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Synthesis, Structures and Reactions of Cyanuric-Sulfanuric Heterocycles

by

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ABSTRACT

This thesis focuses on the synthesis, structural characterization, and reactions of cyanuric-sulfanuric (C-N-S^{VI}-N) heterocycles involving eight or sixteen atoms. Oxidation of the corresponding S(IV) ring systems with *meta*-chloroperoxybenzoic acid, converts S(IV) to S(VI). Characterization of these novel heterocycles is carried out by mass spectrometry, elemental analysis, IR, ^{1}H and ^{13}C NMR. Single crystal X-ray crystallography is also used to determine the solid state structures of the rings and the bond lengths, bond angles, and torsion angles are compared to those of the corresponding C-N-S^{IV}-N heterocycles. Several reactions of the eight-membered cyanuric-sulfanuric rings are investigated including thermolysis, photolysis, and reactions with electrophiles.

X-ray crystallography revealed that oxidation results in replacement of the lone pair of electrons on each sulfur by an oxygen atom without significant change in the conformations of the eight- and sixteen-membered rings. In all the systems the sulfur-nitrogen bond lengths are shorter in the oxidized systems, but C-N distances are unaffected.

Thermolysis of the eight-membered rings at approximately 220°C produces a ring contraction with loss of a sulfanuric group to give a six-membered C_2N_3S ring which is characterized by mass spectrometry, elemental analysis, IR, ^{1}H and ^{13}C NMR.

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LIST OF COMPOUNDS

1. $(NPCl_2)_3$

2. S_4N_4

3. $(NS(O)Cl)_3$

    a. α-isomer

    b. β-isomer

4. $(NPR_2)_n$

    a. R = Cl

    b. R = Me

5. $(SN)_n$

6. $(R_2SiO)_n$

7. $(R_2Si)_n$

8. $Me_3SiN{=}PRR'OCH_2CF_3$

    a. R = R' = Me

9. S_2N_2

10. $Me_3SiN{=}S(O)(R)OR''$

    a. $R = CH_3$, $R'' = CH_2CF_3$

    b. $R = CH_3$, $R'' = OPh$

c. R = Et, R'' = OPh

d. R'' = CH_2CF_3

11. $(NS(O)R)_n$

12. $(NSR)(NPR_2)_2$

13. $(NS(O)R)(NPR_2)_2$

a. R = Cl

14. $(NCR)(NPR_2)_2$

a. R = Cl

15. $[(NS(O)Cl)(NPCl_2)_2]_n$

16. 1,5-$Ph_4P_2N_4(SR)_2$

a. Chair

b. Boat

17. 1,5-$Ph_4P_2N_4(S(O)R)_2$

a. *trans*

b. *cis*

18. $CF_3CH_2OPRR'=N-S(O)R''=NSiMe_3$

19. $CF_3CH_2OPRR'=N-S(O)R''=NH$

20. $(RR'P=N-S(O)R''-N)_n$

21. $[(NCCl)(NPCl_2)_2]_n$

22. $(NSCl)(NCCl)_2$

23. $[(NSCl)(NCCl)_2]_n$

24. $(NS(O)Cl)(NCCl)_2$

25. $[(NS(O)Cl)(NCCl)_2]_n$

26. $Ar_2C_2N_4S_2\ Ar'_2$

a. Ar = 4-BrC_6H_4, Ar' = C_6H_5

b. Ar = 4-$CF_3C_6H_4$, Ar' = C_6H_5

c. Ar = 4-$CF_3C_6H_4$, Ar' = 4-$CH_3C_6H_4$

d. Ar' = NMe_2

27. Z,E,Z-(Ar')SNC(Ar)N=NC(Ar)NS(Ar')

28. $Ar_4C_4N_8S_4Ar'_4$

a. Ar = 4-BrC_6H_4, Ar' = C_6H_5

b. Ar = 4-$CF_3C_6H_4$, Ar' = C_6H_5

c. Ar = 4-$CH_3C_6H_4$, Ar' = C_6H_5

d. Ar = 4-$CF_3C_6H_4$, Ar' = 4-$CH_3C_6H_4$

29. $R_2C_2N_4S_2O_2R'_2$

a. R = 4-BrC_6H_4, R' = Ph

b. R = 4-$CF_3C_6H_4$, R' = Ph

c. R = 4-$CF_3C_6H_4$, R' = 4-$CH_3C_6H_4$

d. R' = NMe_2

e. R' = Cl

30. $[(NCR)(NS(O)R')]_n$

a. R = Ar, R' = Cl

31. 1,3-$ClC_6H_4CO_3H$ - *meta*-Chloroperoxybenzoic acid

32. $(4\text{-}BrC_6H_4)_2C_2N_4S_2O(C_6H_5)_2$

33. $(4\text{-}CF_3C_6H_4)_2C_2N_3S(O)(C_6H_5)$

34. $(4\text{-}CF_3C_6H_4)CN_3S_2(O)_2(C_6H_5)_2$

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b. Ar = 4-$CF_3C_6H_4$, Ar' = C_6H_5

c. Ar = 4-$CF_3C_6H_4$, Ar' = 4-$CH_3C_6H_4$

36. $Ar_4C_4N_8S_4OAr'_4$

37. $Ar_4C_4N_8S_4O_2Ar'_4$

a. vicinal S^{VI} atoms

b. antipodal S^{VI} atoms

38. $Ar_4C_4N_8S_4O_3Ar'_4$

39. $[(NSO)(NPAr)_2]^+[GaCl_4]^-$

40. $(NS(O)Cl)(NCAr)_2$

41. $[(NSO)(NCAr)_2]^+[GaCl_4]^-$

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LIST OF ABBREVIATIONS AND SYMBOLS

Ar	aryl (aromatic) group
d	bond distance
D_{calc}	calculated density
DMF	dimethyl formamide
DSC	Differential Scanning Calorimetry
Et	ethyl, C_2H_5
ESD	Estimated Standard Deviation
FAB-MS	Fast Atom Bombardment Mass Spectrometry
FT-IR	Fourier Transform Infrared Spectroscopy
GPC	Gel Permeation Chromatography
*m*CPBA	*meta*-chloroperbenzoic acid
*m*CBA	*meta*-chlorobenzoic acid
Me	methyl, CH_3
mm	millimetre
Mp	melting point
MS	Mass Spectrometry
NMR	Nuclear Magnetic Resonance
ORTEP	Oakridge Thermal Ellipsoid Plot

Ph	phenyl, C_6H_5
ppm	parts per million
R	reliability factor
R_w	weighted reliability factor
ROP	ring-opening polymerization
T_g	glass transition temperature
THF	tetrahydrofuran
TLC	Thin Layer Chromatography
UV	Ultraviolet
Z	number of molecules in a unit cell

CHAPTER 1

Hybrid Inorganic Heterocycles and Polymers

1.1 Introduction

In recent years, there has been an increased interest in polymers that incorporate inorganic elements in the backbone[1]. This attention comes as a result of their unique properties[2,3]. In general, inorganic systems possess bonds that are stronger, longer, and resistant to free radical cleavage when compared to carbon based organic polymers. This makes them useful because a wide variety of bond lengths and torsion angles are possible. Inorganic elements possess different valencies than carbon which allow for an assortment of different side chains to be incorporated onto the backbone, hence, tuning the polymer for a particular application. Ring-opening polymerization (ROP) is a common route to inorganic polymers due to its versatility[4,5].

The focus of this thesis is the synthesis and characterization of suitable cyclic precursors for the generation of hybrid inorganic polymers involving alternating CN and $S^{VI}N$ groups (cyanuric-sulfanuric systems) in the backbone. By use of previously

established methods[6] of synthesizing eight- and sixteen-membered C-N-S^{IV}-N heterocycles the aim was to use suitable oxidizing agents to convert the sulfur atoms into the S(VI) oxidation state. Once this was achieved it was then important to see if these newly formed heterocycles possess interesting reaction chemistry. With this in mind a variety of experiments were performed on the eight-membered rings to test their applicability as precursors to inorganic polymers.

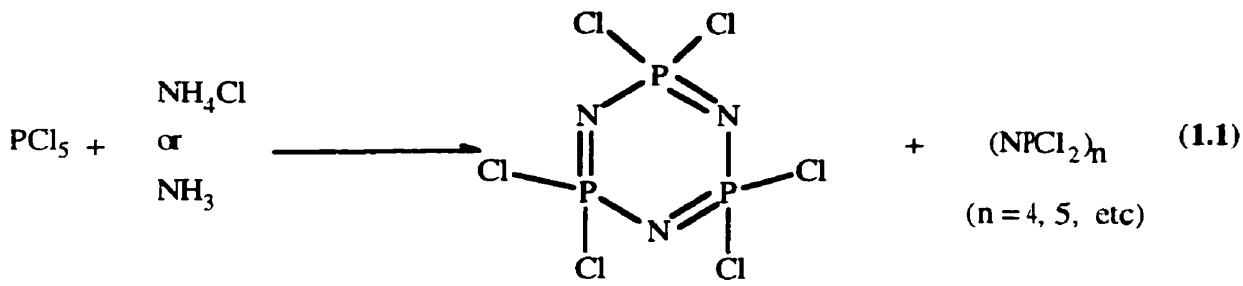
This chapter is therefore designed to give the appropriate background information pertaining to a variety of inorganic heterocycles as well as some related polymer systems. A brief review of some very well known and important inorganic systems, such as cyclic phosphazenes and tetrasulfur tetranitride, is followed by some more recent chemistry of sulfanuric chlorides. In addition, the topic of inorganic polymers is covered with a special emphasis on poly(aryl/alkyloxothiazenes), which have a direct bearing on the hybrid sulfanuric systems. Finally, a review of some recent literature pertaining to hybrid inorganic rings and polymers is presented with the general focus on systems containing sulfur and carbon as part of the hybrid backbone.

1.2 Inorganic Ring Systems

1.2.1 $(NPX_2)_n$ Heterocycles

One of the most studied groups of inorganic heterocycles are those known as cyclic phosphazenes[7,8]. The interest in these ring systems can be attributed to their

stability, variety of chemical reactions, and unique bonding scheme. With the general formula of $(NPX_2)_n$ the alternating backbone of phosphorus and nitrogen can consist of rings as large as seventeen repeating units[9]. The history of cyclic phosphazenes dates back to 1834 when Wohler and Rose observed the reaction of phosphorus pentachloride and ammonia yielded a stable white crystalline solid. At the end of the 1800's Stokes correctly postulated that the reaction yielded $(NPCl_2)_3$ and higher order heterocycles (Equation 1.1)[7].



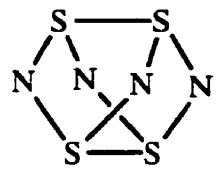
(1.1)

1

Today cyclodichlorophosphazene trimer, $(NPCl_2)_3$, is thought of as the parent compound to many derivatives of substituted cyclic phosphazenes[8]. Phosphazenes contain phosphorus in the +5 oxidation state and are written with an alternating double bond between the nitrogen and phosphorus. This depiction is often misleading because the bonds between nitrogen and phosphorus are essentially equal in length.

1.2.2 S_4N_4

The history of tetrasulfur tetranitride can be compared to that of cyclic phosphazenes. Discovered in the early 1800's it was not until relatively recently that it has been the focus of much chemical attention[10]. Recent interest is due to the fact that S_4N_4 is a useful precursor to a variety of S-N compounds[10a]. The structure of S_4N_4, which was determined by X-ray crystallography in 1963[11], is described as a cage with the nitrogen atoms forming a square arrangement and the sulfur atoms a bisphenoid[10a]. Sulfurs are each three co-ordinate with a sulfur-sulfur bond distance of 2.58 Å and each nitrogen is two co-ordinate with a sulfur-nitrogen bond distance of 1.62 Å.



2

The standard method of synthesis for tetrasulfur tetranitride is by reaction of sulfur halides and ammonia in carbon tetrachloride or dichloromethane[10,12]. An alternative route to S_4N_4 is by reaction of S_2Cl_2 with sulfur and NH_4Cl (Equation 1.2). $S_3N_3Cl_2$ formed in the first step of the reaction is treated with excess chlorine to give the $S_3N_3Cl_3$, which is further reduced with Ph_3Sb to give high yields of S_4N_4 (Equations 1.3 and 1.4). Other metals such as Cu, Sn, and Hg also efficiently reduce $S_3N_3Cl_3$ to S_4N_4[13].

$$S_2Cl_2 + S_8 + NH_4Cl \xrightarrow{160^\circ C} S_3N_2Cl_2 \quad \textbf{(1.2)}$$

$$3\ S_3N_2Cl_2 + 3\ Cl_2 \longrightarrow 2\ S_3N_3Cl_3 + 3\ SCl_2 \quad \textbf{(1.3)}$$

$$4\ S_3N_3Cl_3 + 6\ Ph_3Sb \xrightarrow{CH_3CN} 3\ S_4N_4 + 6\ Ph_3SbCl_2 \quad \textbf{(1.4)}$$

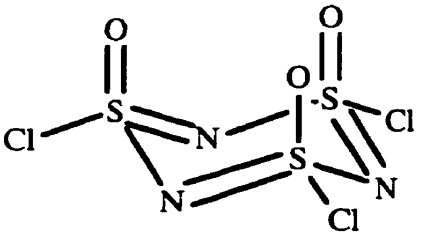
The versatility of S_4N_4 is demonstrated by its ability to undergo a variety of different reactions, e.g. thermal degradation, oxidation, reaction with nucleophiles, and reaction with halides. Perhaps the best known of these is the thermal degradation of S_4N_4 to produce S_2N_2 (see Section 1.3.2).

1.2.3 $[NS(O)Cl]_3$

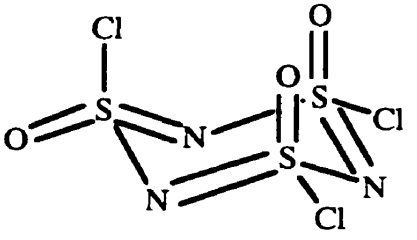
In the early 1900's an attempt by Ephraim and Gurewitsch to make $H_2NSO_2Cl \bullet PCl_3$ led to the synthesis of $Cl_3P{=}NSO_2Cl$ which was correctly identified in the 1950's by Kirsanov[14]. Pyrolysis of trichlorophosphazo-sulfuryl chloride at 140°C yields sulfanuric chloride, $[NS(O)Cl]_3$ with elimination of $OPCl_3$. Today an alternative procedure is used to prepare sulfanuric chloride (Equation 1.5).

$$SOCl_2 + NaN_3 \xrightarrow{CH_3CN} \frac{1}{3}[NS(O)Cl]_3 + N_2 + NaCl \quad \textbf{(1.5)}$$

α- and β-Sulfanuric chloride isomers, **3a** and **3b** form when either above-mentioned synthesis is performed. The more stable α-sulfanuric chloride isomer (**3a**) forms colourless rhombic crystals by cooling a hot solution of the crude mixture in n-heptane while the β-isomer is purified by vacuum sublimation at room temperature. Both the α- and β- derivatives have a chair conformation but the oxygen and chlorine positions differ. The atomic arrangement in α-sulfanuric chloride (**3a**) has all three oxygens in the axial position and chlorines in the equatorial position while β-sulfanuric chloride (**3b**) has only two equatorial chlorines and one oxygen in the equatorial position.



α-sulfanuric chloride
3a

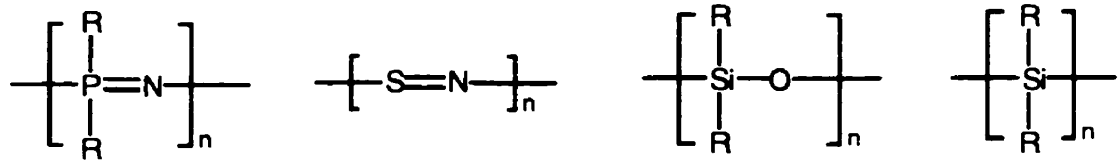


β-sulfanuric chloride
3b

The β-isomer crystallizes as needles with a melting point of 44-46°C and is only stable in crystalline form or in non-polar solvents. If the β-isomer is left in acetonitrile for approximately an hour it will convert to the more stable α-form.

1.3 Inorganic Polymers

A variety of inorganic polymers has been studied to date[1-5]. These inorganic polymers are comprised of main group elements and primarily involve sulfur, silicon, nitrogen, and phosphorus. Polyphosphazene (**4**), poly(sulfur nitride) (**5**) polysiloxane (**6**), and polysilane (**7**) are examples of the most well characterized inorganic polymers.

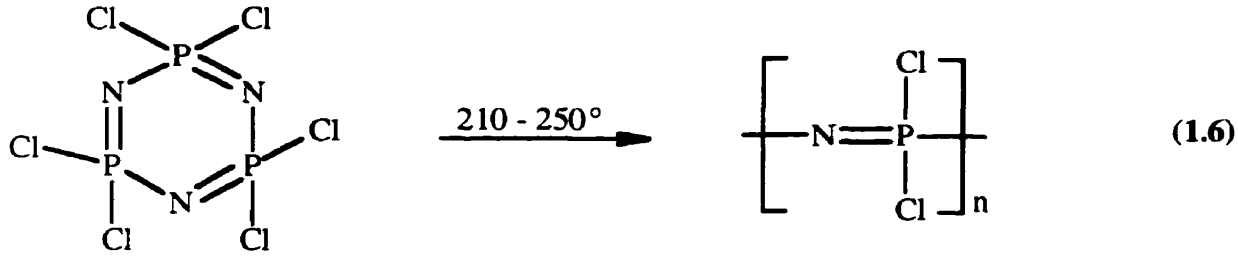


4 **5** **6** **7**

1.3.1 Polyphosphazenes

Substituted polyphosphazenes are the most diverse inorganic polymers investigated to date with several hundred different species synthesized[15]. The polymer backbone consists of alternating phosphorus and nitrogen atoms with four coordinate phosphorus in the +5 oxidation state. A wide variety of substituents have been added to the backbone which result in excellent variability of properties[7]. This is demonstrated by the following properties: low temperature flexibility, liquid crystalline behaviour, and high refractive indices. This wide range of properties is useful in such applications as elastomeric films, flame retardants, and as biomedical materials[16].

As early as the 1830's an "inorganic rubber" was synthesized that incorporated a phosphorus-nitrogen backbone although the exact structure was not known[7]. Today it is understood that the material produced was highly cross-linked poly(dichlorophosphazene). The cross-linked structure of inorganic rubber made it insoluble in common organic solvents thereby making it extremely difficult to work with and, as a result, little interest was given to inorganic rubber chemistry until the synthesis of uncross-linked polyphosphazene was reported by Allcock[15a] (Equation 1.6).



1 **4a** **(1.6)**

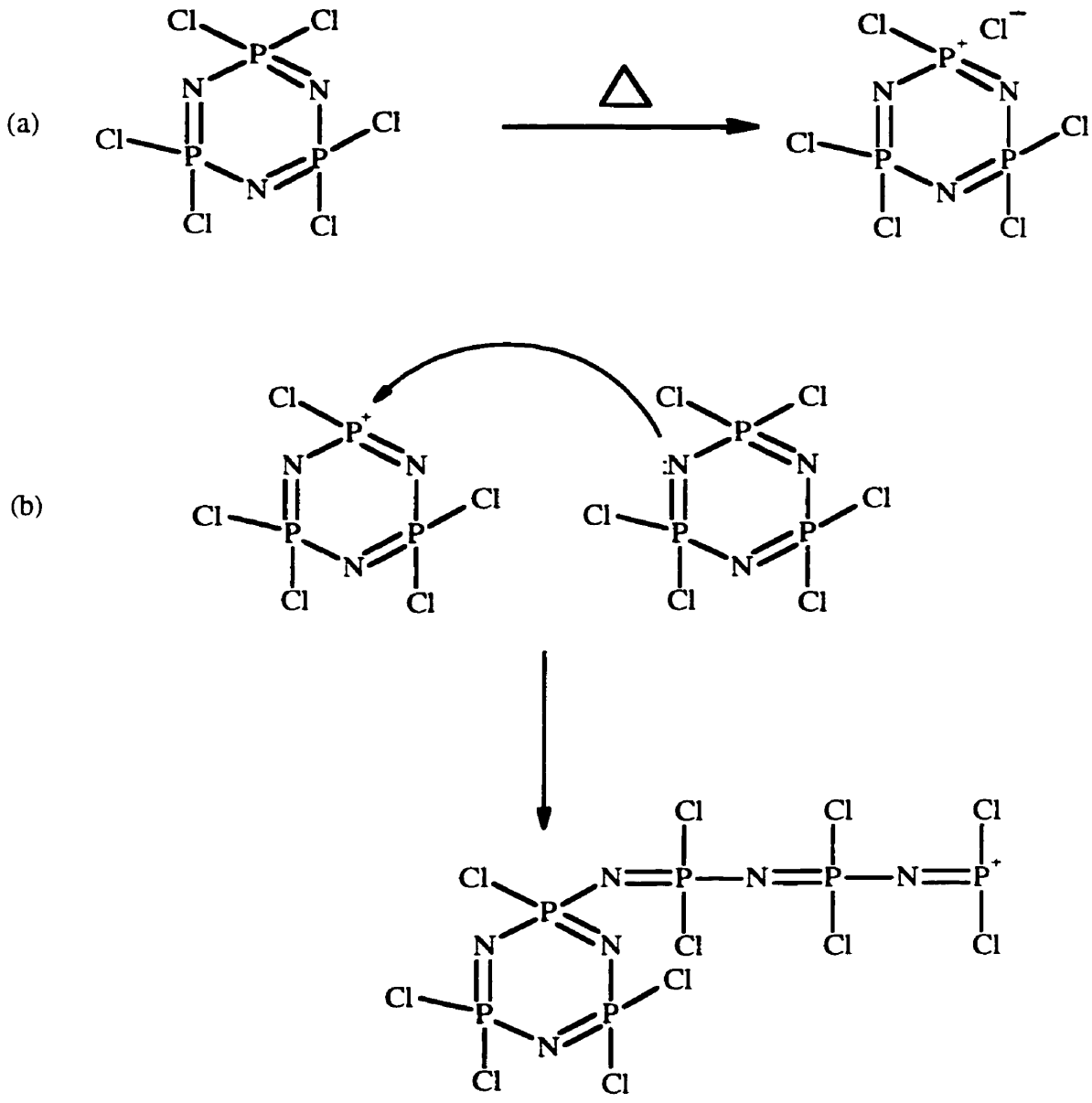
This polymer is an elastomeric material that is very hydrolytically sensitive. However, one of the great advantages of poly(dichlorophosphazene) (**4a**) is the reactivity of the P-Cl bond which allows for a variety of substituents to be added onto the polymer backbone.

The polymerization of the dichlorophosphazene trimer (Equation 1.6) occurs by thermal ring-opening polymerization (ROP), which is the most extensively studied route

for generating inorganic polymers[5,17]. The mechanism of ring opening is believed to involve a cationic initiator formed by the ionization of a P-Cl bond. This cation, $P_3N_3Cl_5^+$, is attacked by the lone pair of electrons on a nitrogen of a second trimer species thereby opening up the ring (Scheme 1.1)[7]. Repetition of this process gives rise to dichlorophosphazene polymer.

In order for initiation and propagation to occur there must be more than one halogen atom on the ring that can be easily ionized. If all the chlorines of the trimer are replaced with organic substituents, e.g. methyl or phenyl, then polymerization will not occur. Large substituents have an adverse effect on polymer formation because of the steric hindrance that occurs through the length of the chain. Impurities such as water or BCl_3 have a catalytic effect on polymerization due to their ability to assist in the initial ionization of the chlorine atom[7].

Many different substituents have been used to replace chlorine on the polymer backbone[18]. Reaction of nucleophiles such as alkoxides, aryloxides, and amines with poly(dichlorophosphazene) results in a facile route to substituted polymers[19]. This process is limited by the size of the nucleophile due to steric reasons, although this impediment may be overcome in most cases by heating the reaction mixture. Interestingly, the substitution of $(NPCl_2)_n$ (**4a**) with selected nucleophiles such as diethylamine or phenoxide results in incomplete chlorine replacement on the polymer backbone. This leads to the possibility of substitution of two different side groups on

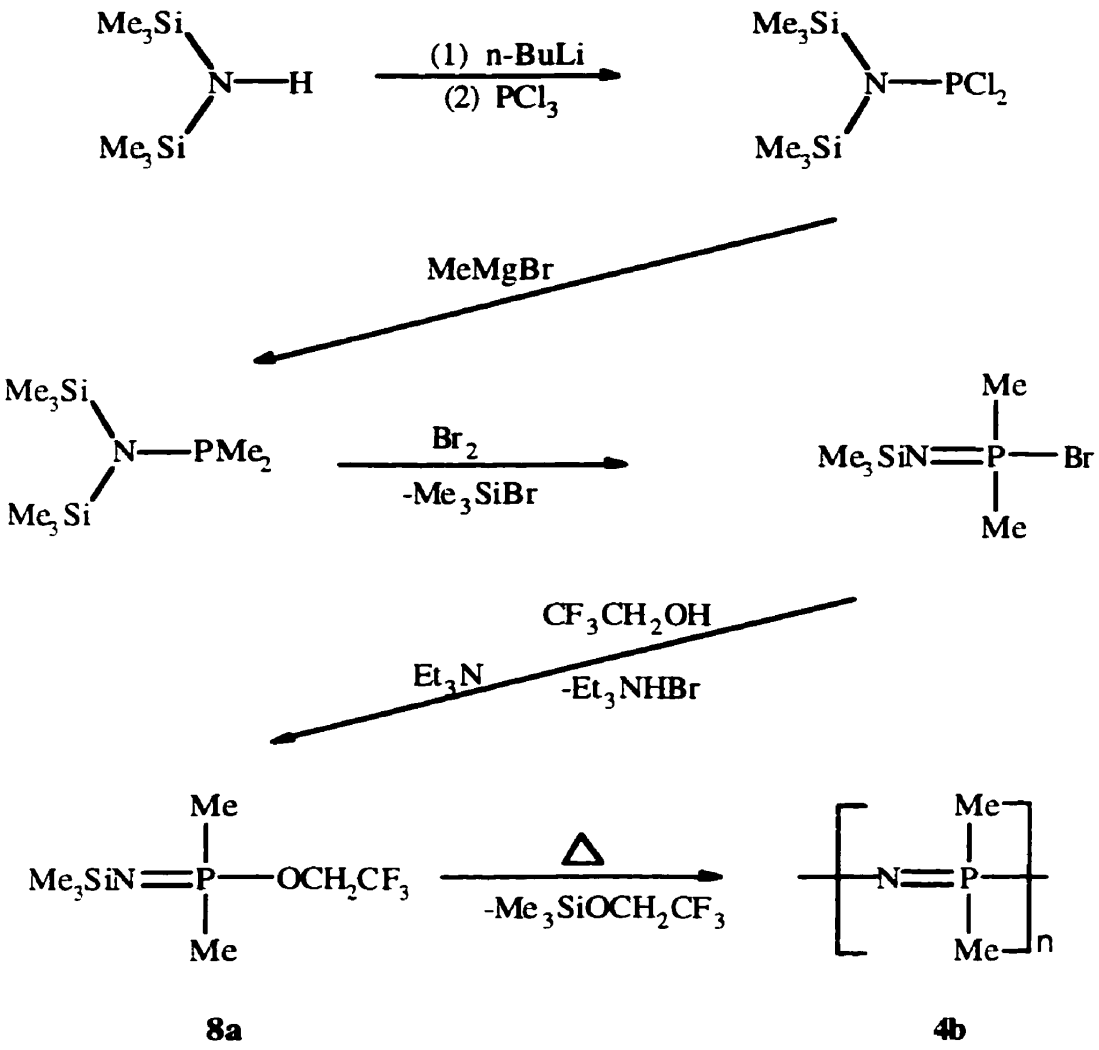


Scheme 1.1 Proposed Ring-Opening Polymerization Mechanism

each phosphorus atom and introduces a variety of properties not previously available by single substitution. Reaction of **4a** with diethylamine, even in excess, leads to replacement of only one chlorine and the subsequent reaction with smaller, less hindered nucleophiles such as methylamine leads to a disubstituted species.

Studies have also been performed that involve the use of fluorine rather than chlorine on the polymer backbone[7]. Synthesis of the fluorinated species involves the treatment of $(NPCl_2)_n$ (**4a**) with sodium fluoride. The usefulness of $(NPF_2)_n$ is limited, however, due to its lack of solubility in organic solvents other than special fluorocarbons.

An alternative method for the formation of polyphosphazenes involves condensation reactions[20]. The driving force for this method is the elimination of $Me_3SiOCH_2CF_3$ (formation of a strong Si-O bond) from an N-silylphosphoranimine (**8**) (Scheme 1.2). Recently, a variation on this condensation method has been used to prepare diblock[21,22] and triblock[23] copolymers.



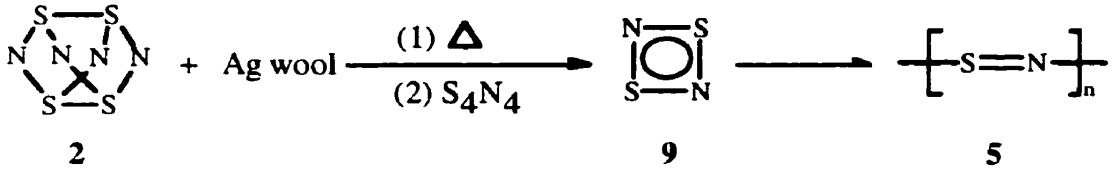
8a **4b**

Scheme 1.2 Condensation Route to Poly(dimethylphosphazene)

1.3.2 Poly(sulfur nitride)

Poly(sulfur nitride) (**5**) is a unique inorganic polymer because of its metallic appearance and behaviour[24]. First synthesized in 1910 by Burt *et al.* it was not until the 1950's that its electrical conductivity properties were realized[24].

Today **5** is prepared by a method very similar to that used by Burt in 1910 with a few minor modifications[25]. Hot vapour of S_4N_4 is passed over silver wool which leads to cleavage of S_4N_4 to produce S_2N_2 (**9**). Cleavage occurs in two steps as depicted in Equation 1.7. In the first step, S_4N_4 reacts with silver to form Ag_2S which acts as a catalyst for further reaction with S_4N_4.



2 **9** **5** (1.7)

The dimer **9** is a clear, colourless, volatile crystalline solid that polymerizes to **5** topochemically. Topochemical polymerization of **9** involves crystal growth at low temperatures followed by warming to 0°C over a period of days. The unique structure of poly(sulfur nitride) confers properties not available from purely organic analogues. The most interesting property involves its conducting and superconducting behaviour. Studies have shown that the metallic conducting behaviour of $(SN)_x$ occurs throughout the temperature range of 300 to 4.2K. As temperatures are further decreased to

approximately 0.26K $(SN)_x$ exhibits superconducting behaviour. The electron configuration of the sulfur and nitrogen atoms allows for conduction through the length of the chain. i.e. sulfur contributes 2 π electrons and nitrogen contributes 1 π electron giving a total of 3 π electrons which fill the valence band and half-fill the conduction band.

