117 cm$^{-1}$ characteristic of the C-O-C stretch of morpholine in the FTIR spectrum of 94 and $^1$H NMR spectrum shows residual peaks in the aliphatic region corresponding to morpholine groups. This is because above a critical level of hydrolysis, the partly hydrolyzed polymer precipitates out due to insolubility and the heterogeneity of the reaction mixture prevents complete hydrolysis. If a complete hydrolysis is achieved by keeping the solution homogeneous, then the *melting point should increase to ca. 429°C* (based on the empirical $T_g/T_m = 0.67$ relationship, both in Kelvins). This would be the *highest melting point reported to date* in poly(aryl ketone) literature. In This would make it very appealing for industrial applications.

Hence, we were able to synthesize a novel poly(aryl ketone ketone sulfone), a combination of functional groups hitherto not synthesized, and the polymers look quite promising from their initial thermal and GPC characterization.
D) A NEW FAMILY OF CHAIN GROWTH MONOMERS: QUINODIMETHANES

1) Background

The synthesis of p-quinodimethane or p-xyylene (95) was first attempted by Thiele in 1904 but all he could produce was a white insoluble powder which he called poly(p-xyylene) (96). He was able to isolate the tetraphenyl substituted p-xyylene 97.116

![Chemical structures]

96 is synthesized by a vapor-coating process which deposits a very thin, uniform, highly crystalline film, which only dissolves in exotic solvents like chlorinated biphenyls at 300°C.117 Union Carbide developed the vapor-coating process and manufactured the various quinodimethane polymers under the trade name 'Parylene'. These display high tensile moduli and thermal transitions. The
parent poly(quinodimethane) 96 has a $T_m$ of 400°C and a $T_g$ of 80°C.\textsuperscript{117}

Yet another interesting quinodimethane is 98, 7, 7, 8, 8-tetracyanoquinodimethane (TCNQ). Its complex (1 : 1) with tetrathialfulvene is known to be highly conductive\textsuperscript{118} and this discovery triggered a burst of scientific activity in the field of 'organic metals'.

\begin{center}
\includegraphics[width=0.3\textwidth]{98.png}
\end{center}

Wheland and Martin\textsuperscript{119} improvised on 98 and synthesized a variety of substituted TCNQs with substituents on the parent phenyl ring. Baghdadchi and Panetta\textsuperscript{120} synthesized TCNQs with an oligomethylenealkoxycarbonyl substituent. Recently Katz\textsuperscript{121} has synthesized a tetrasubstituted quinodimethane with nitrile and 2-pyridyl substituents.

Iwatsuki\textsuperscript{122} has reported a 'spontaneous alternating copolymerization of TCNQ and styrene' and has also synthesized novel quinodimethanes with alkoxy carbonyl, alky- and aryl carbonyl and nitrile substituents and done extensive study of homopolymerizability and copolymerizability of those with styrene and substituted styrenes.\textsuperscript{123 - 129} Hall and coworkers have
synthesized novel captodative quinodimethanes 99 with the capto and the dative ends separated. 130

99 were then homopolymerized and copolymerized with other A-B monomers in an attempt to synthesize dipolar polymers with applications in fields where electrical properties of polymers are important.

2) Synthesis of a novel captodative quinodimethane

When 88 was suspended in dimethylformamide under N2 and 2.2 equivalents sodium hydride added, a vigorous bubbling (evolution of H2) was seen along with a deep red color (that of the delocalized anion). After 2 d of stirring at ambient temperature, the initially heterogeneous mixture was completely homogeneous with the color still deep blood red. The solution was quenched on ice-water and the canary yellow precipitate dried thoroughly to yield 100% of 100.
100 is the first quinodimethane with one dative end and the other captodative end to be synthesized. The $^1$H NMR spectrum (Figure 35) shows it to be a mixture of E and Z isomers. When pure E isomer was crystallized from a mixture of toluene and cyclohexane its $^1$H NMR spectrum (Figure 36) determined in CDCl$_3$ showed peaks at 7.6 (d, 2H), 7.4 (d, 2H), 4.9 (s, 1H), 3.9 - 3.5 (m, 8H) and 2.8 - 2.4 (m, 8H). When the same solution was left overnight and the $^1$H NMR spectrum taken (AP-3-34-18), it showed the same peaks as AP-3-34-15 and some additional peaks at 7.2 - 7.0 (two doublets, AA'BB' pattern), 4.7 (s) and 3.1 (m). This means that the quinodimethane 100 underwent configurational change, presumably via the diradical as shown in Scheme 33. The $^1$H NMR spectra after 16 h, 48 h and 250 h (Figures 37 - 39) show an increase and eventual levelling off of the integral areas of the additional peaks.
Scheme 33: Configurational isomerism of 100 in solution.

The equilibrium population of E : Z was 78 : 22 (± 3%) as detected by $^1$H NMR. The FTIR spectrum of 100 showed peaks at 2230 cm$^{-1}$ (weak) for nitrile, 1507 cm$^{-1}$ for phenyl ring and 1136 cm$^{-1}$ for C-O-C of the morpholine ring. This novel quinodimethane is expected to polymerize\textsuperscript{122 - 127, 131, 132} either free-radically or cationically and the resulting polymer should have interesting dielectric properties; more about this in the FUTURE WORK chapter.
REFERENCES


84) Pandya, A.; Gibson, H. W. manuscript to be submitted to J. Org. Chem.


89) Gibson, H. W. unpublished results.


New York; 1965.


Recently Brunelle and coworkers have shown that under certain circumstances, cyclic oligomers of aromatic carbonates (from bisA chloroformate) can be formed with relative ease via a *pseudohigh* dilution technique by triethylamine catalyzed hydrolysis and condensation.
n = 1 - 20, bisphenol-A based oligomeric macrocycles.


116) Thiele, J.; Balhorn, H. Ber. 1904, 37, 1463.


A) SYNTHESSES OF NOVEL A-A AND A-B BIS(REISSERT COMPOUND) MONOMERS AND POLYMERS:

1) Success and limitations:

Bis(Reissert compound)s \textbf{14a, 15d} and \textbf{16} of the A-A category were synthesized in high yields for the first time, via the TMSCN/\text{CH}_2\text{Cl}_2 technique. Bis(Reissert compound)s \textbf{21 - 25} of the A-B category were synthesized in high yields via the single phase or the two phase technique. \textbf{21, 23 and 24 were polymerized but yielded oligomers due to either rearrangement or side reaction. Thus, the use of difunctional A-B type Reissert compounds is limited as far as novel polymerizations are concerned.}

\textbf{14a, 15d and 16} can be used in a condensation polymerization with dihaloalkanes and with suitable precautions like elimination of the competing rearrangement, high polymers were synthesized. Melvin Rasco, a graduate student in the group, tried out a polymerization on those lines and more data may be found in his thesis.

Novel open chain aliphatic diamine based bis(Reissert compound)s \textbf{52 - 57} were synthesized, as A-A monomers, in high yields from precursor open chain bis(\text{o}-aminonitrile)s \textbf{47 - 51}; the bis(\text{o}-aminonitrile)s were synthesized via a convenient one-pot, multi-step aqueous synthetic route from readily available

146
economic starting materials. 54 yielded novel acylated linear polyamine derivative 70. No polymers resulted when \( R_1 = (CH_2)_2 \) for a variety of \( R_2 - R_4 \). This is attributed to the sterically hindered dianion which is unable to attack the electrophilic end of dihaloalkanes. Therefore, in the opinion of the author, derivatives of 54 can be employed with other dihaloalkanes and novel polymers can result. For example, by the use of hydrophilic diiodides, polymers which may form stable aqueous suspension can be synthesized. This can be advantageous because the chemical industry and EPA are moving towards decreasing the use of toxic and volatile solvents. With more optimization, \( R_4 \) could be p,p'-phenylene sulfonyl; this will lead to improved thermal properties vis a vis 70.

The four independent structural variables (\( R_1 - R_4 \)) in the generic polymer 101, obtained from the polymerization of an A-A open chain bis(Reissert compound) and a dihaloalkane, shown below provide versatility that can be deftly used to optimize the fundamental polymer properties: thermal, mechanical and solubility.
Upon hydrolysis of 101 (removal of acyl moiety), novel linear poly(amine)s may result. These would be unique since linear poly(amine)s are difficult to synthesize due to the problems of branching. The resulting poly(amine)s can be viewed as poly(α-amino-nitrile)s. The susceptibility of the α-amino-nitrile linkage to acids is well established, resulting in carbonyl bearing moieties. In fact, these materials may serve as photo-resist polymers which can be easily removed, by a simple mild acid wash, after appropriate development of the resist.

2) Novel bis(Schiff base) monomers based on alicyclic diamine:

The formation of 58 and 59 is encouraging as both of these are new compounds and 59 can perhaps be condensed with a variety of bisphenols resulting in a novel class of poly(azomethine ether)s 60. There is an interest in the trans-cyclohexane moiety because it imparts properties intermediate to aromatic and aliphatic groups to the resultant polymers. 1,4-trans-Diamino cyclohexane
can be condensed with a variety of (substituted) aldehydes resulting in novel monomers that can be employed for synthesizing polymers containing the trans-cyclohexyl moiety as shown in Scheme 34.

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{NH}_2 \\
\text{+} & \quad \text{2 OH}_\text{R} \\
\text{R} & \quad \text{OH}, \text{COOH}, \text{COOR}_1, \text{CHO}, \text{CN}, \text{etc.}
\end{align*}
\]

**Scheme 34**: Novel bis(Schiff base) monomers based on 1,4-trans-diamino cyclohexane

59 can be condensed with either p-hydroxybenzoic acid or m-aminophenol and the resulting diamine or dicarboxylic acid (102) containing the trans-cyclohexyl moiety can perhaps be incorporated in a *novel polyester or polyamide or polyimide*
syntheses via \textbf{102}. Thus \textbf{59} can either be used for novel monomer or polymer syntheses. This is shown in \textbf{Scheme 35}.

\textbf{102}, \ Y = \text{NH}_2, \text{COOH}.

\textbf{Scheme 35} : Versatility of \textbf{59} toward either novel monomer or polymer syntheses.

3) \textbf{Open chain bis(\alpha-aminonitrile)s based on aromatic diamines} :

By the use of commercially available aromatic diamines, p-phenylene diamine, 4,4'-oxydianiline and 4,4'-methylenedianiline,
novel bis(α-aminonitrile)s 61 and 63 - 66 were synthesized in moderate to high yields. The intention was to manipulate thermal, mechanical and solubility properties vis a vis all-aliphatic backbone systems, i.e., 47 - 51. These dimaines are currently used in potentially post-reaction modifiable copolyamide syntheses. 133 A case in point is shown below.

67 can perhaps be used with success in synthesizing polymers of the type 101 where R1 = p-phenylene; such a polymer may have Tg of ca. 170°C [estimate based on the observed Tg (72°C) of 101] when R1 = n-C6H12.
B) SYNTHESES AND STEREOCHEMISTRY OF BENZOTHIAZOLE REISSERT COMPOUNDS:

Based on the variable temperature $^1$H NMR spectroscopic analysis of 34, the details of its conformational equilibrium in solution were worked out. ASIS results helped consolidate the rationalization; observed upfield shifts for the H$_2$ proton in C$_6$D$_5$CD$_3$ followed a literature precedence. Novel benzothiazole Reissert compounds 31 - 35 were synthesized and methylated in high yields. When the attempted rearrangement of 34 in DMF was carried out and the reaction quenched with iodomethane, a novel compound was isolated and a mechanism proposed. This compound was submitted for mass spectrometric analysis and the latest results will be presented at the time of dissertation defense and added to the dissertation as an appendix.

C) NOVEL NUCLEOPHILIC AROMATIC SUBSTITUTION VIA AMINONITRILES AND OPEN CHAIN REISSERT COMPOUNDS:

1) Model reactions:

Successful quantitative syntheses of 69, 81 and 83 adds one more reaction to the repertoire of synthetic polymer chemist. This reaction uses the umpolung principle and the result is a nucleophilic aromatic substitution under mild reaction conditions based on a carbanion nucleophile. 81 and 83 were hydrolyzed quantitatively to 82 and 84 and while 69 was not hydrolyzed to
yield the corresponding carbonyl compound, there exists a literature precedence to effect that transformation. Not many such nucleophilic aromatic substitution reactions are known except in the case of Grignard reagents and lithio-carbanions both of which show a high propensity to attack a carbonyl moiety; this rules out the synthesis of 83 and possibly 81 via either a Grignard reagent or lithio-carbanion. The aminonitrile carbanion is a hindered soft nucleophile and thus shows no propensity to attack a hard electrophile like the carbonyl group. The result is a highly efficient and selective nucleophilic aromatic substitution.

Although 85, a novel A-B monomer, did not result in the expected polymer 86, it can be used in the syntheses of novel oligo(aryl ketone)fluorides, oligo(aryl ketone sulfone)fluorides and oligo(aryl ketone phosphine oxide)fluorides by successive reactions. This is shown in Scheme 36.
Scheme 36: Utility of 85 in the syntheses of novel oligo(aryl ketone)fluorides, oligo(aryl ketone sulfone)fluorides and oligo(aryl ketone phosphine oxide)fluorides.

2) Novel poly(aryl ketone ketone sulfone)s:
Condensation of 88 and 89 with bis(p-fluorophenyl)sulfone resulted in novel (masked) poly(aryl ketone sulfone)s which were obtained by hydrolysis of the poly(aryl aminonitrile)s. 91
displayed the highest $T_m$ obtained to date in the poly(aryl ketone)s. That 93 displayed a $T_m$ in the first heat was a pleasant surprise because poly(sulfone)s are rarely semi-crystalline. The $T_g - T_m$ window is seemingly narrow (ca. 60°C) for 93 and this is due to the incomplete hydrolysis of the precursor poly(aryl aminonitrile). From the use of 4,4'-difluorobenzophenone instead of bis(p-fluorophenyl)sulfone, the resultant polymer will truly be a poly(aryl ketone) as shown below.

