

THE UNIVERSITY OF CALGARY

Eight-membered PNS Heterocycles Containing S(IV) and S(VI) Centers

by

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## ABSTRACT

This thesis describes the synthesis and structure of new phosphorus-nitrogen-sulfur (PNS) heterocycles and discusses their potential applications as precursors to hybrid inorganic polymers. The use of the eight-membered rings  $1,5\text{-R}_4\text{P}_2\text{N}_4\text{S}_2\text{Cl}_2$  ( $\text{R} = \text{Et}, \text{Ph}$ ) as synthetic precursors to other S,S-disubstituted heterocycles was investigated. The reaction of  $1,5\text{-R}_4\text{P}_2\text{N}_4\text{S}_2\text{Cl}_2$  ( $\text{R} = \text{Et}, \text{Ph}$ ) with  $\text{Me}_2\text{NSiMe}_3$  yields the dimethylamino-substituted derivatives  $1,5\text{-R}_4\text{P}_2\text{N}_4(\text{SNMe}_2)_2$  ( $\text{R} = \text{Et}, \text{Ph}$ ). The structures of the eight-membered rings  $1,5\text{-Et}_4\text{P}_2\text{N}_4\text{S}_2\text{Cl}_2$  and  $1,5\text{-R}_4\text{P}_2\text{N}_4(\text{SNMe}_2)_2$  ( $\text{R} = \text{Et}, \text{Ph}$ ) have been determined by X-ray crystallography. The reaction of  $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{Cl}_2$  with  $\text{AlCl}_3$  gives the dication  $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2^{2+}$ , which was found by X-ray diffraction to have an unexpected planar ring conformation.

The oxidizing agent *m*-chloroperbenzoic acid (*m*CPBA) was found to oxidize S(IV) to S(VI) in these heterocyclic systems. The reaction of *m*CPBA with chair and boat forms of  $1,5\text{-Ph}_4\text{P}_2\text{N}_4(\text{SMe})_2$  yields *trans*- $1,5\text{-Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Me}]_2$  and *cis*- $1,5\text{-Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Me}]_2$ , respectively. In addition to spectroscopic characterization, the structures of *trans*- $1,5\text{-Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{R}]_2$  ( $\text{R} = \text{Me}, \text{Ph}$ ) and *cis*- $1,5\text{-Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Me}]_2$  were determined by X-ray crystallography.

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## **DEDICATION**

To Mom, Dad and Brian. Thank-you for all of your support.

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## LIST OF COMPOUNDS

1.  $(\text{NPCl})_3$

2.  $\text{S}_4\text{N}_4$

3.  $(\text{RR}'\text{PN})_4$

4.  $(\text{RR}'\text{PN})_n$

5.  $(\text{NS}(\text{O})\text{X})_3$

6.  $\text{R}_2\text{PN}_3\text{S}_2$

a.  $(\text{R} = \text{Me}_3\text{SiNH})$

b.  $(\text{R} = \text{Ph})$

c.  $(\text{R} = \text{Me})$

7.  $\text{Ph}_2\text{PN}_3(\text{SCl})_2$

8.  $\text{R}_4\text{P}_2\text{N}_3\text{SX}$

a.  $\text{R} = \text{X} = \text{Cl}$

b.  $\text{R} = \text{Ph}, \text{X} = \text{Cl}$

c.  $\text{R} = \text{Ph}, \text{X} = \text{Br}$

d.  $\text{R} = \text{Ph}, \text{X} = \text{I}$

e.  $\text{R} = \text{X} = \text{Ph}$

f.  $\text{R} = \text{Ph}, \text{X} = \text{NMe}_2$

g.  $\text{R} = \text{Ph}, \text{X} = \text{NEt}_2$

h.  $\text{R} = \text{Ph}, \text{X} = \text{N}(-\text{CH}_2-)_5$

9.  $\text{Ph}_8\text{P}_4\text{N}_6(\text{SNMe}_2)_2$
10.  $\text{Ph}_8\text{P}_4\text{N}_6\text{S}$
11.  $\text{Cl}_2\text{PN}_3[\text{S}(\text{O})\text{Cl}]_2$
12.  $\text{Cl}_4\text{P}_2\text{N}_3\text{S}(\text{O})\text{Cl}$
13. 1,5- $\text{R}_4\text{P}_2\text{N}_4\text{S}_2$
- a.  $\text{R} = \text{Me}$
  - b.  $\text{R} = \text{Ph}$
  - c.  $\text{R} = \text{Et}$
14. 1,3- $\text{R}_4\text{P}_2\text{N}_4\text{S}_2$
- a.  $\text{R} = \text{Me}$
  - b.  $\text{R} = \text{Ph}$
15. 1,5- $\text{R}_2\text{R}'_2\text{P}_2\text{N}_4\text{S}_2$
- a. *exo-R, exo-R*
  - b. *endo-R, endo-R*
  - c. *exo-R, endo-R*
16. 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{X}_2$
- a.  $\text{X} = \text{Br}$
17. 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{Br}^+$
18.  $[\text{1,5}-(\text{Me}_2\text{N})_2\text{C}_2\text{N}_4\text{S}_2\text{Cl}][\text{Cl}_3]$
19.  $[\text{1,5-Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{RLi}(\text{THF})]_2$

20. boat conformation 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>RR'

a. R = R' = Me

21. chair conformation 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>RR'

a. R = R' = Me

b. R = R' = Ph

22. 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>RX

23. (NPCl<sub>2</sub>)NS(O)Cl

24. (NPCl<sub>2</sub>)<sub>4</sub>(NS(O)Cl)<sub>2</sub>

a. *cis*

b. *trans*

25. [(Cl<sub>2</sub>)PN(Cl<sub>2</sub>)PNS(Cl)N]<sub>n</sub>

26. [(Cl<sub>2</sub>)PN(Cl<sub>2</sub>)PNS(O)ClN]<sub>n</sub>

27. [(R<sub>2</sub>)PNS(R')N]<sub>n</sub>

28. [(R<sub>2</sub>)PNS(O)R]<sub>n</sub>

29. 1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>R<sub>2</sub>'

a. R = Et, R' = Cl

b. R = Ph, R' = Cl

c. R = Et, R' = NMe<sub>2</sub>

d. R = Ph, R' = NMe<sub>2</sub>

30. 1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub><sup>2+</sup>

- a. R = Et
  - b. R = Ph
31. 1,5-H<sub>2</sub>E<sub>2</sub>N<sub>4</sub>S<sub>2</sub>
32. 1,5-H<sub>4</sub>E<sub>2</sub>N<sub>4</sub>S<sub>2</sub>
- a. planar conformation
  - b. boat conformation
33. 1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)Cl]<sub>2</sub>
34. 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)R]<sub>2</sub>
- a. *trans*, R = Ph
  - b. *trans*, R = Me
  - b'. *cis*, R = Me
35. *m*-ClC<sub>6</sub>H<sub>4</sub>CO<sub>3</sub>H
36. 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)NMe<sub>2</sub>]<sub>2</sub>
37. 1,5-(Me<sub>2</sub>N)<sub>2</sub>C<sub>2</sub>N<sub>4</sub>S<sub>2</sub>
38. 1,5-(Me<sub>2</sub>N)<sub>2</sub>C<sub>2</sub>N<sub>4</sub>[SON(CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub>
39. 1,5-(Me<sub>2</sub>N)<sub>2</sub>C<sub>2</sub>N<sub>4</sub>[S(O)N(CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub>

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## LIST OF ABBREVIATIONS AND SYMBOLS

Ar	aryl (aromatic) group
d	bond distance
$D_{\text{calc}}$	calculated density
DFT	density functional theory
esd	estimated standard deviation
ESR	Electron Spin Resonance
Et	$\text{C}_2\text{H}_5$ (ethyl)
FTIR	Fourier Transform Infrared Spectroscopy
HOMO	Highest Occupied Molecular Orbital
<i>i</i> Pr	$\text{CH}(\text{CH}_3)_2$ (isopropyl)
LUMO	Lowest Unoccupied Molecular Orbital
<i>m</i> CPBA	<i>meta</i> -chloroperbenzoic acid
Me	$\text{CH}_3$ (methyl)
mp	melting point
MS	Mass Spectrometry
<i>n</i> Bu	$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (butyl)
NMR	Nuclear Magnetic Resonance
ORTEP	Oakridge Thermal Ellipsoid Plot
Ph	$\text{C}_6\text{H}_5$ (phenyl)
ppm	parts per million

ROP	ring opening polymerization
<sup>t</sup> Bu	C(CH <sub>3</sub> ) <sub>3</sub> (tertiary butyl)
T <sub>g</sub>	glass transition temperature
THF	tetrahydrofuran

## CHAPTER 1

### Inorganic Heterocycles and Polymers

#### 1.1 Introduction.

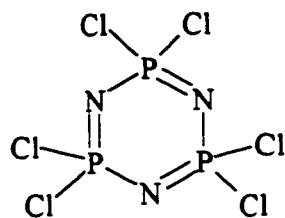
Since the discovery of rubber the research and development of organic polymers has been extensive. Polymers have been made with a wide range of properties and applications which are of interest to industry. The majority of polymers used today are organic polymers such as polyethylene and polypropylene. Inorganic polymers like polysiloxanes and polyphosphazenes have found their places in industry, however they are not used as extensively as their organic counterparts. One day the natural resources used to synthesize organic polymers will be depleted. The loss of these resources creates a need for research into the synthesis of new inorganic polymers which may replace organic polymers. In addition, these polymers could have properties that cannot be found in organic polymers for example, the superconducting properties of poly(sulfur nitride).

This thesis is concerned with making new precursors to hybrid inorganic polymers. A hybrid inorganic polymer is best described as a hybrid of two inorganic polymers like polyphosphazene which has repeating  $-P=N-$  units in the backbone and poly(sulfur nitride), whose repeat units are  $-S=N-$ . The hybrid polymer of these would have the

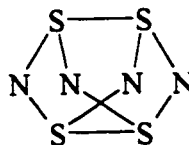
repeat unit  $-P=N-S=N-$ , or some variation of this unit. Inorganic polymers have frequently been made by thermal ring opening polymerization (ROP) of the corresponding cyclic monomer. This same strategy has been used in the synthesis of hybrid inorganic polymers. The thermal ring opening of new inorganic heterocycles could give inorganic polymers with unique properties. The synthesis of new hybrid ring systems that may lead to such polymers is the major focus of this investigation. In order to provide an appropriate background for the discussion of hybrid heterocycles this chapter will start with a brief description of the synthesis and reactivity of some binary PN and SN heterocycles. A discussion of the synthesis and properties of inorganic rings and polymers containing both PN and SN units will follow.