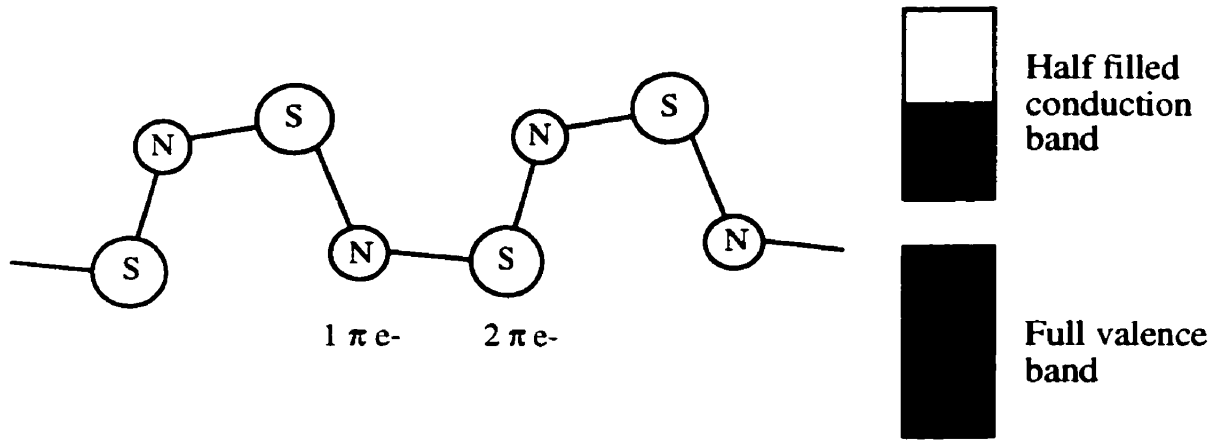


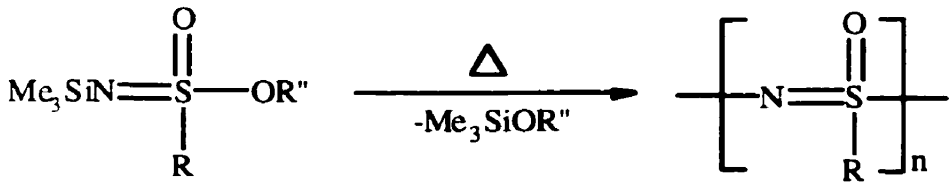
Figure 1.1 Electronic Structure of $(SN)_x$

Although $(SN)_x$ has remarkable properties as a superconductor at low temperatures it is limited by its lack of substituents on sulfur or nitrogen. As we have seen with polyphosphazenes, changing substituents provides a means of tuning the polymer's properties for specific applications. Without these tunable properties poly(sulfur nitride) will remain an excellent conductor, but industrial applications are unlikely.

1.3.3 Poly(alkyl/aryloxothiazenes)

First reported in the 1960's poly(oxothiazenes) were prepared by reaction of $S(O)F_4$ and NH_3 to form the fluoro and amino derivatives[26]. Since then only low molecular weight oligomers of approximately 10 repeating units have been synthesized. In 1993 Roy *et. al.* reported the first synthesis of high molecular weight oxothiazene polymers via a condensation route[27].

Although the thermal ROP of cyclic phosphazenes, $(N{=}PCl_2)_3$, is a typical method of synthesizing poly(phosphazenes) Roy could not utilize the analogous sulfanuric system, namely α-sulfanuric chloride (**3a**) for this purpose, because it decomposes above 250°C. For this reason he turned to the condensation method (c.f. Scheme 1.2). By using the sulfur(VI) compound, N-silylsulfonimidate (**10**), the thermal polycondensation was carried out accordingly (Equation 1.8).



10 **11** **(1.8)**

Various substituents have been used in both uncatalyzed and catalyzed reactions, e.g. R = CH_3, R'' = OCH_2CF_3 (**10a**); R = CH_3, R'' = OPh (**10b**); R = Et, R'' = OPh

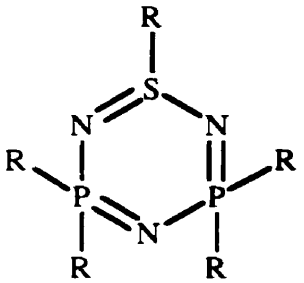
(**10c**). The introduction of a Lewis acid or base as a catalyst moderately enhanced the rate of polycondensation, but it was also determined that control over polydispersity and molecular weight could be achieved through the use of a catalyst. The best combination of high molecular weight, low polydispersity, and increased reaction rate was achieved with $BF_3 \bullet Et_2O$.

The physical properties of these polymers were determined by a variety of different methods, including; (a) tacticity (b) molecular weight (c) glass transition temperature (T_g). ^1H and ^{13}C NMR were used to establish that poly(methyloxothiazene) has both stereoregular and atactic portions. The atactic segments are completely random mixture of isomers i.e. no regularity. By contrast poly(methylphenylphosphazene) is completely atactic. Molecular weight was determined by gel-permeation chromatography (GPC) which uses principles of size exclusion chromatography for product separation. From this study no exact values for molecular weight were reported because the reference and solvent system were not ideal, therefore, only relative comparisons between different substituents were made. For example, polymers in which R = Me (see Equation 1.8) gave the highest molecular weight followed by R = Et and then R = Ph. These data are consistent with the increased steric effects going from Me→Ph and, hence, increased difficulty in polymerization. Glass transition temperatures were determined by differential scanning calorimetry (DSC) and are important in polymer chemistry because they provide information on the elastomeric nature of a polymer. T_g is defined as the

temperature below which the polymer is glass-like[7] and values vary depending on the nature of the backbone and the substituents. The lower the T_g value, the better elastomer a polymer is. It was determined that the T_g for poly(methyloxothiazene) is 55-65°C which is considerably higher than the value of -46°C for poly(dimethylphosphazene), thereby, indicating that the chain flexibility or free space around poly(methyloxothiazene) is lower than poly(dimethylphosphazene).

1.4 Hybrid Inorganic Ring Systems and Polymers

Hybrid inorganic polymers are emerging as a very important class of polymers due to their versatility[4,28,29]. Hybrids are formed by an amalgamation of two inorganic polymers, most commonly, but not exclusively, poly(aryl/alkyloxothiazenes) and polyphosphazene. Thus, they contain both SN and PN groups in the backbone. These materials have been extensively studied due to their prospective properties, which are expected to be a combination of those found in $(NS(O)R)_n$ (**11**) and $(NPR_2)_n$ (**4**). Generally, synthesis of hybrids comes from ROP of the corresponding cyclic heterocycles[30]. A few of the most common examples are thiophosphazene (**12**), thionylphosphazene (**13**), and carbophosphazene (**14**). In these cases phosphorus is four-coordinate in the +5 oxidation state and sulfur may be in the form of either three-coordinate S^{IV} or four-coordinate S^{VI}.



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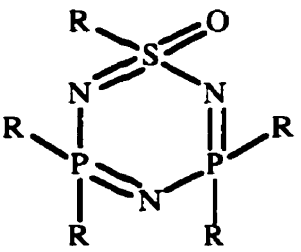

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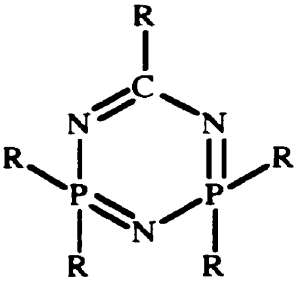


14

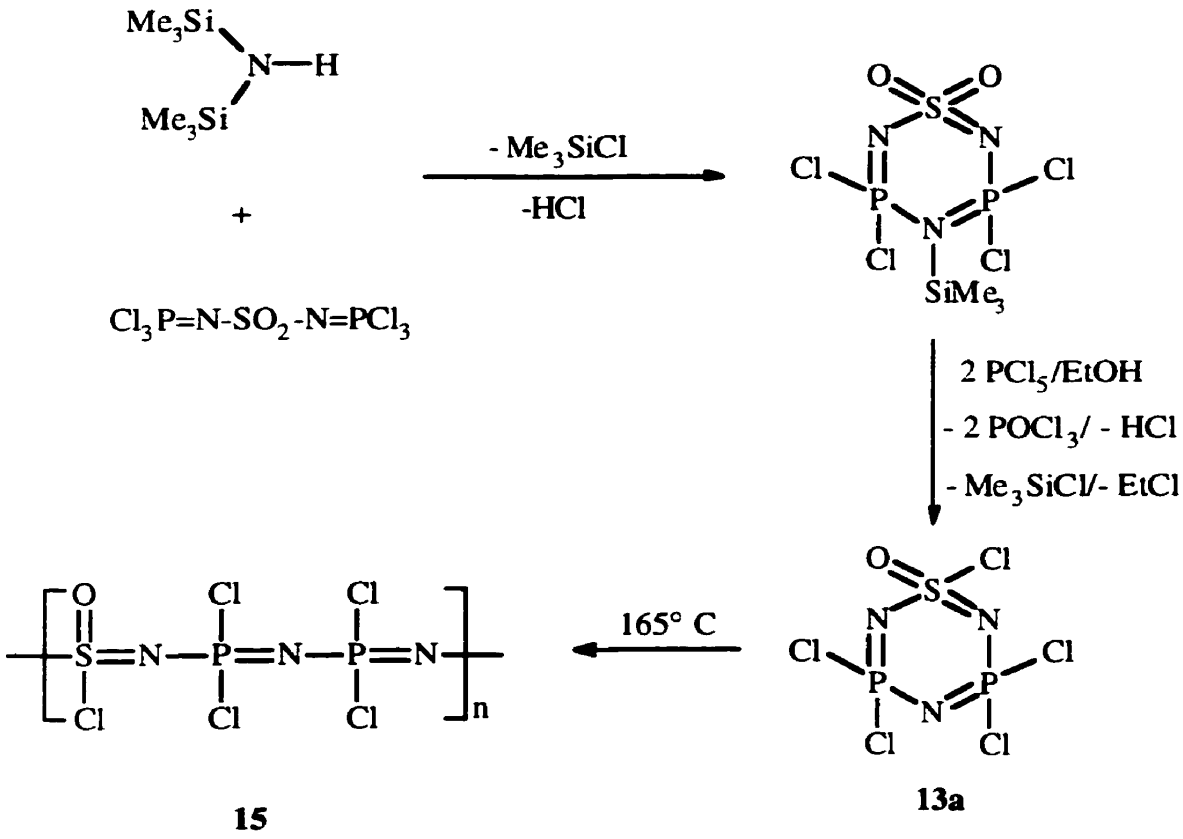
1.4.1 Poly(thiophosphazenes)

Cyclic thiophosphazenes (**12**) were the first hybrid heterocycles to be studied in 1972 when Roesky and coworkers reported the synthesis of the fully chlorinated species (R = Cl)[31]. The product was colourless and hydrolytically unstable. In the 1990's Allcock *et al.* polymerized the chlorinated species by ring opening polymerization at 90°C to form the S^{IV}-N-P-N-P-N- polymer, which is a yellow elastomer[4]. It has been determined that reaction of the polymer with nucleophilic aryloxides gives an elastomeric product that is more hydrolytically stable then the chlorinated species. Substitution with more sterically hindered groups such as *o*-phenylphenoxide improves the stability of the polymer chain and allows for an aqueous work-up of the polymer. Substitution with alkoxy and amine nucleophiles has been unsuccessful as the polymer backbone degrades to oligomers. Although poly(thiophosphazenes) have been well characterized with respect to molecular weight and glass transition temperatures (T_g), they are limited in their usefulness due to extreme hydrolytic instability.

1.4.2 Poly(thionylphosphazenes)

An alternative to thiophosphazenes is a similar hybrid inorganic heterocycle thionylphosphazene (**13**) which has 4-coordinate sulfur in the +6 oxidation state. Van de Grampel and coworkers[30c] determined that the cyclic precursors possess unique stability towards hydrolysis and therefore may be chemically useful. Van de Grampel's early work included a vacuum thermolysis synthesis of the cyclic trimer while Glemser reported a (3+3) cyclocondensation of $SO_2(NH_2)_2$ with $[Cl_3P{=}N{=}PCl_3][PCl_6]$ to give 12% yield. Currently the precursor is synthesized by a (5+1) cyclocondensation reported by Suzuki[32] that provides improved yields of 40-75%. ROP is carried out on white crystalline $(NSOCl)(NPCl_2)_2$ (**13a**) at 165°C to form a moisture-sensitive elastomeric polymer as shown in Scheme 1.3[17].

Chlorinated poly(thionylphosphazene) (**15**) reacts with oxygen-[33] or nitrogen-based[34] nucleophiles to give substituted products. Aryloxide nucleophiles replace the chlorines on the phosphorus atoms while leaving the S^{VI}-Cl bond intact. This is opposite to what is observed in the poly(thiophosphazene) systems in which the S^{IV}-Cl bond reacts preferentially over the P-Cl bonds. This difference in behaviour may be explained by the increased reactivity of the S^{IV}-Cl bond compared to the S^{VI}-Cl bond. Replacement of chlorines attached to phosphorus with aryloxides provides hydrolytic stability and allows for purification by precipitation into water. There is a range of properties available for the aryloxy substituted polymer depending on the steric bulk of the side



15 **13a**

Scheme 1.3 Poly(thionylphosphazene) Synthesis

group[33]. The flexibility of the polymer depends not only on the backbone of the polymer, but also on the nature of the substituents. Compact substituents take up free space and make the chain less flexible while long compliant groups take up less free space close the polymer backbone and therefore increase flexibility.

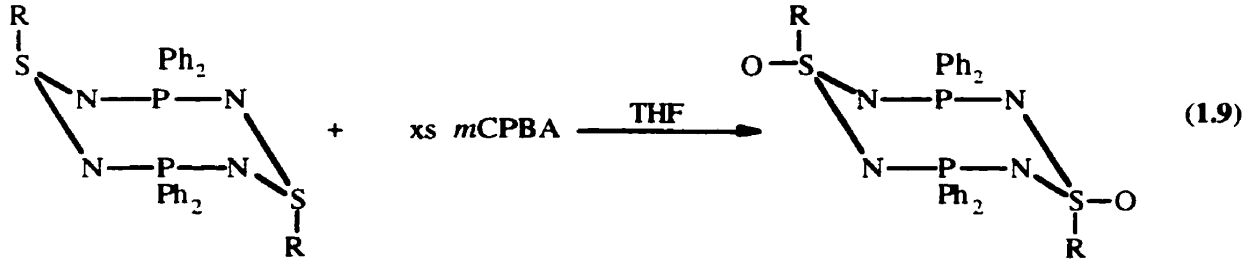
Reaction of **15** with amines has been studied by Van de Grampel and it was found that complete replacement of chlorine at phosphorus occurs while only partial chlorine

replacement at sulfur is observed[34.3]. This is in contrast to the reaction with aryloxides in which there is no chlorine replacement at sulfur. The extent to which the S-Cl is substituted depends on the nature of the amine. For example, the use of methylamine provides 90% chlorine replacement while butylamine only results in 50% replacement. This selective replacement allows the preparation of disubstituted species with a wide variance of properties.

Probably the most important application to emerge for poly(thionylphosphazenes) is their oxygen-pressure sensing properties[3]. The use of cross-linked polysiloxanes in combination with phophorescent sensors based on complexes of transition metal dyes, for example $[Ru(L)_3]^{2-}$ (L= 4,7-diphenyl1,10-phenanthroline) is already established in this field. This method is limited by the fact that it reveals pressure information only at various points on the sample. The key advantages of poly(thionylphosphazenes), more specifically poly[(amino)thionylphosphazenes], are that they can be evenly dispersed by spray-coating a thin film of composite onto the desired surface and they have high solubility and diffusion coefficients for oxygen. In addition to this they offer good compatibility with the phosphorescent dye, high quality films are easily attainable without the need for cross-linking, and they are less costly than the expensive polysiloxane composites.

Thus far ROP has been used on six-membered heterocycles to produce thionylphosphazene polymers with an alternating S-N-P-N-P-N backbone. To achieve a

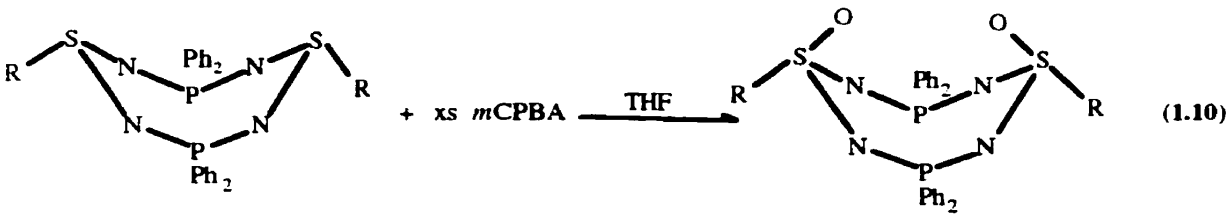
polymer with an alternating S-N-P-N backbone the natural candidate would be an eight-membered ring that could ring-open to form a S^{VI}-N-P-N polymer. Recent literature reports the synthesis of an eight-membered sulfanuric-phosphazene ring with an S^{VI}-N-P-N repeat unit[35]. Chivers *et al.* report the synthesis of *trans*-$Ph_4P_2N_4[S(O)R]_2$ (R = Ph and Me) and *cis*-$Ph_4P_2N_4[S(O)Me]_2$ from the corresponding S(IV) species (Equations 1.9 and 1.10).



(1.9)

16a - chair

17a - *trans*



(1.10)

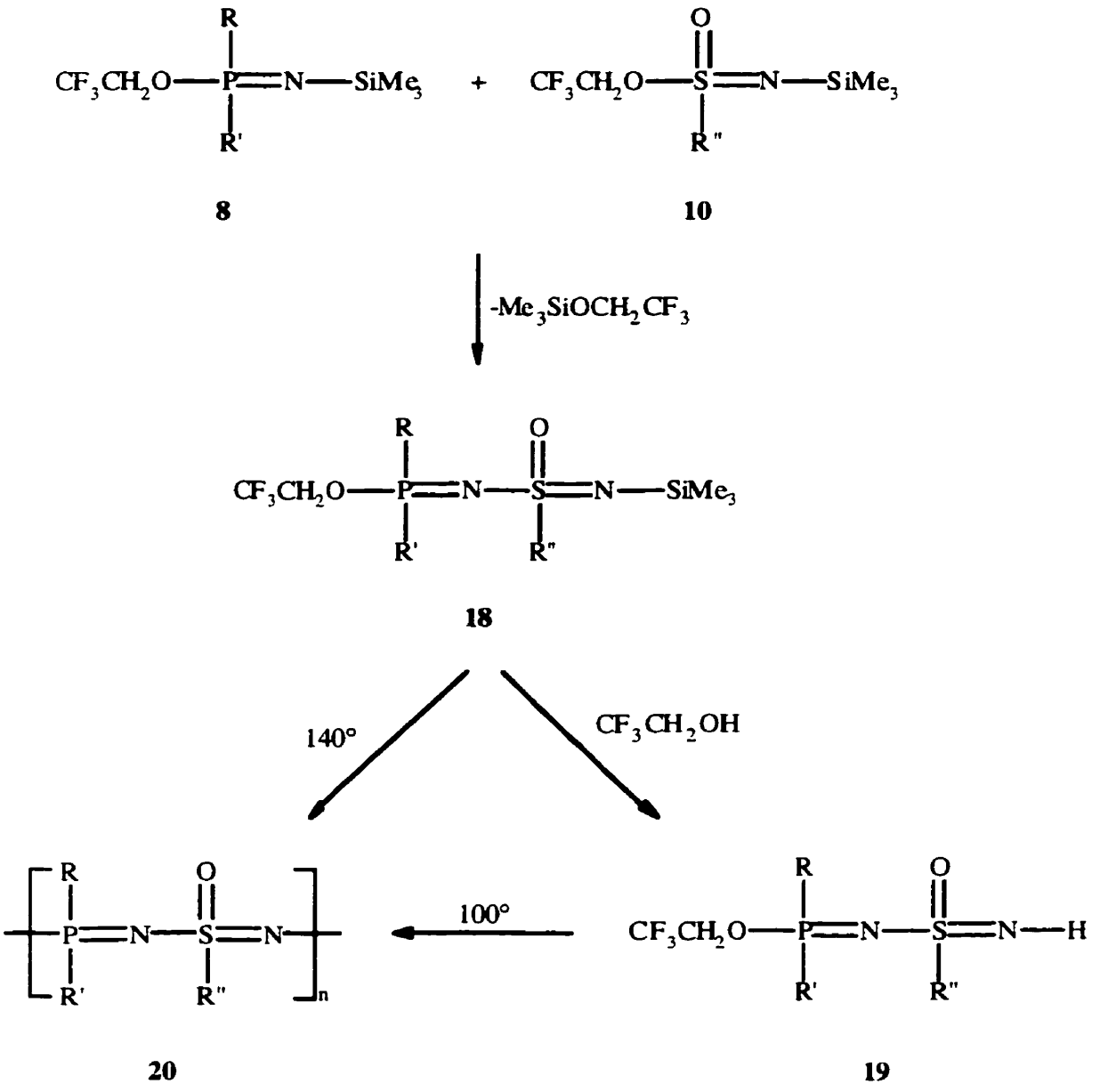
16b - boat

17b - *cis*

In these reactions four equivalents of *m*CPBA are reacted with the S(IV) ring systems (**16**). Interestingly, the chair conformer of 1,5-$Ph_4P_2N_4(SR)_2$ (**16a**) is oxidized to

the *trans*-$Ph_4P_2N_4[S(O)R]_2$ (**17a**) ring whereas the boat conformer of 1,5-$Ph_4P_2N_4(SR)_2$ (**16b**) is converted to the *cis* isomer (**17b**). Both *cis* and *trans* isomers exhibit high thermally stability and, thus, are not suitable candidates for ROP in the formation of thionylphosphazene polymers.

A second important method of poly(thionylphosphazene) synthesis was recently reported by Turner *et al*[36]. In this account they demonstrate the first synthesis of an alkyl or aryl substituted poly(thionylphosphazene) with a S^{VI}-N-P-N repeat unit by a polycondensation reaction that affords a highly regioselective coupling between a N-silylphosphoranimine (**8**) and a N-silylsulfonimidate (**10**). The reaction between **8** and **10** produces **18**, which is a highly reactive species that is very quickly hydrolyzed when exposed to air (Scheme 1.4). Heating of **18** (R = R' = R'' = Me) at 140°C yields **20**, which is a white crystalline solid.



Scheme 1.4 Condensation Route to S^{VI}-N-P-N Poly(thionylphosphazene)

The tacticity of **20** was determined by ^{31}P NMR spectroscopy. Two peaks of equal intensity at δ = 20.57 and 20.74 ppm indicated that equal amounts of isotactic and syndiotactic monomer units are present within the polymer, hence, the polymer is completely atactic (Figure 1.2). This was also confirmed by ^{1}H and ^{13}C NMR in which three doublets in a 1:2:1 ratio are obtained for the methyl groups attached to phosphorus. Evaluation of the polymer end groups by FAB mass spectrometry determined the absolute polymer structure to be $CF_3CH_2O[P\text{-}Me_2{=}N\text{-}S(O)Me{=}N]_nH$ and integration of ^{1}H and ^{31}P NMR spectra determined the absolute molecular weight (M_n) to be 8000.

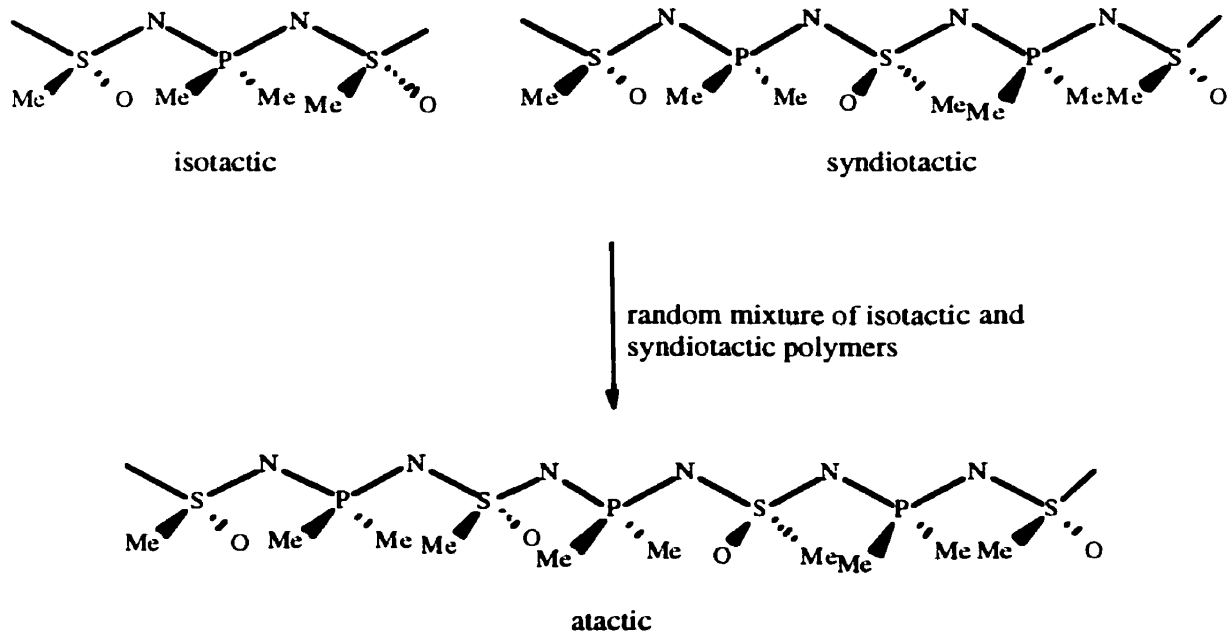
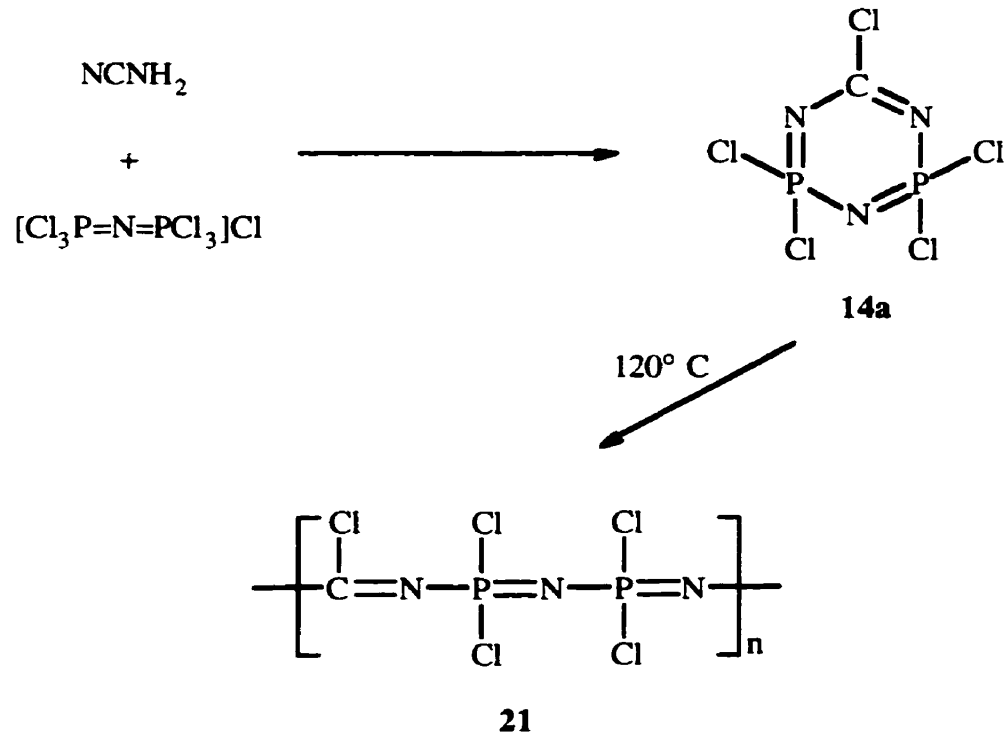


Figure 1.2 Atacticity from Mixing of Isotactic and Syndiotactic Polymers

1.4.3 Poly(carbophosphazenes)

Poly(carbophosphazenes) (**21**) are a class of hybrid inorganic polymers that are receiving attention[37,38]. The backbone is composed of C-N-P-N-P-N repeating units. Unlike the sulfur-containing phosphazene polymers, which may possess mixed properties of $(S(O)RN)_x$ and $(R'_2PN)_x$, there is no $(RCN)_x$ analogue that would contribute unique properties to the system because the triple bond found in the nitrile is very strong and, consequently, polymerization is unlikely[38]. The polymer **21** can be derivatized to tune its properties by changing the substituents on carbon and phosphorus.