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Since the poly(aryl aminonitrile)s precursors to the poly(aryl ketone sulfone)s are very soluble in conventional solvents, it may perhaps be possible to obtain a good coating of the matrix to the fiber for composite manufacture; then a mild acid wash can hydrolyze the aminonitrile transforming the resin into a high performance matrix.

D) QUINODIMETHANE: A NOVEL MONOMER WITH POTENTIAL CAPABILITY TO BE INHERENTLY CONDUCTIVE:

Upon intramolecular dehydrocyanation of 88, a novel quinodimethane 100 was obtained in quantitative yield. It is a
unique quinodimethane in that its one end is donor and the other end is captodative and it is the first synthesis of such a kind of quinodimethane reported to date. It should be easy to polymerize this quinodimethane either free radically or anionically based on literature reports.118 - 124
The polymer obtained initially can be either dehydrocyanated or hydrolyzed and enolized to yield either 100a or 100b both of which are soluble poly(p-phenylene vinylene) modifications. Poly(p-phenylene vinylene) is known to have the among highest conductivities reported to date.

Another approach is to dehydrogenate the aromatic bis(α-aminonitrile) 88 to yield a quinodimethane 100c with both ends captodative. Polymerization of 100c and subsequent hydrolysis of the intermediate polymer should yield a poly(aryl α-diketone) 100d shown below. Such a polymer is expected to be photo-degradable due to the α-diketone linkage.

Thus the aromatic bis(α-aminonitrile) chemistry turned out to be a very fruitful area of research during the author's final year in graduate school. One of the off-shoots, the quinodimethane chemistry yielded some very exciting preliminary results which have opened up many avenues for further research; diversification is also possible in the poly(aryl ketone) area where the use of 4,4'-(difluorophenyl)phenyl phosphine oxide should yield polymers with inherent fire retardancy.
REFERENCES

133) AKZO chemical company, *unpublished results*.
CHAPTER 4

EXPERIMENTAL

A) GENERAL:

Monomers were either triply recrystallized to a constant melting point range or vacuum distilled prior to use. NaI (Fisher Biotech grade, 99+%) was dried at 100°C in vacuo. DMF used for polymerization was purchased from Aldrich (Sure Seal) and used as such. Sodium hydride was used as a 60% dispersion in light mineral oil, as obtained from Aldrich. All yields are for crude products unless otherwise stated. Melting points were determined on a Haake Buchler melting point apparatus and are corrected. Thermogravimetric analyses were carried out on a Perkin Elmer 7700 Thermal Analyses System, interfaced to an IBM PS2 desktop computer and a Hewlett Packard 7550A graphics plotter, in air atmosphere. Glass transitions were determined at a 10°C/min heating rate by a single cell instrument of the Perkin Elmer 7700 Thermal Analyses System interfaced to an IBM PS2 desktop computer and a Hewlett Packard 7550A graphics plotter. Proton NMR and 13C NMR spectra were recorded on a Bruker 270 MHz and 400 MHz instruments interfaced to an Aspect 2000 and a Hewlett Packard 7550A graphics plotter; tetramethysilane was used as the internal standard. FTIR spectra were recorded on a Nicolet MX-1 on KBr pellets. Elemental analyses were performed by Atlantic Microlabs, Norcross, Georgia. Absolute GPC analyses were run
using a Viscotek model #100 differential viscosity detector and a Waters 150C equipped with a RI detector operating at 60°C with DMF (0.5% LiCl) eluant or THF eluant at ambient temperature; this instrument provided polydispersity index ($M_W/M_N$) and Mark-Houwink constants also. Inherent viscosities were measured on a 1.5% by weight solution of the polymer and intrinsic viscosities were measured on polymer solutions by the successive dilution technique beginning with a 1% by weight solution of the polymer in a Cannon-Fenske type viscometer; care was taken to have the measured 't' values between 1.7 - 1.1 t₀.

**1-Cyano-2-benzoyl-1,2-dihydroisoquinoline (1):**
This compound was prepared by the CH$_2$Cl$_2$ / H$_2$O method$^{27}$ and the DMF / KCN method (Table 9, chapter 2). The crude yield for the CH$_2$Cl$_2$ / H$_2$O method was 75%, mp = 124 - 125.5°C (lit.$^{27}$ 125 - 126°C). The DMF / KCN method is given below.

2.49 g (18.5 mmols) of isoquinoline were dissolved in 6.5 mL of dry DMF and 3.8 g (76 mmols) of dry KCN were added to it along with 0.18 g (0.9 mmols) of benzyltrimethylammonium chloride as a phase transfer catalyst. After letting the system stir under N₂ for 10 minutes, 5.4 g (37 mmols) of PhCOCl were quickly added and the system flushed once again with N₂. The flask was then tightly shut with a cork stopper and the reaction mixture was sonicated for 100 hours. Progress of the reaction by means of TLC was
checked at routine intervals. The workup was done by pouring the mixture in 100 mL of H$_2$O, extracting with CH$_2$Cl$_2$, washing the organic layer with H$_2$O, 8% HCl (3X), H$_2$O, satd. NaHCO$_3$ (3X), H$_2$O and drying with MgSO$_4$. On stripping off the organic layer, the weight of the brown oil was found to be 5 g (100%). Crystallization from 95% EtOH gave off-white crystals, m.p = 120 - 123°C (lit.27 125 - 126°C). TLC (20% EtOAc / 80% hexanes) showed a single sharp spot identical to the authentic compound. There was no residue at the starting spot. The $^1$H NMR spectrum was identical with that of an authentic sample.

**General procedure for 14d, 15e and 16**: To a well stirring solution of the heterocycle in dry CH$_2$Cl$_2$, a catalytic amount of AlCl$_3$ was added, followed by the addition of bis(acid chloride) (0.5 molar amount vis a vis heterocycle) under N$_2$ at ambient temperature. After 15 min trimethylsilyl cyanide (equimolar vis a vis heterocycle) was added and the stirring continued for 2 - 4 days.

**Isophthaloyl Bis[2-(1-cyano-1,2-dihydroisoquinoline)] (14d)**:
Yield = 98%. Recrystallized triply from EtOH, mp 120 - 148°C (shrank at ca. 125°C). FTIR (cm$^{-1}$) : 1672, 1628 (amide carbonyl), 1572 (phenyl). $^1$H NMR (CDCl$_3$) : 7.85 - 7.80 δ (m, 3H), 7.63 δ (m, 1H), 7.45 - 7.30 δ (m, 6H), 7.28 - 7.20 δ (m, 2H), 6.65 - 6.45 δ (br. s, 6H).
4H, H₁ and H₃) and 6.13 δ (d, J = 7.7 Hz, 2H, H₄). Elemental analyses, found (calcd. for C₂₈H₁₈N₄O₂). C : 75.51 (76.00), H : 4.27 (4.10), N : 12.60 (12.66).

**Terephthaloyl Bis[1-(2-cyano-1,2-dihydroquinoline)] (15e):**
Yield = 98%. Recrystallized from DMF : EtOH (1:7 v/v), mp = 238 - 241°C (decomposes). FTIR (cm⁻¹) : 1685, 1647 (amide carbonyl), 1572 (phenyl). ¹H NMR (CDCl₃) : 7.36 δ (s, 2H, terephthaloyl-H), 7.28 - 7.22 δ (m, 1H), 7.15 δ (m, 1H), 6.95 δ (m, 1H), 6.85 δ (d, J = 8.8 Hz, 1H), 6.50 δ (d, J = 7.90 Hz, 1H, H₂) and 6.23 - 6.10 δ (m, 2H, H₃ and H₄). Elemental analyses, found (calcd. for C₂₈H₁₈N₄O₂). C : 75.60 (76.00), H : 4.29 (4.10), N : 12.63 (12.66).

**Terephthaloyl Bis[3-(2-cyano-2,3-diydrobenzothiazole)] (16):**
Yield = 100%. Purification was done by Soxhlet extraction with CH₂Cl₂ for 3 d, mp = 250 - 253°C (decomposes). FTIR (cm⁻¹) : 1665 (amide carbonyl), 1610, 1578 (phenyl). ¹H NMR (CDCl₃) : 7.67 δ (s, 4H, terephthaloyl-H), 7.31 δ (br. d, J = 7.9 Hz, 2H, H₇), 7.13 δ (br. m, 2H, H₆), 6.99 δ (br. m, 2H, H₅), 6.75 - 6.50 δ (br. s, 2H, H₄), 6.41 δ (br. s, 2H, H₂). Elemental analyses, found (calcd. for C₂₄H₁₄N₄O₂S₂), C : 63.34 (63.42), H : 3.13 (3.10), N : 12.55 (12.33) and S : 14.02 (14.11).
1-Benzoyl-2-cyano-1,2-dihydroquinoline (18):
This compound was prepared by the CH$_2$Cl$_2$ / H$_2$O method$^{27}$ and the DMF / KCN method (Table 9, chapter 2). The crude yield for the CH$_2$Cl$_2$ / H$_2$O method was 62%, mp = 151.5 - 153.0°C (lit.$^{48}$ 154 - 155°C). The DMF / KCN method is given below.

2.49 g (18.5 mmols) of quinoline were dissolved in 6.5 ml of dry DMF and 3.8 g (76 mmols) of dry KCN were added to it along with 0.18 g (0.9 mmols) of benzyltrimethylammonium chloride as a phase transfer catalyst. After letting the system stir under N$_2$ for 10 minutes, 5.4 g (37 mmols) of PhCOCl were quickly added and the system flushed once again with N$_2$. The flask was then tightly shut with a cork stopper and the reaction mixture was sonicated for 100 hours. Progress of the reaction was followed by means of TLC at routine intervals. The workup was done by pouring the mixture in 100 ml of H$_2$O, extracting with CH$_2$Cl$_2$, washing the organic layer with H$_2$O, 8% HCl (3X), H$_2$O, satd. NaHCO$_3$ (3X), H$_2$O and drying with MgSO$_4$. On stripping off the organic layer, the weight of the brown oil was found to be 5 g (100%). Crystallization from 95% EtOH gave slightly orange crystals, m.p = 149 - 152°C (lit.$^{48}$ 154 - 155°C). TLC showed a single sharp spot (20% EtOAc / 80% hexanes) identical to an authentic specimen with no residue at the starting spot. The $^1$H NMR spectrum was identical with that of an authentic sample.
**2-Cyano-3-benzoyl-2,3-dihydrobenzothiazole (19):**

7.0 g (50 mmols) of benzothiazole were dissolved in 20 ml of CH₂Cl₂ and 7.7 ml (55 mmols) were added and the solution homogenized by stirring. A catalytic amount of AlCl₃ were then added and 7.5 ml (55 mmols) of TMSCN were slowly syringed in. The honey colored solution gave a steady exotherm for about 20 minutes. The stirring was continued for 18 hours. Stripping off the organics gave a red oil which solidified entirely on trituration with EtOH. Yield = 13.3g (100%), mp = 120 - 124°C. It was crystallized from 95% EtOH to give shiny white needle crystals m.p. = 127.5 - 128.5°C (lit. 88 139 - 141°C). FTIR (cm⁻¹) : 1656 (amide carbonyl) and 750, 760 (o-disubstituted benzene). ¹H NMR (CDCl₃) : 7.58 δ (m, 3H), 7.47 δ (m, 2H), 7.30 δ (d, 1H, J = 7.2 Hz), 7.09 δ (dd, 1H, J = 7.5 Hz, J = 7.2 Hz), 6.98 δ (dd, 1H, J = 7.5 Hz, J = 7.2 Hz), 6.90 - 6.50 δ (br. s, 1H), 6.37 δ (s, 1H). ¹³C NMR (CDCl₃) : 170, 138, 135.5, 134.5, 131, 130, 128, 125, 122, 118 and 56 δ.

**2-[p-(Chloromethyl)benzoyl]-1-cyano-1,2-dihydroisoquinoline (22):**

To 25.8 g (200 mmol) of isoquinoline in 150 mL CH₂Cl₂ were added a solution of 40 g (610 mmol) of KCN in 70 mL of H₂O and 1.3 g (7 mmol) of benzyltrimethylammonium chloride while the mixture was being stirred in an ice-water bath. 56.8 g (300 mmol) of p-(chloromethyl)benzoyl chloride were then added dropwise over a period of 75 minutes during which the color of the reaction...
mixture changed to reddish brown. After stirring for an additional
3 h, the organic layer was washed with H2O (1x), 5% HCl (3x, 50 mL
each), H2O (1x), satd. NaHCO3 (3x, 50 mL each), H2O (1x) and after
drying over MgSO4, was evaporated in vacuo. The crude solid
melted at 112 - 180°C and weighed 38.7 g (63%). Recrystallization
from ethanol gave shiny colorless needles mp = 135 - 1360°C. FTIR
(cm⁻¹) : 1654 (amide CO), 1626 (arom. C=C), 1412 (-CH2 scissor),
778 (p-disubs. benzene). ¹H NMR (CDCl3) : 7.65 δ (d, 2H, J = 7.0 hz),
7.50 δ (d, 2H, J = 7.0 hz), 7.45 - 7.21 δ (m, 4H), 6.61 δ (d, 1H, J = 7.5
hz), 6.55 δ (s, 1H), 6.07 δ (d, 1H, J = 7.5 hz) and 4.61 δ (s, 2H).
Elemental analyses, found (calcd. for C₁₈H₁₃ClN₂O) : C : 69.98
(70.02), H : 4.28 (4.24), N : 9.03 (9.08), Cl : 11.54 (11.48).