## 1.2 Inorganic Ring Systems.

The first inorganic heterocycle,  $(NPCl_2)_3$  (**1**), was discovered in 1834 by Wöhler and Rose.<sup>1</sup> One year later, in 1835,  $S_4N_4$  (**2**) was first made by Gregory.<sup>1</sup> Since the 1800's new heterocycles, including siloxanes, phosphazenes and phosphorus-sulfur cages have been developed. The evolution of X-ray crystallography was important because the structures of new heterocycles could be determined which made it easier for chemists to devise new synthetic strategies to prepare novel inorganic heterocycles.<sup>1,2</sup>



1

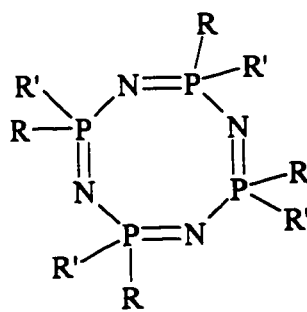


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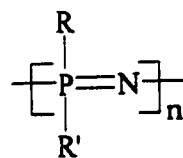
The interest in inorganic ring systems is due to their fundamental chemistry, bonding, and their tendency to form polymers.<sup>1</sup> Some good examples include siloxane ring systems, cyclophosphazenes, and tetrasulfur tetranitride. These ring systems undergo ring-opening polymerization (ROP) to give polymers with interesting properties. Cyclophosphazenes (1) undergo ring-opening to give polyphosphazenes which make up the largest class of inorganic polymers, closely followed by polysiloxanes.<sup>3</sup> Tetrasulfur tetranitride converts readily into  $(SN)_x$ , a polymer that exhibits the superconducting properties of a metal.<sup>3</sup> Current interest in new polymers is a growing industry, but it is mainly devoted to organic polymers which are made from limited resources therefore increasing the need for alternatives based on inorganic sources. In addition, the properties of these polymers, such as the superconductivity of  $(SN)_x$ , and the bioinertness of polyphosphazenes suggests there is potential for further development of new inorganic polymers.

### 1.3 Cyclophosphazenes.

Cyclophosphazene chemistry is so extensive it could be thought of as a branch of inorganic chemistry.<sup>3</sup> The most intensively studied P-N derivatives are the ring or chain phosphazenes with the repeat unit N=PRR' (3 and 4, respectively). A wide variety of ring sizes ranging from  $n = 3-17$  is known for cyclophosphazenes (NPR<sub>2</sub>)<sub>n</sub> (4).



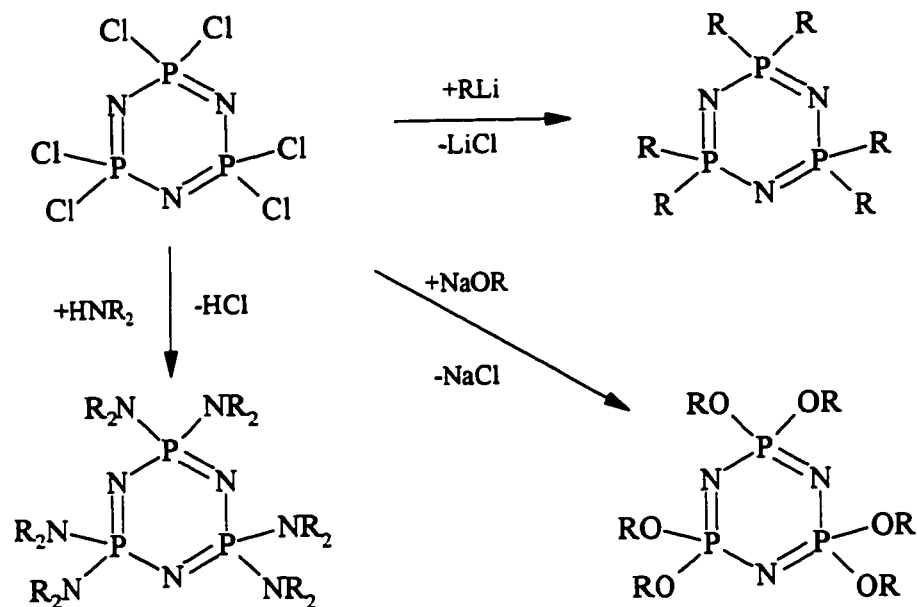
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4

The halophosphazenes ( $R=R' = \text{Cl, F}$ ) are used as synthetic precursors to other substituted phosphazenes because of the reactive P-R bond. The trimer (NPCl<sub>2</sub>)<sub>3</sub> is most commonly prepared by the reaction of PCl<sub>5</sub> with NH<sub>4</sub>Cl.<sup>1</sup> Nucleophilic substitution reactions have led to a large variety of cyclophosphazenes derivatives (Figure 1.1). Substituents placed on the phosphorus include alkoxides, aryloxides, alkylamino, arylamino, alkyl, and aryl; mixed substitution is also possible.

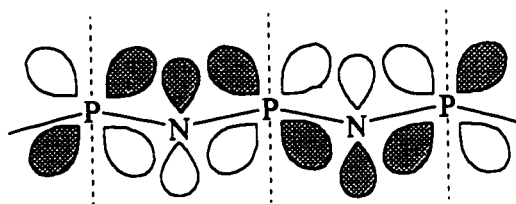




**Figure 1.1.** Some common reactions of cyclophosphazenes where R=alkyl or aryl groups.

The stability of cyclophosphazenes has been attributed to the strong P-N backbone which is derived from  $\pi$  bonding.<sup>1,2</sup> The six-membered ring has  $6\pi$  electrons for 6 atoms making it  $\pi$ -electron precise. One electron from each nitrogen atom and one electron from each phosphorus atom are donated to the  $\pi$  system and the P-N bond distances are equal, within experimental error, suggesting delocalization. The bonding involves a promotion of a phosphorus electron to the 3d level, which can form a  $d\pi$ - $p\pi$  interaction with an electron in the  $p_z$  orbital of nitrogen (Figure 1.2).<sup>1,2</sup> The bonding is predominantly a three center Dewar island type, where every repeating PNP makes up an island with a node at each phosphorus atom.<sup>1</sup> These islands interfere with the possibility

of ring currents commonly found in benzene (absent in the cyclophosphazenes), but still allows the aromatic stabilization of the  $\pi$  electrons.

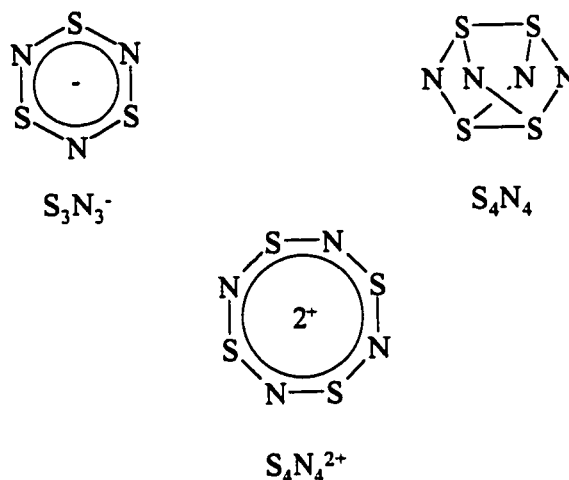


**Figure 1.2.** Dewar island bonding in phosphazenes.

## 1.4 Binary SN Rings.

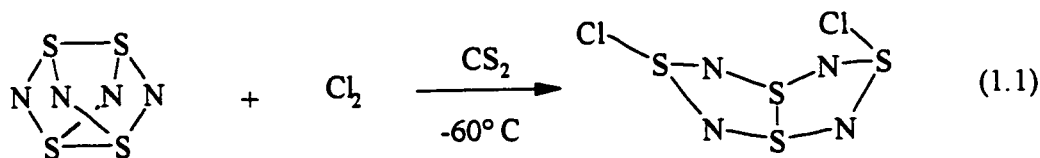
### 1.4.1 Cyclothiazenes.

The cyclothiazenes exhibit interesting bonding and unpredictable reactivity.<sup>1</sup> Some cyclothiazenes are shown in Figure 1.3. Unlike the cyclophosphazenes, these rings are  $\pi$ -electron-rich.<sup>4</sup> Each two-coordinate sulfur donates  $2\pi$  electrons for  $\pi$  bonding, as opposed to  $1\pi$  electron in the case of phosphorus. Their weak S-N bonds, due to partially occupied  $\pi^*$  orbitals, give rise to high reactivity as seen by their tendency to explode releasing the more stable species  $S_8$  and  $N_2$ . The interest in the cyclothiazenes arises from their unusual reaction chemistry and from their tendency to form the polymer  $(SN)_x$  (Section 1.5.2).



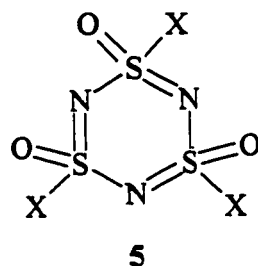
**Figure 1.3.** Some examples of cyclothiazenes

Tetrasulfur tetranitride (**2**) is the most readily prepared S-N compound.<sup>5</sup> It is made by passing  $NH_3$  gas through a solution of  $S_2Cl_2$ . Planar  $S_4N_4$  would be a 12- $\pi$  electron system but it adopts a folded structure with two S-S transannular bonds with a separation of 2.48 Å.<sup>6</sup> At low temperatures, tetrasulfur tetranitride readily undergoes oxidative addition of  $X_2$  ( $X = Cl^7, F^8$ ) to give  $S_4N_4X_2$  with a boat structure as shown in Equation 1.1 ( $X = Cl$ ). The exocyclic chlorine atoms adopt exo-endo positions, possibly to minimize the lone pair interactions of the two substituted sulfurs.<sup>4</sup> The dichlorinated derivative  $S_4N_4Cl_2$  can react further with  $Me_3SiNMe_2$  to give 1,5- $S_4N_4(NMe_2)_2$ .<sup>9</sup>

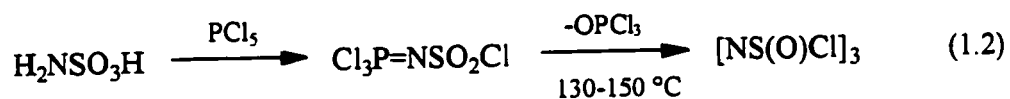


### 1.4.2 Sulfanuric Ring Systems.

Sulfanuric rings contain four-coordinate S(VI) atoms with the characteristic repeat unit  $-N=S(O)X-$  ( $X = Cl, F$ ). The chemistry of these systems has been limited to the six-membered rings, unlike their isoelectronic counterparts, the cyclophosphazenes.<sup>4</sup>



The sulfanuric halides are made by a variety of methods. Sulfanuric chloride (5,  $X = Cl$ ) is most commonly prepared, in 35% yield, by the reaction of  $SOCl_2$  with  $NaN_3$  in  $CH_3CN$ .<sup>10</sup> The original preparation of sulfanuric chloride is a two step synthesis which results in a 17% yield (Equation 1.2).<sup>11</sup> A third pathway to this ring system involves the oxidation of  $(NSCl)_3$  with  $SO_3$ .<sup>12</sup>



The sulfanuric halides undergo nucleophilic substitution at the sulfur-halogen bond. The chlorinated six-membered ring reacts with organomercury compounds to give

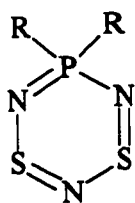
mono-, or di-organo-substituted sulfanuric rings; tri-substituted products are not observed in the reaction with organomercury compounds.<sup>13,14</sup> However, the derivative,  $[\text{NS}(\text{O})\text{Ph}]_3$ , can be synthesized using a Friedel Crafts reaction of  $[\text{NS}(\text{O})\text{F}]_3$  with benzene in the presence of  $\text{AlCl}_3$ .<sup>15</sup> Amino substituted sulfanuric rings are obtained from the reaction of  $[\text{NS}(\text{O})\text{F}]_3$  with secondary amines.<sup>11</sup> Dimethylamine reacts at  $80^\circ\text{C}$ , without a solvent, to give  $[\text{NS}(\text{O})\text{NMe}_2]_3$ . Diethylamine, however, only yields the mono and di-substituted derivatives.