The synthesis of the cyclic precursor **14a** was reported by Fluck and coworkers[39] in 1975 and polymerization was discovered in 1989 by Allcock and coworkers[38] (Scheme 1.5). Thermal ring opening polymerization of the cyclic precursor at 120°C produces a polymer with repeating C-N-P-N-P-N units in the backbone. Due to the hydrolytic instability of the chlorinated species (**21**), reaction with a nucleophile is required to stabilize the polymer. Sodium phenoxide[40] and aniline[38] are two examples of nucleophiles that have been used. The reaction of **21** with excess sodium phenoxide proceeds easily in THF at room temperature while more vigorous conditions are required for aniline. The T_g of the phenoxide polymer is 18°C while that of the amino substituted polymer is 112°C. These higher T_g values suggest that carbon makes the chain less flexible than the sulfur analogue. Upon reaction with amines complete replacement of chlorine on both the



Scheme 1.5 Preparation of Poly(chlorocarbophosphazene)

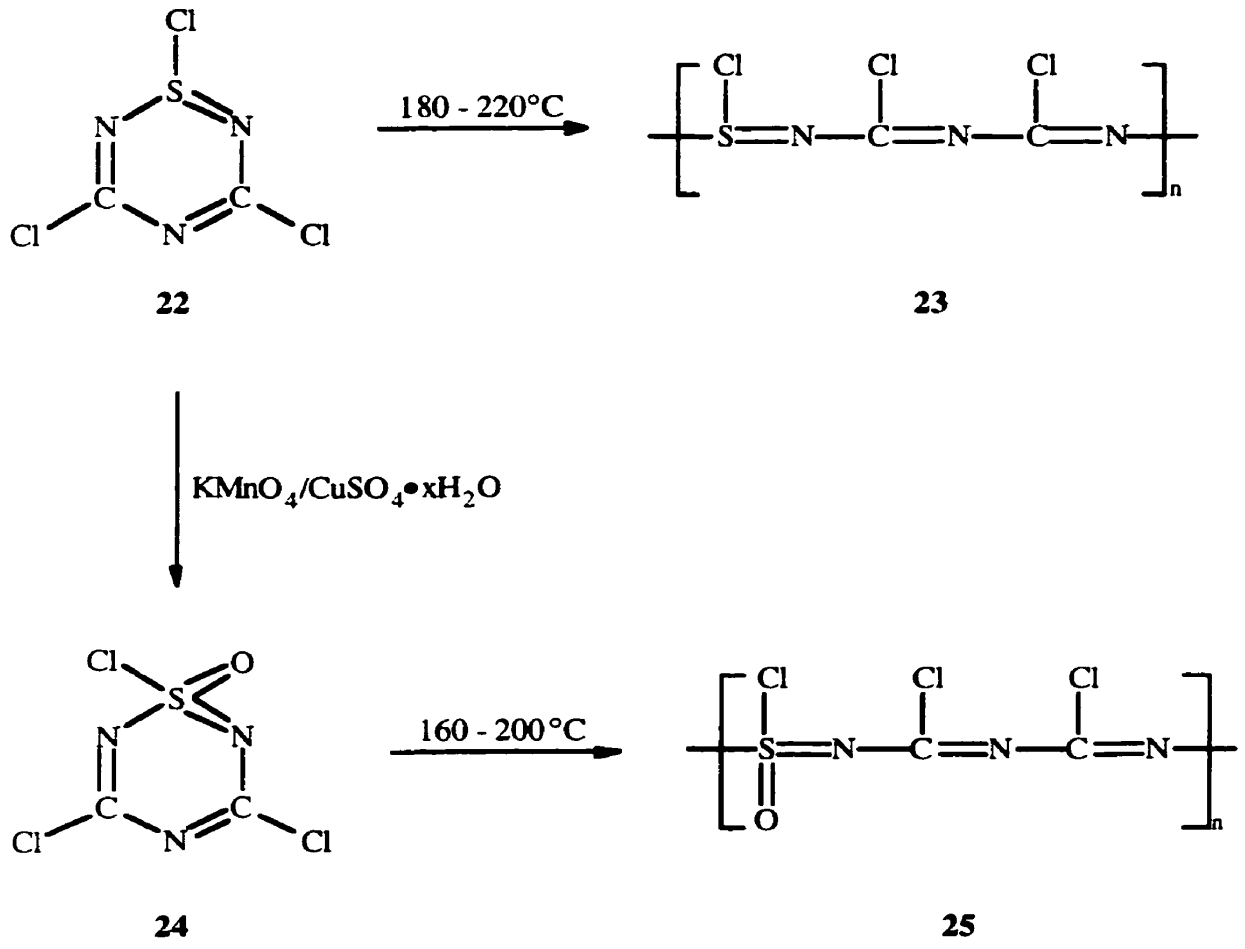
phosphorus and carbon occurs, which is in contrast to the poly(thionylphosphazenes) where amines completely replace chlorines on phosphorus but only partially substitute chlorine on sulfur. In order to determine if any preferential chlorine replacement occurs, one equivalent of nucleophile was added and it was observed that nucleophilic substitution was equally likely at both the carbon and the phosphorus and therefore heterodisubstituted species are inaccessible by this method.

1.4.4 Six-Membered Cyanuric-Sulfanuric Rings

The most common hybrid rings and polymers are those derivatives of phosphazenes containing sulfur or carbon (see Sections 1.4.2 and 1.4.3). In 1999 Chivers *et al.* reported the synthesis of a six-membered cyanuric-sulfanuric rings and the corresponding polymer with a S^{VI}-N-C-N-C-N repeat unit[41]. The cyanuric-thiazyl six-membered ring (**22**) was prepared from the reaction of $NaN(CN)_2$ with $SOCl_2$ in DMF in the presence of Me_4NCl. Attempts at polymerization of **22** gave **23** an orange, highly moisture-sensitive, gummy material. Reactions of **23** with a variety of sodium aryloxides gave polymers with improved hydrolytic sensitivity, but pure products could not be obtained. Elemental analysis revealed the loss of sulfur as sulfur chlorides during the polymerization.

In an effort to improve the hydrolytic stability of **23** the oxidation of the cyanuric-thiazyl ring **22** to the corresponding cyanuric-sulfanuric system **24** was investigated. Oxidizing agents such as *m*CPBA and $KMnO_4$ were attempted without success but $^nBu_4N(MnO_4)$ gave the first indication that oxidation to **24** had occurred. The most successful oxidant for the preparation of **24** was a mixture of $KMnO_4$ and $CuSO_4 \bullet xH_2O$ (x = 4-6). Interestingly, the presence of the hydrated $CuSO_4$ is required, otherwise no reaction occurs. The novel heterocycle **24** is purified by sublimation onto a cold finger at -78°C to yield a white solid that melts at 20-22°C. Polymerization of **24**

was investigated at 160-200°C but pure **25** could not be obtained due to a partial loss of sulfur during the ring-opening process.



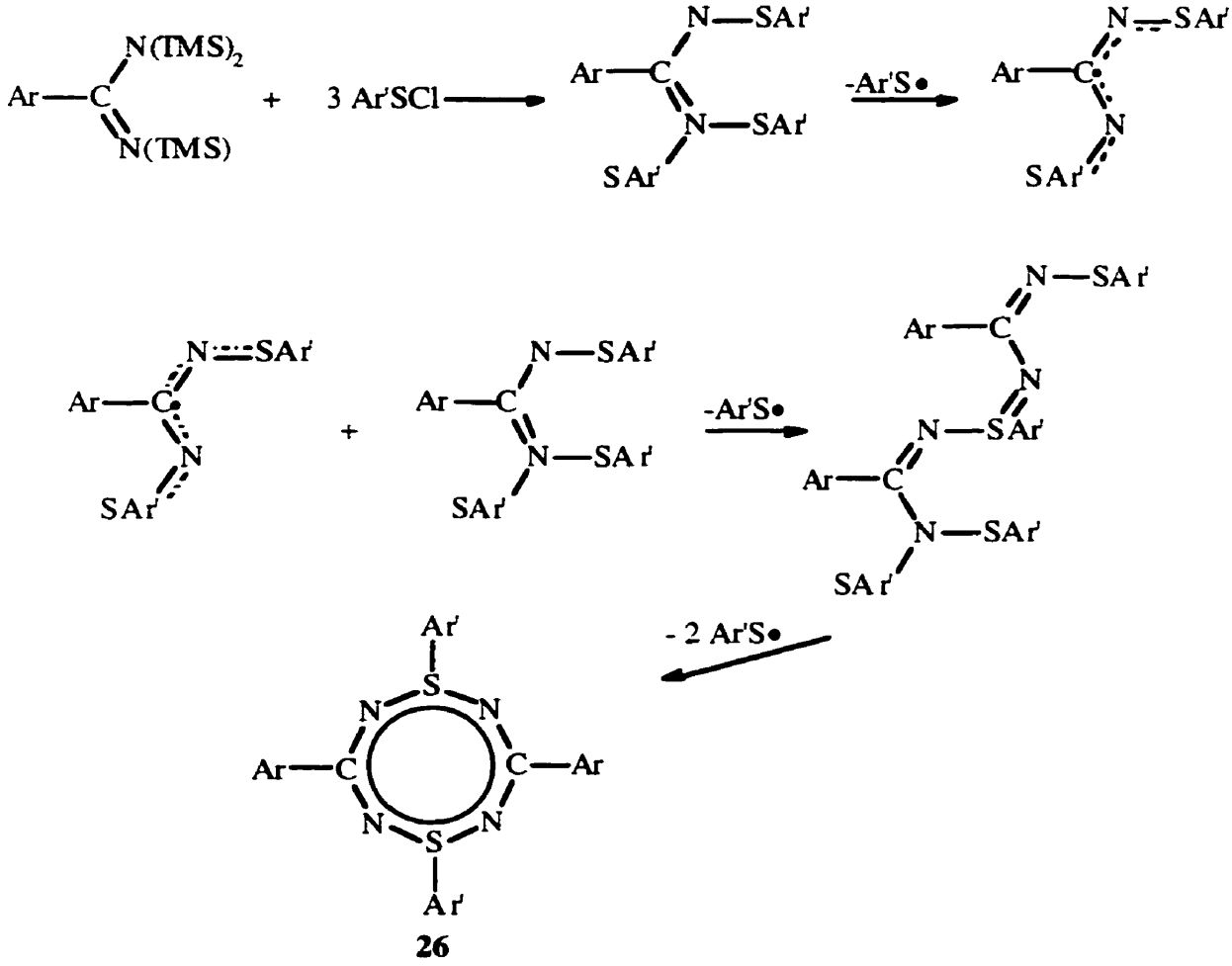
22 **23**

24 **25**

Scheme 1.6 Preparation of Cyanuric-Thiazyl and Cyanuric-Sulfanuric Polymers

1.4.5 Dithiatetrazocines

In the search for hybrid inorganic polymers consisting of a C-N-S-N backbone many potential precursors have been synthesized. In the early 1980's, $C_2N_4S_2$ heterocycles with two-coordinate sulfur were reported, but the formation of polymers



26

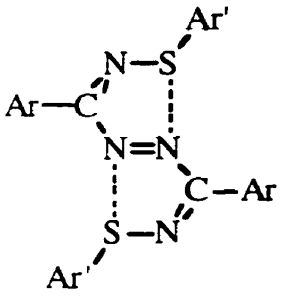
a Ar = 4-BrC_6H_4 Ar' = Ph

b Ar = 4-$CF_3C_6H_4$ Ar' = Ph

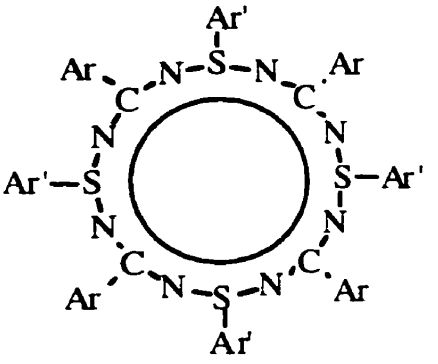
c Ar = 4-$CF_3C_6H_4$ Ar' = 4-$CH_3C_6H_4$

Scheme 1.7 Proposed Mechanism of Formation of $C_2N_4S^{IV}{}_2$ Rings

from these systems was not accomplished[42]. In 1997 the synthesis of heterocycles with three coordinate sulfur in the +4 oxidation state was achieved[6]. These systems consist of alternating C-N-S^{IV}-N rings of eight and sixteen atoms that have boat or cradle ring conformations, respectively. The rings are prepared by the reaction of a trisilylated benzamidine with three equivalents of an arene sulfenyl chloride at very low temperatures (Scheme 1.7). Variation of concentration of reactants, temperature, and reaction time determined the conditions for optimum yields of the eight- and sixteen-membered rings.



27

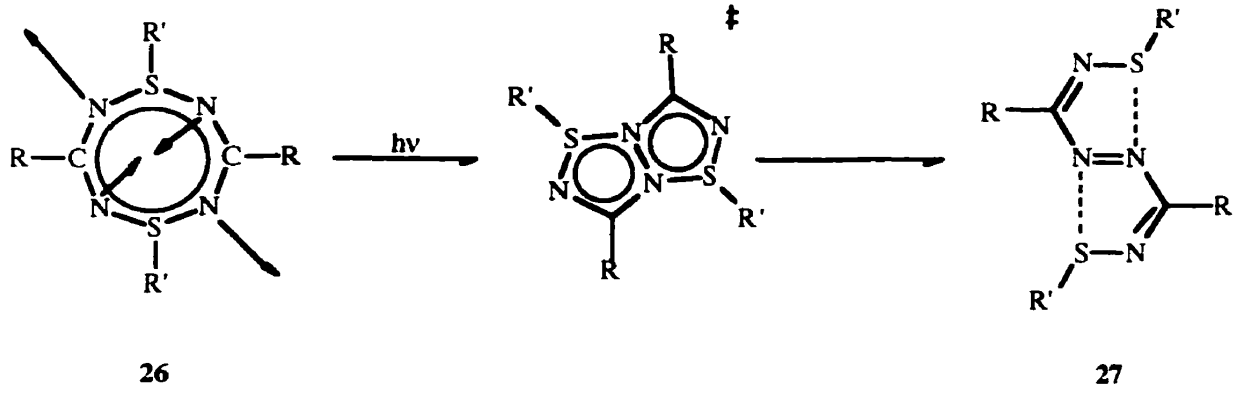


28

a Ar = 4-BrC_6H_4 Ar' = Ph
b Ar = 4-$CF_3C_6H_4$ Ar' = Ph
c Ar = 4-$CH_3C_6H_4$ Ar' = Ph
d Ar = 4-$CH_3C_6H_4$ Ar' = 4-$CF_3C_6H_4$

The formation of the eight-membered rings known as dithiatetrazocines (**26**), is optimized by carrying out the addition at -100°C followed by warming the reaction mixture to -78°C for 16 hours. Under these conditions the yields of the eight- and sixteen-membered rings are 80 and 10%, respectively. An increase in the yield of sixteen-membered ring is observed when the reaction time is increased to 40 hours. The intensely coloured diazene **27** is the major product of all room temperature reactions. This can be explained by considering at elevated temperatures, the relatively high concentration of radical $ArC(NSPh)_2\bullet$ increases the chances of a second order reaction to form the diazene by radical coupling. At low temperatures, the decomposition of $ArCN_2(SPh)_3$ is slow, consequently the concentration of $ArC(NSPh)_2\bullet$ is low and, therefore, the reaction of radical with trithiolated benzamidine prevails forming the longer chains which then cyclize to form the eight-membered ring.

An interesting feature of the eight-membered ring **26** is the photoisomerization to produce the corresponding diazene[43]. The process is shown in Scheme 1.8. Photochemical isomerization is a well known process in heterocyclic chemistry but only a few examples involving C-N-S systems have been studied[43]. The driving force behind the isomerization is the formation of the N=N double bond at the expense of the



26 27

Scheme 1.8 Mechanism for Photoisomerizaiton of Substituted Dithiatetrazocine to a Diazene

S-N bonds which are ultimately lengthened. The resulting diazene has two weak S•••N interactions. It is interesting to note that the sixteen-membered species does not undergo this photochemical isomerization suggesting that a ring-opening process does not occur.

1.5 Thesis Objectives

The objectives of this thesis are two-fold. Firstly, the effects of oxidation on a series of eight- and sixteen-membered C-N-S^{IV}-N rings with different substituents on the cyclic carbon and sulfur atoms will be examined. The varying substituents will include para-substituted phenyl rings, more specifically; C_6H_5, 4-BrC_6H_4, 4-$CH_3C_6H_4$, 4-$CF_3C_6H_4$. These systems are related to the eight-membered P-N-S-N rings mentioned in Section 1.4.2 and a similar approach will be taken to obtain S(VI) species. Oxidation with

*m*CPBA will yield rings with S(VI) atoms which are expected to be more stable with respect to hydrolysis than their S(IV) analogues. Changes in ring conformation, bond lengths d(C-N) and d(S-N), as well as torsion angles as determined by X-ray crystallography will be considered.

The second main focus of this thesis is an investigation into the ring-opening polymerization of the cyanuric-sulfanuric systems under a variety of reaction conditions with a view to generating hybrid polymers with alternating C-N and S^{VI}-N functionalities. These experiments will include thermolysis, photolysis, and reactions with electrophiles.

CHAPTER 2

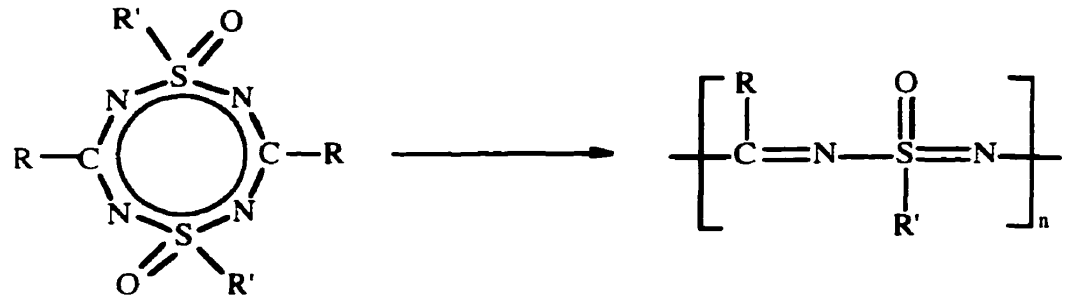
Synthesis, Structures and Reactions of Eight-Membered Cyanuric-Sulfanuric Heterocycles

2.1 *Introduction*

The potential for cyanuric-sulfanuric heterocycles to serve as precursors for inorganic polymers with a C-N-S^{VI}-N backbone (Equation 2.1) is the focus of research described in this chapter. Thus far, hybrid rings and polymers have been shown to be useful for a variety of interesting applications[1,2,3].

The preparation of eight- and sixteen-membered C-N-S^{VI}-N ring systems was reported in 1997[6]. The oxidation of these heterocycles to the corresponding S(VI) systems is investigated in this thesis. In an effort to evaluate the reactivity of the cyanuric-sulfanuric rings a number of different experiments were carried out, namely, thermolysis, photolysis, and reactions with electrophiles. The ring (4-$CF_3C_6H_4)_2C_2N_4S_2O_2(C_6H_5)_2$ was chosen to study the reaction chemistry in view of its

greater ease of preparation compared to the other heterocycles. Each of the aforementioned reactions will be discussed giving a detailed account of the results.



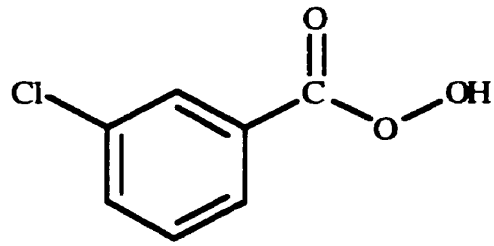
(2.1)

29 **30**

a R = 4-BrC_6H_4 R' = Ph
b R = 4-$CF_3C_6H_4$ R' = Ph
c R = 4-$CH_3C_6H_4$ R' = 4-$CF_3C_6H_4$

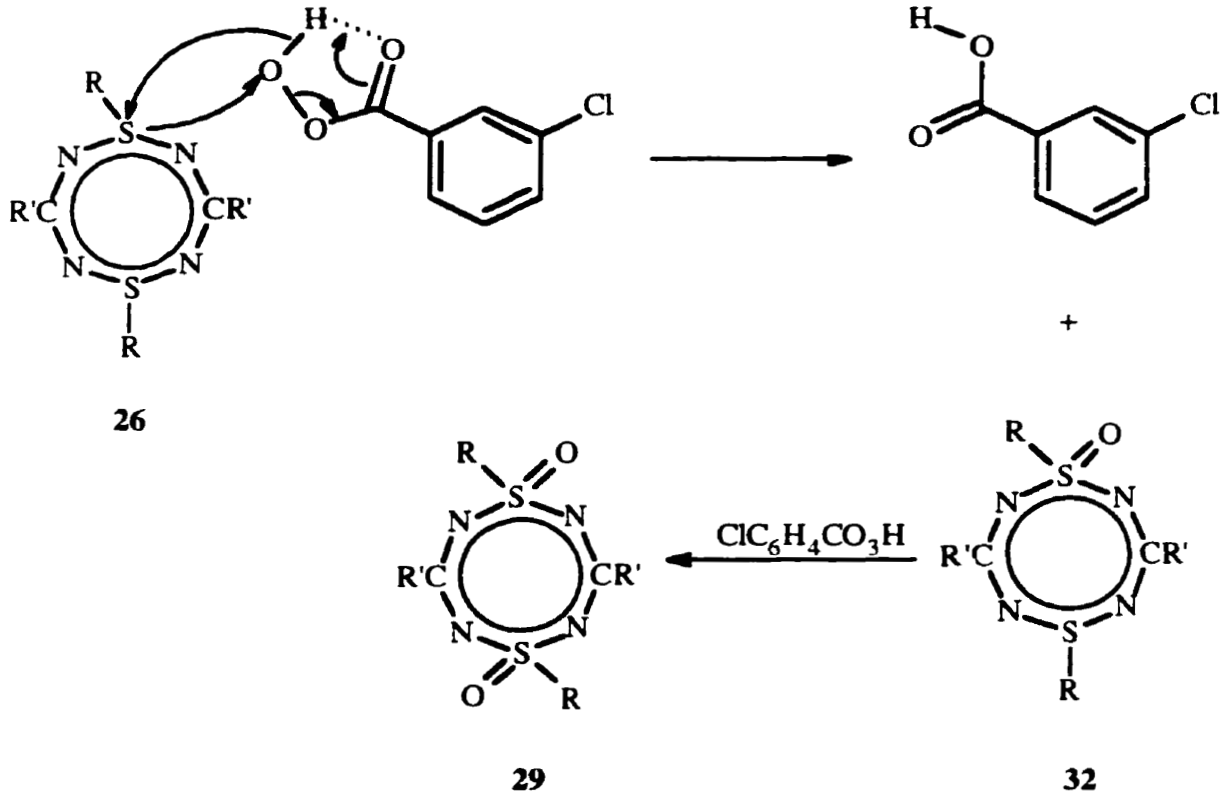
2.2 Synthesis and Spectroscopic Characterization of Eight-Membered Cyanuric-Sulfanuric Rings

Eight-membered cyanuric-sulfanuric rings were prepared by the reaction of the corresponding dithiatetrazocine with *meta*-chloroperbenzoic acid **31** (*m*CPBA) in either THF or, more commonly, CH_2Cl_2 (Scheme 2.1). The reactions were carried out for a variety of substituted rings: (4-BrC_6H_4)$_2C_2N_4S_2(C_6H_5)_2$ (**26a**), (4-$CF_3C_6H_4$)$_2C_2N_4S_2(C_6H_5)_2$ (**26b**) and (4-$CF_3C_6H_4$)$_2C_2N_4S_2$(4-$CH_3C_6H_4$)$_2$ (**26c**).



31

As an oxidant *m*CPBA is well known in organic chemistry and is widely used in epoxide formation from a variety of functional groups including olefins[44] and also in the conversion of ketones to esters[45]. In inorganic heterocyclic chemistry *m*CPBA has been shown to oxidize mixed sulfur(IV)-phosphorus-nitrogen ring systems to give the corresponding sulfanuric-phosphazenes[35]. The weak O-O bond of the peracid undergoes attack from the sulfur atom's electron pair. The consequence is an oxygen transfer from the *m*CPBA to the sulfur contained within the ring. A second equivalent of *m*CPBA reacts in the same manner resulting in the oxidation of the second heterocyclic sulfur atom.



Scheme 2.1 Proposed Mechanism for Dithiatetrazocine Oxidation by *m*CPBA

*m*CPBA is dissolved in CH_2Cl_2 and then added to a slurry of the dithiatetrazocine in CH_2Cl_2. After stirring the reactants for approximately 15 minutes the pale yellow coloured solution becomes colourless indicating that oxidation is complete. Step-wise addition of *m*CPBA determined that a minimum of six equivalents is required to convert both S(IV) atoms to S(VI). Removal of excess *m*CPBA and by-products was achieved by one of two methods. The first method is an aqueous extraction with $NaHCO_3$ followed by recrystallization in CH_2Cl_2/hexane. This method often proved unsatisfactory in

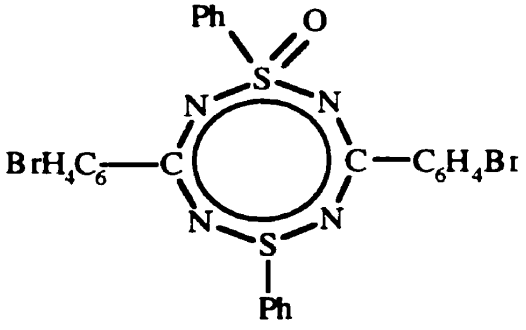
completely removing unwanted by-products and had to be repeated resulting in relatively low yields. An alternative method of by-product removal involves the reaction of the product mixture with gaseous ammonia[46]. After oxidation is complete an excess of $NH_{3(g)}$ is bubbled through the reaction flask for approximately 15 to 30 minutes. Upon $NH_{3(g)}$ introduction a white precipitate forms in the reaction flask. Careful filtration of the reaction mixture with a very fine frit removes ammonium *meta*-chlorobenzoate leaving the oxidized ring in solution. Solvent reduction by high vacuum results in an eight-membered cyanuric-sulfanuric ring that is a white crystalline air-stable solid. Samples were stored in screw cap vials for months with no signs of degradation.

Oxidation with $KMnO_4/CuSO_4 \bullet xH_2O$ was also investigated in an attempt to convert the S(IV) to S(VI) in the eight-membered rings. $KMnO_4/CuSO_4 \bullet xH_2O$ (x = 4-6) in a 2:1 weight ratio is known to be successful in the oxidation of sulfides and selenides[47]. In early 1999 the oxidation of $Cl_2C_2N_3SCl$ by $KMnO_4/CuSO_4 \bullet xH_2O$ to the corresponding sulfanuric system $Cl_2C_2N_3S(O)Cl$ in ≤20% yields was reported by Chivers *et al.*[41]. However, in this work no reaction was observed between **26a** and $KMnO_4/CuSO_4 \bullet xH_2O$ in CH_2Cl_2. Other peracids such as H_2O_2 and $^tBuO_2H$ are known to oxidize sulfides[45] but were unsuccessful when tried on **26a**.

^1H NMR spectra were obtained for all cyanuric-sulfanuric eight-membered rings (**29**). In each instance a typical A_2B_2 pattern was obtained in the aromatic region with peaks shifted slightly upfield compared to those of the dithiatetrazocines. Integration

identified two doublets each corresponding to four protons for the *para*-substituted phenyl rings in **29a** and **29b** and a multiplet representing five protons for the C_6H_5 rings. Strong molecular ions were observed in the electron-impact mass spectra of **29a**, **29b**, and **29c**. Elemental analyses (CHN) of these systems were in good agreement with the calculated values. ^{13}C NMR was used to identify the heterocyclic carbon atom for **29a**, **29b**, and **29c**. The chemical shift determined for these systems was approximately 166 ppm compared to the value of approximately 167 ppm for the corresponding dithiatetrazocines. The infra-red spectra exhibited bands at approximately 1095 cm^{-1} and 1310 cm^{-1}, attributed to S-N and S=O stretching vibrations, respectively.

The reaction of $(4\text{-}BrC_6H_4)_2C_2N_4S_2(C_6H_5)_2$ (**26a**) in THF proceeded considerably more slowly than in CH_2Cl_2. A total time of 2 hours was required for the yellow colour of the dithiatetrazocine to disappear. In this case *m*CPBA (**31**) oxidized only one of the S(IV) atoms to S(VI) while leaving the other unaffected. The result is a mixed eight-membered S(IV)/S(VI) cyanuric heterocycle (**32**).



32

The ^{1}H NMR spectrum of **32** shows two multiplets at approximately δ = 8.25 ppm which represent the two different environments for phenyl protons on the sulfur atoms (Figure 2.1) while the rest of the spectrum remains essentially the same as that of the dioxidized species (i.e. A_2B_2 pattern for the *para*-substituted phenyl rings).

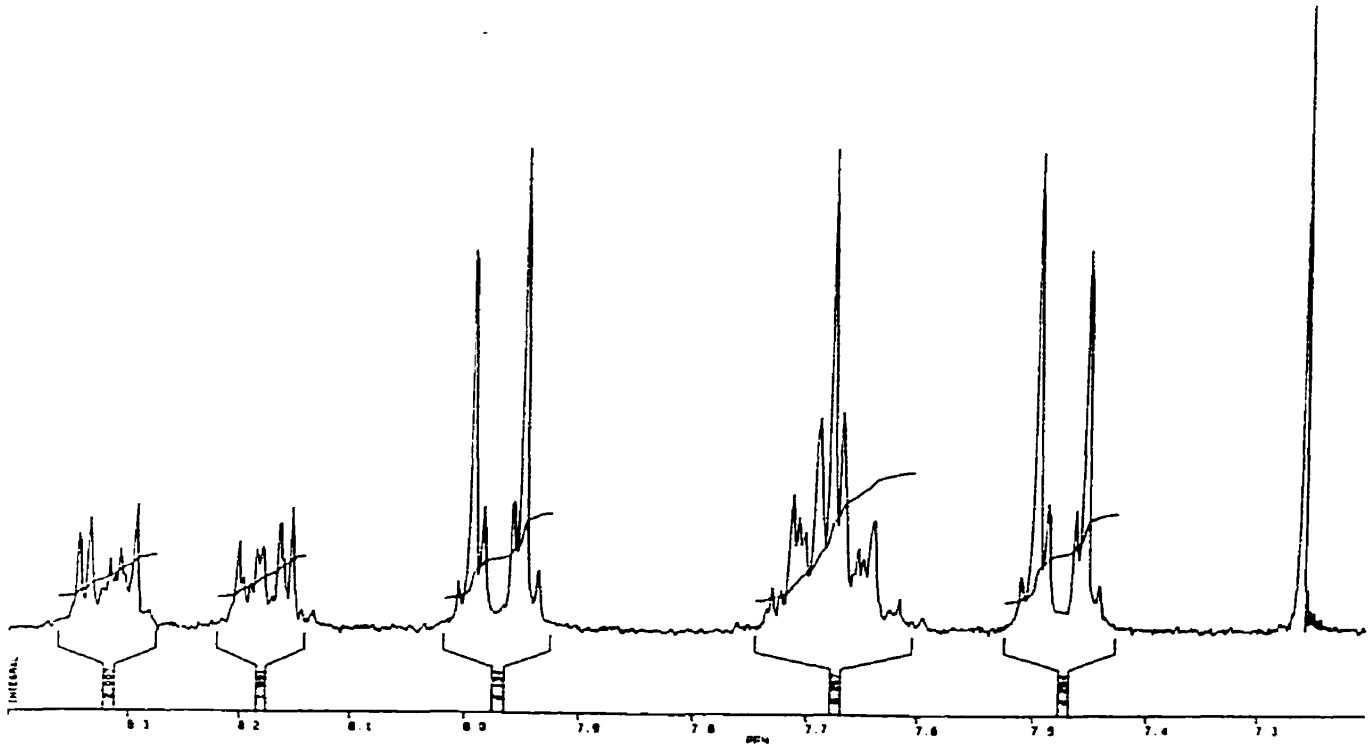


Figure 2.1 ^{1}H NMR Spectrum of $(4\text{-}BrC_6H_4)_2C_2N_4S_2O(C_6H_5)_2$ **(32)**

The formation of the mono-oxidized product is thought to occur because of solvent effects since different products are obtained depending whether CH_2Cl_2 or THF is used.

2.3 X-ray Structures of Eight-Membered Cyanuric-Sulfanuric Rings

2.3.1 $(4\text{-}BrC_6H_4)_2C_2N_4S_2O(C_6H_5)_2$ (32)

Colourless prisms of **32** were grown from slow evaporation of a CH_2Cl_2/hexane solution at room temperature. A crystal was mounted outside the glove-box on a glass fibre in epoxy resin. The crystallographic data for **32** are summarized in Table 2.1. ORTEP drawings are illustrated in Figures 2.2 and 2.3. Selected bond lengths, bond angles, and torsion angles are given in Table 2.2. Data collection was carried out at low temperatures to reduce crystal decomposition and thermal motion. Further details of the structure solution and refinements may be obtained from Dr. T. Chivers.