**Attempted synthesis of 1-Cyano-2-(4-
hydroxymethylbenzoyl)-1,2-dihydroisoquinoline (22a)** :
0.5 g (1.65 mmol) of 22 was suspended in 5 mL of methanol and 1.1
g (1.7 mmol, 40 weight % in water) of tetrabutylammonium
hydroxide were added and the mixture heated to steady reflux;
homogeneity was attained. The reaction was stopped after 15 h,
20 mL CH₂Cl₂ added to it and the organic layer was washed with
H₂O (25 mL, 6X), satd. NaHCO3 (10 mL, 2X) and H₂O (25 mL, 2X).
After drying the CH₂Cl₂ layer with MgSO4 and evaporation, a pale
brown oil was obtained, 190 mg (89% based on isoquinoline). The
¹H NMR spectrum was identical to an authentic sample of
isoquinoline.
2-[m-(Chloromethyl)benzoyl]-1-cyano-1,2-dihydro-
isoquinoline (23):
Application of the two phase method\(^{27}\) (as in the synthesis of 22) 
produced this monomer in 48% crude yield, \(mp = 168 - 172^\circ\)C. It 
was extracted twice from ethanol and the resulting light brown 
solid melted at 177.0 - 178.5\(^{\circ}\)C (lit.\(^{86}\) 179 - 180.5\(^{\circ}\)C). FTIR (cm\(^{-1}\)) : 1670 (amide CO), 1628 (arom. C=C) and 778 (m-disubstituted 
phenyl). \(^1\)H NMR (CDCl\(_3\)) : 7.70 - 7.20 \(\delta\) (m, 8H), 6.65 \(\delta\) (br. d, 1H), 
6.55 \(\delta\) (s, 1H), 6.10 \(\delta\) (d, 1H, \(J = 7.71\) hz), 4.63 \(\delta\) (s, 2H).

2-[p-(Iodomethyl)benzoyl]-1-cyano-1,2-dihydro-
isoquinoline (24) (the exchange method):
3.1 g (10 mmol) of 22 were dissolved in 25 mL of dry acetone along 
with 1.55 g (10.5 mmol) of NaI and the solution was refluxed for 4 
h. After filtration, the acetone was removed in vacuo to yield 4 g 
(100%) of brownish crude solid which was recrystallized from 
ethyl acetate/hexane to yield shiny white needles, \(mp = 168-
170^\circ\)C. FTIR (cm\(^{-1}\)) : 1665 (amide CO), 1625 (arom. C=C), 774 (p-
disubs. phenyl). \(^1\)H NMR (CDCl\(_3\)) : 7.57 - 7.28 \(\delta\) (m, 7H), 7.22 \(\delta\) (d, 
1H, \(J = 6.42\) hz), 6.61 \(\delta\) (br. d, 1H), 6.55 \(\delta\) (s, 1H), 6.07 \(\delta\) (d, 1H, \(J = 
7.22\) hz) and 4.46 (s, 2H).
3-[m-(Chloromethyl)benzoyl]-2-cyano-2,3-dihydro-benzothiazole (25) (the one phase method):
13.5 g (100 mmol) of benzothiazole were dissolved in 80 mL of dry CH₂Cl₂ under N₂ and 20.7 g (104 mmol) of m-(chloromethyl)benzoyl chloride were added along with a trace of AlCl₃. The solution was stirred for 15 min while being cooled in an ice-H₂O bath. 15 mL (104 mmol) of Me₃SiCN were then slowly syringed in and the solution was stirred for 48 h. A small amount of shiny solid had precipitated out. The solvent was evaporated in vacuo to yield an off-white solid, 33.2 g (100%). Recrystallization from dimethylformamide : ethanol (1:6 v/v) yielded shiny white crystals, mp = 143.5 - 145.0°C. FTIR (cm⁻¹) : 1652 (amide CO), 1466 (aromatic C=C), 747 (m-disubstituted benzene), 691 (C-Cl str.). ¹H NMR (CDCl₃) : 7.60 - 7.57 δ (m, 2H), 7.57 - 7.43 δ (m, 2H), 7.32 δ (d, 1H, J = 7.7 Hz), 7.17 - 7.04 δ (dd, 1H, J = 7.7 Hz, J = 7.0 Hz), 7.01 - 6.93 δ (dd, 1H, J = 7.7 Hz, J = 7.0 Hz), 6.81 - 6.62 δ (br. s, 1H, no exchange with D₂O), 6.37 δ (s, 1H) and 4.58 δ (s, 2H). Elemental analyses, found (calcd. for C₁₆H₁₁ClN₂OS) : C : 61.08 (61.05), H : 3.63 (3.52), N : 8.71 (8.90), Cl : 11.97 (11.26).

3-[m-(Iodomethyl)benzoyl]-2-cyano-2,3-dihydro-benzothiazole (26) (the exchange method):
An identical procedure as for 24 gave 26 in 100% yield, mp = 149.0 - 150.0°C. FTIR (cm⁻¹) : 1648 (amide CO), 1580 (arom. C=C), 1464 (CH₂ scissor) and 753 (m-disubs phenyl). ¹H NMR (CDCl₃) : 7.57 δ
(m, 2H), 7.45 δ (m, 2H), 7.31 δ (d, 1H, J = 6.5 Hz), 7.10 δ (dd, 1H, J = 6.5 Hz, J = 8.0 Hz), 7.02 δ (dd, 1H, J = 7.0 Hz, J = 8.0 Hz), 6.80 - 6.57 δ (br. s, 1H, no exchange with D₂O), 6.38 δ (s, 1H), and 4.42 δ (s, 2H).

**Attempted polymerization of 2-[p-(chloromethyl)-benzoyl]-1-cyano-1,2-dihydroisoquinoline (22) with n-Butyllithium in THF:**

To a flame dried three necked polymerization vessel that was cooled under N₂ purge, was added 2.00 g (6.50 mmols) of 22 and 20 mL freshly distilled dry THF. The mixture was stirred gently and cooled to -78°C in a dry ice acetone bath. After about 15 minutes, 1.56 mL (6.51 mmols) of 1.49 M nBuLi/hexane was added dropwise through a gas tight syringe. The color turned deep red immediately and the stirring was continued for 3 hours and the mixture was slowly warmed up to ambient temperature. The workup was done after a total reaction time of 24 hours. The reaction mixture had a very light orange color that had persisted for at least 6 hours; it was quenched by pouring into a ten fold excess of H₂O (150 mL) with stirring; the resulting solid was filtered upon a fritted disc funnel, 2.72 g (136% !). Obviously there was H₂O left in it. The solid was dissolved in THF and precipitated in 10 fold excess of MeOH. This procedure was repeated thrice and the resulting solid was dried in a drying pistol overnight. The yield was 0.35 g (17%). The appearance was a pale yellow powder; the solid turned brownish around 275°C and retained that color until 325°C. The
DSC of this solid showed a Tg at 117°C (2nd heat). The TGA showed 15% weight loss at 275°C and an additional 25% loss at 420°C. The $M_n$ was determined to be 3542 g/mol (GPC, PS standards, THF, 13 repeat units) and the PD was 1.29. FTIR (cm$^{-1}$): 1684 (C=N), 1670, 1636 (amide carbonyl), 1610 (aromatic C=C) and 1261 (C-N, amines). $^1$H NMR (CDCl$_3$): 6.8 - 7.8 δ (10H, multiplet), 6.35 δ (1H, multiplet), 5.65 δ (1H, multiplet), 3.5 - 3.8 δ (2H, broad) and 2.15 δ (1H, broad).

**Attempted polymerization of 1-cyano-2-[p-(iodomethyl)-benzoyl]-1,2-dihydroisoquinoline (24):**

1.01 g (2.51 mmol) of 24 was dissolved in 10 mL of dry DMF under $N_2$ and the mixture was cooled to 0°C in an ice bath. 0.11 g (2.8 mmol) of NaH (60% dispersion in mineral oil) was added quickly and the reaction continued for one day. It was quenched by pouring into 100 mL ice-cold H$_2$O. The solid [wt = 0.96g (96%)] was collected by filtration and the TLC showed no trace of the starting material. FTIR (cm$^{-1}$): 1672 (amide carbonyl), 1632 (aromatic C=C), 1270 (C-N amines) and 778 (o-disubstituted benzene). The solid was partially soluble in CH$_2$Cl$_2$, THF, acetone, EtOAc, EtOH and CHCl$_3$. $^1$H NMR (CDCl$_3$): 8.0 - 6.0 δ (m), 5.1 δ (d, J = 6.9 Hz), 4.7 δ (d, J = 6.9 Hz), 4.6 δ (d, J = 13.1 Hz), 4.3 δ (d, J = 13.1 Hz), 3.5 - 2.8 δ (m). The integration of the aromatic region exceeds the theoretical amount vis a vis aliphatic region. Inherent viscosity, 0.04 dl/g (NMP, 25°C).
2-Cyano-3-(o-chlorobenzoyl)-2,3-dihydrobenzothiazole (33):

9.5 g (66 mmol) of benzothiazole were dissolved in 60 mL CH$_2$Cl$_2$ in a dry round bottom flask under N$_2$ and 9.0 mL (68 mmol) of o-chlorobenzoyl chloride were added and the mixture homogenized by stirring. A catalytic amount of AlCl$_3$ was then added and 9.5 mL (69 mmol) of trimethylsilyl cyanide (TMSCN) were slowly syringed in. The honey colored solution gave a steady exotherm for about 20 minutes and within an hour white solid started forming. The stirring had stopped in one more hour and the heterogeneous mixture was allowed to stand for 8 hours at the end of which the solvent and other volatiles were stripped off and the yield of the pale yellow solid was 20.2 g (100%), m.p. (crude) = 179.5 - 181.5°C. 10 g of the crude solid was crystallized from 3:7 (v:v) DMF:EtOH (100 mL) to obtain 7 g shiny white crystals, mp 182.5 -184.0°C. Two more crystallizations yielded shiny white crystals, mp 183.5 - 185.0°C. FTIR (cm$^{-1}$) : 1664 (carbonyl), 1464 (arom. C=C), 750 (C-Cl) and 740 (o-disubstituted benzene). $^1$H NMR (CDCl$_3$) : 7.75 - 7.40 δ (br., unresolved), 7.40 - 7.20 δ (br. multiplet), 7.20 - 7.00 δ (br. singlet), 6.95 - 6.65 δ (br. singlet), 6.20 - 5.90 δ (br. singlet). Elemental analysis, found (calcd. for C$_{15}$H$_9$CIN$_2$OS) , C : 59.90 (59.90), H : 2.99 (3.02), N : 9.35 (9.32).
2-Cyano-3-o-toluyl-2,3-dihydrobenzothiazole (34):
To a solution of 10.2 g (71 mmol) of benzothiazole in 60 mL CH₂Cl₂ were added 9.5 mL (72 mmol) of o-toluyl chloride with a catalytic amount of AlCl₃ and the solution stirred for 20 minutes under N₂. Upon the completion of the slow addition of 10.4 mL (75 mmol) trimethylsilyl cyanide (TMSCN), an exotherm was detected for 20 minutes. The stirring was continued for 8 hours and a TLC showed no presence of starting material. The solvent and other volatiles were removed under reduced pressure to obtain 20.2 g (100%) off white solid, mp 152.5 - 154°C (crude). 10 g of the crude were crystallized from 1 : 18 (v:v) DMF : EtOH (95 mL) to obtain 8 g of shiny white solid, mp 156 - 158°C. Two more recrystallizations yielded shiny white solid, mp 157.0 - 158.5°C. FTIR (cm⁻¹) : 1662 (carbonyl), 1465 (arom. C=C), 1325 (CH₃ attached to a phenyl ring) and 737 (o-disubstituted benzene). ¹H NMR (CDCl₃) : 7.8 - 7.4 δ (m), 7.4 - 7.2 δ (d, unresolved), 7.2 - 7.0 δ (br. t), 7.0 - 5.5 δ (3 broad peaks), 2.9 -1.8 δ (2 br. humps). Elemental analysis, found (calcd. for C₁₆H₁₂N₂O₂S), C : 68.53 (68.55), H : 4.32 (4.32), N : 10.01 (10.00).

2-Cyano-3-p-toluyl-2,3-dihydrobenzothiazole (35):
To 10.2 g (71 mmol) benzothiazole in 50 mL CH₂Cl₂ were dissolved 9.8 mL (72 mmol) of p-toluyl chloride and a catalytic amount of AlCl₃ was added and the solution stirred for 30 minutes under N₂. 10.2 mL (73 mmol) of TMSCN were syringed in quickly and the
solution stirred for 16 hours. Upon removal of the solvent and the volatiles, a pale honey colored oil was obtained, 20.7 g (100%). This was triturated with EtOH and all of it was recrystallized from 1:28 (v:v) DMF : EtOH (290 mL) to obtain 15 g of off-white shiny crystals, mp 153.4 - 154.2 °C (lit.\textsuperscript{88} 158 - 160°C). \textsuperscript{1}H NMR (CDCl\textsubscript{3}) : 7.48 δ (d, 2H, J = 7.0 Hz), 7.40 - 7.22 δ (m, 3H), 7.15 - 6.95 δ (m, 2H), 6.90 - 6.60 δ (br. s, 1H), 6.35 δ (s, 1H) and 2.45 δ (s, 3H).

**2-Cyano-3-(p-t-butylbenzoyl)-2,3-dihydrobenzothiazole (36)**

To 8.8 g (61.5 mmol) benzothiazole in 45 mL CH\textsubscript{2}Cl\textsubscript{2} were dissolved 12.5 mL (62.3 mmol) of p-t-butylbenzoyl chloride and a catalytic amount of AlCl\textsubscript{3} was added and the solution stirred for 30 minutes under N\textsubscript{2}. 9 mL (64.2 mmol) of TMSCN were syringed in quickly and the solution stirred for 16 hours. Upon removal of the solvent and the volatiles, a reddish oil was obtained, 20.3 g (100%). Upon trituration with EtOH, a creamy solid was obtained which was recrystallized from 95% EtOH to obtain shiny white crystals, mp 131 - 132°C. Two more recrystallizations gave a shiny white solid, mp 131 - 132°C. FTIR (cm\textsuperscript{-1}) : 2237 (v. weak, CN), 1654 (carbonyl), 1464 (arom. C=C) and 1352, 1332 (t-butyl). \textsuperscript{1}H NMR (CDCl\textsubscript{3}) : 7.55 δ (d, 2H, J = 8.4 Hz), 7.47 δ (d, 2H, J = 8.4 Hz), 7.28 δ (d, 1H, J = 8.2 Hz), 7.10 δ (dd, 1H, J = 7.5 Hz, 7.7 Hz), 7.01 δ (dd, 1H, J = 7.5 Hz, 7.4 Hz), 6.97 - 6.77 δ (br. s, 1H), 6.33 δ (s, 1H) and 1.38 δ
(s, 9H). Elemental analysis, found (calcd. for C_{19}H_{18}N_{2}OS), C : 70.71 (70.77), H : 5.66 (5.63), N : 8.67 (8.69).