## 1.5 Hybrid Phosphorus, Nitrogen and Sulfur Heterocycles.

### 1.5.1 Six-Membered PNS Rings [two- or three- coordinate S(IV)].

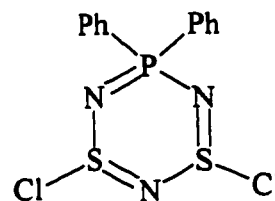
Rings containing both SN and PN units are well known. These heterocycles are usually found with phosphorus in the +5 oxidation state, although some P(III) rings have been isolated in complexes with transition metals.<sup>16,17</sup> The six-membered ring  $\text{R}_2\text{PS}_2\text{N}_3$  (**6a**) ( $\text{R} = \text{Me}_3\text{SiNH}$ ) was the first known hybrid heterocycle of this type. It was isolated from the reaction of  $\text{S}_4\text{N}_4$  with  $(\text{Me}_3\text{Si})_2\text{NP}(\text{NSiMe}_3)_2$ .<sup>18</sup> The synthesis of **6b** and **6c** involves the reaction of  $\text{R}_2\text{PPR}_2$ <sup>19,20</sup> or  $\text{Ph}_2\text{PH}$ <sup>21</sup> with  $\text{S}_4\text{N}_4$ . More recently, these rings have been made from the reaction of  $\text{R}_2\text{P}[\text{N}(\text{SiMe}_3)_2](\text{NSiMe}_3)$  ( $\text{R} = \text{Ph}, \text{Me}$ ) with  $(\text{NSCl})_3$  (**6b** and **6c**) in *ca.* 88% yields.<sup>22</sup> These six-membered rings are characteristically purple in color and both **6a** and **6b** have been characterized crystallographically.<sup>19,20</sup> The intense purple color of  $\text{R}_2\text{PS}_2\text{N}_3$  rings has been attributed to a  $\text{HOMO}(\pi^*) \rightarrow \text{LUMO}(\pi^*)$  transition in the  $8\pi$ -electron system. From the X-ray structure analysis of **6b** it was found

that the  $S_2N_3$  portion of the ring is planar (within 0.05 Å) with the P atom 0.28 Å out of this plane. Adducts of **6** have been made by 1,3-cycloaddition of norbornadiene allowing the isolation of the less stable rings (R = F, PhO, Me).<sup>20</sup> The chlorinated derivative **7** is obtained from the oxidative addition of  $Cl_2$ , in the form of  $SO_2Cl_2$  or  $PhICl_2$ , to **6b**.<sup>23</sup>



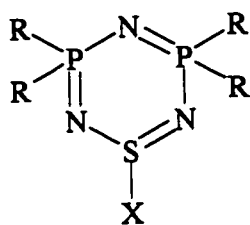
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**6a**, R =  $Me_3SiNH$   
**6b**, R = Ph  
**6c**, R = Me



7

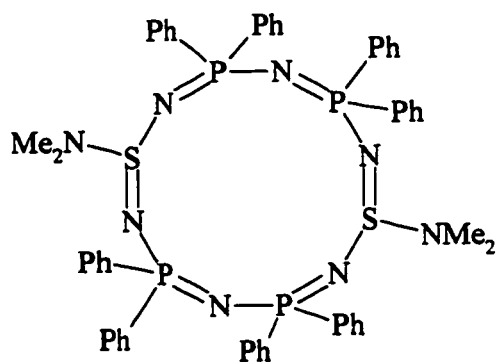
When R = Ph the six-membered ring **8a**, containing two  $R_2P$  moieties, has been synthesized in a number of ways. One approach is to react  $Ph_2PCl$  with  $S_4N_4$  in a ratio of 3:1.<sup>24</sup> The fully chlorinated ring **8a** can be synthesized from  $PCl_5$ <sup>25</sup> or, preferably,  $[Cl_3P=N-PCl_3]^+[Cl]^-$ <sup>26</sup> and  $Me_3SiN=S=NSiMe_3$ . The long S-Cl bond distance (2.357 Å) of **8b**, determined by crystallographic analysis, suggests it has some ionic character.<sup>27</sup> The trithiazyl derivative  $S_3N_3Cl_3$  ( $d(S-Cl) = 2.084$  Å and 2.150 Å)<sup>28</sup> is thought to have covalent S-Cl bonds while the S-Cl interaction of  $S_4N_3Cl$  [ $d(S-Cl) = 2.811$  Å]<sup>29</sup> is predominantly ionic.

**8**

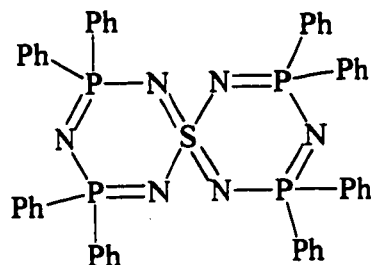
- 8a**, R = X = Cl  
**8b**, R = Ph, X = Cl  
**8c**, R = Ph, X = Br  
**8d**, R = Ph, X = I  
**8e**, R = X = Ph  
**8f**, R = Ph, X = NMe<sub>2</sub>  
**8g**, R = Ph, X = NEt<sub>2</sub>  
**8h**, R = Ph, X = N(-CH<sub>2</sub>)<sub>5</sub>

The reactions of this ring occur at the S-Cl bond. The formation of the monocation results from the treatment of **8** with SbCl<sub>5</sub>.<sup>30</sup> Halogen exchange reactions of **8b** with X<sub>2</sub> (X=Br, I), produce **8c** and **8d**, by the formation of [(Ph<sub>2</sub>PN)<sub>2</sub>SN<sup>+</sup>][X<sub>3</sub><sup>-</sup>] followed by thermal decomposition of the trihalide salt.<sup>30</sup> Treatment of **8b** with diphenylmercury gives **8e** in good yields. The amino substituted derivatives **8f-h** are obtained by reaction of **8b** with the appropriate secondary amine (**8g** and **8h**) or by treating **8b** with Me<sub>3</sub>SiNMe<sub>2</sub> (**8f**).<sup>31</sup>

The ring **8f** undergoes a spontaneous ring expansion to give the twelve-membered heterocycle **9** in CH<sub>3</sub>CN at room temperature. Heating **9** at 150-180°C gives the spiro compound **10**.<sup>31</sup> The ring opening dimerization of **8f** is thought to be promoted by the electron-releasing -NMe<sub>2</sub> groups.



9



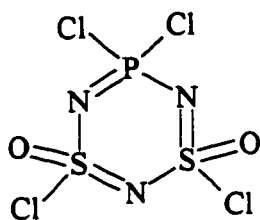
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### 1.5.2 Six-Membered Mixed Phosphazene-Sulfanuric Rings (four-coordinate S(VI))

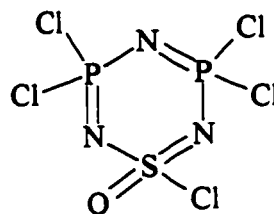
The mixed phosphazene-sulfanuric six-membered rings **11** and **12** are known.

They can be obtained by treating  $[\text{Cl}_3\text{P}=\text{N}=\text{PCl}_3][\text{PCl}_6]$  with  $\text{H}_2\text{NSO}_3\text{H}$ <sup>32</sup> or  $\text{SO}_2(\text{NH}_2)_2$ .<sup>33</sup>

The reaction with  $\text{H}_2\text{NSO}_3\text{H}$  gives a 1:1 mixture of **11** and **12**. The structures of these heterocycles have been determined by X-ray crystallography.<sup>34,35</sup> It should be noted that the stereochemistry of **11** at the sulfur (VI) centers leads to cis and trans isomers.



11



12

The regiochemistry of these rings is of considerable interest because the reactivity at sulfur and phosphorus differs. Aminolysis reactions of **11** show that preferential

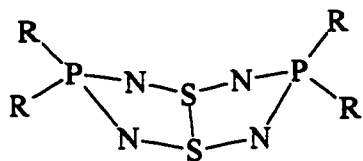


substitution occurs at the phosphorus site but, as the size of the amino group or the polarity of the solvent increases this selectivity at sulfur is decreased and substitution at sulfur is observed.<sup>36,37</sup> It is believed that nucleophilic substitution reactions at phosphorus go through an  $S_N2$  pathway while those at sulfur occur via an  $S_N1$  process.<sup>33</sup> The steric bulk of the reactants along with the polarity of the solvent can determine which site will be attacked and this selectivity can lead to non-geminal substitution.<sup>38</sup> The steric effect observed in the aminolysis of **11** is more dominant than that of **12**. This property can lead to many different kinds of substituted phosphazene-sulfanuric rings.

Recently the reactivity of the heterocycle  $(Cl_2PN)_2NS(O)Cl$ , with sodium alkoxides was investigated.<sup>39</sup> The selectivity of the substitution was preferential to P, but substitution at S could be achieved by using stronger nucleophiles like  $NaOCH_2CF_3$ . The reaction of this ring with aryloxides usually leads to substitution only at the P-Cl bond.

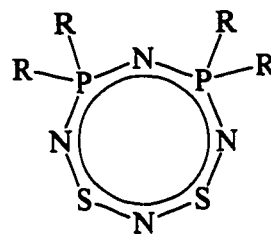
### 1.5.3 Eight-membered PNS rings [two- or three- coordinate S(IV)].

The eight-membered PN/SN systems have the composition  $P_2N_4S_2$ . Two possible isomers exist for this formula. The 1,5 isomer **13** has a folded bicyclic structure with two five-membered rings sharing a common S-S transannular bond [ $d(S-S) \sim 2.5 \text{ \AA}$ ].<sup>40</sup> The 1,3 isomer **14** has a structure that resembles that of the six membered ring  $R_2PN_3S_2$  (see Section 1.5.1). It consists of a planar  $S_2N_3$  unit, while the phosphorus atoms lie on either side of this plane.<sup>21</sup>