The structure of **32** is unique when compared to those of **29b** and **29c** (see Sections 2.3.2 and 2.3.3) in that only one sulfur is oxidized. The oxygen is disordered such that its occupancy is 50% on one sulfur and 50% on the other sulfur. The pseudo C_{2v} symmetry of the molecule allowed for faster data collection as only half the number of reflections had to be collected. The second half of the molecule was generated by symmetry and is the mirror image of the first half. The large estimated deviation values may be attributed to the fact that the sulfur positions were calculated by this method. The eight-membered $C_2N_4S^{VI}_2$ ring in **32** has a boat conformation similar to that of the corresponding dithiatetrazocine. Torsion angles can be used to determine the extent of twisting that occurs in the boat conformation. In **32** the C-N-S-N torsion angles are -81(2) and 68(2)° which compare to values of -81.6(7) and 87.7(7)° in **26a**. Similarly, the

S-N-C-N torsion angles are -4(3) and 14(3)° in **32** while the corresponding values for **26a** are -11.1(1) and 7(1)°. From these data a slightly twisted boat conformation compared to that of the dithiatetrazocine is evident. The phenyl rings attached to sulfur and carbon are perpendicular to the C_2 axis going through the centre of the $C_2N_4S_2$ ring. Table 2.3 lists selected average bond lengths, bond angles, and torsion angles of **32** and the corresponding dithiatetrazocine **26a** for comparison. Oxidation of $(4\text{-}BrC_6H_4)_2C_2N_4S_2(C_6H_5)_2$ to **32** shortens the S-N bond from 1.656(6) Å to 1.62(5) Å while d(C-N) remains approximately the same at 1.32(2) Å [cf. 1.334(6) Å for $(4\text{-}BrC_6H_4)_2C_2N_4S_2(C_6H_5)_2$]. The S=O distance of 1.44(2) Å is consistent with an S^{VI}=O double bond [cf. d(SO) = 1.417(3) Å in $1,5\text{-}(Me_2N)_2C_2N_4[S(O)N(CF_3)_2]_2$[48] and 1.445(3) Å in *trans*-$Ph_4P_2N_4[S(O)Ph]_2$[35]].

Table 2.1 Crystallographic Data for $(4\text{-}BrC_6H_4)_2C_2N_4S_2O(C_6H_5)_2$ (**32**), $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(C_6H_5)_2$ (**29b**), and $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(4\text{-}CH_3C_6H_4)_2$ (**29c**)

	32	**29b**	**29c**
Formula	$C_{26}H_{18}N_4S_2OBr_2$	$C_{28}H_{18}N_4F_6S_2O_2$	$C_{30}H_{22}N_4F_6S_2O_2 \bullet C_7H_{16}$
Formula Weight	626.38	620.59	748.84
Crystal Habit	colourless, prism	colourless, block	colourless, prism
Dimensions (mm)	0.48 x 0.30 x 0.22	0.35 x 0.25 x 0.18	0.50 x 0.40 x 0.37
Crystal System	orthorhombic	monoclinic	triclinic
a (Å)	12.246(5)	7.316(2)	12.849(4)
b (Å)	7.818(4)	29.508(5)	12.863(4)
c (Å)	25.402(8)	12.910(2)	12.610(7)
α (°)	90	90	110.61(3)
β (°)	90	101.30(2)	105.77(3)
γ (°)	90	90	62.77(2)
V (Å^3)	2431(1)	2733(1)	1719(1)
Space Group	Pbcn (#60)	$P2_1/a$ (#14)	$P\bar{1}$ (#2)
Z	4	4	2
D_{calc} (gcm^{-3})	1.71	1.508	1.447
Temperature (°C)	-103.0	23.0	-103.0
R	0.0438	0.0855	0.0692
R_w	0.0434	0.250	0.1937

Table 2.2 Selected Bond Lengths (Å), Bond Angles (°), and Torsion Angles (°) for (4-$BrC_6H_4)_2C_2N_4S_2(O)(C_6H_5)_2$ (**32**)

Atoms	Bond Length	Atoms	Bond Angle
S(1)-N(1)	1.61(2)	S(1)-N(1)-C(1)	123(1)
S(1)-N(2)	1.62(2)	S(1)-N(2)-C(1)*	122(1)
N(1)-C(1)	1.33(2)	N(1)-S(1)-N(2)	115.1(8)
N(2)-C(1)*	1.30(2)	N(1)-C(1)-N(2)*	13691)
S(1)-O(1)	1.44(2)	C(8)-S(1)-O(1)	118(1)
S(1)-C(8)	1.75(2)	N(1)-S(1)-N(2)-C(1)*	68(2)
C(1)-C(2)	1.52(2)	N(2)-S(1)-N(1)-C(1)	-81(2)
		S(1)-N(1)-C(1)-N(2)*	14(3)
		S(1)-N(2)-C(1)*-N(1)*	-4(3)

Table 2.3 Comparison of Bond Lengths (Å), Bond Angles (°), and Torsion Angles (°) for (4-$BrC_6H_4)_2C_2N_4S_2(C_6H_5)_2$ (**26a**) and (4-$BrC_6H_4)_2C_2N_4S_2O(C_6H_5)_2$ (**32**)

	26a	**32**
d(S-N) Range (Å)	1.650(7) - 1.661(7)	1.61(2) - 1.62(2)
d(S-N) Average (Å)	1.656(6)	1.62(5)
d(C-N) Range (Å)	1.328(9) - 1.339(10)	1.30(2) - 1.33(2)
d(C-N) Average (Å)	1.334(6)	1.32(2)
∠S-N-C Range (°)	118.0(6) - 118.6(6)	123(1) - 122(1)
∠S-N-C Average (°)	118.3(3)	122.5(5)
∠N-S-N-C Range (°)	87.7(7) - -81.6(7)	68(2) - -81(2)
∠S-N-C-N Range (°)	7(1) - -11(1)	14(3) - -4(3)

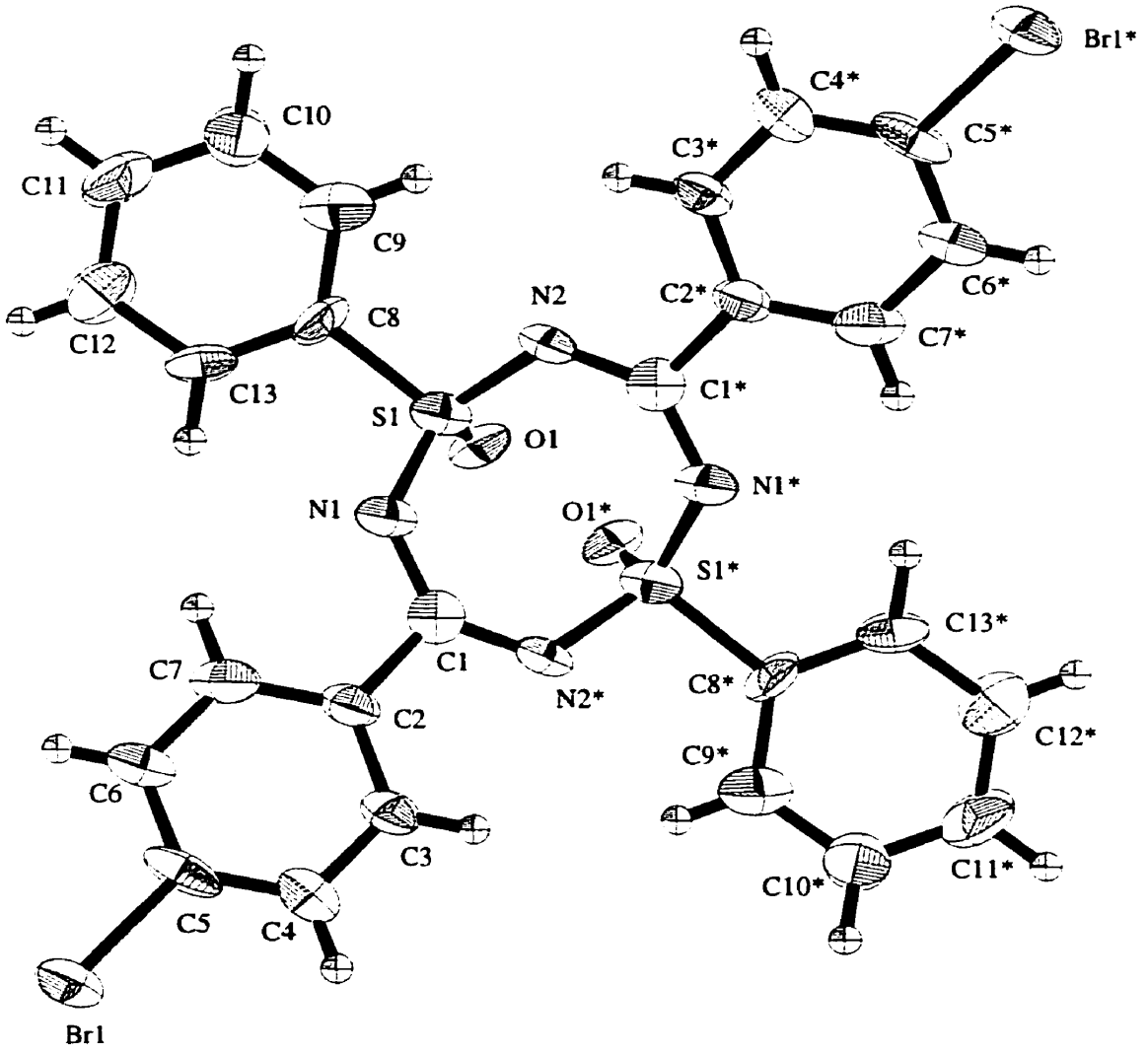
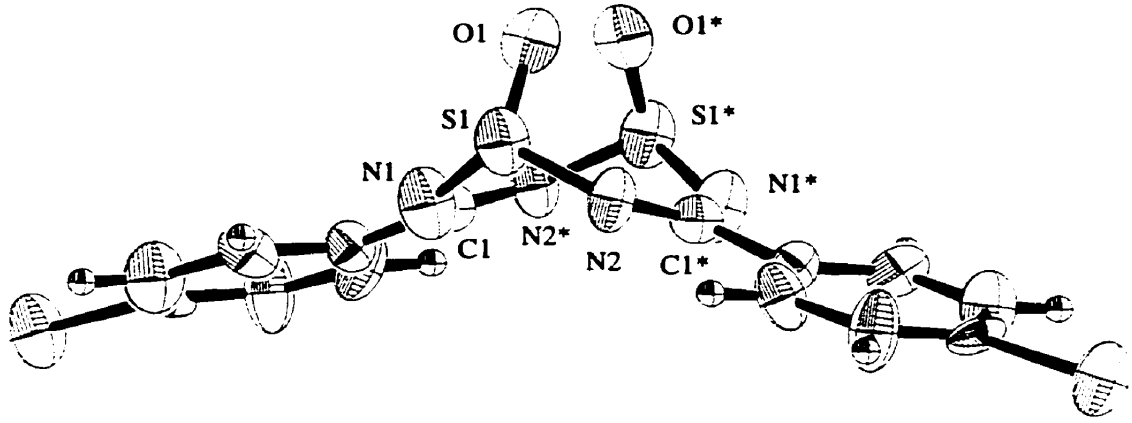


Figure 2.2 ORTEP Diagram of $(4\text{-}BrC_6H_4)_2C_2N_4S_2(O)(C_6H_5)_2$ **(32)**

(a)



(b)

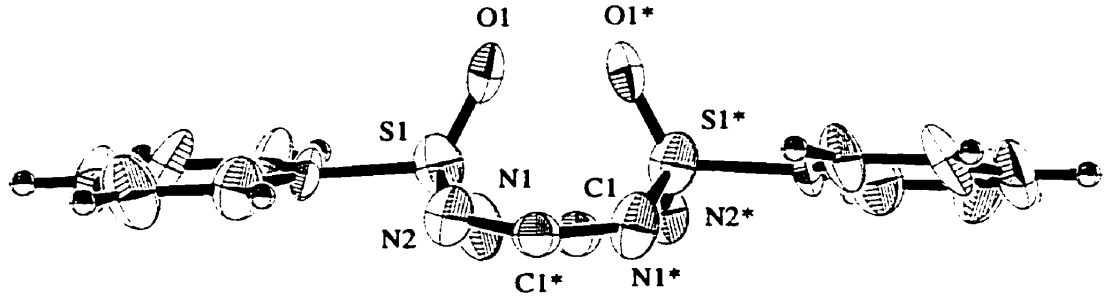


Figure 2.3 ORTEP Diagram of $(4\text{-}BrC_6H_4)_2C_2N_4S_2(O)(C_6H_5)_2$ (**32**) with (a) Ph rings on sulfur omitted and (b) $(4\text{-}BrC_6H_4)$ rings on carbon omitted for clarity

2.3.2 $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(C_6H_5)_2$ (29b)

Crystals of **29b** were grown as colourless blocks from slow evaporation of a CH_2Cl_2/hexane solution at room temperature. The crystal was mounted outside the glove-box on a glass fibre in epoxy resin. The crystallographic data for **29b** are summarized in Table 2.1. ORTEP drawings are illustrated in Figures 2.4 and 2.5. Selected bond lengths, bond angles, and torsion angles are given in Table 2.4. Data collection was carried out at room temperature. Further details of the structure solution and refinements may be obtained from Dr. T. Chivers.

The oxygen atoms bonded to sulfur in **29b** are *cis* to each other with respect to the $C_2N_4S_2$ ring. The presence of two oxygens has a pronounced effect on the boat conformation of the ring. In the corresponding dithiatetrazocine a regular boat conformation is observed but the boat has a distinct twist in the cyanuric-sulfanuric system. The presence of the oxygens on sulfur appear to skew the sulfur atoms from their original position in the dithiatetrazocine thus distorting the boat and relieving the steric hindrance felt by the oxygen atoms. Torsion angles of **29b** and the corresponding dithiatetrazocine (**26b**) are listed in Table 2.5. The distortion of the boat conformation of the $C_2N_4S_2$ ring is reflected in the difference in the values of the S-N-C-N and N-S-N-C torsion angles. Interestingly, the plane of the phenyl ring attached to S(1) is approximately at right angles to the S(2) phenyl ring plane (Figure 2.4). Table 2.6 is a list of selected bond lengths, bond angles, and torsion angles of **29b** and the corresponding

dithiatetrazocine **26b**. From this table we see that oxidation of S(IV) to S(VI) affects bond lengths, bond angles, and torsion angles. For **29b** the average S-N bond length is 1.589(14) Å which is slightly shorter than the corresponding value of 1.640(12) Å for the dithiatetrazocine. The average C-N bond length remains unchanged from 1.327(14) Å in the dithiatetrazocine to 1.331(23) Å in the cyanuric-sulfanuric ring. The S-N-C bond angles range from 118.1(5) to 125.5(5)° with an average of 121(3)° in the dithiatetrazocine compared to a range of 124.3(8) to 129.0(7)° and average of 126.8(20)° in the cyanuric-sulfanuric ring. The S=O distances of 1.434(8) Å and 1.412(9) Å in **29b** are consistent with an S(VI)=O double bond.

Table 2.4 Selected Bond Lengths (Å), Bond Angles (°), and Torsion Angles (°) for (4-$CF_3C_6H_4)_2C_2N_4S_2(O)_2(C_6H_5)_2$ **(29b)**

Atoms	(Å)	Atoms	(°)
S(1)-N(4)	1.601(10)	N(4)-S(1)-N(1)	113.8(5)
S(1)-N(1)	1.565(10)	N(3)-S(2)-N(2)	112.4(5)
S(2)-N(3)	1.595(10)	S(1)-N(4)-C(9)	129.0(7)
S(2)-N(2)	1.596(10)	S(2)-N(3)-C(9)	126.1(8)
N(3)-C(9)	1.368(13)	S(2)-N(2)-C(1)	124.3(8)
N(4)-C(9)	1.312(13)	S(1)-N(1)-C(1)	127.8(8)
N(1)-C(1)	1.334(13)	N(4)-C(9)-N(3)	124.6(8)
N(2)-C(1)	1.309(14)	N(2)-C(1)-N(1)	130.1(11)
S(1)-O(1)	1.434(8)	C(17)-S(1)-O(1)	108.4(5)
S(2)-O(2)	1.412(9)	C(23)-S(2)-O(2)	110.9(5)
C(1)-C(2)	1.512(12)	S(1)-N(4)-C(9)-N(3)	-18.5(17)
S(1)-C(17)	1.763(8)	S(1)-N(1)-C(1)-N(2)	-31.7(18)
C(9)-C(10)	1.438(9)	S(2)-N(3)-C(9)-N(4)	-33.6(15)
S(2)-C(23)	1.724(7)	S(2)-N(2)-C(1)-N(1)	13.4(14)
		N(4)-S(1)-N(1)-C(1)	89.7(11)
		N(3)-S(2)-N(2)-C(1)	-38.9(13)
		N(2)-S(2)-N(3)-C(9)	98.1(10)
		N(1)-S(1)-N(4)-C(9)	-29.3(13)

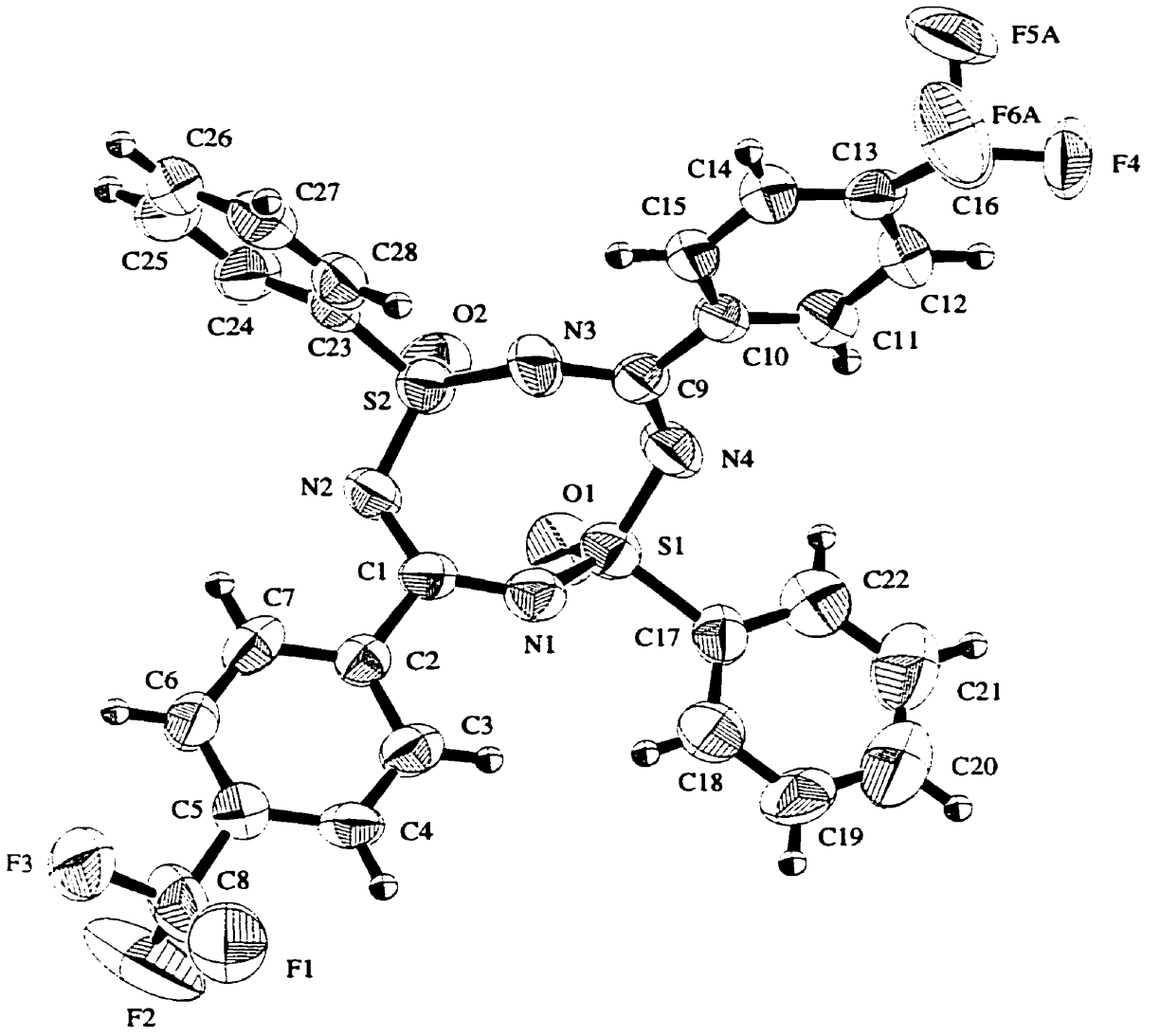


Figure 2.4 ORTEP Diagram of $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2(O)_2(C_6H_5)_2$ **(29b)**

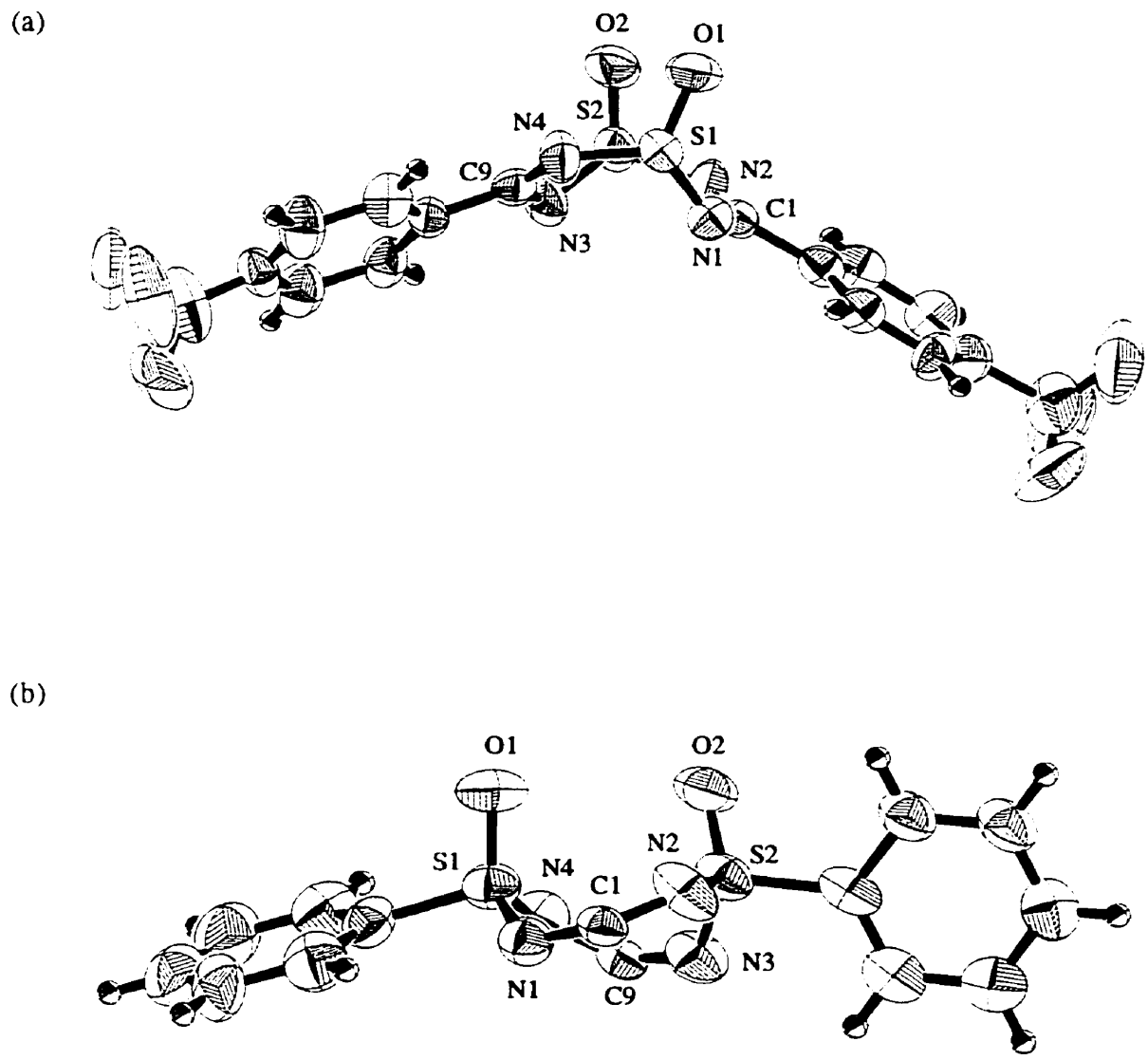


Figure 2.5 ORTEP Diagram of $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2(O)_2(C_6H_5)_2$ **(29b)** with (a) Ph rings on sulfur omitted and (b) $(4\text{-}CF_3C_6H_4)$ rings on carbon omitted for clarity

Table 2.5 Selected Torsion Angles (°) for $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2(C_6H_5)_2$ (**26b**), $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2(O)_2(C_6H_5)_2$ (**29b**), and $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2(O)_2(4\text{-}CH_3C_6H_4)_2$ (**29c**)

	26b	**29b**	**29c**
S(1)-N(4)-C(9)-N(3)	-17(1)	-18.5(17)	31.6(5)
S(1)-N(1)-C(1)-N(2)	6(1)	-31.7(18)	16.0(6)
S(2)-N(3)-C(9)-N(4)	3(1)	-33.6(15)	16.0(6)
S(2)-N(2)-C(1)-N(1)	-15(1)	13.4(14)	29.0(6)
N(4)-S(1)-N(1)-C(1)	-78.6(6)	89.7(11)	38.8(4)
N(3)-S(2)-N(2)-C(1)	82.4(6)	-38.9(13)	-93.6(4)
N(2)-S(2)-N(3)-C(9)	-66.2(7)	98.1(10)	35.8(4)
N(1)-S(1)-N(4)-C(9)	93.3(6)	-29.3(13)	-94.7(3)

Table 2.6 Comparison of Bond Lengths (Å), Bond Angles (°), and Torsion Angles (°) for $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2(C_6H_5)_2$ (**26b**), and $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(C_6H_5)_2$ (**29b**), and $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(4\text{-}CH_3C_6H_4)_2$ (**29c**)

	26b	**29b**	**29c**
d(S-N) Range (Å)	1.623(5)-1.652(5)	1.565(10)-1.601(10)	1.579(3)-1.605(3)
d(S-N) Average (Å)	1.640(12)	1.589(14)	1.592(10)
d(C-N) Range (Å)	1.312(7)-1.348(7)	1.309(14)-1.368(13)	1.326(5)-1.348(4)
d(C-N) Average (Å)	1.327(14)	1.331(23)	1.336(9)
∠S-N-C Range (°)	118.1(5)-125.5(5)	124.3(8)-129.0(7)	122.4(3)-127.1(3)
∠S-N-C Average (°)	121.6(16)	126.8(20)	124.8(20)
∠N-S-N-C Range (°)	-78.6(6)-93.3(6)	-39.8(13)-98.1(10)	-93.6(4)-38.8(4)
∠S-N-C-N Range (°)	-17(1)-6(1)	-33.6(15)-13.4(14)	16.0(6)-31.6(5)

2.3.3 $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(4\text{-}CH_3C_6H_4)_2 \bullet C_7H_{16}$ (29c)

Colourless prisms of **29c** were grown from slow evaporation of a CH_2Cl_2/ hexanes (the hexanes may have contained methyl substituted hexane) solution at room temperature. A crystal was mounted outside of the glove-box on a glass fibre in epoxy resin. Special care was given during mounting because the crystals began to crack and became opaque. It is thought that the cracking was due to slow solvent evaporation from the crystal matrix. The crystallographic data for **29c** are summarized in Table 2.1. ORTEP drawings are illustrated in Figures 2.6 and 2.7. Selected bond lengths, bond angles, and torsion angles are given in Table 2.7. Data collection was carried out at low temperature to reduce crystal decomposition and thermal motion. Further details of the structure solution and refinements may be obtained from Dr. T. Chivers.

In the absence of X-ray data direct comparison cannot be made with the corresponding dithiatetrazocine, but a comparison with $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2(C_6H_5)_2$ (**26b**) and $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2(O)_2(C_6H_5)_2$ (**29b**) is made in Table 2.6 (see Section 2.3.2). The torsion angles are considerably different from those of both **26b** and **29b** indicating that the cyanuric-sulfanuric ring is distorted compared to those in both **26b** and **29b**. The orientation of the phenyl rings in **29c** is different from that in **26b** and **29b**. The 4-$CF_3C_6H_4$ groups on carbon are parallel with each other, but at right angles to the 4-$CH_3C_6H_4$ groups on sulfur (Figure 2.6). Comparison of bond lengths and bond angles

of **29b** and **29c** show similar trends, i.e. d(S-N) becomes shorter upon oxidation and d(C-N) remains essentially the same. The S=O distances of 1.434(3) Å and 1.432(3) Å are consistent with an S^{VI}=O double bond.