**2-Cyano-2-methyl-3-(o-chlorobenzoyl)-2,3-dihydrobenzothiazole (37)**:

1.91 g (6.3 mmol) of 2-cyano-3-(o-chlorobenzoyl)-2,3-dihydrobenzothiazole (33) was dissolved with slight application of heat in 15 mL of DMF and upon cooling to 0 - 5°C, 2.4 mL (38 mmol) of Mel were added and the mixture was stirred until homogeneous. 0.28 g (7 mmol) of NaH (60 % dispersion in mineral oil) was added quickly in one aliquot and no color change was seen. A pale yellow color was seen after 10 minutes along with slight solid formation. 3 mL of DMF were added and the stirring continued for 3 hours at the end of which the reaction was quenched by pouring into 200 mL of ice cold water. A pale yellow oil settled on the bottom; this was washed with water and hexanes and dried to obtain 1.7 g (85%) of gummy solid. Trituration with EtOH yielded an off white soild which was crystallized from 95% EtOH, mp 163.8 - 164.8°C. FTIR (cm\(^{-1}\)) : 2237 (v. weak, CN), 1657 (carbonyl), 1471 (arom. C=C), 1350 (CH\(_3\) antisym. def.) and 741 (o-disubs. benzene). \(^1\)H NMR (CDCl\(_3\)) : 7.65 - 7.34 \(\delta\) (m, 4H), 7.15 \(\delta\) (d, 1H, J = 7.9 Hz), 6.98 \(\delta\) (dd, 1H, J = 7.9 Hz, 6.4 Hz), 6.75 \(\delta\) (dd, 1H, J = 6.4 Hz, 7.0 Hz), 6.02 \(\delta\) (d, 1H, J = 7.0 Hz) and 2.60 - 2.15 \(\delta\) (br. s, 3H). Elemental analysis, found (calcd. for C\(_{16}\)H\(_{11}\)N\(_2\)OS), C : 61.10 (61.04), H : 3.57 (3.52).
2-Cyano-2-methyl-3-o-toluyl-2,3-dihydrobenzothiazole (38):
1.91 g (6.8 mmol) of 2-cyano-3-o-toluyl-2,3-dihydrobenzothiazole (34) were dissolved with slight application of heat in 12 mL of DMF and upon cooling to 0 - 5°C, 2.1 mL (35 mmol) of MeI were added and the mixture stirred until homogeneous. 0.30 g (7.2 mmol) of NaH (60 % dispersion in mineral oil) was added quickly in one aliquot. No color change was seen along with the vigorous bubbling due to H₂ evolution. A pale yellow color was seen after 10 minutes along with slight solid formation. The stirring was continued for 4 hours at the end of which the reaction was quenched by pouring in 200 mL of ice cold water. A pale yellow lumpy solid settled on the bottom; it was washed with water and hexanes and dried to obtain 1.7 g (85%) of gummy solid. Trituration with EtOH yielded an off white solid which was crystallized from 95% EtOH, mp 110.8 - 111.8°C. FTIR (cm⁻¹): 2236 (v. weak, CN), 1659 (carbonyl), 1470 (arom. C=C), 1320 (CH₃ attached to benzene ring) and 737 (o-disubs. benzene). ¹H NMR (CDCl₃): 7.40 δ (m, 2H), 7.30 δ (m, 2H), 7.15 δ (d, 1H, J = 7.8 Hz), 6.95 δ (dd, 1H, J = 7.8 Hz, 8.7 Hz), 6.70 δ (dd, 1H, J = 8.7 Hz, 7.8 Hz) 5.90 δ (d, 1H, J = 7.8 Hz) and 2.45 δ (br. s, 6H). Elemental analysis, found (calcd. for C₁₇H₁₄N₂O₅), C: 69.45 (69.36), H: 4.81 (4.79).
2-Cyano-2-methyl-3-benzoyl-2,3-dihydrobenzothiazole
(39):
To a solution of 2.0 g (7.5 mmol) of 2-cyano-3-benzoyl-2,3-
dihydrobenzothiazole (19) in 20 mL dry DMF under N2 were added
1.9 mL (30.1 mmol) of Mel and the solution stirred for 20 minutes
at 0 - 5°C. Upon the addition of 0.33 g (8.3 mmol) of NaH (60 %
dispersion in mineral oil), vigorous bubbling was seen and a faint
yellow color was seen at the end of 30 minutes. The reaction
mixture was stirred for 2 h and quenched by pouring into 300 mL of
ice cold water. The pale oil was dissolved in 40 mL CH2Cl2,
 washed with water (10X, 50 mL each), dried over MgSO4 and upon
removal of the solvent yielded an off white oil, 2.22g (100%) which
was recrystallized from EtOAc/hex. to yield a white powdery solid,
mp 112 - 115°C. 1H NMR (CDCl3) : 7.71 - 7.63 δ (m, 2H), 7.63 - 7.52
δ (m, 1H), 7.51 - 7.39 δ ( m, 2H), 7.18 δ (d, 1H, J = 7.4 Hz), 6.96 δ
(dd, 1H, J = 6.8, 7.4 Hz), 6.78 δ (dd, 1H, J = 7.9, 7.4 Hz), 6.13 δ (d,
1H, J = 7.9 Hz) and 2.33 δ (s, 3H). Elemental analysis, found (calcd.
for C16H12N2OS), C : 68.68 (68.55), H : 4.30 (4.31).

2-Cyano-2-(p-chlorobenzyl)-3-benzoyl-2,3-dihydro-
benzothiazole (40):
To a solution of 5.01 g (18.83 mmol) of 2-cyano-3-benzoyl-2,3-
dihydrobenzothiazole (19) in 15 mL dry DMF under N2 were added
4.74 g (18.81 mmol) of p-chlorobenzyl iodide and the solution was
cooled to -23°C (CCl4 / dry ice slush) with stirring for 30 minutes.
Upon the addition of 0.61 g (21 mmol) of NaH (80% dispersion in mineral oil), a vigorous bubbling was seen and the mixture was stirred for 3 h. A light brown solid, 7.31 g (100%), was collected after quenching the reaction in ice cold water. Multiple recrystallizations from EtOH gave off white shiny needles, mp 172 - 174°C. FTIR (cm⁻¹) : 1655 (carbonyl), 1468 (arom. C=C), 1319 (methylene rock) and 748 (o-disubs. benzene). \(^1\)H NMR (CDCl₃) : 7.72 - 6.70 δ (m, 12H), 6.03 δ (d, 1H), 3.95 δ (d, 1H, J = 13.2 Hz) and 3.72 δ (d, 1H, J = 13.2 Hz). Elemental analysis, found (calcd. for C₂₂H₁₅ClN₂O₂S), C : 67.66 (67.59), H : 3.92 (3.87), N : 7.17 (7.17) and S : 8.21 (8.20).

2-Cyano-1-(o-tolyl)-1,2-dihydroquinoline (41) :

To a solution of 4.60 g of quinoline (35.2 mmol) in 22 mL of dry CH₂Cl₂ in a dry flask under N₂ were quickly added 4.80 mL of o-tolyl chloride (36.3 mmol) with a catalytic amount of AlCl₃ and the solution was stirred at ambient temperature for 20 minutes. 5.0 mL of Me₃SiCN (36.6 mmol) were then quickly added and after 5 minutes an exotherm lasted 20 minutes. The reaction was complete in 6 h as indicated by TLC (5% EtOAc : 95% hexanes). The volatiles were removed to obtain a pale honey colored oil, 9.72 g (100%). Multiple recrystallizations yielded shiny white crystals, mp 131 - 132°C. FTIR (cm⁻¹) : 2225 (v. weak, nitrile), 1656 (amide carbonyl), 1489 (phenyl), 1457 (CH₂ scissor) and 762 (o-disubstituted phenyl). \(^1\)H NMR (CDCl₃) : 7.8 - 5.9 δ (m, 11H) and 3.4
- 1.2 δ (br., 3H). Elemental analysis, found (calcd. for C_{18}H_{14}N_{2}O), C : 78.85 (78.81), H : 5.19 (5.14) and N : 10.22 (10.21).

Open chain bis(aminonitrile)s 47 - 51 were all synthesized by an aqueous one-pot multi-step synthetic procedure. The typical procedure is given for 47 and spectral details for 48 - 51 are included.

**N,N'-Bis(α-cyanobenzyl)-1,2-ethanediamine (47):**
To a solution of 19.8 g (192 mmol) of NaHSO₃ in 300 mL of water were added 19.6 mL (192 mmol) of benzaldehyde and the mixture was stirred vigorously for two h to give a homogeneous colorless solution of the bisulfite addition product. 5.8 g (96 mmol) of 1,2-ethanediamine were then added in one aliquot and the stirring continued for two h to give a colorless solution to which were added 9.6 g (192 mmol) of NaCN in one aliquot. The stirring was then continued for 8 h, the sticky solid was extracted with CH₂Cl₂. The organic layer was washed with water (6x, 100 mL each), dried over Na₂SO₄ and concentrated to give a pale oil that crystallized upon standing, 27.8 g (100%). Recrystallization from EtOAc gave shiny white needles, mp 118 - 119.5°C [lit.¹⁰² 118 - 123°C (dec.)]. FTIR (cm⁻¹) : 3344 (sh., NH), 2233 (str., CN), 1495 (phenyl), 1451 (CH₂ scissor), 1129 (str., C-N) and 737, 697 (monosubstituted benzene). ¹H NMR : 7.6 - 7.4 δ (m, 5H), 4.8 δ (s, 1H), 3.1 - 2.9 δ (m, 2H), 1.9 δ (br. s, 1H), 1.6 δ (br. s, 1H).
**N,N'-Bis(α-cyanobenzyl)-1,4-butanediamine (48):**

Yield = 100%, recrystallized from EtOAc, mp 89.0 - 90.5°C (lit. 101 88°C). FTIR (cm⁻¹): 3345 (NH), 2228 (nitrile), 1478 (phenyl), 1450 (CH₂ scissor), 1119 (C-N, amine), 744, 697 (monosubstituted benzene). ¹H NMR (CDCl₃): 7.6 - 7.4 δ (m, 5H), 4.8 δ (s, 1H), 2.9 - 2.7 δ (m, 2H), 1.7 δ (br. s, 2H) and 1.6 δ (br. s, 1H).

**N,N'-Bis(α-cyanobenzyl)-1,6-hexanediamine (49):**

The crude product was isolated in 100% yield as an oil and was difficult to recrystallize (lit. 101 68°C). FTIR (cm⁻¹): 3316 (NH), 2226 (nitrile), 1482 (phenyl), 1453 (CH₂ scissor), 1114 (C-N, amine), 752, 695 (monosubstituted benzene). ¹H NMR (CDCl₃): 7.50 - 7.30 δ (m, 5H), 4.75 δ (s, 1H), 2.85 - 2.60 δ (m, 2H) and 1.60 - 1.30 δ (m, 5H).

**N,N'-Bis(α-cyano-p-methoxybenzyl)-1,2-ethanediamine (50):**

Yield = 99%. Recrystallization from EtOAc yielded an off white powdery solid, mp 107 - 109°C (lit. 102 95 - 97°C (dec.)). FTIR (cm⁻¹): 3325 (NH, secondary amine), 2846 (aliphatic C-H stretch), 1588 (arom. C=C), 1467 (methylene scissor), 1244 (arom.-alkyl ether), 1177 (C-N, amines) and 818 (p-disubstituted benzene). ¹H NMR (CDCl₃): 7.42 δ (d, 2H, J = 6.9 hz), 6.91 δ (d, 2H, J = 6.9 hz),
4.74 δ (s, 1H), 3.85 δ (s, 3H), 3.10 - 2.90 δ (m, 2H) and 1.80 δ (br., 1H).

**N,N'-Bis(α-cyano-p-fluorobenzyl)-1,2-ethanediamine (51):**

Yield = 100%. Recrystallized from ethyl acetate, mp 123.8 - 125.8°C. FTIR (cm⁻¹) : 3317 (NH), 2222 (nitrile), 1604, (arom. C=C), 1489 (phenyl), 1245 (C-N amine) and 826 (p-disubstituted benzene). ¹HNMR (CDCl₃) : 7.5 δ (m, 2H), 7.1 (m, 2H), 4.9 (s, 1H), 3.0 (m, 2H) and 1.9 (br. s, 1H). Elemental analyses, found (calcd. for C₁₈H₁₆F₂N₄), C : 66.30 (66.24), H : 4.94 (4.94) and N : 17.22 (17.17).

Open chain bis(Reissert compound)s 52 - 57 were all synthesized by amidification of the bis(aminonitrile)s 47 - 50 in dry pyridine solution with the appropriate acid chloride. The typical procedure is given for 52 and spectral details for 53 - 57 are included.

**N,N'-Bis(α-cyanobenzyl)-N,N'-dibenzoyl-1,2-ethanediamine (52):**

5.8 g (20 mmol) of 47 were dissolved in 30 mL of dry pyridine under N₂ and cooled to 0 - 5°C. To the faint yellow solution were then added 5.0 mL (43 mmol) of benzoyl chloride. The solution was stirred overnight and quenched by pouring in 250 mL ice-water. The white solid was filtered, washed thoroughly with water and
dried, 10.2 g (100%). It was very insoluble in a variety of common solvents and therefore was purified by placing it in a Soxhlet extractor and extracting with acetone, mp 225 - 227°C. FTIR (cm⁻¹) : 2243 (v. weak, CN), 1659, 1644 (amide carbonyl), 1601 (aromatic C=C). ¹H NMR (CDCl₃) : 7.6 - 7.2 δ (m, 11H), 3.8 δ (br. d, 1H), 3.5 - 3.3 δ (br. s, 1H). Elemental analyses, found (calcd. for C₃₂H₂₆N₄O₂), C : 76.98 (77.09), H : 5.28 (5.26), N : 11.29 (11.24).