13

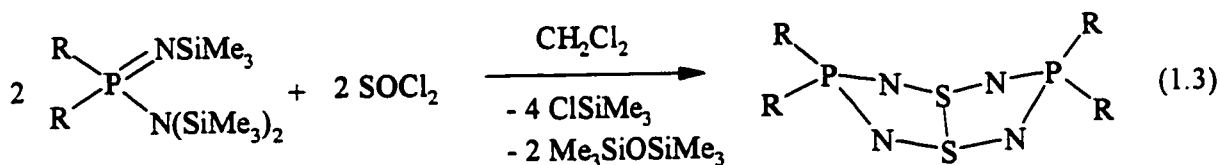
13a, R = Me  
13b, R = Ph  
13c, R = Et



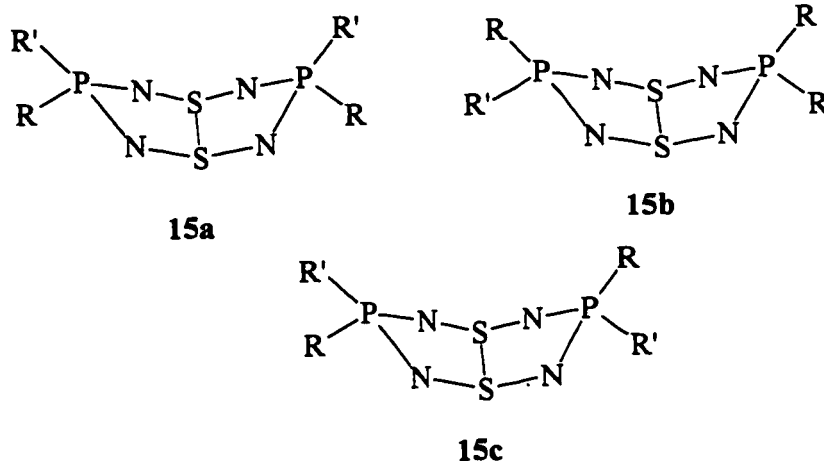
14

14a, R = Me  
14b, R = Ph

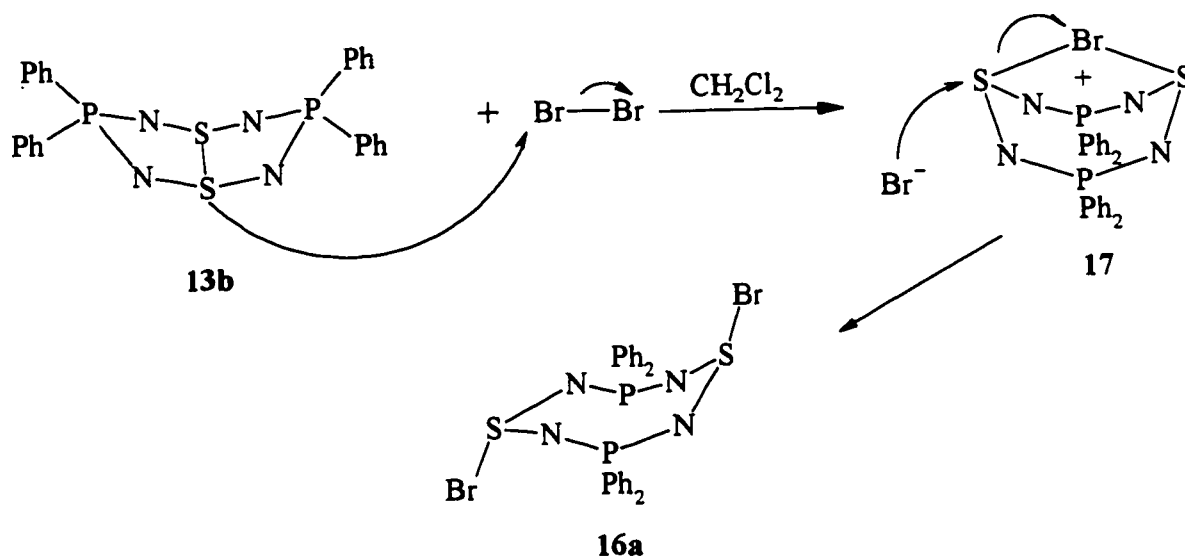
The discovery of 1,5-Me<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> (**14a**) was a result of studies of the decomposition of the six-membered ring Me<sub>2</sub>PN<sub>3</sub>SN<sub>2</sub> (**6c**).<sup>40,41</sup> The reaction of S<sub>4</sub>N<sub>4</sub> with Ph<sub>2</sub>PH or Ph<sub>2</sub>PPH<sub>2</sub> gives a mixture of **13b** and **14b** in low yields.<sup>41</sup> In order to investigate the reactions of **13** and **14**, improved syntheses were developed. The reaction of R<sub>2</sub>P[(NSiMe<sub>3</sub>)<sub>2</sub>](NSiMe<sub>3</sub>) with SOCl<sub>2</sub> or SOCl<sub>2</sub> gave better yields for **13** and allowed for the synthesis of other derivatives (R = Et, nBu) (Equation 1.3).<sup>22,41</sup>



This strategy can also be used to synthesize derivatives of **13** with different substituents on P and three isomers **15a**, **15b** and **15c** have been identified in two cases.<sup>41</sup>

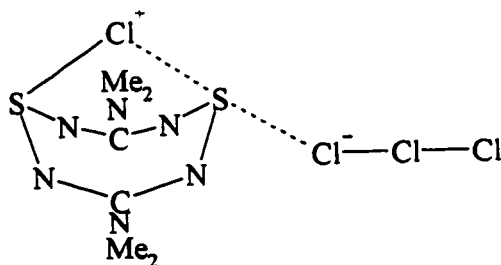


Oxidative addition of halogens to the electron-rich ring **13** occurs across the S-S transannular bond.<sup>42</sup> The addition of  $X_2$  results in the formation of 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{X}_2$  (**16**). Characterization by X-ray crystallography shows the bromine atoms adopt a trans configuration with respect to the ring. It has been suggested that initial attack occurs by a bromonium ion (Figure 1.4) across the S-S  $\sigma$  (MO) to form the bridged intermediate **17**. Subsequent attack of **17** by a bromide ion will then occur from the other side of the ring giving a trans orientation of the bromine atoms.



**Figure 1.4.** Proposed mechanism of oxidative addition of halogens across the S-S bond.

A similar mechanism has been proposed for the chlorination of S<sub>4</sub>N<sub>4</sub> to 1,5-Cl<sub>2</sub>S<sub>4</sub>N<sub>4</sub>.<sup>43</sup> The endo-exo geometry of S<sub>4</sub>N<sub>4</sub>Cl<sub>2</sub> arises from electrophilic attack of Cl<sup>+</sup> on the S-S bonding orbital of S<sub>4</sub>N<sub>4</sub>. Evidence for this mechanism was obtained through mechanistic studies of the addition of Cl<sub>2</sub> across the S-S transannular bond of 1,5-(Me<sub>2</sub>N)<sub>2</sub>C<sub>2</sub>N<sub>4</sub>S<sub>2</sub> which produces the ionic compound [1,5-(Me<sub>2</sub>N)<sub>2</sub>C<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sup>+</sup>][Cl<sub>3</sub><sup>-</sup>] (18).<sup>44</sup> A structural resemblance between this product and the proposed intermediate 17 is evident.



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Some other S,S disubstituted rings have been made recently. The reaction of  $\text{Ph}_2\text{P}[\text{N}(\text{SiMe}_3)_2](\text{NSiMe}_3)$  with  $\text{PhSCl}$  in  $\text{CH}_2\text{Cl}_2$  at  $0^\circ\text{C}$  gives  $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{Ph}_2$  in *ca.* 60% yields.<sup>45</sup> The formation of the ring is presumed to occur by the decomposition of  $\text{R}_2\text{PN}_2(\text{SPh})_3$  with the loss of  $\text{PhSSPh}$ . It was later found that in the absence of solvent this yield is increased to 80%.<sup>46</sup> The  $\text{P}_2\text{N}_4\text{S}_2$  ring in  $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{Ph}_2$  adopts a chair conformation, as shown by X-ray crystallographic analysis, with the phenyl groups attached to sulfur adopting a trans orientation similar to that of  $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{Br}_2$ .<sup>42</sup> Each of the sulfur atoms is  $0.938(5)$  Å out of and on opposite sides of the  $\text{P}_2\text{N}_4$  least squares plane. The first synthesis of  $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{Me}_2$  used  $\text{Me}_2\text{S}(\text{NBr})_2$ , an explosive reagent, and  $(\text{Ph}_2\text{PN})_2\text{SMe}_2$ .<sup>47</sup> Improved syntheses of these heterocycles are significant because the development of safer routes allows for further study of their reactivity.

Recently other synthetic approaches to the S,S diorgano derivatives have been developed. Treatment of **13b** with  $\text{Li}[\text{BEt}_3\text{H}]$  gives the dianion  $[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2]^{2-}$  as its dilithium derivative. The reaction of this reagent with 2 equivalents of  $\text{CH}_3\text{I}$  produce  $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{Me}_2$  in excellent yields.<sup>48</sup> An alternative synthetic approach allows for

unsymmetrical S,S substitution. The reaction of RLi with **13b** gives the organolithium adduct  $[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{R}^-]\text{Li}^+$  (**19**).<sup>49</sup> The monoanion is obtained as a dimeric THF adduct (Figure 1.5) and the  $\text{P}_2\text{N}_4\text{S}_2$  ring is in a boat conformation. Subsequent treatment of **19** with R'I produces the boat conformer of 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{RR}'$  (**20**), as the kinetic product. Conversion to the chair conformer (**21**) occurs upon heating in boiling  $\text{CH}_2\text{Cl}_2$ . This transformation is easily monitored by  $^{31}\text{P}$  NMR; the boat conformer **20a** has a singlet at  $\delta = +27.0$  ppm and the chair conformer **21a** at  $\delta = +14.7$  ppm. Treatment of the monoanion **19** with  $\text{X}_2$  (X= Cl, Br) gives the unsymmetrically substituted rings 1,5- $\text{Ph}_4\text{P}_2\text{N}_4(\text{SR})(\text{SX})$  **22**.<sup>50</sup>

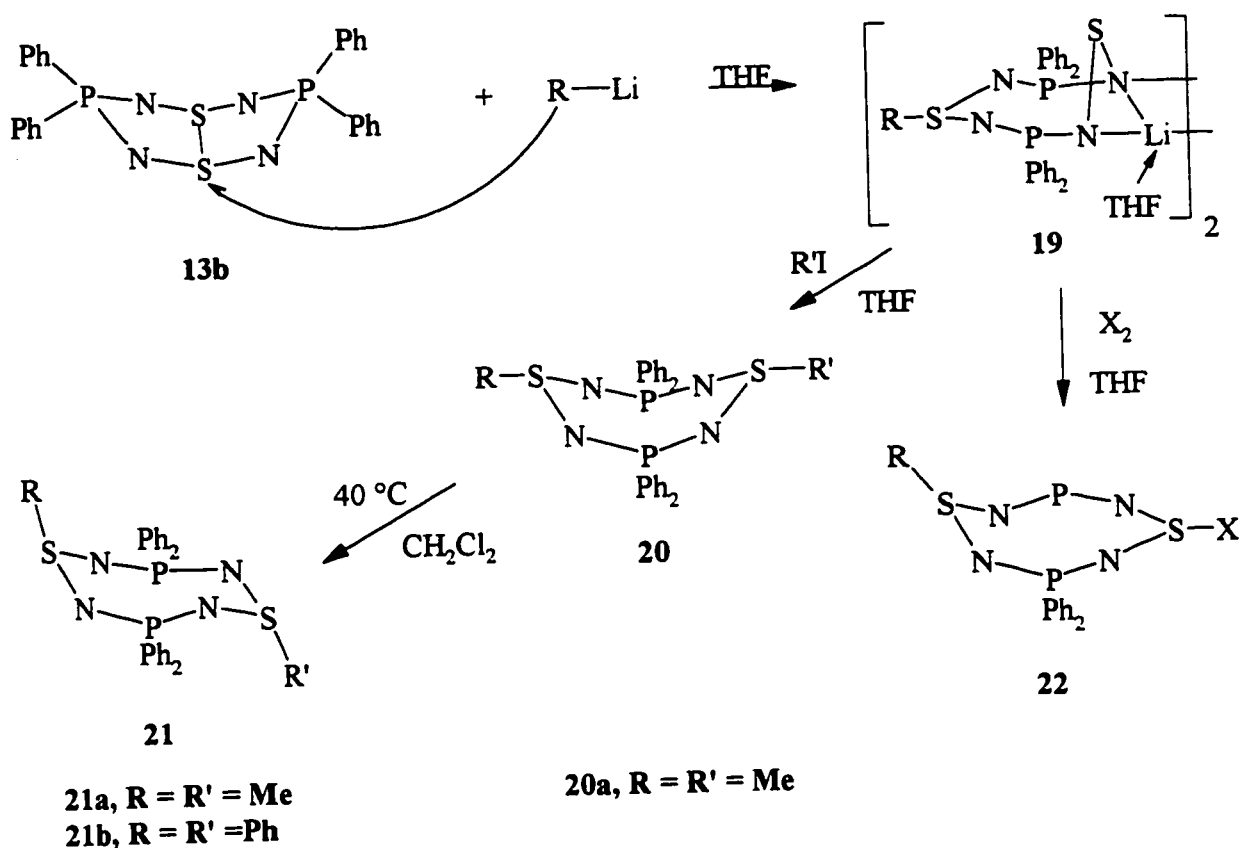
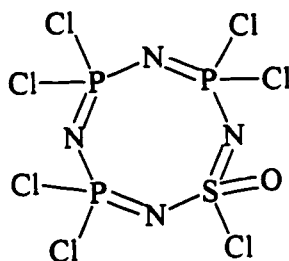


Figure 1.5. Synthesis of the boat and chair conformers of  $\text{Ph}_4\text{P}_2\text{N}_4(\text{SR})(\text{SR}')$ .