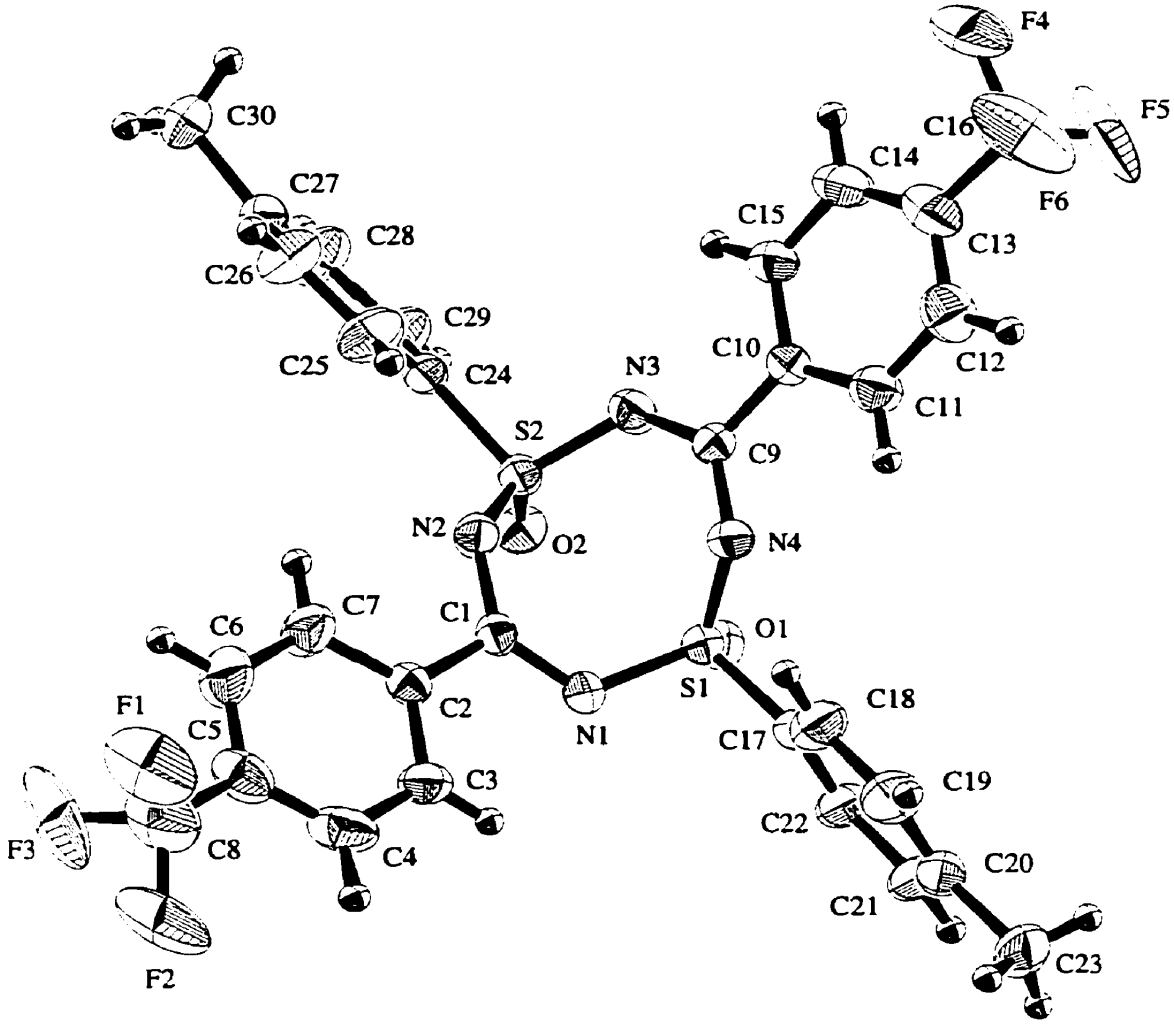


Figure 2.6 ORTEP Diagram of $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2(O)_2(4\text{-}CH_3C_6H_5)_2$ **(29c)**

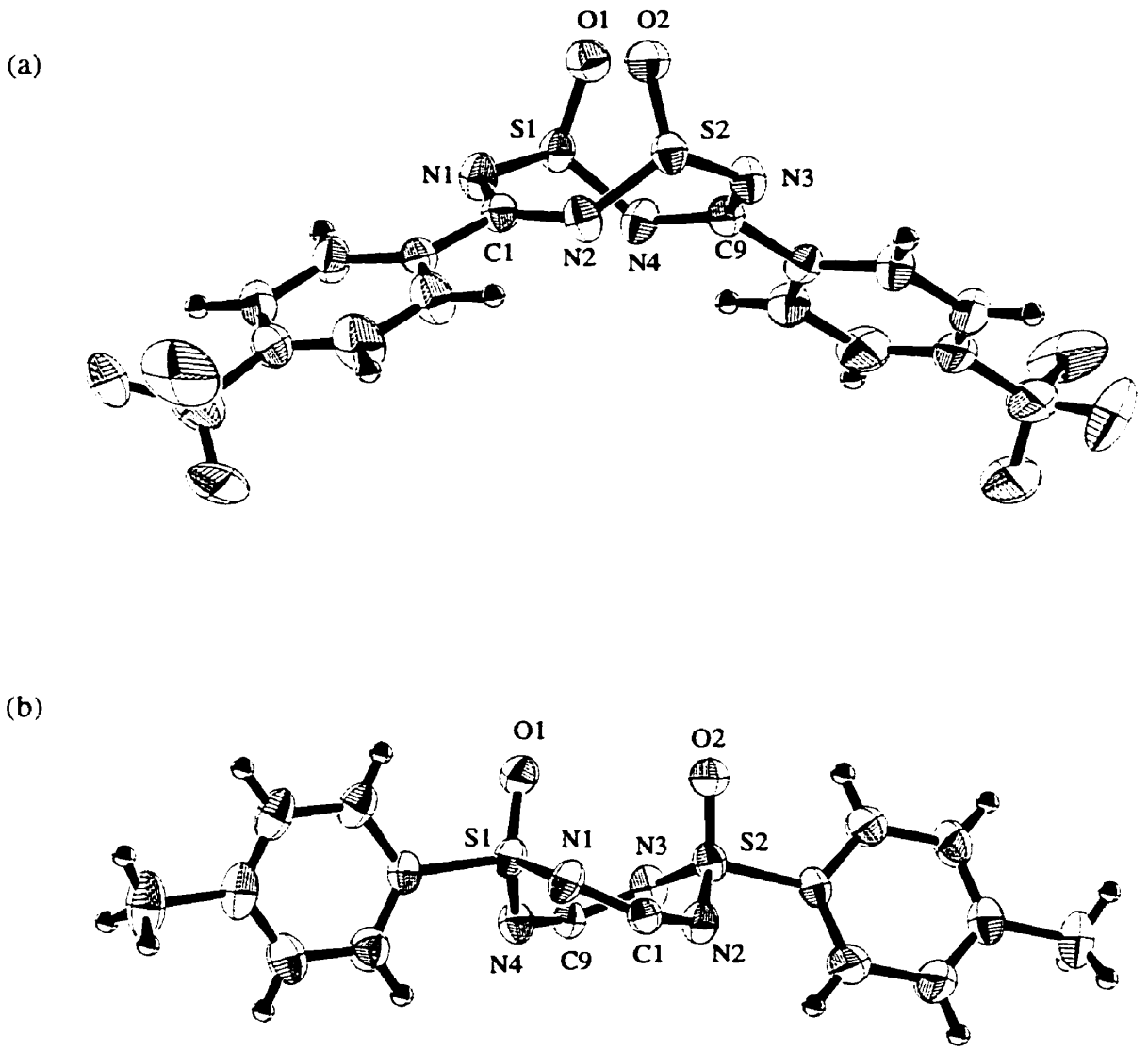


Figure 2.7 ORTEP Diagram of $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2(O)_2(4\text{-}CH_3C_6H_5)_2$ (**29c**) with (a) $(4\text{-}CH_3C_6H_5)$ rings on sulfur omitted and (b) $(4\text{-}CF_3C_6H_4)$ rings on carbon omitted for clarity

Table 2.7 Selected Bond Lengths (Å), Bond Angles (°), and Torsion Angles (°) for (4-$CF_3C_6H_4)_2C_2N_4S_2(O)_2$(4-$CH_3C_6H_5)_2$ (**29c**)

Atoms	(Å)	Atoms	(°)
S(1)-N(4)	1.584(3)	N(4)-S(1)-N(1)	112.19(19)
S(1)-N(1)	1.599(3)	N(3)-S(2)-N(2)	112.79(19)
S(2)-N(3)	1.605(3)	S(1)-N(4)-C(9)	125.9(3)
S(2)-N(2)	1.579(3)	S(2)-N(3)-C(9)	124.0(2)
N(3)-C(9)	1.329(5)	S(2)-N(2)-C(1)	127.1(3)
N(4)-C(9)	1.348(4)	S(1)-N(1)-C(1)	122.4(3)
N(1)-C(1)	1.326(5)	N(4)-C(9)-N(3)	128.8(3)
N(2)-C(1)	1.343(5)	N(2)-C(1)-N(1)	130.3(4)
S(1)-O(1)	1.434(3)	C(17)-S(1)-O(1)	109.09(16)
S(2)-O(2)	1.432(3)	C(23)-S(2)-O(2)	108.41(15)
C(1)-C(2)	1.494(4)	S(1)-N(4)-C(9)-N(3)	31.6(5)
S(1)-C(17)	1.743(2)	S(1)-N(1)-C(1)-N(2)	16.0(6)
C(9)-C(10)	1.475(3)	S(2)-N(3)-C(9)-N(4)	16.0(6)
S(2)-C(23)	1.752(2)	S(2)-N(2)-C(1)-N(1)	29.0(6)
		N(4)-S(1)-N(1)-C(1)	38.8(4)
		N(3)-S(2)-N(2)-C(1)	-93.6(4)
		N(2)-S(2)-N(3)-C(9)	35.8(4)
		N(1)-S(1)-N(4)-C(9)	-94.7(3)

2.4 Reactions of Eight-Membered Cyanuric-Sulfanuric Rings

2.4.1 Thermolysis of $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(C_6H_5)_2$

The thermolysis of $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(C_6H_5)_2$ **(29b)** was investigated to determine whether thermal ring-opening was a valid method of polymerization for these systems. A small amount of sample, often 100 mg or less, was placed into a long tube which was then evacuated. The tube was placed in a temperature-controlled furnace at a temperature above its melting point, approximately 220°C. The experimental set-up is shown in Figure 2.8.

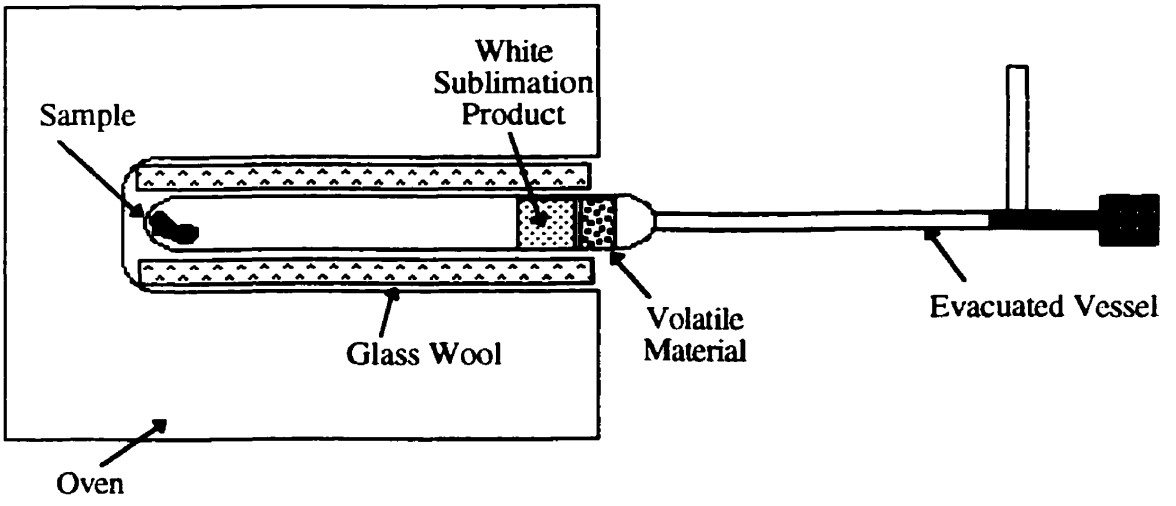


Figure 2.8 Thermolysis Experiment

The sample turned black upon heating and then remained as a liquid melt. The reaction was monitored by ^1H NMR at regular intervals until it was observed that no

eight-membered ring **29b** remained in the tube. After approximately 31 hours at 220°C all starting material was converted to the product. A characteristic doublet at δ = 8.67 ppm was used as a guide for product formation because it was distinct from the other peaks in the aromatic region (see Figure 2.9).

At the end of the tube closest to the outside of the furnace a white crystalline material sublimed and a yellow liquid that solidified upon cooling was also observed. ^{1}H NMR analysis indicated that the latter contained large amounts of diphenyl disulfide as well as some 4-$CF_3C_6H_4CN$. The ^{1}H NMR analysis of the white compound showed it was the same as the black residue. In an effort to purify the black product it was sublimed at 120°C under vacuum (*ca.* 10^{-2} mmHg) for 48 hours. To determine the optimum temperature for sublimation the vessel was gradually heated until the white material was observed to form on the cold finger of the apparatus. Attempts to recrystallize the white sublimate have been unsuccessful. Many different solvents in varying ratios were attempted but the crystals that were obtained were not of X-ray quality. However, this product was identified by a variety of spectroscopic methods, in addition to elemental analysis and molecular weight determination, as indicated below.

The presence of the yellow volatile material inside the reaction vessel, in addition to the white sublimate, indicates that the cyanuric-sulfanuric ring is not simply isomerizing as was the case when dithiatetrazocines are heated above their melting points[43]. The most likely explanation of the experimental observations is a ring

contraction reaction. Ring contraction is known to occur for other sulfur-nitrogen ring systems e.g., 1,3-$(Me_2NCN)_2(NSCl)_2$ loses Me_2NCN to form $(Me_2NCN)(NSCl)_2$[49] and 1,3-$(Ph_2PN)_2(NSCl)_2$ loses a NSCl unit to form the six-membered ring $(Ph_2PN)_2(NSCl)$[50]. In view of the detection of both $(PhS)_2$ and 4-$CF_3C_6H_4CN$ in the yellow volatile product two decomposition pathways should be considered (Scheme 2.2). The loss of a sulfanuric unit, NS(O)R, is indicated by the formation of $(PhS)_2$. In 1968 Maricich reported a synthesis of $(NS(O)Ph)_3$ from the reaction of (PhS(O)Cl) and NaN_3[51]. In this synthesis it is believed that $(NS(O)Ph)_3$ is formed by the trimerization of the monomeric (PhS(O)N). A by-product of this reaction is $(PhS)_2$ although no explanation is given as to how it is formed. It is suggested that loss of both the sulfanuric group NS(O)Ph and the nitrile 4-$CF_3C_6H_4CN$ occur simultaneously upon thermolysis of **29b**. Since $(PhS)_2$ is formed in larger amounts than 4-$CF_3C_6H_4CN$ pathway (a) (Scheme 2.2) appears to be favoured for ring contraction of **29b**.

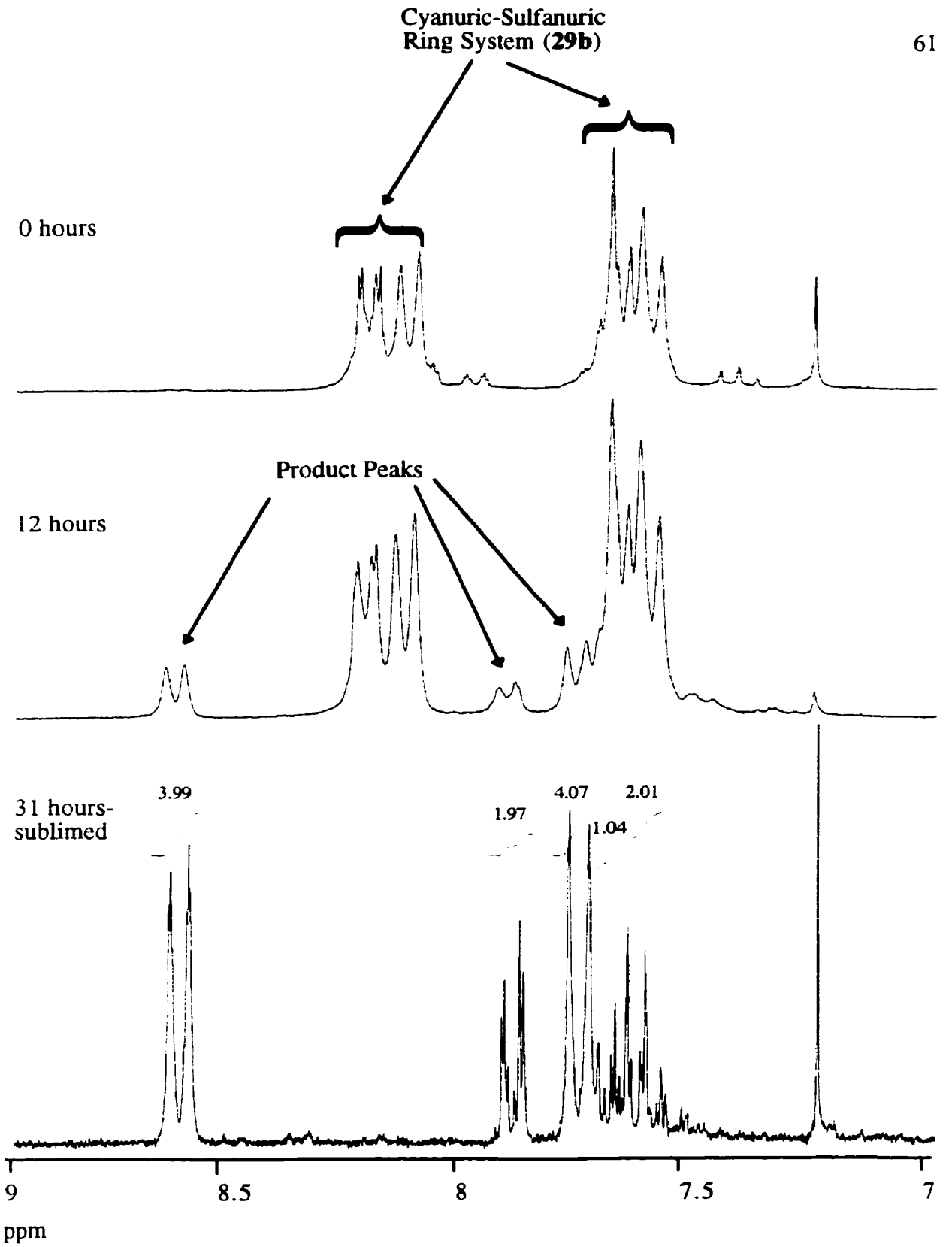
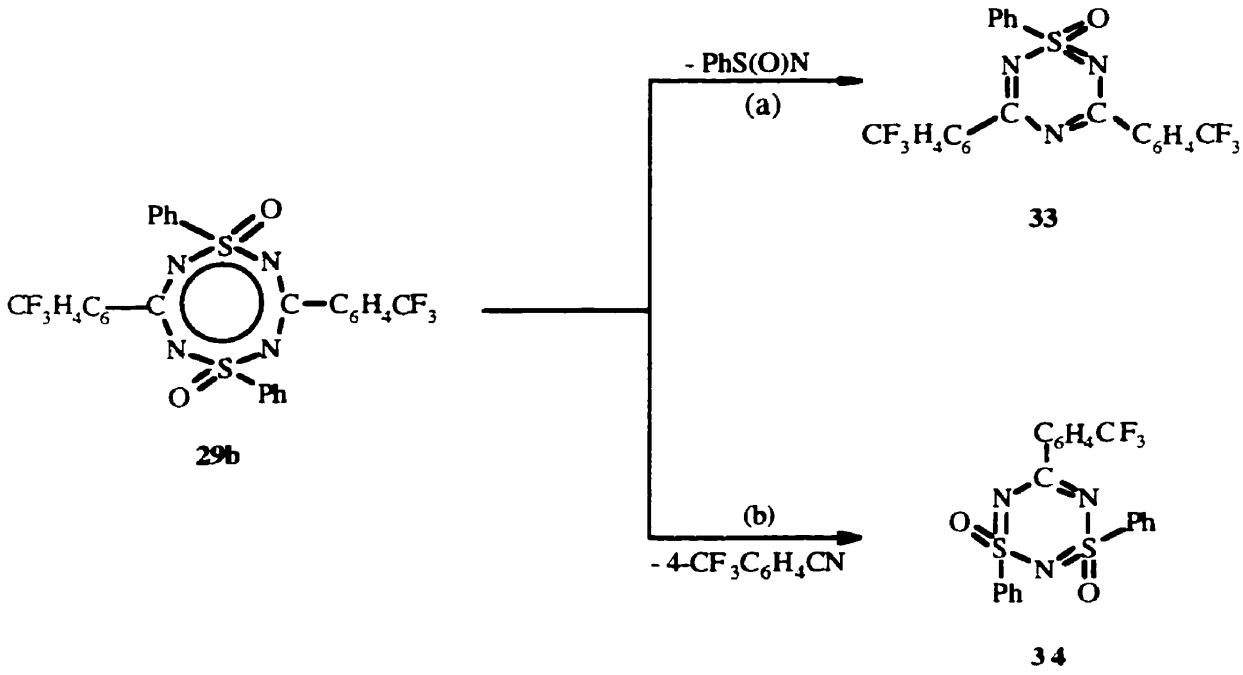


Figure 2.9 ^{1}H NMR Spectra of Products of Thermolysis of **29b** at Various Intervals



Scheme 2.2 Possible Pathways for Ring Contraction of **29b**

The white sublimate has been identified as the six-membered cyanuric-sulfanuric ring system (**33**) on the basis of mass spectra, CHNS elemental analysis, molecular weight measurements, ^{1}H and ^{13}C NMR. The ^{1}H NMR spectrum exhibits the typical A_2B_2 pattern for the substituted phenyl rings on carbon and a characteristic multiplet for the C_6H_5 rings attached to sulfur. Peak integration shows a 8:5 ratio which corresponds to that expected for **33**. Mass spectrometry gives a molecular ion peak at 481 as expected for the six-membered sulfanuric-cyanuric ring **33**. Further evidence supporting the formation of **33** is the elemental analysis data. C,H,N and S analysis fit well with the

calculated values for **33** rather than the alternative **34**. Thus pathway (a) (Scheme 2.2) is the predominant ring contraction process for the eight-membered cyanuric-sulfanuric ring **29b**. The preferred loss of NS(O)Ph rather than 4-$CF_3C_6H_4CN$ is surprising, particularly in view of the previously reported preference for elimination of $Me_2NC{\equiv}N$ from eight-membered cyanuric-thiazyl ring 1,3-$(Me_2NCN)_2(NSCl)_2$[49].

2.4.2 Thermolysis of $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(4\text{-}CH_3C_6H_4)_2$

In an effort to confirm that the ring contraction of $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(C_6H_5)_2$ (**29c**) upon thermolysis is not unique and to provide better crystals for X-ray analysis, the thermolysis of $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(4\text{-}CH_3C_6H_4)_2$ was examined. A small amount of sample, less than 100 mg, was placed in a tube, evacuated and heated for 31 hours at 220°C (Figure 2.8). It was observed by ^1H NMR that the eight-membered ring disappeared and a product with a prominent doublet in the 8.6 ppm region was formed. Mass spectrometry analysis of the sublimed thermolysis product showed a molecular ion peak at m/z = 495 corresponding to the six-membered ring, $(4\text{-}CF_3C_6H_4)_2C_2N_3S(O)(4\text{-}CH_3C_6H_4)$. Thus ring contraction with loss of the sulfanuric fragment $(4\text{-}CH_3C_6H_4)S(O)N$ is also observed in this case.

2.4.3 Photolysis of $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(C_6H_5)_2$

The photolysis of $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(C_6H_5)_2$ (**29b**) was examined in an effort to determine whether the eight-membered cyanuric-sulfanuric ring undergoes photoisomerization similar to that observed for dithiatetrazocines[43]. Alternatively, UV-induced ring-opening polymerization is a possibility. A small amount of $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(C_6H_5)_2$ was dissolved in toluene and transferred into a quartz UV cell. The UV cell was suspended in a photoreactor, which was equipped with a sample rotator to ensure the sample was evenly irradiated at a wavelength of 254 nm (Figure 2.10).

The reaction was monitored by ^1H NMR at regular intervals until it was observed that no eight-membered ring remained. The sample turned from a very pale yellow to a bright yellow colour after 45 minutes of irradiation. Further irradiation yielded a darker yellow solution that became cloudy. With continued irradiation, up to 1325 minutes, ^1H NMR spectra showed the disappearance and appearance of a variety of different signals. It is interesting to note that one set of peaks that is observed is the doublet at δ = 8.67 ppm that was observed in the thermolysis of $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(C_6H_5)_2$ and has been assigned to **33**. Throughout the reaction it was observed that these peaks grew in intensity and then with increasing irradiation began to disappear (Figure 2.11).

^{19}F NMR analysis was performed to identify the number of products contained in the sample. The spectra revealed that there are numerous peaks in the δ = -63 ppm

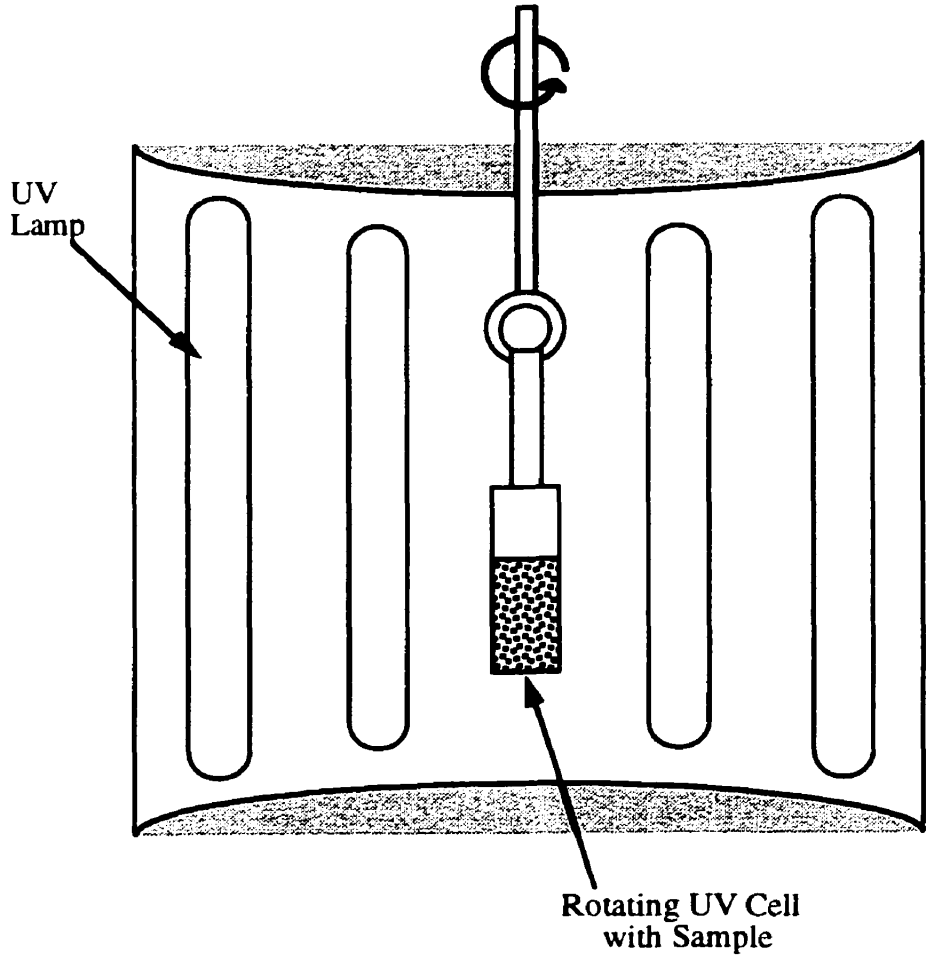


Figure 2.10 Schematic of the Photoreactor Used in Photolysis of $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(C_6H_5)_2$ (**29b**)

region and consequently a large variety of different products formed (Figure 2.12). Thus it appears that photolysis engenders ring contraction to give the six-membered ring (**33**), but other processes that generate additional products also occur under these conditions. The thermolysis reaction gives rise to a much cleaner ring contraction process.

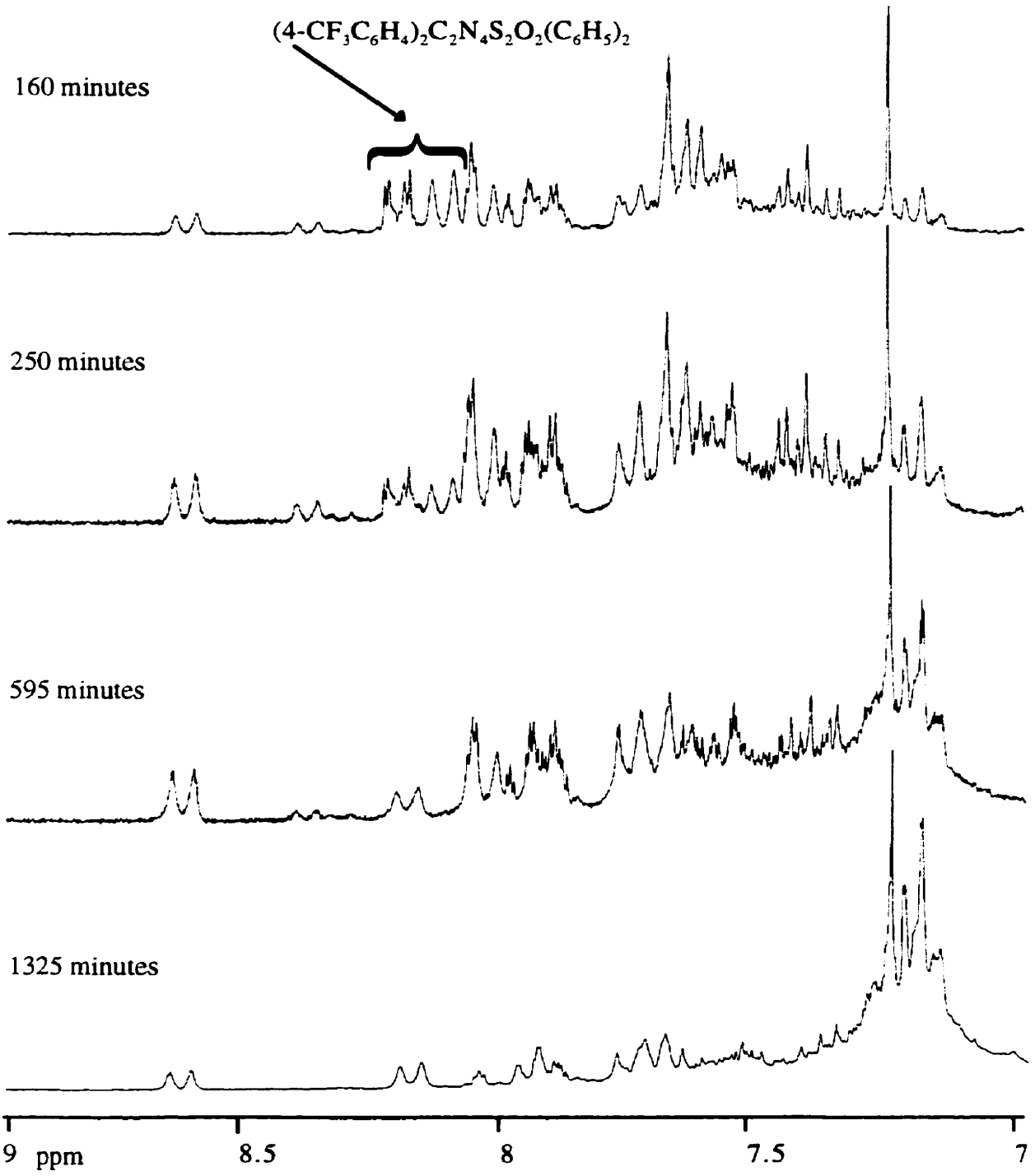


Figure 2.11 ^{1}H NMR Spectra of Photolysis Products of **29b** in $CDCl_3$ at Various Intervals

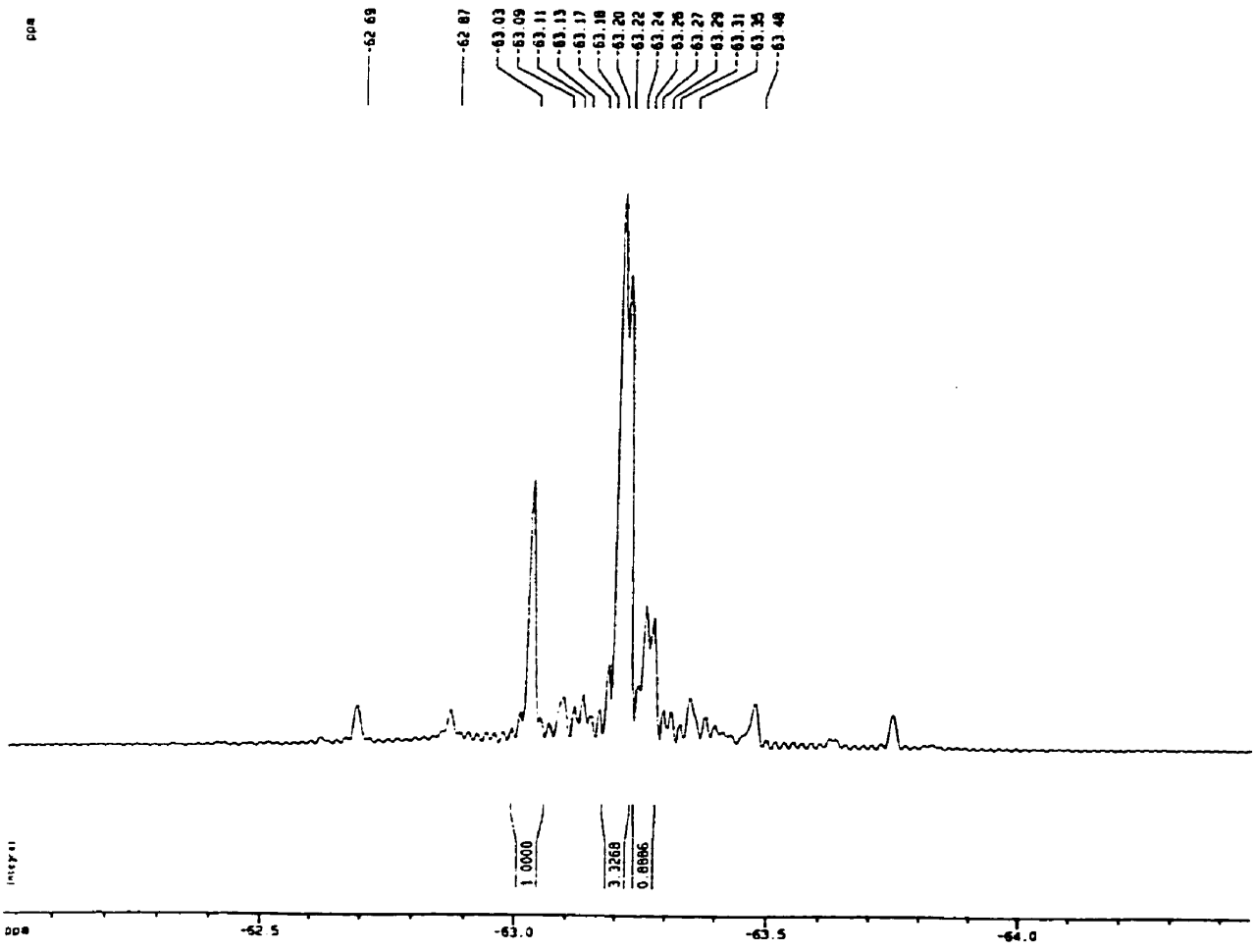


Figure 2.12 ^{19}F NMR Spectrum the Products from Irradiation of **29b**

2.4.4 Reaction of Cyanuric-Sulfanuric Rings with Electrophiles

In ring-opening polymerization the driving force for ring-opening is the strain that is contained within the ring system[7]. Eight-membered rings are less strained than the

corresponding six-membered systems and, therefore, other methods of inducing ring-opening need to be investigated. Along these lines, the interaction of the eight-membered cyanuric-sulfanuric rings with two electrophiles, CF_3SO_3Me and CF_3SO_3H[45], was investigated. Methylation or protonation of ring N atoms might lead to weakening of the S-N bond and, hence, ring-opening. In both of these cases the reaction was monitored by ^1H and ^{13}C NMR. The NMR spectra revealed that, even in the presence of a large excess of the electrophile and with heating, no reaction occurred. Consequently, this approach to ring-opening polymerization was not pursued.