**N,N'-Bis(α-cyanobenzyl)-N,N'-dibenzoyl-1,4-butane-diamine (53)**:
Yield = 100%. Recrystallized from ethanol-DMF, mp 202.5 - 203.5°C. FTIR (cm⁻¹) : 2243 (v. weak, CN), 1636 (amide carbonyl), 1600 (aromatic C=C). ¹H NMR (CDCl₃) : 7.6 - 7.2 δ (m, 11H), 3.4 - 2.8 δ (br. s, 2H) and 1.5 - 0.9 (br. s, 1H). Elemental analyses, found (calcd. for C₃₄H₃₀N₄O₂), C : 77.28 (77.54), H : 5.78 (5.74), N : 10.57 (10.64).

**N,N'-Bis(α-cyanobenzyl)-N,N'-dibenzoyl-1,6-hexane-diamine (54)**:
Yield = 100%. Recrystallized from ethanol-DMF, mp 169.0 - 170.5°C. FTIR (cm⁻¹) : 2243 (v. weak, CN), 1639 (amide carbonyl), 1600 (aromatic C=C) and 1427 (CH₂ scissor). ¹H NMR (CDCl₃) : 7.6 - 7.4 δ (m, 11H), 3.4 - 2.9 δ (br. m, 2H) and 1.5 - 0.8 (br. s, 4H). Elemental analyses, found (calcd. for C₃₆H₃₄N₄O₂), C : 77.90 (77.95), H : 6.23 (6.18), N : 10.18 (10.10).
N,N'-Bis(α-cyanobenzyl)-N,N'-bis(t-butylcarbonyl)-1,6-hexanediamine (55):
Yield = 77%. Recrystallized from absolute ethanol, mp 162 - 163°C. FTIR (cm⁻¹) : 1628 (amide carbonyl), 1479 (phenyl) and 1405, 1210 (t-butyl) and 752 (monosubstituted benzene). ¹H NMR (CDCl₃) : 7.50 - 7.35 δ (s, 5H), 6.65 δ (s, 1H), 3.55 - 3.40 (m, 1H), 3.15 - 3.00 (m, 1H) and 1.8 - 0.9 (m, 13H). Elemental analyses, found (calcd. for C₃₂H₄₂N₄O₂), C : 74.61 (74.67), H : 8.14 (8.22), N : 11.00 (10.88).

N,N'-Bis(α-cyanobenzyl)-N,N'-bis(p-t-butylbenzoyl)-1,6-hexanediamine (56):
Yield = 42%. Recrystallized from ethanol-DMF, mp 174.5 - 175.5°C. FTIR (cm⁻¹) : 1643 (amide carbonyl), 1490 (phenyl), 1405, 1189 (t-butyl), 843 (p-disubstituted benzene) and 734, 696 (monosubstituted benzene). ¹H NMR (CDCl₃) : 7.8 - 5.5 δ (br. m, 10H), 3.5 - 2.9 δ (br. m, 2H) and 1.7 - 0.7 δ (br. m, 13H). Elemental analyses, found (calcd. for C₄₄H₅₀N₄O₂), C : 79.19 (79.24), H : 7.50 (7.56), N : 8.49 (8.40).

N,N'-Bis(α-cyano-p-methoxybenzyl)-N,N'-bis(p-t-butylbenzoyl)-1,2-ethanediameine (57):
Yield = 95%. Crystallization from 3:1 EtOH:DMF (v:v) gave shiny white crystals, mp 251 - 252°C. FTIR (cm⁻¹) : 1651 (amide
carbonyl), 1612 (arom. C=C), 1253 (Ar-O-C) and 852 (p-disubs. benzene). $^1$H NMR (CDCl$_3$) : 7.7 - 5.8 $\delta$ (m, 9H), 3.8 $\delta$ (s, 3H), 3.7 - 2.7 $\delta$ (br. s, 2H) and 1.35 $\delta$ (s, 9H). Elemental analysis, found (calcd. for C$_{42}$H$_{44}$N$_4$O$_2$), C : 75.28 (75.19), H : 6.79 (6.91) and N : 8.54 (8.35).

Bis(Schiff base)s 58 and 59 were synthesized by an aqueous synthetic route rather than the conventional azeotropic route. A typical synthesis is given for 58 and spectral details for 59 are included.

**N,N'-bisbenzyldiene-trans-1,4-diaminocyclohexane (58)**: (by the aqueous route)

To an aqueous solution of NaHSO$_3$ (7.3 g, 72 mmol) were added 7.6 mL (69 mmol) of benzaldehyde and the mixture was stirred for 2 h to produce a homogeneous solution. 4 g (34.5 mmol) of trans-1,4-diaminocyclohexane were dissolved in 50 mL of water and the solution was added to the reaction mixture over a period of 1 h in 15 aliquots and the reaction was stirred for 8 h more. The off-white crude was collected and dried to yield 3.5 g (35%) product, mp 165 - 170°C. Crystallization from EtOH-toluene yielded shiny white crystals, mp 172 - 174°C. FTIR (cm$^{-1}$) : 1643 (imine C=N), 1619 (arom. C=C), 1579 (phenyl), 1449 (methylene scissor) and 758, 691 (unsubstituted benzene). $^1$H NMR (CDCl$_3$) : 8.4 $\delta$ (s, 1H), 7.8 $\delta$ (m, 2H), 7.4 $\delta$ (m, 3H), 3.4 - 3.2 $\delta$ (m, 1H) and 2.0 - 1.7 $\delta$ (m,
4H). Elemental analyses, found (calcd. for C_{20}H_{22}N_{2}), C : 82.49 (82.72), H : 7.62 (7.64), N : 9.58 (9.64).

**N,N'-Bis(p-fluorobenzylidene)-trans-1,4-diaminocyclohexane (59):**
Yield = 17%. Crystallization from EtOH-toluene yielded shiny white crystals, mp 179 - 181°C. FTIR (cm\(^{-1}\)) : 1645 (imine C=N), 1599 (arom. C=C), 1505 (phenyl), 1452 (methylene scissor) and 837 (p-disubs. benzene). \(^1\)H NMR (CDCl\(_3\)) : 8.4 δ (s, 1H), 7.8 - 7.7 δ (m, 2H), 7.1 - 7.0 δ (m, 2H), 3.4 - 3.2 δ (m, 1H) and 2.0 - 1.7 δ (m, 4H). Elemental analyses, found (calcd. for C_{20}H_{20}F_{2}N_{2}), C : 73.39 (73.60), H : 6.17 (6.18), N : 8.51 (8.58).

The multi-step, one-pot aqueous route that was successfully used to synthesize 47 - 51 failed with 61 - 66; a typical procedure is given below for 64. Therefore, aromatic bis(aminonitrile)s 61 - 66 were synthesized by a one step, one-pot procedure involving the reflux of an ethanolic solution of the aromatic diamine and appropriate cyanohydrin. A typical procedure is given for 61.

**Attempted synthesis of N, N'-bis(α-cyanobenzyl)-4,4'-oxydianiline (64) (by the aqueous one-pot route):**
To a solution of 4.9 g (47 mmol) of sodium bisulfite in 50 mL of water were added 5.1 g (47 mmol) of benzaldehyde and the mixture stirred for two h when a homogeneous clear solution appeared.
g (23.5 mmol) of 4,4'-oxydianiline were then added and the mixture was stirred for two h; a thickening of the reaction mixture was observed. 2.3 g (47 mmol) of sodium cyanide were then added in one aliquot and a clearing of the reaction mixture was observed in the first 20 m. In 15 more minutes, precipitation of the reaction product was seen. This was dissolved in CH₂Cl₂, washed with water (6x), dried over sodium sulfate and the solvent was stripped off to obtain 7.8 g (78%) of a sticky solid. The ¹H NMR spectrum showed peaks corresponding to the bis(Schiff base), starting material and the product. The amounts according to the ¹H NMR spectrum were ca. 50% for the bis(Schiff base), ca. 13% for the expected product and 37% starting material.

**N, N'-Bis(α-cyanoethyl)-1,4-diaminobenzene (61):**

To a solution of 2.16 g (20 mmol) of 1,4-diaminobenzene in 25 mL ethanol were added 2.9 g (40 mmol) lactonitrile in one aliquot and the solution refluxed for 11 h. A light gray precipitate was formed upon cooling the solution. The product was collected and the yield was 3.6 g (87%), mp (crude) = 183 - 189°C (dec.). Purification was done by washing the crude solid with 95% ethanol and drying in a vacuum pistol. FTIR (cm⁻¹) : 3244 (NH), 2223 (nitrile), 1524 (phenyl), 1242 (aromatic amines), 1161 (C-N of amines) and 838 (p-disubstituted benzene). ¹H NMR (dmso-d₆) : 6.70 δ (s, 2H), 5.65 δ (d, 1H, J = 7.2 hz), 4.55 - 4.40 δ (m, 1H) and 1.55 δ (br. d, 3H, J = 7.2
hz). Elemental analyses, found (calcd. for C_{12}H_{14}N_{4}), C : 67.29 (67.26), H : 6.61 (6.59).

**N. N'-Bis(α-cyanobenzyl)-1,4-diaminobenzene (62):**
Yield = 83%, mp (crude) = 182 - 187 °C (dec., lit.\textsuperscript{106} 163 °C). FTIR (cm\textsuperscript{-1}) : 3371 (NH), 2234 (weak, nitrile), 1516, 1492 (phenyl), 1270 (C-N, aromatic amines), 816 (p-disubstituted benzene) and 750, 695 (monosubstituted benzene). \textsuperscript{1}H NMR (CDCl\textsubscript{3}) : 7.6 δ (m, 2H), 7.5 - 7.4 δ (m, 3H), 6.8 δ (s, 2H), 5.4 δ (s, 1H), 3.9 - 3.7 δ (br. s, 1H).

**N. N'-Bis(α-cyanoethyl)-4,4' -oxydianiline (63):**
Yield = 55%. Fractional crystallization from ethyl acetate-hexanes gave an off-white solid, mp = 132.0 - 133.5 °C. Two more crystallizations gave an off-white solid, mp = 132.0 - 134.5 °C. FTIR (cm\textsuperscript{-1}) : 3332 (NH stretch), 2237 (v. weak, nitrile stretch), 1501 (aromatic C= C) and 1232 (aromatic C= O). \textsuperscript{1}H NMR (CDCl\textsubscript{3}) : 6.95 δ (d, 2H, J = 7.5 Hz), 6.71 δ (d, 2H, J = 7.5 Hz), 4.25 δ (m, 1H), 3.72 δ (d, 1H, J = 6.9 Hz) and 1.65 δ (d, 3H, J = 6.9 Hz). Elemental analyses, found (calcd. for C\textsubscript{18}H_{18}N\textsubscript{4}O), C : 70.37 (70.55), H : 5.96 (5.92), N : 18.18 (18.29).

**N. N'-Bis(α-cyanobenzyl)-4,4' -oxydianiline (64):**
Yield = 62%. Recrystallization could not be done due to gumming up of the product in a variety of common solvents. \textsuperscript{1}H NMR (CDCl\textsubscript{3}) :
7.7 - 7.4 δ (m, 5H), 6.9 δ (d, 2H, J = 9.3 hz), 6.8 δ (d, 2H, J = 9.3 hz), 5.4 δ (s, 1H) and 4.3 - 3.2 δ (br. s, 1H).

N. N'-Bis(α-cyanoethyl)-4,4'-methylenedianiline (65):
Yield = 75%. Crystallization from 95% ethanol gave off-white solid, mp = 142.0 - 143.5°C. One more crystallization after carefully removing the pale yellowish green oil by slow addition of hexanes to the solution in hot ethyl acetate gave an off-white solid, mp = 144 - 145°C. FTIR (cm⁻¹) : 3361 (NH), 2229 (nitrile), 1617 (arom. C=C), 1521 (phenyl), 1161 (C-N of amines) and 801 (p-disubstituted benzene). 1H NMR (CDCl₃) : 7.05 δ (d, 2H, J = 8.1 hz), 6.65 δ (d, 2H, J = 8.1 hz), 4.25 δ (m, 1H), 3.85 δ (s, 1H), 3.71 δ (d, 1H, J = 6.7 hz) and 1.65 δ (d, 3H, J = 6.7 hz). Elemental analysis, found (calcd. for C₁₉H₂₀N₄), C : 74.26 (74.97), H : 6.64 (6.62), N : 18.30 (18.41).

N. N'-Bis(α-cyano benzyl)-4,4'-methylenedianiline (66):
Yield = 79%. Crude mp = 51 - 57°C. Numerous efforts to crystallize from various solvents including EtOH, EtOAc, CHCl₃ and THF/hexane failed as these invariably yielded gums. 1H NMR (CDCl₃) : 7.7 - 7.4 δ (m, 5H), 7.1 δ (d, 2H, J = 8.6 hz), 6.7 δ (d, 2H, J = 8.6 hz), 5.4 δ (s, 1H) and 4.1 - 3.8 δ (m, 3H).
N,N'-Bis(α-cyanobenzyl)-N,N'-bis-p-toluoyl-1,4-diamino-benzene (67):
The procedural details for the synthesis of this open chain aromatic bis(Reissert compound) are the same as for 52 - 57. Yield = 100%. Recrystallization from ethanol-DMF yielded white shiny crystals, mp 231.5 - 232.5°C. FTIR (cm⁻¹) : 1664 (amide carbonyl), 1611 (arom. C=C), 1311 (CH₃ attached to benzene) and 829 (p-disubstituted benzene). ¹H NMR (CDCl₃) : 7.4 - 7.1 δ (m, 8H), 6.9 δ (m, 2H), 6.7 - 6.4 δ (br. s, 2H) and 2.4 δ (s, 3H). Elemental analysis, found (calcd. for C₃₈H₃₀N₄O₂), C : 79.52 (79.42), H : 5.35 (5.26), N : 9.74 (9.75).