#### 1.5.4. Larger Mixed Phosphazene-Sulfanuric Rings.

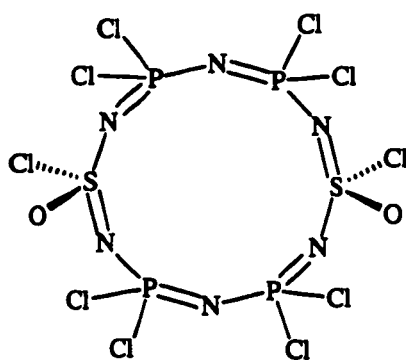
Only one eight-membered phosphazene-sulfanuric ring  $(\text{NPCl}_2)_3\text{NS(O)Cl}$  (**23**) has been prepared.<sup>51</sup> It was obtained from the reaction  $\text{SO}_2(\text{NH}_2)_2$  with  $[\text{Cl}_3\text{P=N-PCl}_2=\text{N-PCl}_3]^+\text{PCl}_6^-$  at room temperature over a few days and was crystallized from pentane. No further information has been reported.



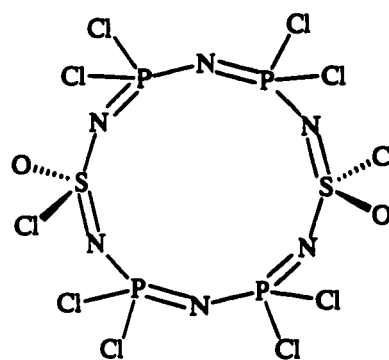
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In 1995 Manners and coworkers reported the synthesis of twelve and twenty-four membered cyclic phosphazene-sulfanuric rings, which were isolated from the thermolysis of  $(\text{Cl}_2\text{PN})_2\text{SOCl}$  (**12**) by recrystallization and sublimation.<sup>52</sup> Two isomers of the twelve membered ring, *cis* (**24a**) and *trans* (**24b**), were found in the crystal structure. X-ray analysis on the twenty-four membered ring was also performed. It is the largest inorganic heterocycle to be characterized by X-ray crystallography. The crystal contained only one isomer, (*cis, trans, cis, trans*), but rotational disorder of the molecule is observed. These ring systems are important intermediates in the ROP of **12** to give phosphazene-sulfanuric polymers (see Section 1.6)





24a



24b

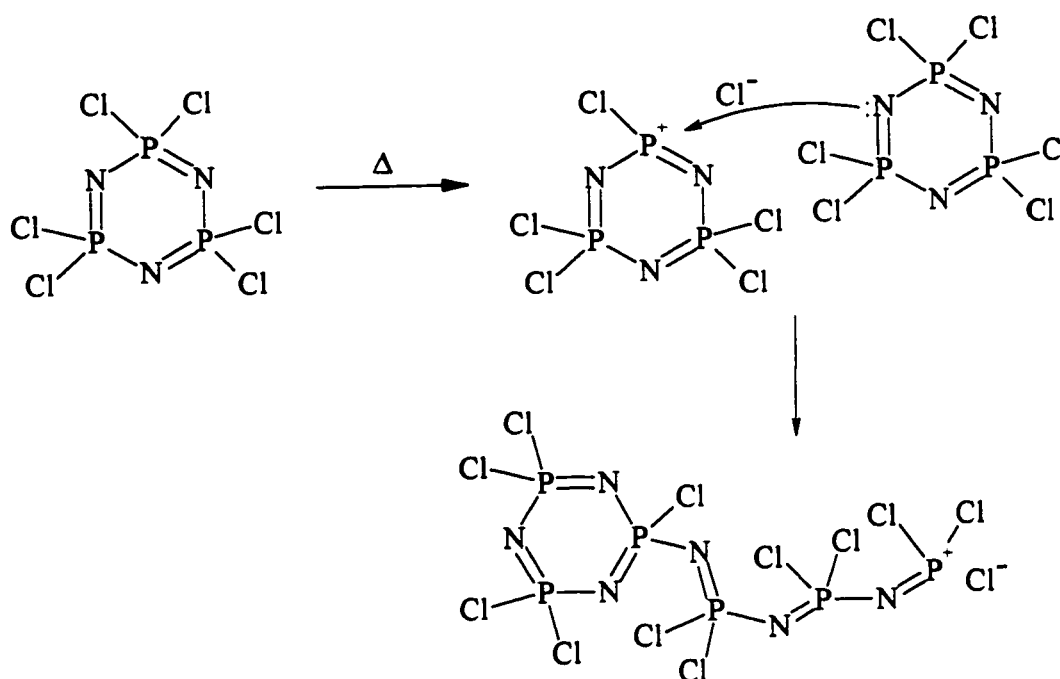
## 1.6 Inorganic Polymers.

### 1.6.1 Polyphosphazenes.

A variety of methods is utilized to synthesize inorganic polymers.

Polyphosphazenes can be made via condensation polymerization or thermal ROP.

Condensation polymerization occurs when two reactive sites on the monomeric precursor condense to form a polymer, e.g.  $R_2P(OR')=N(SiMe_3)$  eliminates  $R'OSiMe_3$  giving  $-[P(R_2)=N]_n-$ .<sup>3</sup> Ring opening polymerization of  $(PCl_2N)_3$  is proposed to occur by an ionic mechanism in which a cationic P center undergoes nucleophilic attack by a N on another ring (Figure 1.6).<sup>3</sup>



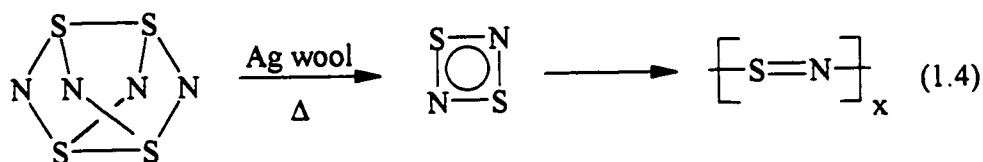
**Figure 1.6.** Mechanism of ring opening polymerization of chlorophosphazenes.<sup>3</sup>

The polychlorophosphazenes can go under nucleophilic substitution to replace the substituents on phosphorus, with, for example alkoxy or amino groups *cf.* cyclohalophosphazenes (Figure 1.1).<sup>1-3</sup> This reactivity has allowed chemists to synthesize hundreds of different polyphosphazenes with their own distinct properties. The diverse properties of the polyphosphazenes are comparable to those of organic polymers. Over 300 different polyphosphazenes have been synthesized and characterized to date.<sup>3</sup> The different side groups, R, allow for the preparation of polymers which have different properties ranging from bioinert to bioactive materials, electrical conductors to insulators, elastomers to glasses, and water-soluble to hydrophobic polymers.<sup>3</sup> Applications include

solvent-resistant materials, elastomers, pharmaceuticals, hydrogels, textiles, and implantable devices like heart valves.

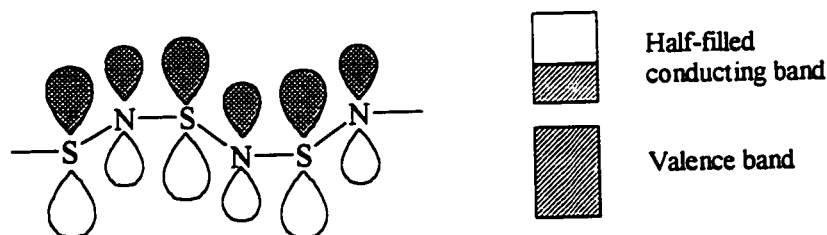
### 1.6.2 Poly(sulfur nitride).

The crystalline polymer  $(\text{SN})_x$  is prepared from  $\text{S}_4\text{N}_4$ . When  $\text{S}_4\text{N}_4$  is vaporized and passed through silver wool  $\text{S}_2\text{N}_2$  is formed and, subsequently, it undergoes solid state polymerization to  $(\text{SN})_x$  (Equation 1.4).<sup>5</sup> Interest in this polymer is due to its metallic properties.<sup>3</sup>



Each repeat unit of poly(sulfur nitride) has  $3\pi$  electrons for two atoms, creating a partially filled valence band. The p orbitals of the sulfur and nitrogen allow for the delocalization of these electrons along the chain of the polymer (Figure 1.7). The crystals are lustrous, soft and malleable, like a metal. In addition, the polymer has the conducting properties of a metal. At very low temperatures  $(\text{SN})_x$  becomes a superconductor. The addition of bromine vapor to  $(\text{SN})_x$  results in the formation of  $(\text{SNBr}_{0.40})_x$  which has better conductivity, by an order of magnitude, than  $(\text{SN})_x$ .<sup>53</sup> In an inert atmosphere the polymer

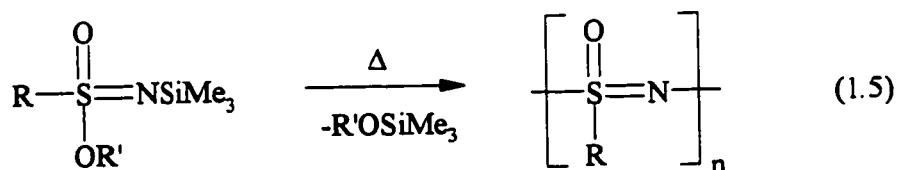
$(\text{SN})_x$  is stable up to  $140^\circ\text{C}$ . Unfortunately,  $(\text{SN})_x$  is easily oxidized and at temperatures above  $240^\circ\text{C}$  the polymer will explode. Applications of this polymer are limited due to its instability.