2.5 Conclusions

Eight-membered cyanuric-sulfanuric rings can be prepared in good yields by the oxidation of the corresponding dithiatetrazocines. A number of mono- and di-oxidized species were synthesized and their X-ray structures were solved, namely; $(4\text{-}BrC_6H_4)_2C_2N_4S_2O(C_6H_5)_2$ (**32**), $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(C_6H_5)_2$ (**29b**), and $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(4\text{-}CH_3C_6H_4)_2$ (**29c**). The dioxidized ring system $(4\text{-}BrC_6H_4)_2C_2N_4S_2O_2(C_6H_5)_2$ (**29a**) was also prepared, but the structure was not elucidated as it was expected to be similar to that of the other eight-membered rings.

The investigations into the reactions of these rings has also proven to be informative. Thermolysis of **29b** gives rise to a novel eight- to six-membered ring contraction process involving the loss of a sulfanuric unit. The six-membered ring (**33**)

was characterized by mass spectrometry, elemental analysis, ^{1}H and ^{13}C NMR. This product is also observed in the photolysis of **29b**, although many additional products are formed and separation is very difficult. The reactions of **29b** with electrophiles were inconclusive apparently owing to incomplete reactions.

2.6 Experimental

2.6.1 Reagents and General Procedures

Reactions were carried out under an argon atmosphere with reaction vessels covered in aluminum foil to minimize exposure to light. The air-stable ring systems were manipulated in air with an effort to reduce possible decomposition by storing in sealed vessels. All solvents used were distilled over appropriate drying agents and then stored over molecular sieves; dichloromethane (P_2O_5, CaH_2), pentane (Na), hexane (Na, benzophenone), diethyl ether (Na, benzophenone), THF (Na, benzophenone). The reagents 4-XC_6H_4CN (X = Br, CH_3, CF_3), H_2O_2, $^tBuO_2H$, Ph_2S_2, $KMnO_4$, and Me_3SiCl were used as received from Aldrich. SO_2Cl_2 was received from Aldrich and distilled prior to use. Literature methods were used to prepare and purify the following reagents before use; *meta*-chloroperbenzoic acid (*m*CPBA)[52], PhSCl[53], and 4-$XC_6H_4CN_2(SiMe_3)_3$ (X = Br, CH_3, CF_3)[54]. $LiN(SiMe_3)_2$ was obtained from Aldrich and the monoetherate adduct was prepared by dissolving $LiN(SiMe_3)_2$ in hexanes and adding 1.1 equivalents of diethyl ether. The adduct $LiN(SiMe_3)_2 \bullet Et_2O$ was then precipitated out of solution, washed with

hexane, and stored in the dry-box. All dithiatetrazocines were prepared by the reaction of a trisilylated benzamidine with three equivalents of an arene sulfenyl chloride at very low temperatures as reported in literature[6]. The product mixtures were separated and purified by multiple recrystallizations in CH_2Cl_2/hexane and also by column chromatography using 170 - 250 Å mesh silica gel.

2.6.2 Instrumentation

All ^1H and ^{13}C NMR spectra were recorded on a Bruker ACE 200 spectrometer or Varian XL-200 and analyzed using the Tecmag PowerMac 7300/180 software. All samples were run in deuterated solvents and referenced with respect to the residual protons. Chemical shifts are quoted relative to tetramethylsilane at 0 ppm. Infrared spectral data were collected on a Mattson 4030 FT-IR spectrometer and samples were prepared on KBr plates in a Nujol mull. Electron-impact mass spectra were obtained using a VG 7070F Micromass spectrometer running at 70 eV. All chemical analyses (i.e. mass spectra and elemental analysis) were carried out by the Analytical Services department at the University of Calgary. X-ray data collections were carried out on a Rigaku AFC6S diffractometer equipped with a low temperature device. Structures were solved and refined by Dr. Masood Parvez using the teXsan[55] program. Further details of the structure solution and refinements may be obtained from Dr. T. Chivers.

2.6.3 Preparation of $(4\text{-}BrC_6H_4)_2C_2N_4S_2O(C_6H_5)_2$ (32)

To a Schlenk vessel containing $(4\text{-}BrC_6H_4)_2C_2N_4S_2(C_6H_5)_2$ (0.116 g, 0.190 mmol) in 50 ml THF was added *m*CPBA (0.197 g, 1.14 mmol) also dissolved in 50 ml of THF. Before *m*CPBA addition the reaction solution is a very pale purple due to trace amounts of a diazene (see Section 1.4.4) and after two hours the solution is colourless. It was determined through stepwise addition that 6 equivalents of *m*CPBA are required for complete reaction to occur. The reaction was monitored using thin layer chromatography (TLC) with a dichloromethane/hexane solvent mixture in a 3:1 ratio. Unreacted *m*CPBA and the by-product *meta*-chlorobenzoic acid (*m*CBA) were removed from the reaction mixture by an aqueous extraction with 10 equivalents of $NaHCO_3$ followed by $MgSO_4$. The product is obtained as a colourless powder (0.0907 g, 0.145 mmol, 76.3%). It was recrystallized from a mixture of CH_2Cl_2 and hexane at -20°C to yield clear colourless crystals. X-ray quality crystals were obtained by slow evaporation of this solvent mixture at room temperature. Mp: 221°C (turns red upon melting). Elemental Analysis: Calculated for $C_{26}H_{18}N_4S_2OBr_2$: C, 49.86; H, 2.90; N, 8.94. Found: C, 49.85; H, 2.81; N, 9.10. ^{1}H NMR (in $CDCl_3$, δ): 8.33 (m, 1H), 8.19 (m, 1H), 7.98 (d, $4\text{-}BrC_6(H_a)_2(H_b)_2$, 2H), 7.69 (m, 3H), 7.48 (d, $4\text{-}BrC_6(H_a)_2(H_b)_2$, 2H). ^{13}C NMR (in $CDCl_3$, δ): 165.09 (heterocyclic tertiary C), 143.79, 143.65, 139.88, 136.70, 132.96, 132.48, 132.20, 131.74, 129.85, 129.12, 126.62, 125.98. IR (cm^{-1}): 2722 (w), 2674 (w), 2352 (w), 1579 (s), 1515 (s), 1311 (s), 1297 (m), 1284 (m), 1261 (w), 1194 (m), 1173 (m), 1157 (m), 1094 (m),

1066 (w), 1024 (w), 1004 (m), 969 (w), 922 (w), 844 (w), 809 (m), 723 (s), 681 (m), 626 (w), 576 (s). MS: m/z = 625 (M^+).

2.6.4 Preparation of (4-$BrC_6H_4)_2C_2N_4S_2O_2(C_6H_5)_2$ (29a)

To a Schlenk vessel containing (4-$BrC_6H_4)_2C_2N_4S_2(C_6H_5)_2$ (0.100 g, 0.164 mmol) dissolved in 50 ml CH_2Cl_2 was added *m*CPBA (0.169 g, 0.983 mmol) also dissolved in 50 ml CH_2Cl_2. The reaction mixture was stirred one hour under a flow of argon. Unreacted *m*CPBA and the by-product *m*CBA were removed from the reaction mixture by several recrystallizations in a 2:1 pentane/CH_2Cl_2 mixture. In addition, it was sometimes necessary to perform an aqueous extraction with 10 equivalents of $NaHCO_3$ followed by $MgSO_4$ to completely remove the unwanted materials. The product obtained is a colourless powder (0.0775 g, 0.121 mmol, 73.6%). It was recrystallized from a mixture of CH_2Cl_2/pentane at -20°C to yield colourless crystals of X-ray quality. Mp: 232°C (turns red upon melting). Elemental Analysis: Calculated $C_{26}H_{18}N_4S_2O_2Br_2$: C, 48.76; H, 2.83; N, 8.75. Found: C, 48.26; H, 2.44; N, 8.62. ^{1}H NMR (in $CDCl_3$, δ): 7.48 (d, 4-$BrC_6(H_a)_2(H_b)_2$, 2H), 7.89 (d, 4-$BrC_6(H_a)_2(H_b)_2$, 2H), 8.22 and 7.67 (m, C_6H_5, 5H). ^{13}C NMR (in $CDCl_3$, δ): 167.31 (heterocyclic tertiary C), 143.74, 135.46, 132.91, 131.68, 131.57, 129.31, 128.73, 125.91. IR (cm^{-1}): 2726 (w), 1579 (m), 1547 (w), 1503 (m), 1332 (s), 1252 (m), 1184 (w), 1096 (w), 1064 (m), 1008 (m), 973 (w), 922 (w), 852 (m), 832 (m), 773 (m), 749 (w), 721 (w), 682 (m), 584 (m), 541 (w). MS: m/z = 642 (M^+).

2.6.5 Preparation of $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(C_6H_5)_2$ (29b)

To a Schlenk tube containing $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2(C_6H_5)_2$ (0.537 g, 0.912 mmol) dissolved in 50 ml CH_2Cl_2 was added *m*CPBA (0.944 g, 5.47 mol) also dissolved in 50 ml CH_2Cl_2. The reaction was stirred for an hour under a flow of argon. Unreacted *m*CPBA and the by-product *m*CBA were removed from the product mixture by several recrystallizations in a 2:1 pentane/CH_2Cl_2 mixture. In addition, it was sometimes necessary to perform an aqueous extraction with 10 equivalents of $NaHCO_3$ followed by $MgSO_4$. The product obtained is a colourless powder (0.529 g, 0.853 mmol, 93.4%). Colourless crystals of X-ray quality were grown by slow evaporation of CH_2Cl_2/hexane solution. Mp: 183°C. Elemental Analysis: Calculated $C_{28}H_{18}N_4S_2O_2F_6$: C, 54.19; H, 2.93; N, 9.03. Found: C, 53.80; H, 2.86; N, 9.23. ^{1}H NMR (in $CDCl_3$, δ): 8.15 (d, 4-$CF_3C_6(H_a)_2(H_b)_2$, 2H), 8.23 and 7.52 (m, C_6H_5, 5H), 7.63 (d, 4-$CF_3C_6(H_a)_2(H_b)_2$, 2H). ^{19}F NMR (in $CDCl_3$, δ): -63.50. ^{13}C NMR (in $CDCl_3$, δ): 166.79 (heterocyclic tertiary C), 143.26, 139.54, 132.97, 130.15, 129.23, 125.77, 125.26, 125.17. IR (cm^{-1}): 2360 (w), 2342 (w), 1593 (w), 1527 (s), 1356 (m), 1319 (s), 1248 (m), 1158 (m), 1134 (s), 1109 (s), 1067 (s), 1015 (m), 931 (w), 852 (m), 788 (m), 764 (m), 749 (m), 722 (w), 700 (w), 686 (w), 686 (w), 629 (w), 583 (m), 579 (m), 542 (w). MS: m/z = 620 (M^-).

2.6.6 Preparation of $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(4\text{-}CH_3C_6H_4)_2$ (29c)

To a Schlenk tube containing $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2(4\text{-}CH_3C_6H_4)_2$ (0.345 g, 0.559 mmol) dissolved in 50 ml CH_2Cl_2 was added *m*CPBA (0.579 g, 3.356 mmol) also dissolved in 50 ml CH_2Cl_2. The reaction was stirred one hour under a flow of argon. A ^1H NMR spectrum was recorded the following day to ensure the product reacted, but it was observed that no shift occurred in the $4\text{-}CH_3C_6H_4$ resonance (at 2.53 ppm). Unreacted *m*CPBA and by-product *m*CBA were removed from the reaction mixture by several recrystallizations in a 2:1 pentane/CH_2Cl_2 mixture. In addition, it was sometimes necessary to perform an aqueous extraction with 10 equivalents of $NaHCO_3$ followed by $MgSO_4$. The product obtained is a colourless powder (0.355 g, 97.8%). Colourless crystals of X-ray quality were grown from a slow evaporation of a CH_2Cl_2/hexane solution. Mp: 187 °C (melts to yellow liquid). Elemental Analysis Calculated for $C_{30}H_{22}N_4S_2O_2F_6$: C, 55.55 ; H, 3.42 ; N, 8.64. Found: C, 55.16; H, 3.28; N, 7.84. ^1H NMR (in $CDCl_3$, δ): 8.15 (d, $4\text{-}CH_3C_6(H_c)_2(H_d)_2$, 2H), 8.11 (d, $4\text{-}CF_3C_6(H_a)_2(H_b)_2$, 2H), 7.61 (d, $4\text{-}CH_3C_6(H_c)_2(H_d)_2$, 2H), 7.45 (d, $4\text{-}CF_3C_6(H_a)_2(H_b)_2$, 2H), 2.53 (s, $4\text{-}CH_3C_6H_4$, 3H). ^{13}C NMR (in $CDCl_3$, δ): 166.52 (heterocyclic tertiary C), 143.87, 140.45, 139.69, 133.82, 130.12, 129.79, 128.26, 125.82, 125.18, 125.10. IR (cm^{-1}): 1700 (w), 1592 (w), 1512 (m), 1349 (m), 1317 (s), 1263 (m), 1233 (w), 1190 (w), 1169 (m), 1130 (m), 1107 (m), 1065 (ms), 1016 (m), 925 (w), 845 (m), 806 (w), 782 (w), 758 (m), 721 (w), 695 (w), 654 (w). MS (M^+): m/z = 649 (M^+).

2.6.7 Preparation of $(4\text{-}CF_3C_6H_4)_2C_2N_3S(O)(C_6H_5)$ (33)

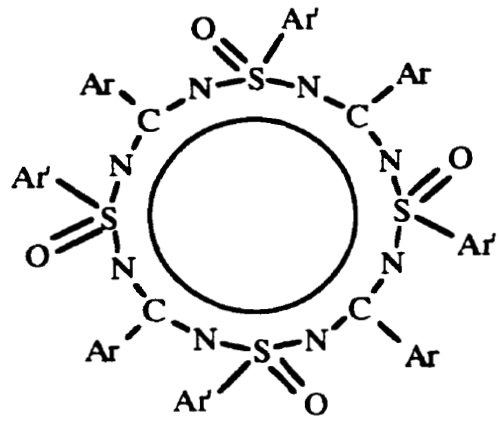
A long Schlenk tube containing $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2(O)_2(C_6H_5)_2$ (0.173 g, 0.279 mmol) was evacuated and placed in a 220°C oven for 31 hours. A black liquid melt formed at the bottom of the tube while white crystalline material sublimed at the cool end of the tube. Along with the white product some yellow volatile material formed on the inside of the tube that was outside the oven. The black material was sublimed at 120°C under vacuum for 48 hours to give a white sublimate (0.098 g, 0.203 mmol, 73.1%) and a small amount of black residue at the bottom of the apparatus. Mp: 214-216 °C. Elemental Analysis: Calculated for $C_{22}H_{13}N_3SOF_6$: C, 54.88; H, 2.72; N, 8.73; S, 6.65. Found: C, 55.00; H, 2.74; N, 8.73; S, 7.92. ^{1}H NMR (in $CDCl_3$, δ): 8.65 and 7.78 (d, C_6H_4, 8H), 7.92 (m, $C_6(H_a)_2(H_b)_3$, 2H), 7.66 (m, $C6(H_a)_2(H_b)_3$, 3H). ^{13}C NMR (in $CDCl_3$, δ): 168.91 (heterocyclic tertiary C), 139.86, 138.84, 134.92, 134.34, 129.59, 129.28, 127.89, 125.43, 125.36. IR (cm^{-1}): 1695 (s), 1596 (w), 1574 (w), 1305 (m), 1263 (m), 1140 (w), 1099 (w), 1074 (w), 1027 (w), 917 (w), 897 (w), 849 (w), 808(w), 750 (m), 720 (s), 667 (w), 652 (w), 545 (w). MS: m/z = 481 (M^+). Molecular Weight (in CH_2Cl_2): 452.

CHAPTER 3

Synthesis and Structures of Sixteen-Membered Cyanuric-Sulfanuric Heterocycles

3.1 Introduction

The investigations into sixteen-membered cyanuric-sulfanuric heterocycles described in this chapter have somewhat different objectives than those discussed in the previous chapter for the eight-membered species. Study of the eight-membered rings was aimed at finding a viable route to C-N-S^{VI}-N polymers. The sixteen-membered $C_4N_8S_4$ ring has very little ring strain compared to that of the eight-membered system and even less than that of a six-membered species. Consequently, ROP is an unlikely method of obtaining such polymers. In light of this, the factors that are of interest are the changes in ring conformation, bond angles, and bond lengths of the S(VI) heterocycles when compared to their S(IV) counterparts which have a cradle conformation. The possibility of identifying ring systems with sulfur in different oxidation states is another consideration for these macrocycles.



35

a Ar = 4-$CH_3C_6H_4$, Ar' = Ph
b Ar = 4-$CF_3C_6H_4$, Ar' = Ph
c Ar = 4-$CH_3C_6H_4$, Ar' = 4-$CF_3C_6H_4$

3.2 Synthesis and Spectroscopic Characterization of Sixteen-Membered Cyanuric-Sulfanuric Rings

Sixteen-membered cyanuric-sulfanuric rings (**35**) were prepared by the reaction of the corresponding S(IV) systems with *meta*-chloroperbenzoic acid (*m*CPBA) in CH_2Cl_2. The reactions were carried out for three different substituted rings: (4-$CF_3C_6H_4)_4C_4N_8S_4(C_6H_5)_4$ (**28b**), (4-$CH_3C_6H_4)_4C_4N_8S_4(C_6H_5)_4$ (**28c**), and (4-$CF_3C_6H_4)_4C_4N_8S_4$(4-$CH_3C_6H_4)_4$ (**28d**).

An excess of *m*CPBA was dissolved in CH_2Cl_2 and then added to a slurry of the $C_4N_8S^{IV}{}_4$ ring in CH_2Cl_2. After addition of *m*CPBA the reaction mixture was stirred for 1

hour to ensure complete oxidation of the sixteen-membered ring. Step-wise addition of *m*CPBA determined that a minimum of twenty-four equivalents is required to convert all S(IV) atoms to S(VI) in the formation of **35a** and **35b**, and sixteen equivalents are required for **35c**. Removal of excess *m*CPBA and the by-products, presumably *meta*-chlorobenzoic acid, was achieved by one of two methods. The first method was an aqueous extraction with $NaHCO_3$ followed by recrystallization of the product from CH_2Cl_2/hexane. This method often proved inadequate for the complete removal of unwanted by-products and had to be repeated resulting in relatively low yields. An alternative method of by-product removal involved the reaction of the product mixture with gaseous ammonia[46]. After oxidation was complete an excess of $NH_{3(g)}$ is bubbled through the reaction flask for approximately 15 to 30 minutes. Passage of $NH_{3(g)}$ produced a white precipitate. Careful filtration of the reaction mixture with a very fine frit removed ammonium *meta*-chlorobenzoate leaving the oxidized sixteen-membered ring. These novel compounds are white crystalline powders that are stable in air for long periods of time. Samples are stored in screw top vials with no signs of degradation after many months.

^1H NMR analysis was carried out on all three sixteen-membered cyanuric-sulfanuric heterocycles. The presence of a doublet at $\delta = 6.8$-7.2 ppm is characteristic for these systems (Figure 3.1). A typical A_2B_2 pattern is obtained for all *para*-substituted rings (**35**). ^{13}C NMR analysis of these systems (**35**) revealed a resonance for the

heterocyclic tertiary carbons at approximately δ = 170 ppm which compares to the S(IV) systems at 180 ppm. The presence of a single resonance in the ^{13}C NMR is unexpected when the solid state structure is considered. From a consideration of the symmetry of the structure of **35a** (Figure 3.4) two different environments for the heterocyclic carbon atoms are predicted because the carbons adjacent to each other are not equivalent. The presence of only a single resonance at δ = 170 ppm indicates a fluxional process is occurring in the solution that causes all the carbon environments to be the same. A ring-flipping type process can be envisioned that would promote equivalence of carbon atoms. Although molecular ions were not observed in the electron-impact mass spectra, fast atom bombardment (FAB) mass spectrometry gave molecular ions corresponding to those expected for **35a**, **35b**, and **35c**. Elemental analyses (CHN) of these systems are in good agreement with the calculated values with the exception of consistently low carbon values for **35a**. Infra-red spectra exhibit bands at approximately 1096 cm^{-1} and 1316 cm^{-1}, tentatively assigned to S-N and S=O vibrations, respectively.

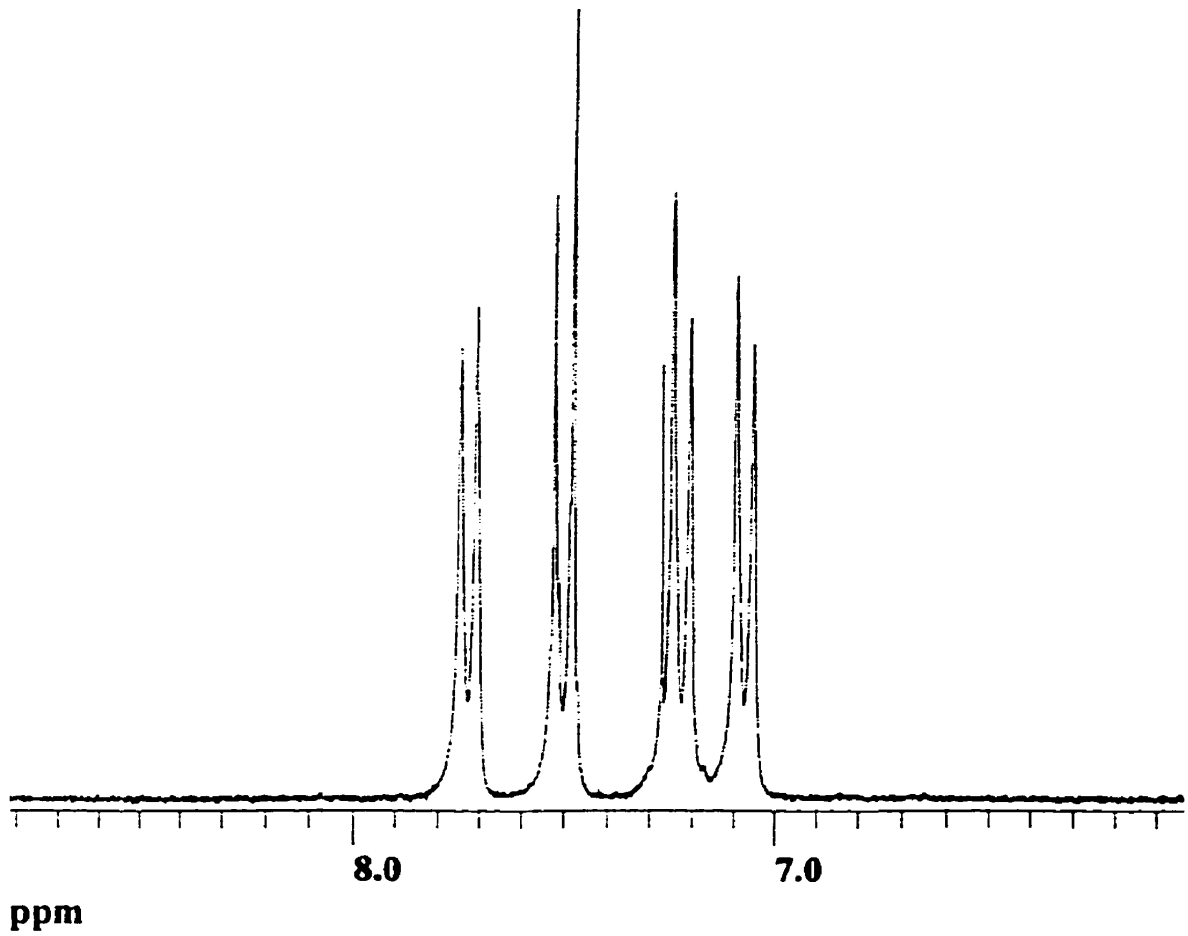


Figure 3.1 Typical ^{1}H NMR Spectrum for Sixteen-Membered Heterocycles (**35**)

3.3 X-ray Structures of Sixteen-Membered Cyanuric-Sulfanuric Rings

3.3.1 $(4\text{-}CH_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ (35a)

Colourless plates of **35a** were grown by slow evaporation of a CH_2Cl_2/hexane solution at room temperature. A crystal was mounted outside the glove-box on a glass fibre in epoxy resin. The crystallographic data for **35a** are summarized in Table 3.1. ORTEP drawings are illustrated in Figures 3.2, 3.3, and 3.4. Selected bond lengths, bond angles, and torsion angles are given in Table 3.2. Data collection was carried out at low temperatures to reduce crystal decomposition and thermal motion. Further details of the structure solution and refinements may be obtained from Dr. T. Chivers.

The pseudo C_2 symmetry of the molecule allowed for faster data collection as only half the number of reflections had to be collected. The second half of the molecule was generated by symmetry. The range and average bond lengths, bond angles, and torsion angles are given in Table 3.3 for $(4\text{-}CH_3C_6H_4)_4C_4N_8S_4(C_6H_5)_4$ (**28c**), $(4\text{-}CH_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ (**35a**), and the $(4\text{-}CF_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ (**35b**). The average d(S-N) for **35a** is 1.595(12) Å compared to a value of 1.664(5) Å for **28c**. By contrast the C-N bond lengths are essentially unchanged upon oxidation from S(IV) to S(VI). Similar observations were noted for the eight-membered cyanuric-sulfanuric systems (see Section 2.3). The average S-N-C bond angle becomes larger for **35a** [122(5)°] upon sulfur oxidation [cf. S(IV) 114.2(6)° for **28c**] while the average N-C-N bond angle remains the same. Torsion angles can be used to determine the extent of

Table 3.1 Crystallographic Parameters for $(4\text{-}CH_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ (**35a**) and $(4\text{-}CF_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ (**35b**)

	35a	**35b**
Empirical Formula	$C_{56}H_{48}N_8S_4O_4$	$C_{56}H_{36}N_8S_4O_4F_{12}\bullet CH_2Cl_2$
Formula Weight	1025.29	1326.11
Colour, Crystal Habit	colourless, plate	colourless, plate
Crystal Dimensions (mm)	0.60 x 0.40 x 0.20	0.50 x 0.32 x 0.09
Crystal System	orthorhombic	triclinic
a (Å)	22.657(2)	12.647(3)
b (Å)	10.570(2)	19.137(3)
c (Å)	10.664(3)	12.5498(17)
α (°)	90	105.765(11)
β (°)	90	93.610(15)
γ (°)	90	88.877(16)
V (Å^3)	2554(1)	2917.2(9)
Space Group	Pba2 (#32)	P $\bar{1}$ (#2)
Z	2	2
D_{calc} (gcm^{-3})	1.333	1.510
Temperature (°C)	-103.0	-103.0
R	0.0562	0.067
R_w	0.156	0.058

distortion of the cradle conformation. The S(IV) system **28c** has a range of 127.2(5) to 123.3(5)° for N-S-N-C while the corresponding values for **35a** are -156.2(7) to 146.4(7)°. Similarly, the S-N-C-N torsion angles range from -168.4(5) to 170.9(5)° for **28c** compared to -179.5(6) to 1.8(11)° for **35a**. Oxidation of the $C_4N_8S^{IV}_4$ ring also affects the size of the cavity formed by the cradle conformation. For example, the N-N distance across the ring is 3.96 Å in the S(IV) ring compared to 5.05 Å in the S(VI) system. Similarly, the S-S distance across the ring increases from 5.54 Å to 6.05 Å. The conclusions that can be drawn from the above information are that oxidation of the sixteen-membered ring shortens the S-N bonds and opens the ring giving a larger cavity in the cradle conformation. The mean S=O distance of 1.438(5) Å is consistent with an S^{VI}=O double bond.