N-(α-Cyano-p-anisyl)methylamine (68a):
To a solution of 11.0 g (100 mmol) of NaHSO₃ in 150 mL of water were added 12.5 mL (100 mmol) of p-anisaldehyde and the mixture was stirred for 2 h. Upon the addition of 8.00 g (100 mmol) of MeNH₂ (40 wt. % solution in water) in one aliquot and stirring, a brief milkiness was seen and a homogeneous clear solution resulted after 2 h of stirring. NaCN (5.5 g, 105 mmol) was added in one aliquot and the mixture stirred overnight to obtain a white chunky solid, which when dried looked faint yellow and weighed 16 g (91%) mp 40 - 43°C. Attempts to recrystallize the crude solid from EtOH, THF and EtOAc/hexane were unsuccessful, probably due to the low melting point. ¹H NMR (CDCl₃) : 7.45 δ (d, 2H), 6.95 δ (d, 2H), 4.71 δ (s, 1H), 3.82 δ (s, 3H), 2.55 δ (s, 3H) and 1.65 - 1.35 δ.
(br. s, 1H). This is a new compound but due to difficulty in purification, it was decided to convert it to the open chain Reissert compound 68 and characterize 68 in more detail.

**N-(p-t-Butylbenzoyl)-N-(α-cyano-p-anisyl)methylamine (68)**:

11.7 g (67.1 mmol) of N-(α-cyano-p-anisyl)methylamine were dissolved in 45 mL of dry pyridine in a dry flask under N₂ and 14.0 g (73.2 mmol) of p-t-butylbenzoyl chloride were added in one aliquot and the stirring was continued. An exotherm was felt in 5 min which lasted for a good 25 min. The reaction mixture was stirred for 10 h, diluted with 20 mL of pyridine and quenched in 700 mL ice cold water (8% HCl) in a blender. The brown sticky mass which separated out was dissolved in EtOAc and dried over MgSO₄. Upon removal of the solvent, this yielded 20.8 g (95%) of red brown oil which was triturated with 95% EtOH to yield a yellow solid. Recrystallization of this solid from 95% EtOH (with decolorizing charcoal) yielded off white shiny crystals, mp 77 - 80°C. Multiple recrystallizations from the same solvent yielded shiny off white crystals, mp 83 - 84°C. FTIR (cm⁻¹): 1643 (amide carbonyl), 1512 (phenyl), 1248 (Ar-O-C) and 809 (p-disubstituted benzene). ¹H NMR (CDCl₃): 7.51 δ (m, 8H), 6.95 δ (d, 2H), 3.85 δ (s, 3H), 2.92 δ (s, 3H) and 1.38 δ (s, 9H). Elemental analysis. found (calcd. for C₂₁H₂₄N₂O₂), C: 75.04 (74.97), H: 7.21 (7.19), N: 8.36 (8.33).
Attempted rearrangement of N-(p-t-butylbenzoyl)-N-(α-cyano-p-anisyl)methylamine (68):

1.96 g (5.80 mmol) of 68 were dissolved in 10 mL of dry DMF and the solution equilibrated at 95°C for 10 minutes. Addition of 0.26 g (6.39 mmol) of NaH (60% dispersion in mineral oil) caused evolution of H₂ and a blood red color developed instantly. The stirring was continued for 48 h and the solution was quenched in 100 mL ice-cold water. The off-white crude solid was dried and after turning to a sticky mass, it resolidified, weight = 1.87 g (96%). Recrystallization from ethanol afforded white needle crystals, mp 82 - 83°C. A mixed melting point with authentic 68 was recorded at 82.0 - 83.5°C. FTIR and ¹H NMR spectra were identical to authentic 68.

Attempted reaction of N-(p-t-butylbenzoyl)-N-(α-cyano-p-anisyl)methylamine (68) with bis(p-chlorophenyl) sulfone:

3.51 g (10.42 mmol) of N-(p-t-butylbenzoyl)-N-(α-cyano-p-anisyl)methylamine (68) were dissolved in 15 mL of dry DMF in a N₂ atmosphere along with 1.50 g (5.21 mmol) of bis(chlorophenyl) sulfone. Upon the addition of 0.46 g (23 mmol) of NaH (60% dispersion in mineral oil), a deep red color and the evolution of H₂ was seen. The reaction mixture was stirred for 120 h at ambient temperature at the end of which a TLC (30% EtOAc : 70% hexanes) showed a considerable amount of the starting material.
Attempted reaction of $N$-(p-t-butylibenzoyl)-$N$-(α-cyano-p-anisyl)methylamine (68) with bis(fluorophenyl) sulfone:

An identical procedure with slightly different amounts of starting materials at ambient temperature gave an incomplete reaction at the end of 72 h by TLC.

Repeat above at 90°C: Synthesis of 4,4'-Bis[α-cyano-α-(N-methyl-N-p-t-butylibenzoylamino)-p-methoxybenzyl]-diphenyl sulfone (69):

2.94 g (8.75 mmol) of the open chain Reissert compound 68 and 1.13 g (4.38 mmol) of the bis(4-fluorophenyl) sulfone were dissolved in 10 mL of DMF in a dry flask under N₂ and 0.39 g (9.13 mmol) of NaH (60% dispersion in mineral oil) was added quickly, whereupon a deep red color and evolution of H₂ were seen. The temperature of the reaction mixture was raised to 90°C and the stirring was continued for 48 h, at the end of which TLC (30% EtOAc: 70% hexanes & 20% EtOAc: 80% hexanes) showed only one sharp spot corresponding to the product. The reaction was quenched in 125 mL of ice cold water. After filtration, the pale brown solid was dissolved in CH₂Cl₂ and precipitated into 10 fold excess hexanes. The pale brown powder, mp 162 - 185°C (diastereomeric), showed a sharp single spot on the TLC (30% EtOAc: 70% hexanes) and did not recrystallize from
EtOAc/hexanes, benzene, THF or toluene/hexanes. The crude solid was purified by column chromatography (silica gel, gradient elution with 25% EtOAc / 75% hexanes as the highest polarity solvent mixture) to obtain an off-white solid, mp 170 - 225°C. FTIR (cm⁻¹) : 1662, 1654 (amide carbonyl), 1511 (phenyl), 1453 (-CH antisymmetric deformation), 1258 (Ar-O-C) and 1327 (sulfone). ¹H NMR (CDCl₃) : 7.90 δ (d, 2H, J = 8.4 Hz), 7.62 δ (m, 4H), 7.47 δ (d, 2H, J = 8.4 Hz), 7.40 δ (d, 2H, J = 8.8 Hz), 6.90 δ (d, 2H, J = 8.8 Hz), 3.81 δ (s, 3H), 2.83 δ (s, 3H) and 1.35 δ (s, 9H). Elemental analyses, found (calcd. for C₅₄H₅₄N₄O₆S), C : 72.52 (73.11), H : 6.15 (6.14), N : 6.08 (6.32) and S : 3.58 (3.62).

**Attempted rearrangement of N,N'-Bis(α-cyanobenzyl)-N,N'-dibenzoyl-1,6-hexanediamine (54)**:

1.51 g (2.71 mmol) of 54 were dissolved in 15 mL of dry DMF under N₂ at 75 - 80°C and upon addition of 0.24 g (5.61 mmol) of NaH (60% dispersion in mineral oil), a blood red color was seen with vigorous evolution of H₂. The stirring was continued for 72 h, at the end of which the deep red color was still visible. The reaction was quenched in 200 mL ice-cold water. The off-white solid was dried and after turning to a sticky mass, it resolidified, weight = 1.39 g (92%). Two recrystallizations from ethanol-DMF yielded a white solid, mp 169 - 171°C. FTIR and ¹H NMR spectra were identical to authentic 54. Elemental analyses, found (calcd. for 54 C₃₆H₃₄N₄O₂), C : 77.42 (77.95), H : 6.19 (6.18), N : 10.19 (10.10).
Polymer syntheses (from Reissert monomers):
The monomers were weighed accurately on an analytical balance to
a stoichiometric equivalence and dissolved in DMF. NaI was added
and then NaH [2.2 equivalents per bis(Reissert monomer)] was
added. After stirring for over 3 days at ambient temperature, the
mixture was quenched in ice-water. The resulting polymers were
purified by dissolving in DMF-THF (1:6) and precipitation into
tenfold excess H$_2$O-MeOH (2:1 v/v) three times and dried in vacuum
20° below T$_g$.

Synthesis of (70) by the use of diiodoalkane:
3.9631 g (7.1504 mmol) of 49 were dissolved in 18 mL of dry DMF
in a flame dried flask with the application of heat under N$_2$. The
colorless solution was allowed to cool to ambient temperature and
then 2.8163 g (7.1514 mmol) of 1,10-diiododecane were quickly
added and the mixture stirred under N$_2$. After about 15 min, 0.63 g
(15.8 mmol) of NaH (60% suspension in oil) were quickly added and
evolution of H$_2$ and a deep red color (of the dianion) were
immediately noticeable. An exotherm was felt over a period of 15
m. The reaction mixture had completely gelled in about 18 h
(looked like an orange 'jello'). The gel was dissolved in 80 mL of
DMF with heating and quenched by pouring into 12 fold excess
brine-ice-MeOH (3:8:1 v/v) in a high speed blender to yield 4.97 g
(100%) of pale yellow solid. Precipitation from THF-DMF (8:1 v/v)
into 12 fold H$_2$O-MeOH (2:1 v/v) was carried out three times. The resulting pale brown polymer was dried at 50°C in a vacuum oven overnight. FTIR (cm$^{-1}$) : 1654, 1647 (amide carbonyl), 1612 (phenyl) and 1446 (methylene scissor). $^1$H NMR (CDCl$_3$) : 7.8 - 7.0 δ (m, 5H) and 3.6 - 0.2 δ (br. m, 8H). Intrinsic viscosity (NMP, 29°C) : 0.48 dl/g. TGA : 10% weight loss (in air) at 305°C and a complete loss of material occurs at 600°C. DSC analysis displayed a Tg of 72°C. Absolute GPC (NMP, 60°C) yielded an $M_n$ of 14K and $M_W$ of 162K; $\alpha$ (Mark-Houwink's constant) = 0.48.

**Synthesis of (70) by the use of dibromoalkane and NaI:** 4.0100 g (7.2304 mmol) of 49 were dissolved in 31 mL of dry DMF in a flame dried flask with the application of heat under N$_2$. The colorless solution was allowed to cool to ambient temperature and then 2.1704 g (7.2324 mmol) of 1,10-dibromodecane were quickly added along with 3.5 g (23 mmol) of NaI and the mixture stirred under N$_2$. After about 15 min, 635 mg (15 mmol) of NaH (60% suspension in oil) were quickly added, evolution of H$_2$ and a deep red color (of the dianion) were immediately noticeable. The reaction mixture was stirred for 72 h at ambient temperature. An increase in viscosity was noted over the reaction time. The reaction was quenched by pouring into 12 fold excess brine-ice-MeOH (3:8:1 v/v) in a high speed blender to yield 5.00 g (100%) of pale yellow solid. Precipitation from THF-DMF (8:1 v/v) into 12 fold H$_2$O-MeOH (2:1 v/v) was carried out three times. FTIR and $^1$H
NMR spectra were analogous to 70 made by the use of diiododecane. TGA: 10% weight loss at 305°C. Intrinsic viscosity (NMP, 25°C) was determined to be 0.35 d/l/g. Absolute GPC (NMP, 60°C) yielded an $M_n$ of 7700 and $M_W$ of 33000; $\alpha$ (Mark-Houwink's constant) = 0.47.

$\alpha$-(N-Morpholino)benzyl cyanide (80):
NaHSO$_3$, 10.5 g (100 mmol), was dissolved in 150 mL of water and 11 mL (100 mmol) of benzaldehyde were added and the mixture was stirred for 2 h until homogeneous. 8.7 mL (100 mmol) of morpholine were added in one aliquot and the stirring was continued for two more h. Finally, 5 g (100 mmol) of NaCN were added and the solution was stirred for 6 h, at the end of which shiny, white solid had precipitated out. The yield was 19.8 g (98%), mp = 66.8 - 67.8°C. It was recrystallized from 150 mL (1:1) hexane : EtOAc to yield shiny, white platelets, mp = 67 - 68°C (lit.$^{134}$ 68 - 70°C). FTIR (cm$^{-1}$) : 2228 (nitrile), 1454 (methylene scissor), 1117 (C-O-C), 739, 703 (monosubstituted benzene). $^1$H NMR (CDCl$_3$) : 7.55 - 7.35 $\delta$ (m, 5H), 4.82 $\delta$ (s, 1H), 3.78 - 3.65 $\delta$ (m, 4H), 2.59 - 2.56 $\delta$ (t, 4H, J = 4.7 Hz).