**Figure 1.7.** Bonding in poly(sulfur nitride).

### 1.6.3. Poly(alkyl/aryloxothiazenes).

The existence of linear polymers of the form  $[-\text{N}=\text{S}(\text{O})\text{F}-]_n$  has been speculated but detailed characterization is lacking.<sup>15,54</sup> In 1993 Roy and coworkers at Dow Chemical Company reported the synthesis of high molecular weight polymers with the formula  $[-\text{N}=\text{S}(\text{O})\text{R}-]_n$  using the condensation polymerization of N-silylsulfonimidates (Equation 1.5).<sup>55</sup> Preliminary evidence indicates that the  $\text{S}=\text{N}$  backbone ( $\text{R} = \text{Me}$ ,  $T_g = 55\text{-}65^\circ\text{C}$ ) is less flexible than that of the polyphosphazenes ( $\text{R} = \text{Me}$ ,  $T_g = -46^\circ\text{C}$ ).<sup>55</sup> Since 1993, no papers on these polymer systems have been published.

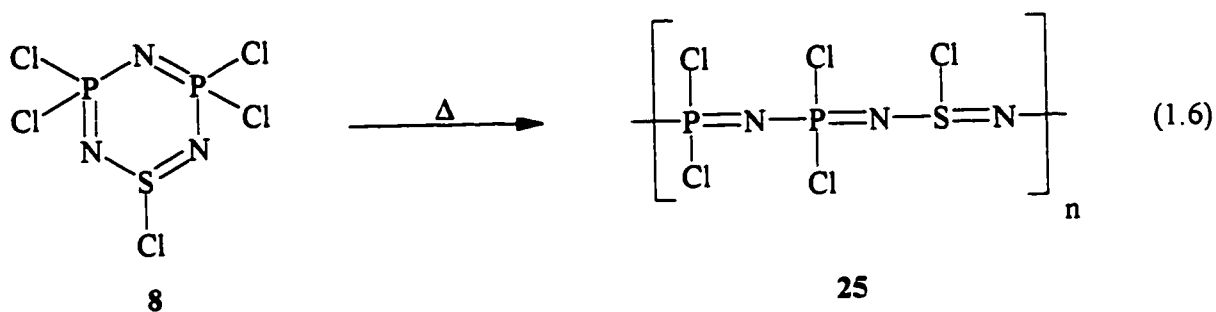


## 1.7 Hybrid Inorganic Polymers.

### 1.7.1 Poly(thiophosphazenes).

Poly(thiophosphazenes) were first isolated by Allcock and coworkers in 1990.<sup>56</sup>

The polymer is made by thermal ROP of **8** to give the chlorinated, moisture-sensitive polymer (**25**). Replacement of the halogen substituents with small aryloxy groups leads to a more stable polymer, but the polymer is still moisture sensitive. A moisture stable polymer is obtained when very bulky aryloxy groups, such as *o*-phenylphenoxide, are used, but only partial substitution occurs.<sup>57</sup>

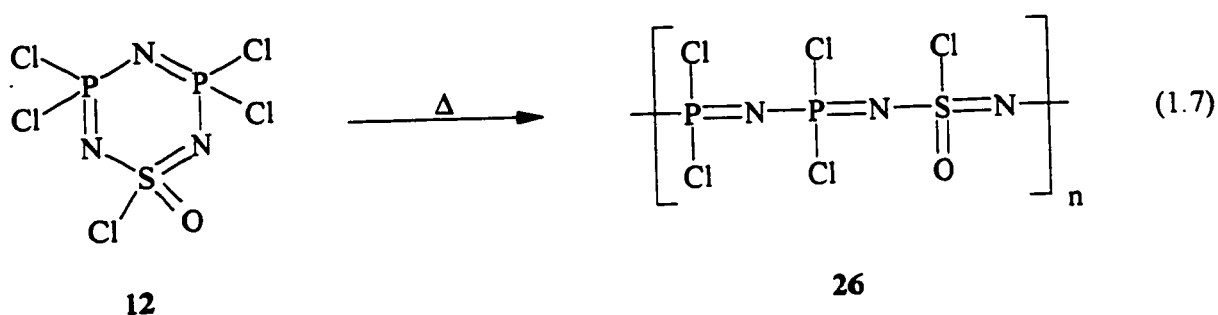


Further investigations of the nucleophilic reactions of poly(thiophosphazenes) with alkoxides and amines were performed. The weak polymer backbone was found to

breakdown and no stable polymers were obtained limiting the applications of these polymers.<sup>57</sup> However it was found that the S-Cl bond is more reactive towards nucleophiles than the P-Cl bonds. Although this property opens up the potential for a large number of different substituted poly(thiophosphazenes) with one type of substituent on S and a different substituent on P the polymer backbone is susceptible to hydrolysis thus limiting the development of this polymer system.<sup>58</sup>

### 1.7.2 Poly(thionylphosphazenes).

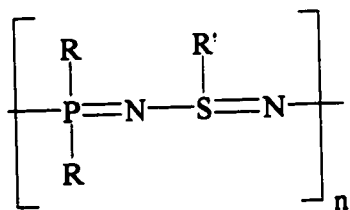
Poly(thionylphosphazenes) (**26**) represent another class of P-N-S polymer, which contain four-coordinate S(VI) atoms rather than three-coordinate S(IV). The polymer **26** is prepared by ROP of  $(Cl_2PN)_2(S(O)X)$  ( $X = Cl^{59}, F^{60}$ ) to give halogenated polymers of high molecular weight (Equation 1.7). Hydrolytically stable poly(thionylphosphazenes) are prepared by reacting the halogenated polymer with aryloxy nucleophiles, however only the chlorine atoms on phosphorus are replaced leaving the S-Cl bonds intact. Recently it was shown that substitution of Cl on S with an aryloxy can be achieved for the six-membered ring  $[(ArO)_2PN]_2(SOX)$  when treated with NaOPh and stirred vigorously for one week.<sup>39</sup> Full substitution was also achieved by using stronger nucleophiles such as  $NaOCH_2CF_3$  or  $NaO^nBu$ . Given these results the full substitution of these polymers should be possible.



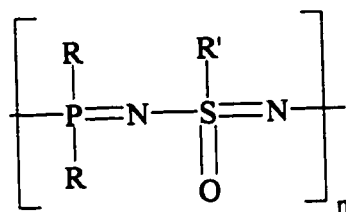
Reactions of the halogenated poly(thionylphosphazenes) with primary amines yield poly[(amino)thionylphosphazenes] which are hydrolytically stable. Substitution of the Cl atoms on P and S is achieved.<sup>61</sup> The stereochemistry of the substituted polymer was found to be atactic (irregular stereochemistry) through the use of <sup>31</sup>P NMR. Further studies into the properties of these novel polymers are still under investigation.

### 1.8 Thesis Objectives

The hybrid inorganic polymers containing both P-N and S-N components prepared to date have the characteristic repeating unit -P=N-P=N-S=N-. The synthesis of these polymers involves thermal ROP of the corresponding six membered ring. The synthesis of a thiazylphosphazene polymer such as 27 has not been reported. It is predicted that the eight-membered ring 1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> could be a precursor to this type of polymer as these rings already contain the required (P=N-S=N) repeating units.



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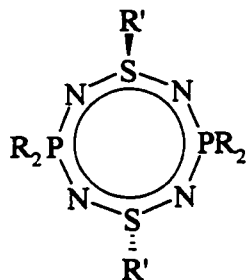


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The eight-membered ring 1,5- $\text{R}_4\text{P}_2\text{N}_4\text{S}_2$  does not have considerable ring strain but the isolation of the heterocycles **24a** and **24b** indicate that larger rings are intermediates in the formation of high molecular weight polymers. This is evidence that ring strain is not essential in order for ROP to occur.

The substitution of a dimethylamino group at the S-Cl bond of **8** promotes spontaneous ring-opening to give the twelve membered ring **9**.<sup>31</sup> The synthesis the of new [S,S] disubstituted derivatives **29c** and **29d** could provide rings that are susceptible to ring opening to give larger heterocycles or, in view of the bifunctional nature of **29c** and **29d**, novel PNS(IV)N polymers. In Chapter 2 the reaction of **29a** and **29b** with  $\text{Me}_2\text{SiMe}_3$  will be discussed along with the tendency of the electron-donating group ( $-\text{NMe}_2$ ) to promote the formation of larger heterocycles. Also, the reaction of **29a** with  $\text{AlCl}_3$  will be described.





- 29a**, R = Et, R' = Cl  
**29b**, R = Ph, R' = Cl  
**29c**, R = Et, R' = NMe<sub>2</sub>  
**29d**, R = Ph, R' = NMe<sub>2</sub>

**29**

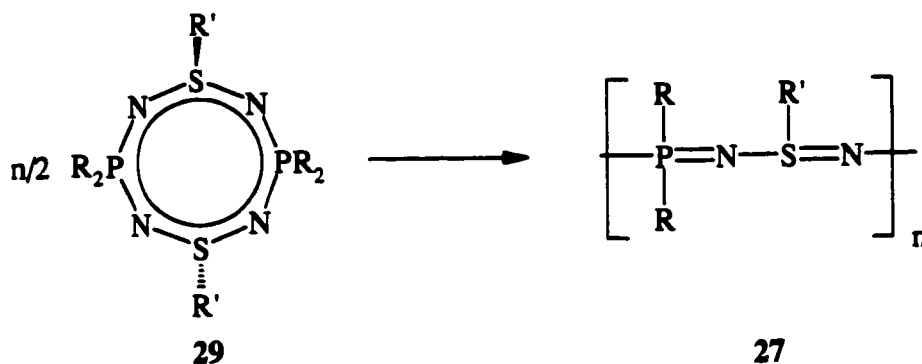
The investigations into the hybrid polymers **25** and **26** have shown that the four-coordinate S(VI) sites in **26** stabilize the [-P=N-P=N-S=N-] backbone.<sup>58</sup> It is predicted that four-coordinate S(VI) polymers of the type **28** will be more stable than the three-coordinate S(IV) polymers of the type **27**. The synthesis of eight-membered P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> rings containing four-coordinate S(VI) centers could provide precursors to S(VI) containing polymers **28**. The synthesis and structures of three new eight-membered phosphazene-sulfanuric heterocycles are described in Chapter 3.

## CHAPTER 2

Synthesis and Reactions of 1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub>

## 2.1 Introduction.

Heterocycles like 1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>R<sub>2</sub>' (**29**) have two PNSN repeat units with substituents on the P and S atoms. To date the only isolated rings of this type are those where R and R' are alkyl or aryl groups. The potential for **29** to be a precursor to a PNSN polymer creates a need to synthesize new S,S disubstituted versions of **29** which could lead to different types of PNSN polymers (**27**) whose properties would vary depending upon the substituents on S and P.