Table 3.2 Selected Bond Lengths (Å), Bond Angles (°), and Torsion Angles (°) for (4-$CH_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ (**35a**)

Atoms	(Å)	Atoms	(°)
S(2)-N(3)	1.597(7)	N(2)-S(1)-N(1)	105.2(4)
S(2)-N(4)	1.596(7)	N(4)-S(2)-N(3)	105.1(4)
S(1)-N(1)	1.577(6)	S(1)-N(2)-C(15)	116.1(6)
S(1)-N(2)	1.611(7)	S(2)-N(3)-C(15)	127.4(5)
N(3)-C(15)	1.326(10)	S(2)-N(4)-C(1*)	117.5(6)
N(2)-C(15)	1.325(8)	S(1*)-N(1*)-C(1*)	127.4(6)
N(4*)-C(1)	1.366(10)	N(3)-C(15)-N(2)	121.9(6)
N(1*)-C(1)	1.311(10)	N(1)-C(1)-N(4*)	121.2(7)
S(2)-O(2)	1.433(6)	N(1)-S(1)-N(2)-C(15)	-69.7(7)
S(1)-O(1)	1.444(6)	N(2)-S(1)-N(1)-C(1)	146.4(7)
		N(3)-S(2)-N(4)-C(1*)	75.9(7)
		N(4)-S(2)-N(3)-C(15)	-156.2(7)
		S(2)-N(3)-C(15)-N(2)	-164.8(6)
		S(1*)-N(1*)-C(1*)-N(4)	179.5(6)
		S(1*)-N(2*)-C(15*)-N(3*)	1.8(11)

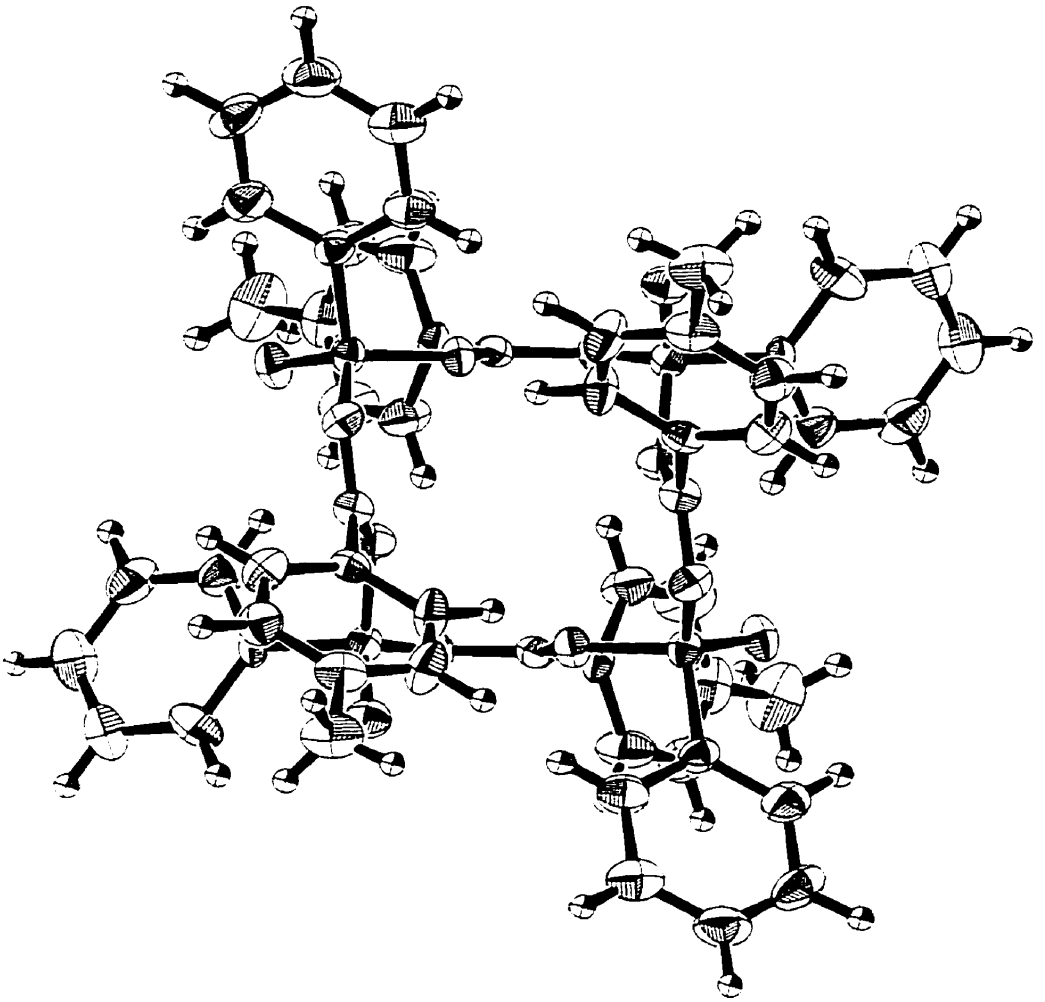


Figure 3.2 ORTEP diagram for Top View of $(4\text{-}CH_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ **(35a)**

including phenyl and *p*-tolyl groups

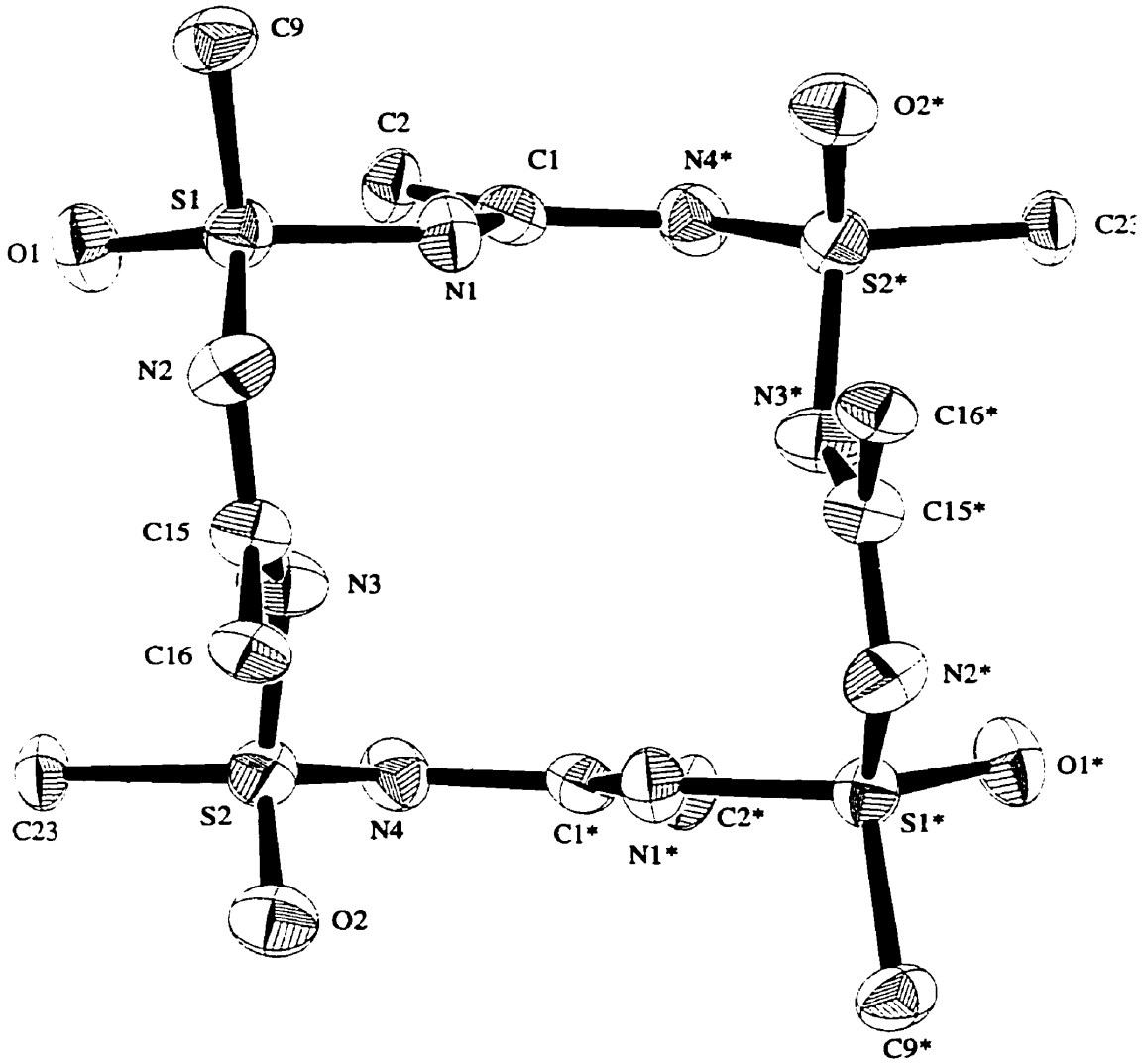
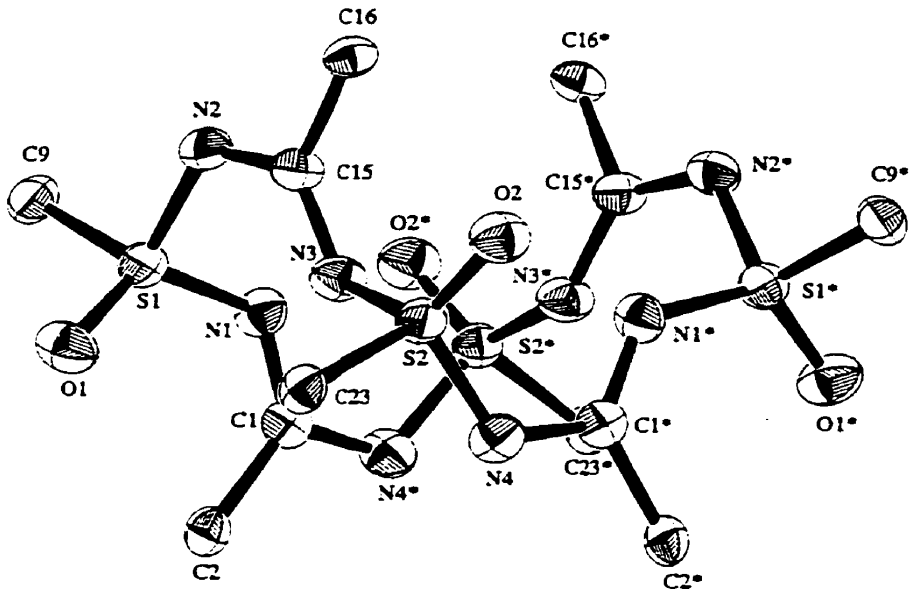


Figure 3.3 ORTEP diagram for Top View of $(4\text{-}CH_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ **(35a)**

with only *-ipso* carbons of aryl groups shown

(a)



(b)

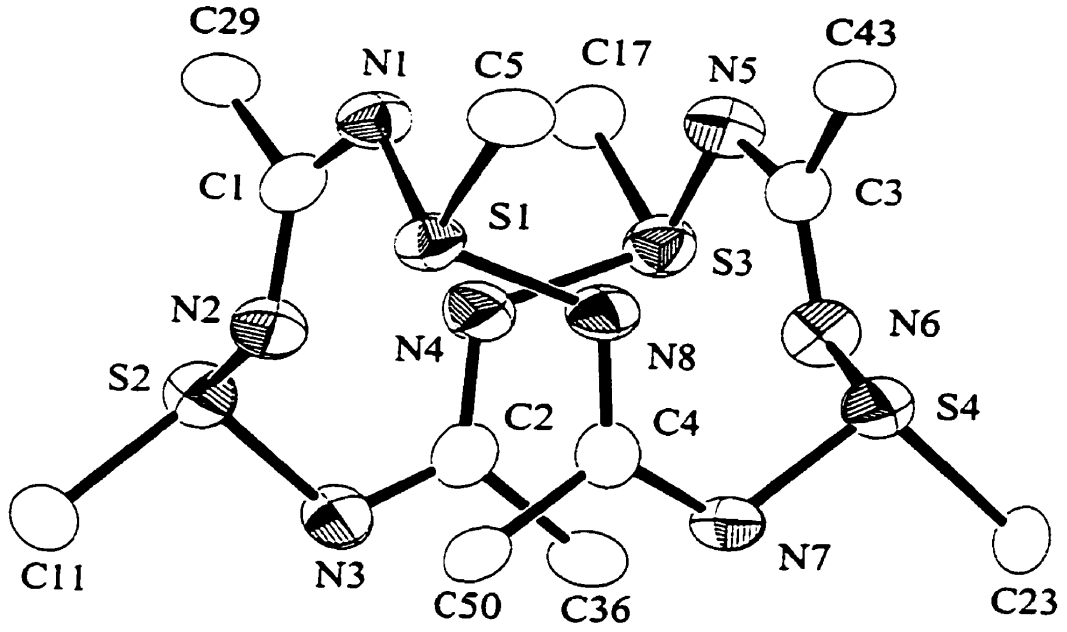


Figure 3.4 ORTEP diagram for (a) $(4\text{-}CH_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ **(35a)** and (b) $(4\text{-}CH_3C_6H_4)_4C_4N_8S_4(C_6H_5)_4$ **(28c)** with only *-ipso* carbons from aryl groups shown

Table 3.3 Comparison of Bond Lengths (Å), Bond Angles (°), and Torsion Angles (°) for $(4\text{-}CH_3C_6H_4)_4C_4N_8S_4(C_6H_5)_4$ **(28c)**, $(4\text{-}CH_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ **(35a)**, and $(4\text{-}CF_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ **(35b)**

	28c	**35a**	**35b**
d(S-N) Range (Å)	1.644(5)-1.693(5)	1.577(6)-1.611(7)	1.561(9)-1.623(10)
d(S-N) Average (Å)	1.664(5)	1.592(12)	1.601(22)
d(C-N) Range (Å)	1.317(7)-1.352(7)	1.311(10)-1.366(10)	1.310(14)-1.352(14)
d(C-N) Average (Å)	1.332(8)	1.332(20)	1.330(13)
∠S-N-C Range (°)	110.8(5)-117.3(5)	116.1(6)-127.4(6)	117.0(8)-131.5(9)
∠S-N-C Average (°)	114.2(6)	122(5)	124(6)
∠N-C-N Range (°)	121.1(6)-122.5(6)	121.2(7)-121.9(6)	119.6(11)-122.2(11)
∠N-C-N Average (°)	121.7(6)	121.5 (35)	121(1)
∠N-S-N-C Range (°)	127.2(5)-123.3(5)	-156.2(7)-146.4(7)	-136.1(11)-131.6(10)
∠S-N-C-N Range (°)	-168.4(5)-170.9(5)	-179.5(6)-1.8(11)	-172.6(9)-177.5(9)

3.3.2 $(4\text{-}CF_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4 \bullet CH_2Cl_2$ (35b)

Colourless plates of **35b** were grown by slow evaporation of a CH_2Cl_2/hexane solution at room temperature. A crystal was mounted outside the glove-box on a glass fibre in epoxy resin. Special care was given during mounting because the crystals began to crack and became opaque. It is thought that the cracking was due to slow solvent

evaporation from the crystal matrix The crystallographic data for **35b** are summarized in Table 3.1. ORTEP drawings are illustrated in Figures 3.5 and 3.6. Selected bond lengths, bond angles, and torsion angles are given in Tables 3.4 and 3.5. Data collection was carried out at low temperatures to reduce crystal decomposition and thermal motion. Further details of the structure solution and refinements may be obtained from Dr. T. Chivers.

In the absence of X-ray data direct comparison cannot be made with the corresponding S(IV) ring, but a comparison with $(4\text{-}CH_3C_6H_4)_4C_4N_8S_4(C_6H_5)_4$ (**28c**) and $(4\text{-}CH_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ (**35a**) is made in Table 3.3 (see Section 3.3.1). From this Table it is observed that the S-N bond length decreases and the C-N length remains the same upon oxidation. Similarly, the average S-N-C bond angle becomes larger [124(6)° for **35a**] upon sulfur oxidation (cf. 114.2(6)° for **28c**) while the average N-C-N bond angle remains approximately the same at 121(1)°. An increase in the size of the cavity, or widening, is also noted upon oxidation of **28c** with a N-N distance across the ring of 4.35 Å and a S-S distance of 5.77 Å. The mean S=O distance of 1.446(3) Å is consistent with an S^{VI}=O double bond.

Table 3.4 Selected Bond Lengths (Å) and Bond Angles (°) for (4-$CF_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ (**35b**)

Atoms	Bond Length (Å)	Atoms	Bond Angle (°)
S(2)-N(3)	1.610(9)	N(5)-S(3)-N(4)	109.0(5)
S(2)-N(2)	1.561(9)	N(3)-S(2)-N(2)	112.2(5)
S(1)-N(1)	1.623(10)	N(1)-S(1)-N(8)	106.7(5)
S(1)-N(8)	1.571(9)	N(7)-S(4)-N(6)	106.2(5)
S(4)-N(7)	1.622(9)	N(5)-C(3)-N(6)	122.2(11)
S(4)-N(6)	1.603(10)	N(7)-C(4)-N(8)	120.5(11)
S(3)-N(4)	1.599(9)	N(1)-C(1)-N(2)	119.6(11)
S(3)-N(5)	1.616(10)	N(3)-C(2)-N(4)	121.5(10)
N(2)-C(3)	1.326(13)	S(3)-N(4)-C(2)	126.2(8)
N(4)-C(2)	1.336(13)	S(3)-N(5)-C(3)	120.4(9)
N(5)-C(3)	1.310(14)	S(4)-N(6)-C(3)	126.8(9)
N(6)-C(3)	1.314(13)	S(4)-N(7)-C(4)	117.0(8)
N(7)-C(4)	1.352(14)	S(1)-N(8)-C(4)	131.0(9)
N(8)-C(4)	1.326(13)	S(1)-N(1)-C(1)	118.3(8)
N(1)-C(1)	1.344(14)	S(2)-N(2)-C(1)	131.5(9)
N(2)-C(1)	1.331(13)	S(2)-N(3)-C(2)	117.5(8)
S(1)-O(1)	1.443(8)		
S(2)-O(2)	1.443(8)		
S(3)-O(3)	1.451(8)		
S(4)-O(4)	1.445(8)		

Table 3.5 Selected Torsion Angles (°) for $(4\text{-}CF_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ (**35b**)

	Torsion Angle (°)		Torsion Angle (°)
S(2)-N(3)-C(2)-N(4)	-9.7(16)	N(1)-S(1)-N(8)-C(4)	122.7(12)
S(2)-N(2)-C(1)-N(1)	169.7(9)	N(2)-S(2)-N(3)-C(2)	67.9(10)
S(3)-N(4)-C(2)-N(3)	176.5(9)	N(3)-S(2)-N(2)-C(1)	-109.9(11)
S(3)-N(5)-C(3)-N(6)	-1.9(17)	N(4)-S(3)-N(5)-C(3)	-59.9(11)
S(4)-N(6)-C(3)-N(5)	177.5(9)	N(5)-S(3)-N(4)-C(2)	131.6(10)
S(4)-N(7)-C(4)-N(8)	-0.3(16)	N(6)-S(4)-N(7)-C(4)	75.0(10)
S(1)-N(1)-C(1)-N(2)	0.1(15)	N(7)-S(4)-N(6)-C(3)	-136.1(11)
S(1)-N(8)-C(4)-N(7)	-172.6(9)	N(8)-S(1)-N(1)-C(1)	-77.2(10)

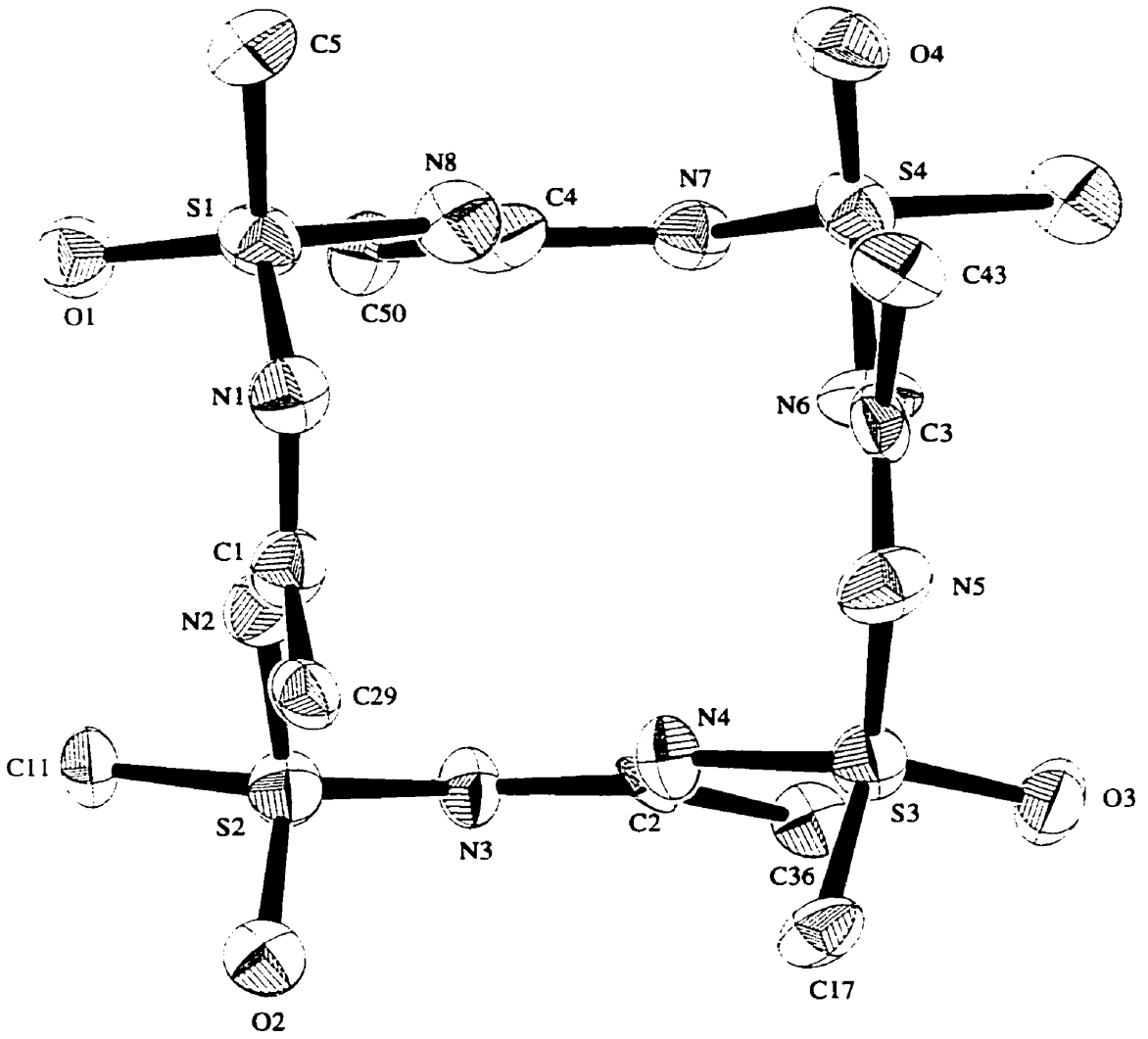


Figure 3.5 ORTEP diagram for Top View of $(4\text{-}CF_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ **(35b)** with only *-ipso* carbons of the aryl groups shown

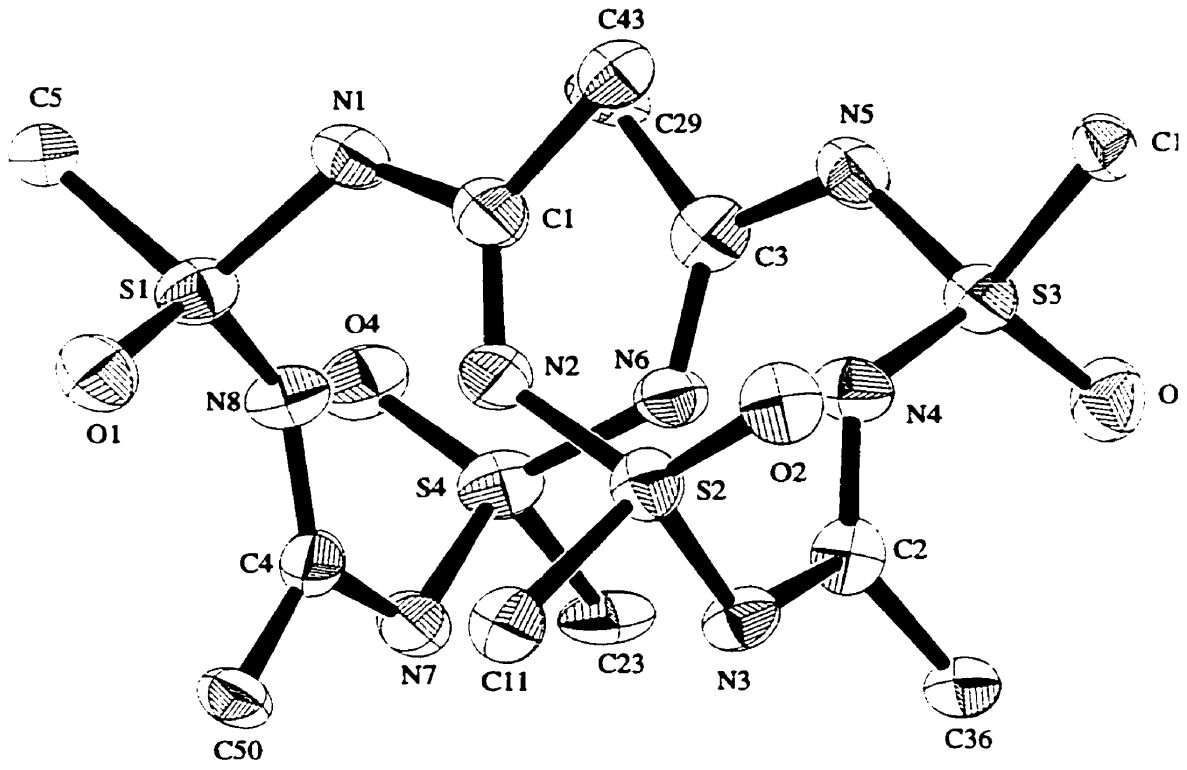
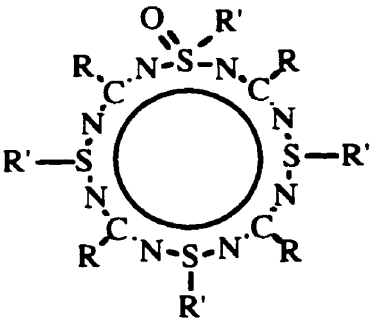


Figure 3.6 ORTEP diagram for $(4\text{-}CF_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ **(35b)** with only *-ipso* carbons from aryl groups shown

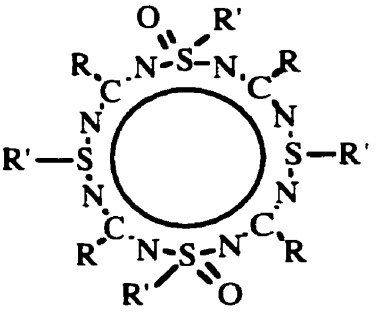
3.4 Formation of Intermediates in the Oxidation of $C_4N_8S_4$ Ring Systems

It was determined by ^{1}H NMR analysis of the reaction of *m*CPBA with **28c** that intermediate species are formed if less than 24 equivalents of *m*CPBA are added. It is believed that these species may include the mono-, di-, and tri-oxidized species **36**, **37a,b** and **38**, respectively (Figure 3.7). For each intermediate it is assumed that the oxygen

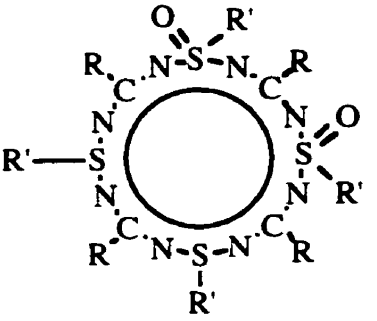
atoms take up the former position of the lone pair on sulfur atoms, as observed for the tetra-oxidized species (*vide supra*) (see Figures 3.3 and 3.4). Thus only one isomer is possible for the mono- and tri-oxidized species while two positional isomers (vicinal and antipodal) can be envisioned for the dioxide. An investigation into the formation of these intermediate species was carried out on an NMR scale (i.e. in an NMR tube) using $CDCl_3$ as a solvent. Aliquots of *m*CPBA were added, four equivalents at a time, and the ^1H NMR spectrum was recorded after mixing the reagents for 20 minutes. Figure 3.8 shows the ^1H NMR resonances for the CH_3 groups of *p*-tolyl substituents attached to carbon. After four equivalents of *m*CPBA were added three major resonances were observed. Addition of another eight equivalents of *m*CPBA gave rise to the same three resonances, but with different relative intensities. Addition of 12 more equivalents of *m*CPBA, produced a single resonance with a chemical shift $\delta = 2.21$ ppm identical to that observed for the tetra-oxidized species **35a** (*vide infra*). From previous work[56] it is known that the resonance at $\delta = 2.25$ ppm (middle peak in Figure 3.8 (a and b)) is attributed to the $C_4N_8S^{IV}_4$ ring **28c**. From examination of the possible intermediates **36**, **37a**, **37b**, and **38** (Figure 3.7) it is likely that the third resonance at $\delta = 2.31$ ppm is due to the antipodal isomer of the dioxidized species **37a**, which has a single *p*-tolyl environment. Compounds **36**, **37b**, and **38** would give two, three (1:2:1) and two resonances, respectively, in the methyl region due the inequivalence of the *p*-tolyl groups resulting from the presence of sulfur in different oxidation states in these sixteen-membered rings.