4.4'-Bis($\alpha$-cyano-$\alpha$-N-morpholino)benzyl Diphenyl Sulfone (81):
1.63 g (8.07 mmol) of $\alpha$-(N-morpholino)benzyl cyanide (80) was dissolved in 12.5 mL of dry DMF along with 1.04 g (4.04 mmol) of
4,4'-difluorophenyl sulfone in a dry round bottom flask under N₂. After 15 m of stirring to homogenize the solution, 366 mg (17.7 mmol) of 60% NaH were added in one aliquot and immediately the vigorous bubbling of H₂, a slight exotherm and a change in color to greenish were observed. Within about 15 m, the color had changed to pale honey and stayed that for the 12 h of stirring that was allowed. Upon quenching the reaction mixture into 125 mL ice-water, a white precipitate was collected and dried, yield = 2.51 g (100%), mp 125 - 165°C (diastereomeric). The crude sample was crystallized thrice from DMF - EtOH to give a white, amorphous solid, mp 222 - 223.5°C; found (calcd. for C₃₆H₃₄N₄O₄S): C : 69.15 (69.88), H : 5.46 (5.54), N : 9.04 (9.06), S : 6.01 (5.18). Apparently some decomposition and/or hydrolysis had taken place and hence the sample was recrystallized from benzene - hexane 3 times to yield white, shiny flakes mp 145 - 220°C, found: C : 70.96, H : 5.65, S : 4.89. This analysis fits very well with C₃₆H₃₄N₄O₄S(1/2 C₆H₆) i.e., with 1 molecule of benzene as solvent of crystallization for every two moles of the compound. Calculated for C₃₆H₃₄N₄O₄S/0.5C₆H₆): C : 71.21, H : 5.67, S : 4.87. FTIR (cm⁻¹): 1450 (methylene scissor), 1324, 1161 (sulfone), 1117 (C-O-C), 747 (monosubstituted benzene). ¹H NMR (CDCl₃): 7.95 - 7.85 δ (m, 4H), 7.65 - 7.55 δ (m, 2H), 7.4 - 7.2 δ (m, 2H), 3.8 - 3.7 δ (m, 4H), 2.7 - 2.5 δ (m, 4H).
4,4'-Bis(benzoyl)diphenyl Sulfone (82):
1 g of 4,4'-bis(α-cyano-α-N-morpholino)benzyl diphenyl sulfone (81) was suspended in 25 mL of 70% AcOH and the mixture was refluxed. Within about 10 min, the solid had dissolved and in 5 more min, white solid started separating out. The mixture was cooled and the solid collected. Dry wt. = 0.63 g (83%), mp 192 - 195°C. It was recrystallized thrice from toluene-EtOH (9:1) to give shiny, colorless, fluffy crystals, mp 203.5 - 204°C. FTIR (cm⁻¹) : 1668 (CO), 1654 (C=C arom.), 1331, 1165 (sulphone) and 704 (monosubstituted benzene).¹H NMR (CDCl₃) : 8.11 δ (d, 2H, J = 8.2 hz), 7.92 δ (d, 2H, J = 8.2 hz), 7.79 δ (d, 2H, J = 7.5 hz), 7.65 δ (dd, 1H, J = 7.5, 7.3 hz), 7.51 δ (dd, 2H, J = 7.5, 7.3 hz). Elemental analysis, found (calcd. for C₂₆H₁₈O₄S), C : 73.16 (73.22), H : 4.30 (4.25), S : 7.77 (7.52).

4,4'-Bis[α-cyano-α-N-morpholinoazldyne]benzophenone (83):
1.85 g (9.16 mmol) of α-(N-morpholino)benzyl cyanide (80) was dissolved in 12 mL of dry DMF along with 1.00 g (4.58 mmol) of 4,4'-difluorobenzophenone in a dry round bottom flask under N₂. After 15 min of stirring, 405 mg (9.23 mmol) of 60% NaH were added to the solution in one aliquot and immediately the vigorous bubbling of H₂, a slight exotherm and a change in color to greenish were observed. Within about 15 min, the color had changed to pale honey which remained for the 12 h of stirring that was allowed.
Upon quenching the reaction mixture into 125 mL ice-water, a white precipitate was collected and dried, yield = 2.67 g (100%), mp 80 - 122°C (diastereomeric). The crude sample was purified by column chromatography (silica gel, gradient elution with 35% EtOAc / 65% hexanes as the highest polarity solvent mixture) and the white shiny solid, mp 125 - 142°C, was thoroughly dried (in vacuo at 110°C for 16 h) and elementally analyzed, found (calcd. for C₃₇H₃₄N₄O₃), C : 75.31 (76.27), H : 5.97 (5.88), N : 9.35 (9.61). Apparently some ethyl acetate was incorporated as solvent of crystallization because this analysis fits very well with C₃₇H₃₄N₄O₃(1/4 CH₃CO₂C₂H₅), i.e., with 1 molecule of ethyl acetate as solvent of crystallization for every four moles of the compound. Calculated for C₃₇H₃₄N₄O₃/0.25CH₃CO₂C₂H₅, C : 75.48, H : 6.00, N : 9.27. FTIR (cm⁻¹) : 2227 (v. weak, nitrile), 1734 (CO), 1664 (benzophenone derivative), 1606, 1492 (phenyl), 1449 (methylene scissor), 1117 (C-O-C), 1008 (alicyclic ring vibration) and 754, 703 (monosubstituted benzene). ¹H NMR (CDCl₃) : 7.85 - 7.65 δ (m, 6H), 7.45 - 7.20 (m, 3H), 3.90 - 3.70 δ (m, 4H), 2.75 - 2.45 δ (m, 4H).

4,4'-(Bisbenzoyl)benzophenone (84) :
A procedure analogous to synthesis of 82 from 81 was used to obtain 84 from 83 in 100% crude yield. Recrystallization from ethanol-DMF afforded shiny off-white crystals, mp 231 - 232°C (lit.¹¹³ 226 - 228°C). FTIR (cm⁻¹) : 1648 (CO), 793 (p-
disubstituted benzene) and 693 (monosubstituted benzene). $^1$H NMR (dmsO): 8.0 - 7.9 δ (m, 4H), 7.8 δ (m, 2H), 7.75 (d, 1H) and 7.6 (m, 2H).

α-(N-Morpholino)-p-fluorobenzyl cyanide (85):
Procedural details are the same as for the synthesis of 80. Yield = 91%, mp 60 - 62°C. Recrystallization from EtOAc/hexanes gave shiny white crystals, mp 64 - 64°C (lit.135 60 - 63°C). FTIR (cm$^{-1}$): 2228 (nitrile), 1611 (arom. C=C), 1507 (phenyl), 1457 (methylene scissor), 1229 (C-O-C alicyclic compounds) and 1113 (C-O-C). $^1$H NMR (CDCl3): 7.51 δ (m, 2H), 7.10 δ (m, 2H), 4.79 δ (s, 1H), 3.73 δ (m, 4H) and 2.57 δ (t, J = 4.5 hz, 2.5 hz).

α,α'-Dicyano-α,α'-bis(N-morpholino)-p-xylene (88):
To a solution of 11.05 g (100 mmol) of NaHSO3 in 300 mL of H2O were added 6.85 g (50 mmol) of terephthalaldehyde and the mixture was stirred for 2 h to give a solution. 9.15 mL (100 mmol) of morpholine were syringed in at this time and the solution was stirred for 2 h to give a solution of the bis(aminal). A solution of 5.2 g (100 mmol) of NaCN in 100 mL of H2O was then added over a period of two h and the stirring was continued for overnight. The pale cream solid was filtered and the dry crude solid weighed 16 g (100%), mp 224 - 227°C. It was recrystallized from DMF - EtOH twice to yield off-white, shiny crystals, mp 230 - 232°C. FTIR (cm$^{-1}$): 2230 (nitrile), 1510 (aromatic C=C), 1458 (methylene
scissor), 1112 (C-O-C) and 803 (p-disubstituted benzene). \(^1\)H NMR (CDCl₃) : 7.61 \(\delta\) (s, 2H), 4.85 \(\delta\) (s, 1H), 3.85 - 3.69 \(\delta\) (m, 4H), 2.7 - 2.52 \(\delta\) (m, 4H). Elemental analysis, found (calcd. for C₁₈H₂₂N₄O₂), C : 66.50 (66.23), H : 6.75 (6.80), N : 17.23 (17.17).

\(\alpha,\alpha'-\text{Dicyano-}\alpha,\alpha'-\text{bis(N-morpholino)-m-xylene} \ (89)\) :
To a solution of 11.2 g (100 mmol) of NaHSO₃ in 200 mL of H₂O were added 7.0 g (50 mmol) of isophthalaldehyde (98%) and the mixture stirred to homogeniety for 2 h. 10 mL (106 mmol) of morpholine were then added in one aliquot and the solution was stirred for 2 h. 5.5 g (105 mmol) of NaCN were then added in one aliquot and the beaker was transferred to a steam bath where it was heated for 8 h with occassional stirring. The filtered pale yellow solid was dried to yield 15.9 g (100%) of product which was recrystallized twice from 95% EtOH to obtain a pale yellow powder, mp 118.5 - 135.5°C. After thorough drying, it was placed in a fritted disc funnel, washed with 200 mL of 95% EtOH by gravity filtration and dried in a vacuum oven at 60°C overnight. FTIR (cm\(^{-1}\)) : 2228 (v. v. weak, CN), 1456 (phenyl), 1113 (C-O-C) and 760 (m-disubs. phenyl). \(^1\)H NMR (CDCl₃) : 7.70 \(\delta\) (d, 1H, \(J = 12\) hz), 7.59 \(\delta\) (d, 2H, \(J = 7.5\) hz), 7.50 - 7.44 \(\delta\) (m, 1H) 4.85, 4.84 \(\delta\) (1H, diastereomeric acidic proton), 3.9 - 3.7 \(\delta\) (m, 8H) and 2.8 - 2.5 \(\delta\) (m, 8H). Decoupling experiments consisted of irradiating the signal at 7.70 and then at 7.59. None of the peaks changed but a change in the coupling of the multiplet was observed when the 7.59 signal
was irradiated. This proved that the peak at 7.70 is \( H_1 \) and it is diastereomeric in nature. Elemental analysis, found (calcd. for \( C_{18}H_{22}N_4O_2 \), C : 66.23 (66.24), H : 6.80 (6.80) and N : 17.14 (17.17).

**Polymerization of Bis(4-fluorophenyl) Sulfone and \( \alpha,\alpha'-\text{Dicyano-}\alpha,\alpha'-\text{bis(N-morpholino)}\)-p-xylene (88) to form Poly(\( \alpha \)-aminonitrile) 90 :**

a) At ca. 105°C

3.0260 g (9.2711 mmol) of \( \alpha,\alpha'-\text{dicyano-}\alpha,\alpha'-\text{bis(N-morpholino)}\)-p-xylene 88 were dissolved along with 2.3574 g (9.2719 mmol) of bis(4-fluorophenyl) sulfone at 105°C (solution temperature) in a flame dried flask in dry DMF under \( N_2 \). Upon the addition of 830 mg (21 mmol) of 60% NaH, a vigorous bubbling and an immediate color change to deep maroon was seen. The solution was stirred for a total of 69 h and quenched in ice cold 5% aqueous NaCl to yield 4.97 g (99%) of a pale brown solid. Purification was done by dissolving it in 1:1 DMF:acetone and precipitation in water thrice. It was dried in a vacuum oven at 50°C overnight. TGA: 10% weight loss (in air) at 252°C followed by a 60% weight retention up to 500°C and complete weight loss at 600°C. FTIR (cm\(^{-1}\)) : 1676 (weak, CO), 1594 (arom. C=O), 1456 (methylene scissor), 1327, 1160 (sulfone) and 1117 (C-O-C). \(^1\)H NMR (CDCl\(_3\)) : 8.12 - 7.48 \( \delta \) (m, 12H), 3.97 - 3.63 \( \delta \) (br. s, 8H), 2.72 - 2.38 \( \delta \) (m, 8H). Absolute molecular weight
determination by GPC (in NMP at 60°C) yielded a $M_n$ of 345 g/mol and $M_W$ of 3300 g/mol respectively.

**b) At ca. 25°C**

3.6223 g (11.098 mmol) of $\alpha,\alpha'$-dicyano-$\alpha,\alpha'$-bis(N-morpholino)-p-xylene (88) were suspended along with 2.8216 g (11.098 mmol) of bis(4-fluorophenyl) sulfone at ambient temperature in a flame dried flask in 25 mL dry DMF under N$_2$. The mixture was stirred for 20 minutes and stayed heterogeneous because of the insolubility of the bis(aminonitrile) at the reaction temperature. Upon the addition of 1.02 g of 60% NaH (23.0 mmol), a vigorous bubbling and an immediate color change to deep maroon were seen. The solution was stirred for a total of 120 h and quenched into 250 mL ice cold 5% aqueous NaCl to yield 6.05 g (100%) of a pale yellow solid. Purification was done by dissolving it in DMF and precipitation in water once. Then it was twice precipitated from a CHCl$_3$ solution into ten fold excess ice cold MeOH. It was dried in a vacuum oven at 50°C overnight. TGA : 10% weight loss (in air) at 268°C followed by a 60% weight retention up to 500°C and complete weight loss at 640°C. DSC analysis showed no transitions up to 250°C, beyond which degradation started. FTIR (cm$^{-1}$) : 1678 (weak, CO), 1591 (arom. C=C), 1452 (methylene scissor), 1331, 1158 (sulfone) and 1114 (C-O-C). $^1$H NMR (CDCl$_3$) : 8.1 - 7.3 $\delta$ (m, 12H), 4.0 - 3.6 $\delta$ (br. s, 8H), 2.7 - 2.4 $\delta$ (m, 8H). An absolute
molecular weight determination by GPC yielded an $M_n$ of 5,000 g/mole and an $M_w$ of 15,000 g/mole.

**Poly(sulfonyl-p-phenylene carbonyl-p-phenylene carbonyl-p-phenylene)** (91):

1.00 g of 90 was refluxed in 25 mL 30% AcOH for 1.5 h. The resultant solid was filtered and dried thoroughly after washing exhaustively with water and MeOH, 0.65 g (100%). A reduction in total mass of 35% corresponds to quantitative hydrolysis of the aminonitrile groups. TGA showed a 10% weight loss at 491°C (i.e., an increase of 233°C relative to 90). It was insoluble in almost any solvent that was tried, including toluene, DMF, acetone and THF. FTIR (cm$^{-1}$): 1668 (carbonyl), 1594, 1500 (phenyl) and 1328, 1164 (SO$_2$). Absence of the prominent C-O-C peak at ca. 1117 cm$^{-1}$ indicated removal of the aminonitrile moiety. The first heat in DSC showed a $T_g$ of 199°C, a crystallization exotherm at 266°C and an (endothermic) melting transition at 415°C. After cooling at 10°C/min, the second heat displayed a $T_g$ of 228°C and a melting peak at 414°C. When heated after quench cooling, only a $T_g$ at 225°C was discernible. Wide angle x-ray analysis (appendix 2, pg. 212) was indicative of semicrystallinity in the polymer as isolated from the reaction mixture.