The eight-membered ring  $1,5\text{-R}_4\text{P}_2\text{N}_4\text{S}_2\text{Cl}_2$  can be used as a synthetic precursor to new S,S disubstituted derivatives  $1,5\text{-R}_4\text{P}_2\text{N}_4\text{S}_2\text{R}_2'$ . The S-Cl bond provides a reactive site which can be attacked by various nucleophiles, for instance  $\text{R}_2\text{NSiMe}_3$  or MOR (M = Na, K). The S-Cl bonds in  $\text{S}_4\text{N}_4\text{Cl}_2$  and in  $\text{Ph}_4\text{P}_2\text{N}_3\text{SCL}$  (**8a**) undergo nucleophilic substitution with  $\text{Me}_2\text{NSiMe}_3$  to produce the corresponding dimethylamino derivatives  $\text{S}_4\text{N}_4(\text{NMe}_2)_2$ <sup>9</sup> and  $\text{Ph}_4\text{P}_2\text{N}_3\text{SNMe}_2$  (**8f**), respectively.<sup>31</sup> In the case of **8f** the dimethylamino group on S promotes ring opening to give the twelve-membered ring  $\text{Ph}_8\text{P}_4\text{N}_6(\text{SNMe}_2)_2$  (**9**), so it follows that the synthesis of the S,S dimethylamino derivatives  $1,5\text{-R}_4\text{P}_2\text{N}_4(\text{SNMe}_2)_2$  might lead to larger rings which could potentially give polymers.<sup>24</sup>

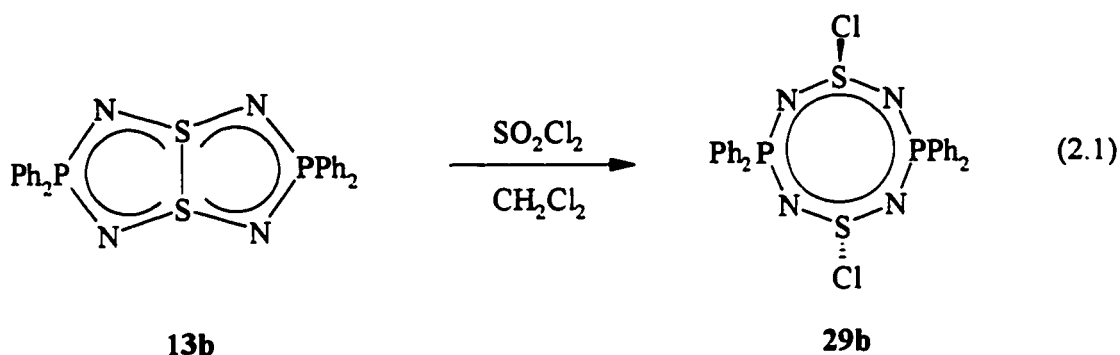
The synthesis of other S-substituted derivatives using the reactive S-Cl bond of  $\text{Ph}_4\text{P}_2\text{N}_3\text{SCL}$  (**8a**) has been reported (see Section 1.4.1). The heterocycle  $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{Cl}_2$  has been shown to react with alkyllithium reagents to give  $1,5\text{-Ph}_4\text{P}_2\text{N}_4(\text{SR})(\text{SCL})$  and  $1,5\text{-Ph}_4\text{P}_2\text{N}_4(\text{SR})_2$ . However, the dichlorides  $1,5\text{-R}_4\text{P}_2\text{N}_4\text{S}_2\text{Cl}_2$  (R = Et, Ph) have not been investigated for their reactivity towards other nucleophiles like  $\text{R}_2\text{NSiMe}_3$  and alkoxides.<sup>50</sup>

This chapter contains the description of the synthesis and X-ray structures of new eight-membered PNS(IV) heterocycles (**29**). The synthetic strategy adopted uses the reactive S-Cl bonds of  $1,5\text{-R}_4\text{P}_2\text{N}_4\text{S}_2\text{Cl}_2$  to give new S-substituted derivatives. The S,S-dimethylamino substituted heterocycles are prepared in order to determine if the electron donating group  $\text{-NMe}_2$  bonded to S can promote ring opening like that observed for

$\text{Ph}_4\text{P}_2\text{N}_3\text{S}(\text{NMe}_2)$  (**8f**). Also the synthesis of the the dications  $1,5\text{-R}_4\text{P}_2\text{N}_4\text{S}_2^{2+}$  via the reaction of  $1,5\text{-R}_4\text{P}_2\text{N}_4\text{S}_2\text{Cl}_2$  with  $\text{AlCl}_3$  will be described.

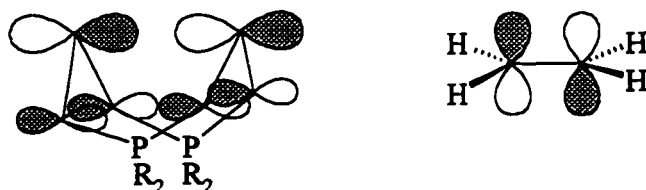
## 2.2 Synthesis of $1,5\text{-R}_4\text{P}_2\text{N}_4\text{S}_2\text{Cl}_2$ ( $\text{R} = \text{Et}$ , **29a**; $\text{R} = \text{Ph}$ , **29b**).

The synthesis of  $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{Cl}_2$  involves the oxidative addition of  $\text{Cl}_2$  (as  $\text{SO}_2\text{Cl}_2$ ) across the S-S transannular bond of the eight-membered ring  $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2$  (**13b**) (Equation 2.1).<sup>42</sup>



It has been shown that the LUMO of  $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2$  is the antibonding  $\sigma^*$  (S-S) orbital, which has similar symmetry properties to the  $\pi^*$  orbital (LUMO) of ethylene (Figure 2.1).<sup>62</sup> The oxidative addition of halogens across the S-S bond is believed to involve a bridged halogen cation like those observed in the oxidative addition of halogens to ethylene.<sup>43</sup> This is supported by the structure of  $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{Br}_2$  in which the bromine atoms adopt a trans orientation. Trans products are also isolated from the oxidative addition of halogens to ethylene.<sup>42</sup> The isolation and X-ray structure of  $[1,5\text{-(Me}_2\text{NC)}_2\text{N}_4\text{S}_2\text{Cl}]^+[\text{Cl}_3]^-$  provides further evidence for a bridging chloronium ion in the

oxidative addition of  $\text{Cl}_2$  to 1,5- $(\text{Me}_2\text{NC})_2\text{N}_4\text{S}_2$ .<sup>44</sup> The structure of the cation  $[\text{Me}_2\text{NC})_2\text{N}_4\text{S}_2\text{Cl}]^+$  can be described as a pseudo-bridged chloronium cation (See Section 2.2.1 and Figure 2.3).



**Figure 2.1.** LUMO of 1,5-diphosphadithiatetrazocines and LUMO of ethylene.

The synthesis of 1,5- $\text{Et}_4\text{P}_2\text{N}_4\text{S}_2\text{Cl}_2$  (**29a**) involves similar reaction conditions to those used for the preparation of 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{Cl}_2$ .<sup>63</sup> A solution of 1,5- $\text{Et}_4\text{P}_2\text{N}_4\text{S}_2$  (**13c**) in  $\text{CH}_2\text{Cl}_2$  was stirred at room temperature while  $\text{SO}_2\text{Cl}_2$  was added. The solution turns from pale yellow to orange-red and, upon completion, a bright yellow color. The reaction is easily monitored by  $^{31}\text{P}$  NMR with the disappearance of the resonance of 1,5- $\text{Et}_4\text{P}_2\text{N}_4\text{S}_2$  (**13c**) at +136.1 ppm and the appearance of a new resonance for 1,5- $\text{Et}_4\text{P}_2\text{N}_4\text{S}_2\text{Cl}_2$  (**29a**) at +27.4 ppm. Recrystallization is not necessary as the product is very pure (as indicated by  $^{31}\text{P}$  NMR) upon removal of  $\text{CH}_2\text{Cl}_2$ . Furthermore, hydrolysis can occur during the recrystallization step. The moisture-sensitive product can however, be recrystallized from  $\text{CH}_3\text{CN}$  at  $-20^\circ\text{C}$  to give pale yellow crystals. The  $\text{CH}_2\text{Cl}_2$  used for the reaction must be

very dry or the product will hydrolyze. The hydrolysis product is very difficult to remove from **29a**.

The pale yellow crystals of **29a** are light-sensitive and decompose to an orange species. The product also exhibits thermal instability. The colorless crystals of **29a** become orange at 80 °C, red at 85 °C and continue to deepen in color until they melt at 115-116 °C.

### 2.2.1 X-ray Structure of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub>.

Crystals of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29a**) were obtained from a saturated CH<sub>3</sub>CN solution at -20°C. Crystallographic parameters are summarized in Table 2.1. Figure 2.2 shows an ORTEP diagram with the numbering of the atoms. Bond distances, bond angles and torsion angles can be found in Tables 2.2 and 2.3. There are two major features of the structure. The first is the shape of the P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> ring and the second is the difference in the two S-Cl bond lengths. The eight-membered ring can be described as a distorted boat, which is different from the chair conformation found previously for the P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> ring of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Br<sub>2</sub> (**16a**).<sup>43</sup> The two P atoms and four N atoms of **16a** are almost planar, with the S atoms ~ 0.50 Å out and on opposite sides of the P<sub>2</sub>N<sub>4</sub> plane. The structures of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29a**) and 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Br<sub>2</sub> (**16a**) are similar in that the halogen atoms are in trans (*axial, axial*) positions, but the S-Cl bond distances in 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29a**) differ by 0.18 Å whereas 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Br<sub>2</sub> (**16a**) has equal S-Br bond lengths. The values of the S-Cl distances [d(S(1)-Cl(1)) = 2.235(1) Å and d(S(2)-Cl(2)) = 2.419(1) Å] in **29a** can be compared to those of S<sub>4</sub>N<sub>4</sub>Cl<sub>2</sub> [d(S-Cl) = 2.18 Å].<sup>6</sup> However, the six-membered

ring  $\text{Ph}_4\text{P}_2\text{N}_3\text{SCl}$  contains a significantly longer S-Cl bond [ $d(\text{S-Cl}) = 2.357(2) \text{ \AA}$ ] attributed to ionic character suggesting that the S(2)-Cl(2) bond [ $d(\text{S-Cl}) = 2.419(1) \text{ \AA}$ ] of **29a** also has some ionic character.