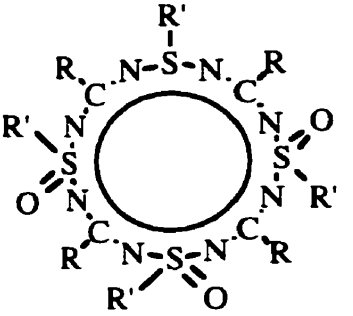
MONO-OXIDE
36



DI-OXIDE
37a
(antipodal)



DI-OXIDE
37b
(vicinal)



TRI-OXIDE
38

R = 4-$CH_3C_6H_4$, R' = Ph

Figure 3.7 Possible Intermediate Products Formed During the Oxidation of **28c**

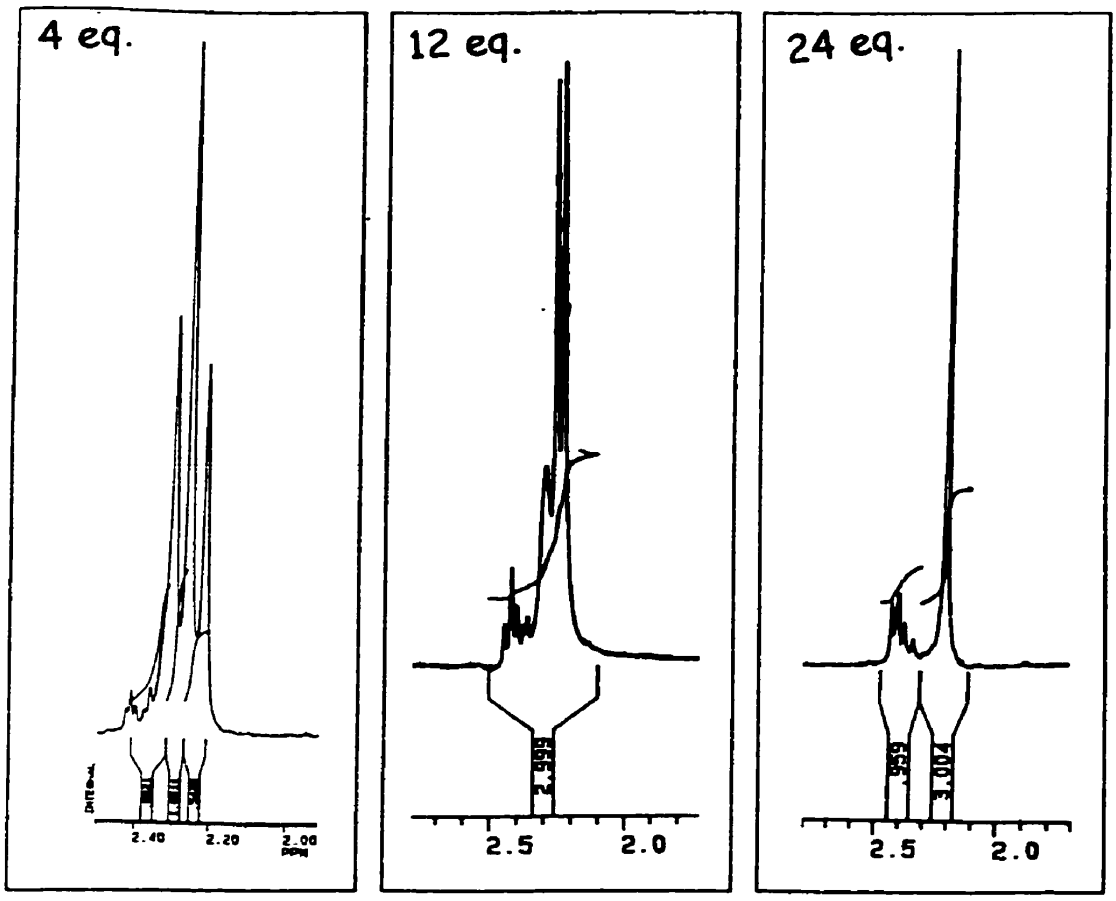


Figure 3.8 ^{1}H NMR Spectra of Intermediate Species formed in the Oxidation of **28c**

Thin-layer chromatography (TLC) on silica plates in a variety of CH_2Cl_2/hexane solvent mixture ratios indicated that partially oxidized intermediates could not be separated by column chromatography because the compounds elute too closely to each other. This is not surprising considering their similar ring sizes. Attempted recrystallization of the product mixture from CH_2Cl_2/hexane at -20°C did not afford a pure product. This multiple product formation was also observed in the oxidation of **28b**, but it was much more difficult to monitor in the absence of a suitable ^{1}H NMR probe.

3.5 Conclusions

Sixteen-membered cyanuric-sulfanuric rings can be prepared in good yields (55-80%) by the oxidation of the corresponding S(IV) heterocycles. The X-ray structures of $(4\text{-}CH_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ (**35a**) and $(4\text{-}CF_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ (**35b**) were determined. The tetra-oxidized species $(4\text{-}CF_3C_6H_4)_4C_4N_8S_4O_4(4\text{-}CH_3C_6H_4)_4$ (**35c**) was also prepared. The conformation of the sixteen-membered ring is retained upon oxidation with a slight opening of the cradle structure. In both **35a** and **35b** the S-N distance becomes shorter upon oxidation, but d(C-N) remains about the same. The S=O distances are consistent with typical S^{VI}=O double bond values.

The partial oxidation of S(IV) sixteen-membered rings is attainable if less than sixteen (**28d**) or twenty-four equivalents (**28b** and **28c**) are used. It is believed that, as was observed for the tetra-oxides, the oxygen atoms take the place of the lone pair of electrons on the sulfur in these partially oxidized systems. ^{1}H NMR evidence for partially oxidized $C_4N_8S_4$ rings was obtained but pure samples of these mixed oxidation state systems could not be isolated.

3.6 Experimental

3.6.1 Reagents and General Procedures

See Chapter 2 for details of reagents and general procedures. All sixteen-membered C-N-S^{IV}-N rings were prepared by reaction of the appropriate trisilylated benzamidine and an arene sulfenyl chloride at low temperature as outlined in literature[6].

3.6.2 Instrumentation

All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ACE 200 spectrometer or Varian XL-200 and analyzed using the Tecmag PowerMac 7300/180 software. All samples were run in deuterated solvents and referenced with respect to the residual protons. Chemical shifts are quoted relative to trimethylsilane at 0 ppm. Infrared spectra were collected on a Mattson 4030 FT-IR spectrometer and samples were prepared on KBr plates in a Nujol mull. FAB-mass spectra were obtained using a Kratos MS80 RFA mass spectrometer. All chemical analyses (i.e. mass spectra and elemental analysis) were carried out by the Analytical Services department at the University of Calgary. X-ray data collections were obtained on a Rigaku AFC6S diffractometer equipped with a low temperature device. Structures were solved and refined by Dr. Masood Parvez using the teXsan[55] program. Further details of the structure solution and refinements may be obtained from Dr. T. Chivers.

3.6.3 Preparation of $(4\text{-}CH_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ (35a)

To a Schlenk vessel containing $(4\text{-}CH_3C_6H_4)_4C_4N_8S_4(C_6H_5)_4$ (0.181 g, 0.188 mmol) in 50 ml CH_2Cl_2 was added *m*CPBA (0.780 g, 4.52 mmol) also dissolved in 50 ml of CH_2Cl_2. It was determined through stepwise addition that 24 equivalents of *m*CPBA are required for complete oxidation to occur, i.e. all four sulfurs oxidized to S(VI). The reaction was stirred for one hour under a flow of argon. Unreacted *m*CPBA and the by-product *m*CBA were removed from the reaction mixture by several recrystallizations from a 2:1 pentane/CH_2Cl_2 mixture. In addition to this it was sometimes necessary to perform an aqueous extraction with 10 equivalents of $NaHCO_3$ followed by $MgSO_4$ to completely remove the unwanted materials. The product obtained is a colourless powder (0.107 g, 0.104 mmol, 55.5%). The product was recrystallized from a mixture of CH_2Cl_2 and hexane at -20°C to yield clear colourless crystals. X-ray quality crystals were obtained by slow evaporation of CH_2Cl_2/hexane solvent mixture at room temperature. Mp: 202°C (decomposed to brown material). Elemental Analysis Calculated for $C_{56}H_{48}N_8S_4O_4 \bullet CH_2Cl_2$: C, 61.72; H, 4.55; N, 10.11. Found: C, 62.13; H, 4.47; N, 10.14. ^{1}H NMR (in $CDCl_3$, δ): 7.49 (m, $C_6(H_c)_2(H_d)_3$, 3H), 7.30 (m, $C_6(H_c)_2(H_d)_3$, 2H), 7.89 (d, $4\text{-}CH_3C_6(H_a)_2(H_b)_2$, 2H), 6.81 (d, $4\text{-}CH_3C_6(H_a)_2(H_b)_2$, 2H), 2.22 (s, $4\text{-}CH_3C_6H_5$, 3H). ^{13}C NMR (in $CDCl_3$, δ): 170.44 (heterocyclic tertiary C), 142.45, 140.29, 133.96, 133.69, 132.28, 129.35, 129.02, 128.65, 128.50. IR (cm^{-1}): 1654 (m), 1560 (m), 1489 (m), 1398 (m), 1309 (w), 1227 (m), 1172 (w), 1111 (m), 1095 (s), 1022 (w), 948 (w), 851

(s), 807 (w), 791 (w), 748 (m), 727 (m), 689 (w), 661 (w), 591 (s), 510 (w). FAB-MS (M^-): 1025.

3.6.4 Preparation of $(4\text{-}CF_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ (35b)

To a Schlenk vessel containing $(4\text{-}CF_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ (0.220 g, 0.187 mmol) in 50 ml CH_2Cl_2 was added *m*CPBA (0.774 g, 4.49 mmol) also dissolved in 50 ml of CH_2Cl_2. It was determined through stepwise addition that 24 equivalents of *m*CPBA are required for complete oxidation to occur, i.e. all four sulfurs oxidized to S(VI). The reaction was stirred one hour under a flow of argon. Unreacted *m*CPBA and the by-product *m*CBA were removed from the reaction mixture by several recrystallizations in a 2:1 pentane/CH_2Cl_2 mixture. In addition to this it was sometimes necessary to perform an aqueous extraction with 10 equivalents of $NaHCO_3$ followed by $MgSO_4$ to completely remove the unwanted materials. The product obtained is a colourless powder (0.189 g, 0.152 mmol, 81.4%). The product was recrystallized from a mixture of CH_2Cl_2 and diethyl ether at -20°C to yield clear colourless crystals. X-ray quality crystals were obtained by slow evaporation of CH_2Cl_2/hexane solvent mixture at room temperature. Mp: 226°C. Elemental Analysis Calculated for $C_{56}H_{36}N_8S_4O_4F_{12}$: C, 54.19; H, 2.93; N, 9.03. Found: C, 53.81; H, 2.80; N, 8.81. ^1H NMR (in $CDCl_3$, δ): 7.41 (m, $C_6(H_c)_2(H_d)_3$, 3H), 7.66 (m, $C_6(H_c)_2(H_d)_3$, 2H), 7.92 (d, $4\text{-}CH_3C_6(H_a)_2(H_b)_2$, 2H), 7.19 (d, $4\text{-}CH_3C_6(H_a)_2(H_b)_2$, 2H). ^{13}C NMR (in $CDCl_3$, δ): 170.85 (heterocyclic tertiary C),

141.84, 139.77, 133.51, 130.45, 129.20, 128.91, 126.83, 124.52, 124.49. IR (cm^{-1}): 1655 (s), 1523 (w), 1504 (w), 1416 (s), 1317 (s), 1224 (m), 1127 (m), 1098 (m), 1018 (w), 1003 (w), 861 (m), 820 (m), 684 (w), 653 (m), 629 (w), 617 (w), 582 (w), 499 (w), 545 (w).

3.6.5 Preparation of $(4\text{-}CF_3C_6H_4)_4C_4N_8S_4O_4(4\text{-}CH_3C_6H_4)_4$ (35c)

To a Schlenk vessel containing $(4\text{-}CF_3C_6H_4)_4C_4N_8S_4O_4(4\text{-}CH_3C_6H_4)_4$ (0.161 g, 0.131 mmol) in 50 ml CH_2Cl_2 was added *m*CPBA (0.361 g, 2.10 mmol) also dissolved in 50 ml of CH_2Cl_2. It was determined through stepwise addition that 16 equivalents of *m*CPBA are required for complete oxidation to occur, i.e. all four sulfurs oxidized to S(VI). The reaction was stirred one hour under a flow of argon. Unreacted *m*CPBA and the by-products *m*CBA were removed from the reaction mixture by several recrystallizations from a 2:1 pentane/CH_2Cl_2 mixture. In addition to this it was sometimes necessary to perform an aqueous extraction with 10 equivalents of $NaHCO_3$ followed by $MgSO_4$ to completely remove the unwanted materials. The product obtained is a colourless powder (0.129 g, 0.0996 mmol, 76.3%). The product was recrystallized from a mixture of CH_2Cl_2 and diethyl ether at -20°C to yield clear colourless crystals. X-ray quality crystals were obtained by slow evaporation of CH_2Cl_2/hexane solvent mixture at room temperature. Mp: did not melt up to 270°C. Elemental Analysis Calculated for $C_{60}H_{44}N_8S_4O_4F_{12}$: C, 55.55; H, 3.42; N, 8.64. Found: C, 55.45; H, 3.86; N, 8.99. ^1H

NMR (in $CDCl_3$, δ): 7.75 and 7.17 (d, 4-$CF_3C_6H_4$, 2H) 7.65 and 7.14 (d, 4-$CH_3C_6H_4$, 2H), 2.42 (s, 4-$CH_3C_6H_5$, 3H). ^{13}C NMR (in $CDCl_3$, δ): 170.89 (heterocyclic tertiary C), 144.53, 139.88, 138.96, 130.44, 129.72, 128.96, 126.85, 125.32, 124.41, 124.38. IR (cm^{-1}): 1597 (m), 1575 (m), 1522 (m), 1506 (m), 1418 (s), 1322 (s), 1221 (s), 1125 (s), 1097 (s), 1018 (m), 951 (m), 901 (w), 857 (s), 821 (s), 777 (w), 639 (m), 625 (m), 601 (m), 578 (w), 512 (m), 461 (m).

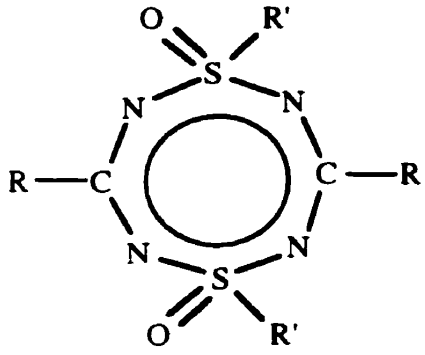
CHAPTER 4

Conclusions and Future Work

4.1 Conclusions

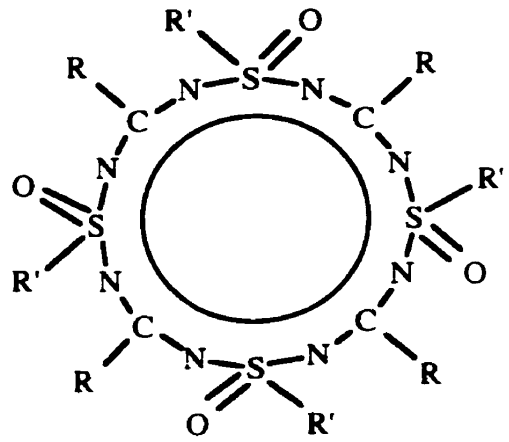
The first objective of this thesis, i.e. the synthesis and structural characterization of eight- and sixteen-membered heterocycles with alternating C-N-S^{VI}-N groups was accomplished. Several eight- and sixteen-membered rings were prepared with varying substituents on both sulfur and carbon (see Figure 4.1).

The cyanuric-sulfanuric rings were prepared by oxidation of the corresponding S(IV) species with *m*CPBA to yield white crystalline powders that are stable towards moisture and oxygen. Single crystals were obtained from CH_2Cl_2/hexane and the structures of **29b**, **29c**, **32**, **35a**, and **35b** were determined by X-ray crystallography. These novel heterocycles were also characterized by elemental analysis, mass spectrometry, IR, ^1H NMR, and ^{13}C NMR. Structural analysis determined that the boat



29

a R = 4-BrC_6H_4, R' = C_6H_5
b R = 4-$CF_3C_6H_4$, R' = C_6H_5
c R = 4-$CF_3C_6H_4$, R' = 4-$CH_3C_6H_4$.



35

a R = 4-$CH_3C_6H_4$, R' = C_6H_5
b R = 4-$CF_3C_6H_4$, R' = C_6H_5
c R = 4-$CF_3C_6H_4$, R' = 4-$CH_3C_6H_4$

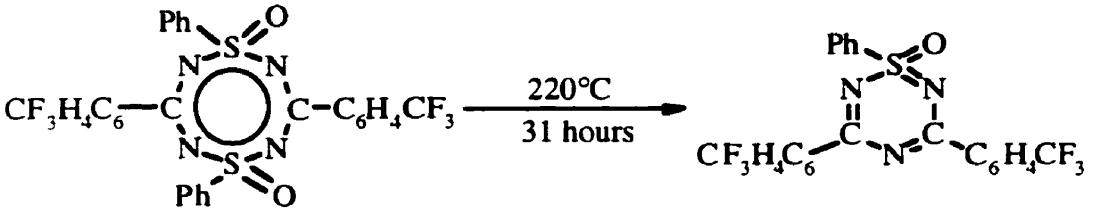
Figure 4.1 Eight- and Sixteen-Membered Cyanuric-Sulfanuric Rings

conformation of the dithiatetrazocine is retained upon oxidation. The presence of two oxygens in a *cis* position above the ring skews the sulfur atoms thus giving a twisted boat structure. In the sixteen-membered systems the cradle conformation is retained upon oxidation of all four sulfur atoms although it is widened.

The second objective of this research was to determine whether the eight-membered cyanuric-sulfanuric rings can be used as precursors for hybrid inorganic polymers. Many hybrid inorganic heterocycles have been known to undergo thermal ring opening to form polymers[3] and this new cyclic system was a potential source of

polymers containing alternating $CN/S^{VI}N$ groups. This investigation revealed that the eight-membered cyanuric-sulfanuric rings undergo ring contraction at approximately 220°C with loss of a sulfanuric group to form the six-membered heterocycle, $(4\text{-}CF_3C_6H_4)_2C_2N_3SO(C_6H_5)$ (**33**), rather than the ring-opening polymerization.

The ring-contraction product (**33**) is a white crystalline material that is not air or moisture-sensitive. Characterization of **33** was carried out by C,H,N,S elemental analysis, mass spectrometry, IR, ^1H NMR, and ^{13}C NMR. Unfortunately, no X-ray quality crystals were obtained for structure determination.

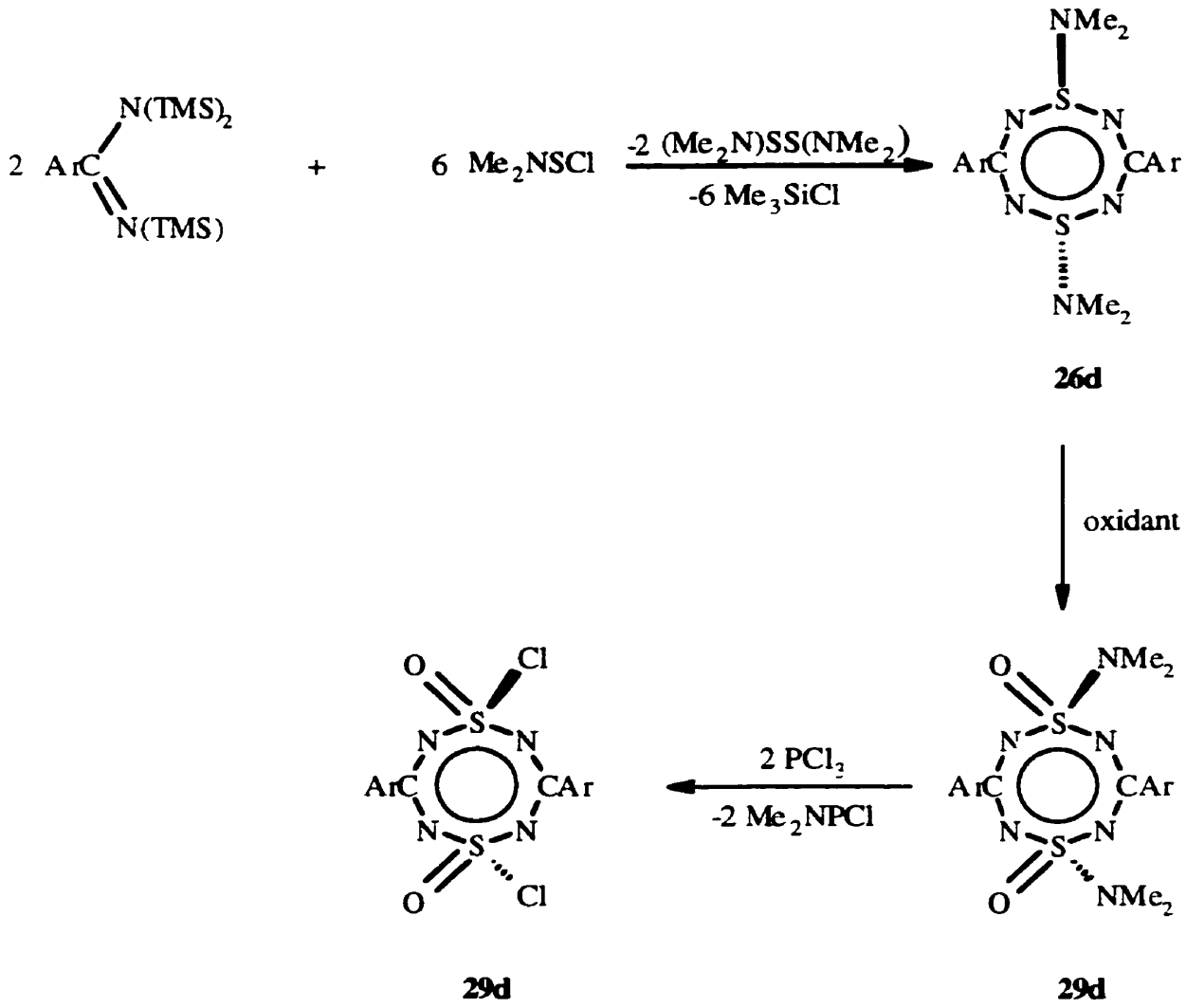


(4.1)

33

4.2 Suggestions for Future Work

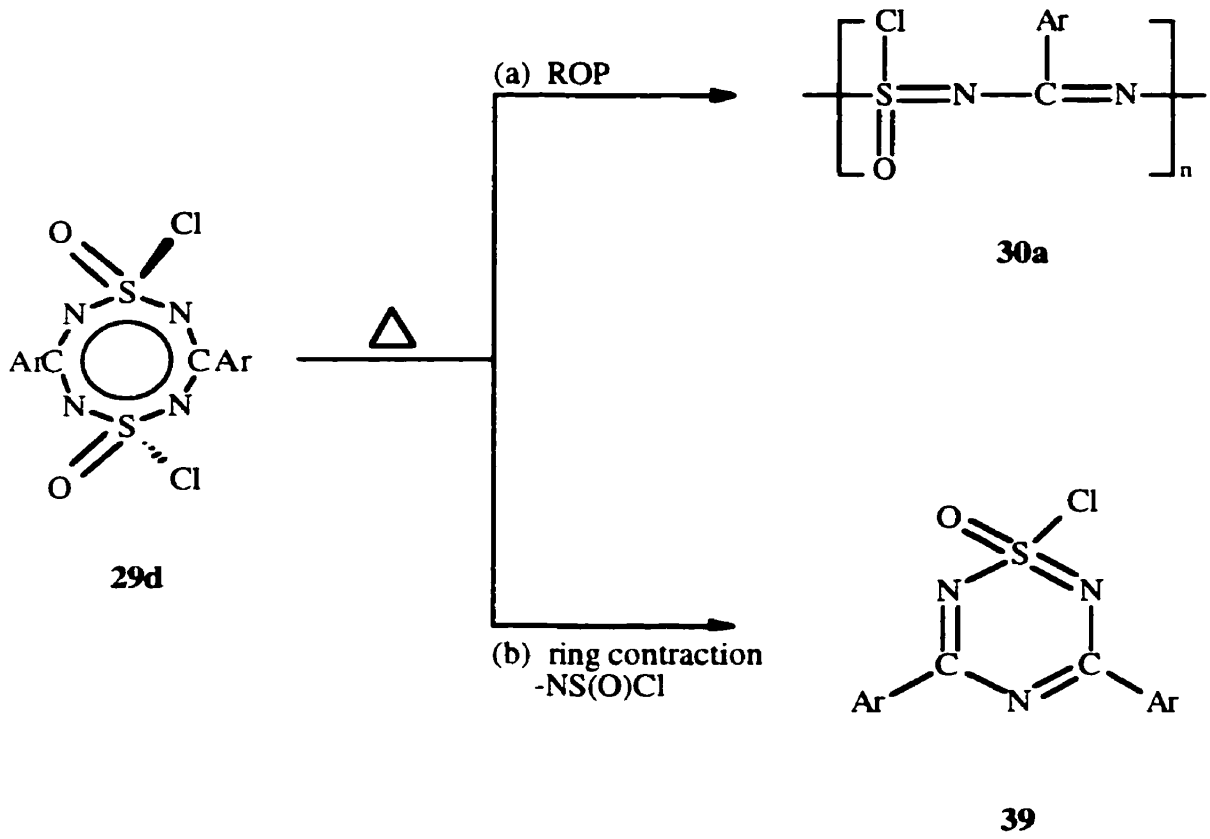
The ultimate goal of the research described in this thesis is the production of polymers with alternating S^{VI}-N-C-N repeating units. Until now only derivatives with aryl substituents attached to carbon and sulfur have been investigated. Although a variety of different heterocycles can be produced by changing these substituents, a major objective of this work involves the development of a versatile system suitable for application to a diverse number of substituents [cf. poly(phosphazenes)[2] (see Section 1.3.1)]. Ideally this would involve Cl as a substituent on the sulfur atom. The presence of Cl instead of the substituted phenyl groups may allow: (a) facile ring-opening polymerization via an ionization mechanism (Section 1.3.1) and (b) nucleophilic substitution of the resulting polymer to give a variety of sulfur-substituted derivatives. Scheme 4.1 gives a proposed method for obtaining a chlorine substituent on sulfur. The formation of the dithiatetrazocine (**26d**) is achieved by the low temperature reaction of a trisilylated benzamidine and three equivalents of dimethylaminosulfenyl chloride, which is prepared by the reaction of dimethylamine with sulfur dichloride[57]. In the second step the oxidation of the S(IV) to S(VI) is accomplished by reaction with a suitable reagent. Typically, *m*CPBA has been successful, but other oxidants such as $KMnO_4/CuSO_4 \bullet xH_2O$ have also been employed[42] in similar systems. Further reaction with a chlorinating agent, PCl_3 for example, will afford a facile replacement of the NMe_2 groups to give the chlorinated species (**29d**).



Scheme 4.1 Proposed Preparation of Sulfur-Chlorinated Cyanuric-Sulfanuric Rings

Upon thermolysis of **29d** two possible reactions may be envisioned: (a) ring-opening polymerization of the eight-membered species to give a polymer with a S^{VI}-N-C-N backbone or (b) ring contraction with the loss of a sulfanuric group to leave

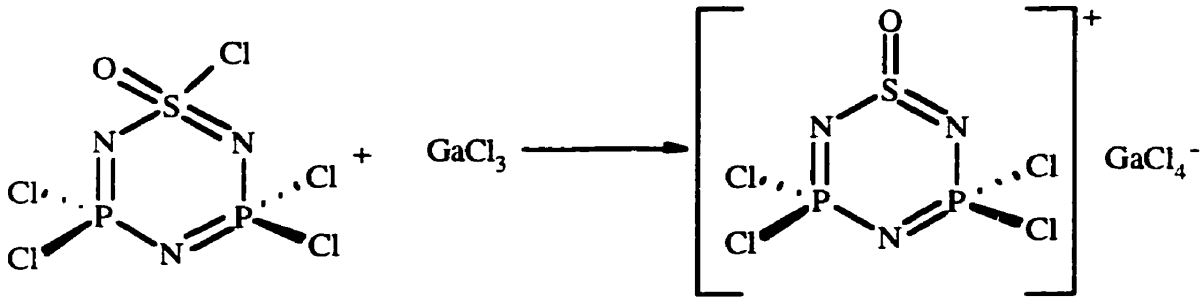
$Ar_2C_2N_3S(O)Cl$. Derivatization of the polymer [route (a)] or six-membered ring [route (b)] is a means to a variety of different hybrid inorganic species.



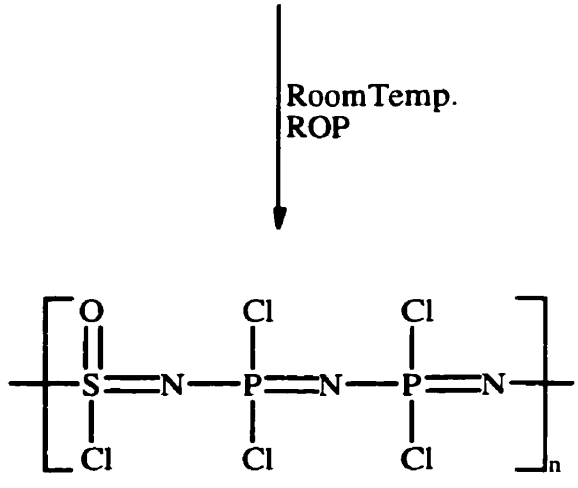
Scheme 4.2 Possible Reaction Pathways for Thermolysis of **29d**

Investigation into the ROP of **39** would also be interesting. However, it is known from previous studies on similar systems[41] that thermal ROP may cause loss of sulfur as sulfur halides. Thus, an alternative method of polymerization needs to be investigated.

Ambient temperature synthesis of polyphosphazenes by polycondensation of phosphoranimines has been reported[58,59]. Recently, Manners *et al.* have described an ambient temperature synthesis of poly(thionyl phosphazenes) from cyclic precursors using $GaCl_3$ as a chloride ion acceptor[60].



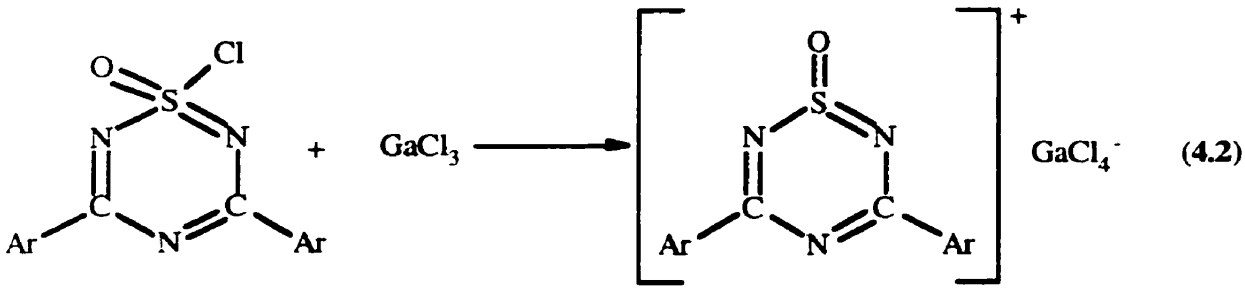
13a **39**



15

Scheme 4.3 Room Temperature ROP of Cyclic Thionylphosphazene

The interaction of **13a** with a Lewis acid generates the cationic centre necessary for ring-opening polymerization (see Scheme 1.1). A similar reaction may be attempted with heterocycle **40** to generate the desired polymer without the need for heating the sample.



40 **41** **(4.2)**

Clearly there are many avenues for future work in the area of cyanuric-sulfanuric heterocyclic chemistry. The generation of inorganic polymers incorporating a C-N-S^{VI}-N alternating backbone is a main focus as these systems have yet to be reported.

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