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Polymerization of Bis(4-fluorophenyl) Sulfone and \(\alpha,\alpha'-\)
Dicyano-\(\alpha,\alpha'-\)bis(N-morpholino)-m-xylene (89) to form
Poly(\(\alpha\)-ammonitrile) 93:
3.6608 g (11.216 mmol) of \(\alpha,\alpha'\)-dicyano-\(\alpha,\alpha'\)-bis(N-morpholino)-m-xylene (89) were dissolved along with 2.8520 g (11.217 mmol) of bis(4-fluorophenyl) sulfone at ambient temperature in a flame dried flask in 25 mL dry DMF under \(\text{N}_2\). The mixture was stirred for 20 minutes and became completely homogeneous at room temperature. Upon the addition of 1.04 g (24.5 mmol) of 60% NaH, a vigorous bubbling and an immediate color change to pale yellowish and then yellowish green were seen. After 24 h, the color of the reaction mixture was brown. The temperature was raised to 50\(^\circ\)C and the stirring was continued. The color changed to a pale orange in 0.5 h and was pale honey after 24 h of stirring at 50\(^\circ\)C. The temperature was then raised to 72\(^\circ\)C and stirring was continued for 24 h, at the end of which an increase in the solution viscosity was evident. The solution was quenched in ice cold 5% aqueous NaCl to yield 6.1 g (100%) of a pale yellow solid. Purification was done by dissolving it in DMF and precipitation into water. Then it was twice precipitated from CHCl\(_3\) solution into ice cold methanol. It was dried in a vacuum oven at 50\(^\circ\)C overnight. TGA: 10% weight loss (in air) at 298\(^\circ\)C. FTIR (cm\(^{-1}\)) : 1678 (weak, CO), 1591 (arom. C=C), 1452 (methylene scissor), 1331, 1158 (sulfone) and 1114 (C-O-C). \(^1\)H NMR (CDCl\(_3\)) : 8.2 - 7.2 \(\delta\) (m, 12H), 4.0 - 3.5 \(\delta\) (br. s, 8H), 2.7 - 2.2 \(\delta\) (br. s, 8H). DSC showed a relatively large exotherm at
278°C, indicative of some reaction, on the first heat. On the second heat, the maximum of the exotherm had shifted beyond the range of heating (i.e., at ca. 370°C). Absolute molecular weight determination by GPC yielded an \( M_n \) of 32.3 kg/mole and an \( M_w \) of 44.0 kg/mole.

**Poly(sulfonyl-p-phenylene) (94):**

1.00 g of 93 was refluxed in 25 mL 30% AcOH for 1.5 h. The solid was filtered and dried thoroughly after washing exhaustively with water and MeOH, 0.65 g (100%). A reduction in total mass of 35% corresponds to quantitative hydrolysis of the aminonitrile groups. FTIR (cm\(^{-1}\)) : 1675, 1663 (carbonyl), 1328, 1155 (SO\(_2\)) and 704 (m-disubstituted benzene). Absence of the prominent C-O-C peak at ca. 1117 cm\(^{-1}\) indicated removal of the aminonitrile moiety. TGA showed a 10% weight loss at 478°C (i.e., an increase of 180°C relative to 93). An absolute molecular weight determination by GPC yielded an \( M_n \) of 16.4 kg/mole and an \( M_w \) of 30.6 kg/mole. The decrease in \( M_n \) is more than expected by theory and this may point to some degradation occurring at the reaction condition (i.e., refluxing 30% AcOH). DSC showed a \( T_g \) of 192°C on the first heat, a crystallization exotherm with a maximum at 242°C and a \( T_m \) of 257°C. On the second heat, a \( T_g \) of 195°C was noted with no signs of \( T_m \).
7-Cyano-7,8-bis(N-morpholino)quinodimethane (100):

a). Using 1.1 Equivalents of NaH

To a well stirred suspension of 1.51 g (4.63 mmol) of α,α'-dicyano-α,α'-bis(N-morpholino)-p-xylene (88) in 10 mL DMF in a dry flask under N₂ was added 0.21 g (5.10 mmol) of NaH (60% dispersion in mineral oil) and an immediate exotherm, evolution of H₂ and a change in color from off-white to deep maroon were seen. After stirring for 48 h, the reaction was quenched by pouring into ice cold aqueous 5% NaCl (100 mL) and an intensely yellow precipitate was obtained. Dry weight = 1.38 g (100%). The partly yellow filtrate was not saved. FTIR and ¹H NMR spectral analysis showed the solid to be predominantly the starting material.

b). Using 2.2 mol NaH:

To a well stirred suspension of 1.51 g (4.63 mmol) of α,α'-dicyano-α,α'-bis(N-morpholino)-p-xylene (88) in 10 mL DMF in a dry flask under N₂ was added 0.41 g (10.20 mmol) of NaH (60% dispersion in mineral oil) and an immediate exotherm, evolution of H₂ and a change in color from off-white to deep maroon were seen. After stirring 48 h, the reaction was quenched by pouring into ice cold aqueous 5% NaCl (100 mL) and an intensely yellow precipitate was obtained. Dry weight = 1.38 g (100%). It was crystallized once from toluene-cyclohexane to obtain a yellow powder, mp 95 - 110°C. ¹H NMR (CDCl₃) : 7.6 δ (d, 2H, J = 7.5 Hz), 7.4 δ (d, 2H, J = 7.5 Hz), 4.9 δ (s, 1H), 3.9 - 3.5 δ (m, 8H) and 2.8 - 2.4 δ (m, 8H).
Upon taking the $^1$H NMR spectrum of the same solution after 24 h, the same peaks along with some extra peaks were seen: 7.2 - 7.0 δ (2d), 4.7 δ (s) and 3.1 δ (m). In fact these extra peaks gained in size (integration) as time progressed. The $^1$H NMR spectra (Figures 37-39) of the same solution (CDCl$_3$) at the beginning (AP-34-15), after 16 h (AP-34-18), after 48 h (AP-34-24) and 250 h (AP-34-25) point to a cis-trans isomerization occurring in solution at ambient temperature. The compound was very soluble in all common solvents except hexanes. Purification was done by precipitating a CHCl$_3$ solution into ten fold excess hexanes and allowing the crystals to appear, mp 188 - 196°C (decomposition). FTIR (cm$^{-1}$): 2230 (v. weak, CN), 1507 (phenyl), 1136 (C-O-C) and 864 (C=C out of plane def.). Elemental analyses, found (calcd. for C$_{17}$H$_{21}$N$_3$O$_2$), C: 68.18 (68.20), H: 7.12 (7.07), N: 13.96 (14.04).

REFERENCES


Numerous attempts to isolate a crystalline product of rearrangement of 19 failed because the gum could neither be recrystallized nor purified by column chromatography. Moreover, not much information was available from the $^1$H NMR spectrum since all signals appeared in the aromatic region. Hence it was decided to employ 35 as the substrate (with the 4-methyl group serving as a tag in the aliphatic region in the $^1$H NMR spectrum) and quench the reaction with methyl iodide.

35 was dissolved in DMF under N$_2$ at 50°C and an equivalent of NaH was added whereupon a vigorous bubbling and a blood red color were seen. The reaction gelled up in ca. half hour and after the addition of 3 equivalents of methyl iodide it was stirred for 1h and allowed to warm up to ambient temperature. It was then quenched by pouring onto ten fold excess ice-cold water and the deep red gum was extracted with ethyl acetate; pale orange crystals were isolated when the solution was allowed to stand overnight. A high resolution mass spectrum of the compound and elemental analysis were indicative of an empirical formula of C$_{25}$H$_{18}$N$_4$O$_3$S$_2$. With Prof. Merola's help, a x-ray crystal structure analysis ascertained the following structure.
2-(2-Benzothiazolyl)-2-(N-p-toluoyl)methylamino-3-cyano-3,4-dehydrobenzothiazine (101):
To a solution of 3.0 g (11.3 mmol) of 35 in 20 mL of dry DMF at 5°C under N₂ was quickly added 0.5 g (12.4 mmol) of NaH (60% dispersion in mineral oil). A vigorous bubbling of H₂ and a deep red color were seen immediately and upon continuing the stirring for ca. 40 m, gelling of the reaction mixture was seen. 2.3 mL (34 mmol) of methyl iodide were syringed in quickly at the end of 2h and the mixture was gently warmed to ambient temperature in 1h and poured over 200 mL of ice-cold water. The maroon-red gum was extracted with ethyl acetate and shiny, pale orange crystals appeared overnight, 0.52 g (17%). Recrystallization from ethyl acetate yielded shiny, pale yellow crystals, mp 233 - 234°C. FTIR (cm⁻¹) : 1637 (secondary amide), 1609 (phenyl), 1352 (CH₃ attached to benzene), 766 and 754 (o-disubstituted benzene). ¹H NMR (CDCl₃) : 8.18 δ (d, 1H, J = 7.8 Hz), 7.94 δ (d, 1H, J = 8.1 Hz), 7.69 - 7.39 δ (m, 6H), 7.09 δ (d, 2H, J = 7.4 Hz), 6.87 δ (d, 2H, J = 7.4
hz), 2.78 δ (s, 3H) and 2.35 δ (s, 3H). Elemental analyses, found (calcd. for C_{25}H_{18}N_4O_2S_2), C : 65.98 (66.06), H : 3.98 (3.99), N : 12.34 (12.33) and S : 14.04 (14.11).

A mechanistic scheme is shown overleaf which invokes the bimolecular reaction of 2-cyanobenzothiazole with the ring opened azomethinethiophenoxide from 35 with subsequent acyl transfer and methylation of the amido anion resulting in the formation of 101.
35. \( \text{Ar} = \text{p-tolyl} \)
APPENDIX 2

A sample of 91 that showed a $T_m$ of 414°C (Figure 26) was subjected to wide angle x-ray analysis and displayed a pattern characteristic of semicrystalline polymers. This is shown below and thus lends more proof to the semicrystallinity of 91 as made.
Figure 2: \( ^1H \) NMR spectrum of 22 in CDCl$_3$ at 250°C.
Figure 3: $^1$H NMR spectrum of 19 in CDCl$_3$ at 25°C.
Figure 4: 1H NMR spectrum of 41 in CDC3 at 25°C.
Figure 5: $^1$H NMR spectrum of 24 in CDCl$_3$ at 25°C.
Figure 6: $^1$H NMR spectrum of 34 in CDCl$_3$ at -60°C.
Figure 7: $^1$H NMR spectrum of 34 in C$_6$D$_5$CD$_3$ at 25°C.
Figure 8: 1H NMR spectrum of 24 in C6D5CD3 at -60°C.
Figure 9: $^1$H NMR spectrum of 39 in CDCl$_3$ at 250°C.
Figure 10: $^1$H NMR spectrum of 39 in CDCl₃ at -60°C.
Figure 11: $^1$H NMR spectrum of 39 in C$_6$D$_5$CD$_3$ at 25°C.
Figure 12: 1H NMR spectrum of 39 in C6D5CD3 at -60°C.
Figure 13: $^1$H NMR spectrum of 6Z in CDCl$_3$ at 250°C.
Figure 14: 1H NMR spectrum of 69 in CDCl3 at 250°C.
Figure 15: $^1H$ NMR spectrum of ZQ in CDCl$_3$ at 25°C.
Figure 16: $^1$H NMR spectrum of 81 in CDCl$_3$ at 25°C.
Figure 18: 1H NMR spectrum of 83 in CDCl$_3$ at 250°C.
Figure 20: $^1$H NMR spectrum of 90 in CDCl$_3$ at 25°C.
**Figure 21**: TGA of 90 and 91 (10ºC / min, in air).
Figure 23: DSC of 91 (scale of 1 g, refer Table 19), first heat after drying at 260°C.
Figure 24: DSC of 90 (scale of 6 g, refer Table 19), first heat after drying at 140°C.
Figure 25: DSC of 90 (scale of 6 g, refer Table 19), second heat after cooling from 260°C.
Figure 26: DSC of 91 (scale of 6 g, refer Table 19), first heat after drying at 240°C.
Figure 27: DSC of 91 (scale of 6 g, refer Table 19), second heat after cooling at 10°C/min.
Figure 28: DSC of 91 (scale of 6 g, refer Table 19), second heat after quench cool from 460°C.
Figure 31: DSC of 93 (scale of 6 g), second heat.
Figure 32: DSC of 94 (scale of 6 g), first heat.
Figure 33: DSC of 94 (scale of 6 g), cooling curve at 10°C / min, from 270 - 130°C.
Figure 34: DSC of 94 (scale of 6 g), second heat after cooling at 10°C / min.
Figure 35: $^1$H NMR spectrum of 100 in CDCl$_3$ at 25°C.
Figure 36: $^1$H NMR spectrum of 100 in CDCl$_3$ at 25°C (single diastereomer).
Figure 37: $^1$H NMR spectrum of 100 in CDCl$_3$ at 250°C (after 16 h).
Figure 38: $^1$H NMR spectrum of 100 in CDCl$_3$ at 25°C (after 48 h).
Figure 39: $^1$H NMR spectrum of 100 in CDCl$_3$ at 25$^\circ$C (after 250 h).
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1) "Formation of bis(aminonitrile)s from aromatic diamines and cyanohydrins", H. W. Gibson and A. Pandya, US patent applied for.

Publications (refereed):


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Presentations:

1) New Step Growth Polymers via Reissert Compound Chemistry, 
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   and Reaction Mechanisms, 201st National Meeting, American Chemical 

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   B. Guilani, A. Pandya and H. W. Gibson, Frontiers Research Symposium, 
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