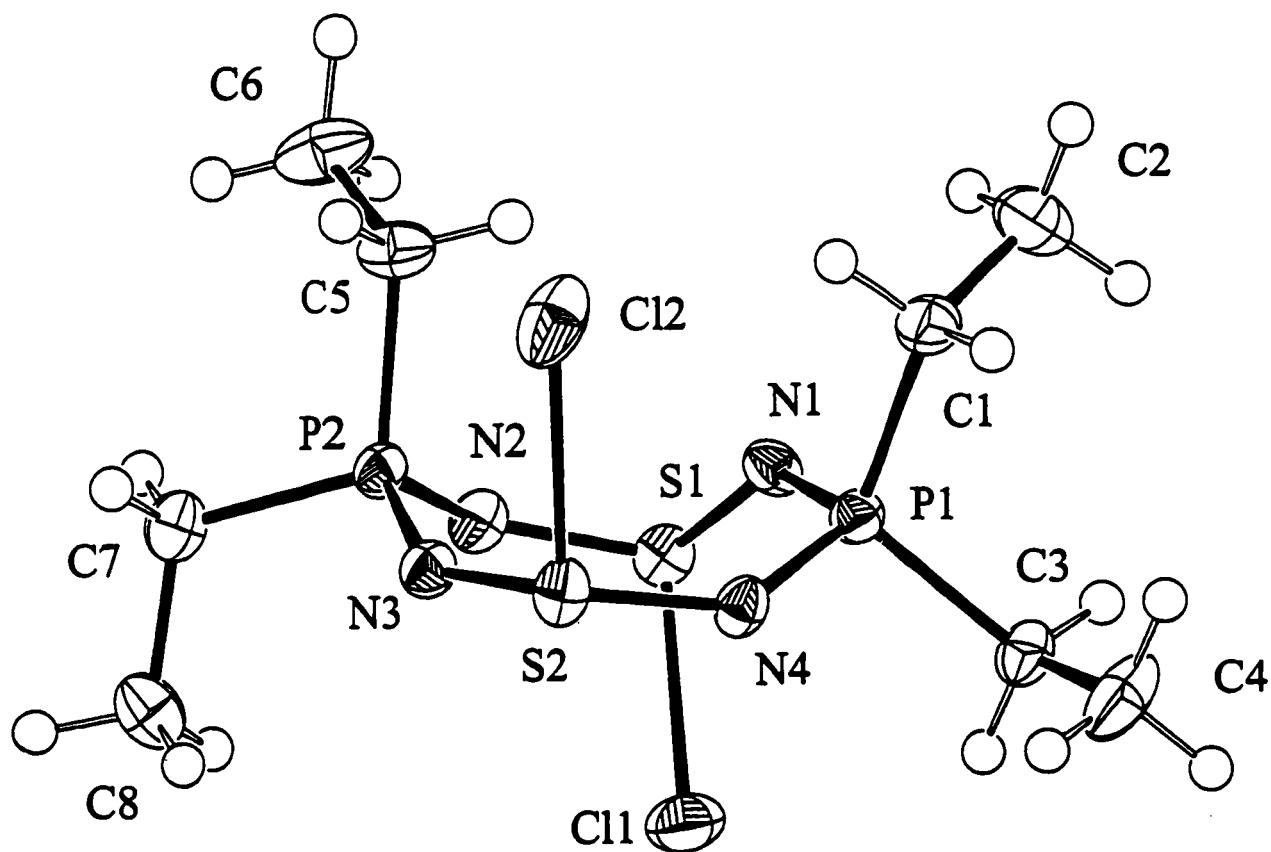


Figure 2.2. ORTEP diagram for 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29a**).

**Table 2.1.** Crystallographic Parameters for 1,5- Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29a**).

<b>29a</b>	
Empirical Formula	C <sub>8</sub> H <sub>20</sub> N <sub>4</sub> P <sub>2</sub> S <sub>2</sub> Cl <sub>2</sub>
Formula Weight	369.25
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.80 X 0.60 X 0.40 mm
Crystal System	triclinic
Lattice Parameters	$a = 8.417(5) \text{ \AA}$ $b = 13.456(6) \text{ \AA}$ $c = 8.130(4) \text{ \AA}$ $\alpha = 99.32(4)^\circ$ $\beta = 109.24(2)^\circ$ $\gamma = 96.58(4)^\circ$ $V = 815.8(9) \text{ \AA}^3$
Space Group	P $\bar{1}$ (#2)
Z value	2
D <sub>calc</sub>	1.503 g/cm <sup>3</sup>
Temperature	-103.0° C
Reflection/Parameter Ratio	14.56
R	0.030
R <sub>w</sub>	0.039



**Table 2.2** Selected Bond Lengths and Bond Angles of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29a**).

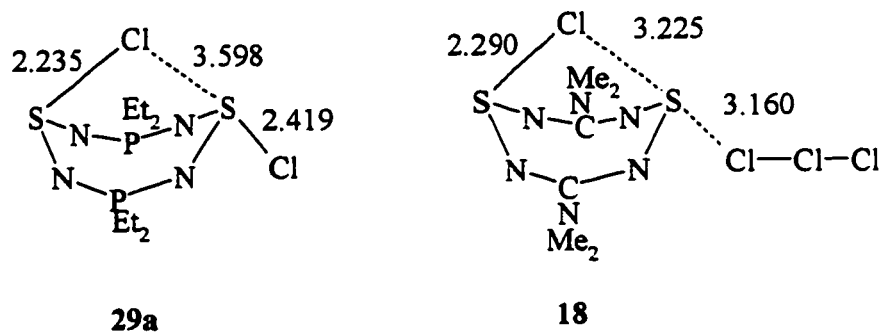
Atoms	Bond Lengths (Å)	Atoms	Bond Angles (°)
S(1)-Cl(1)	2.235(1)	N(1)-S(1)-N(2)	112.8(1)
S(2)-Cl(2)	2.419(1)	N(3)-S(2)-N(4)	119.3(1)
S(1)-N(1)	1.561(3)	S(1)-N(1)-P(1)	136.6(2)
S(1)-N(2)	1.547(2)	S(1)-N(2)-P(2)	128.3(2)
S(2)-N(3)	1.535(3)	S(2)-N(3)-P(2)	144.8(2)
S(2)-N(4)	1.535(2)	S(2)-N(4)-P(1)	134.7(2)
P(1)-N(1)	1.608(3)	N(1)-P(1)-N(4)	117.6(1)
P(1)-N(4)	1.638(2)	N(2)-P(2)-N(3)	118.0(1)
P(2)-N(2)	1.642(2)		
P(2)-N(3)	1.621(2)		

**Table 2.3.** Torsion Angles for the P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> ring of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29a**).

Atoms	Torsion Angles (°)
S(1)-N(1)-P(1)-N(4)	-49.9(3)
S(2)-N(3)-P(2)-N(2)	71.9(3)
P(1)-N(1)-S(1)-N(1)	96.6(2)
P(2)-N(2)-S(1)-N(1)	-25.6(2)
S(1)-N(2)-P(2)-N(3)	-42.5(2)
S(2)-N(4)-P(1)-N(1)	-34.5(3)
P(1)-N(4)-S(2)-N(3)	39.1(3)
P(2)-N(3)-S(2)-N(4)	-44.4(3)

The structure of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29a**) is similar to those reported for the salts [(Me<sub>2</sub>N)<sub>2</sub>C<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl][X].<sup>65</sup> Although the structure of the S,S dichloro derivative is unknown, the structure of the trichloride salt [(Me<sub>2</sub>N)<sub>2</sub>C<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl][Cl<sub>3</sub>] has been reported.<sup>44</sup> The cation (Me<sub>2</sub>N)<sub>2</sub>C<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sup>+</sup> possesses a cationic sulfur center exhibiting a weak (S<sup>+</sup>-Cl)

interaction [ $d(\text{S}^{\cdots}\text{Cl}) = 3.225 \text{ \AA}$ ] while the adjacent sulfur has an S-Cl distance of 2.290(3)  $\text{\AA}$  with the same chlorine atom (Figure 2.3). The structure of **29a** shows similar interactions which are depicted in Figure 2.3. The different S-Cl bond distances found in 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29a**) and the similarity of the structure to that of [(Me<sub>2</sub>N)<sub>2</sub>C<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl][Cl<sub>3</sub>] (**18**) suggests the structure of **29a** can be thought of as an incipient cation, Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sup>+</sup>, bonded ionically to a chloride anion. Therefore the structure of **29a** provides further support for the proposed mechanism of oxidative addition of halogens across the S-S transannular bonds of dithiatetrazocines (see Figure 1.4).



**Figure 2.3.** Diagram of the S-Cl interactions in Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29a**) and [(Me<sub>2</sub>N)<sub>2</sub>C<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl][Cl<sub>3</sub>] (**18**).<sup>63</sup>

The different S-Cl bond distances give rise to significant differences in the NSN components of the P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> ring. The mean S-N distances at S(2) are shorter (1.535(3)  $\text{\AA}$ ) than those at S(1) (1.554(3)  $\text{\AA}$ ) and the corresponding NSN bond angles are substantially different at 119.3(1) $^\circ$  and 112.8(1) $^\circ$  respectively. The SNP bond angles have values

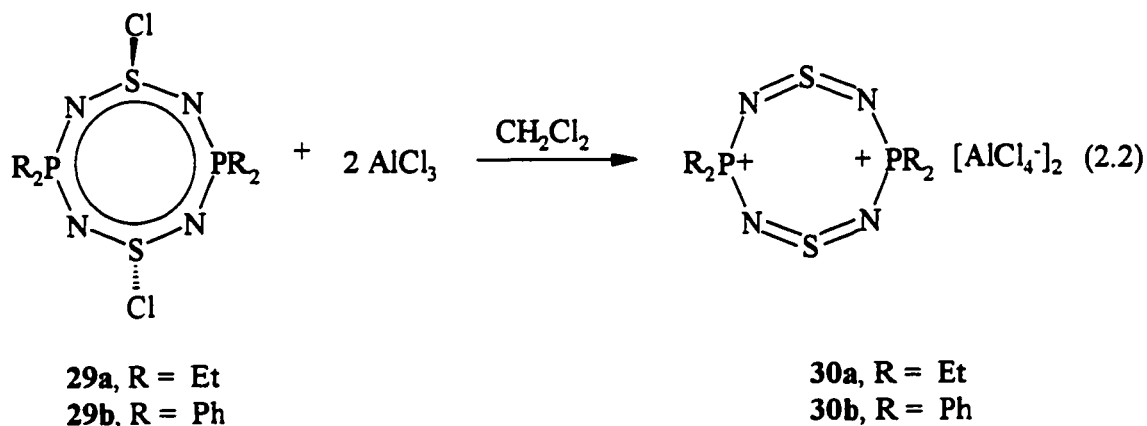
ranging from  $128.3(2)^\circ$  to  $144.8(2)^\circ$ . The mean P-N distances of of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29a**) do not vary significantly from the P-N distances of of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> (**13c**), 1.627(2) Å and 1.616(8) Å<sup>42</sup>, respectively. However, the NPN bond angle is larger in 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29a**) [  $117.8(1)^\circ$  ] due to the loss of the S-S transannular bond in 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> (**13c**) [  $\angle(\text{NPN}) 109.8(4)^\circ$  ].<sup>41</sup>

The different S-Cl bond distances result in different S-Cl stretching vibrations in the IR spectrum of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29a**). A recent correlation between  $\nu(\text{S-Cl})$  and  $d(\text{S-Cl})$  reported by Passmore et al. facilitated the assignment of two stretching frequencies.<sup>66</sup> The formula,  $\nu(\text{S-Cl}) [\text{cm}^{-1}] = 1913.90 - 696.54 d(\text{S-Cl}) [\text{Å}]$ , gave calculated stretches at 357 and 229 cm<sup>-1</sup> for S(1)-Cl(1) and S(2)-Cl(2), respectively. The experimental IR spectrum exhibited stretching frequencies at 358 and 225 cm<sup>-1</sup>, which are tentatively assigned to the short and long S-Cl bonds, respectively.

### 2.3 Synthesis of [1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>][AlCl<sub>4</sub>]<sub>2</sub> (R =Et, **30a**; R =Ph, **30b**).

The dianion Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub><sup>2-</sup> is known and has been used to prepare various coordination complexes with transition metals,<sup>67</sup> so it was of some interest to prepare the corresponding dication 1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub><sup>2+</sup>. The dications R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub><sup>2+</sup> can be obtained by the reaction of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29a**) or 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29b**) with two equivalents of AlCl<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> at 23° C (Equation 2.2).<sup>63</sup> As the reaction proceeds the products [1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>][AlCl<sub>4</sub>]<sub>2</sub> (**30a**) and [1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>][AlCl<sub>4</sub>]<sub>2</sub> (**30b**) precipitate from solution in the form of orange, moisture-sensitive crystals which can be isolated by filtration. The

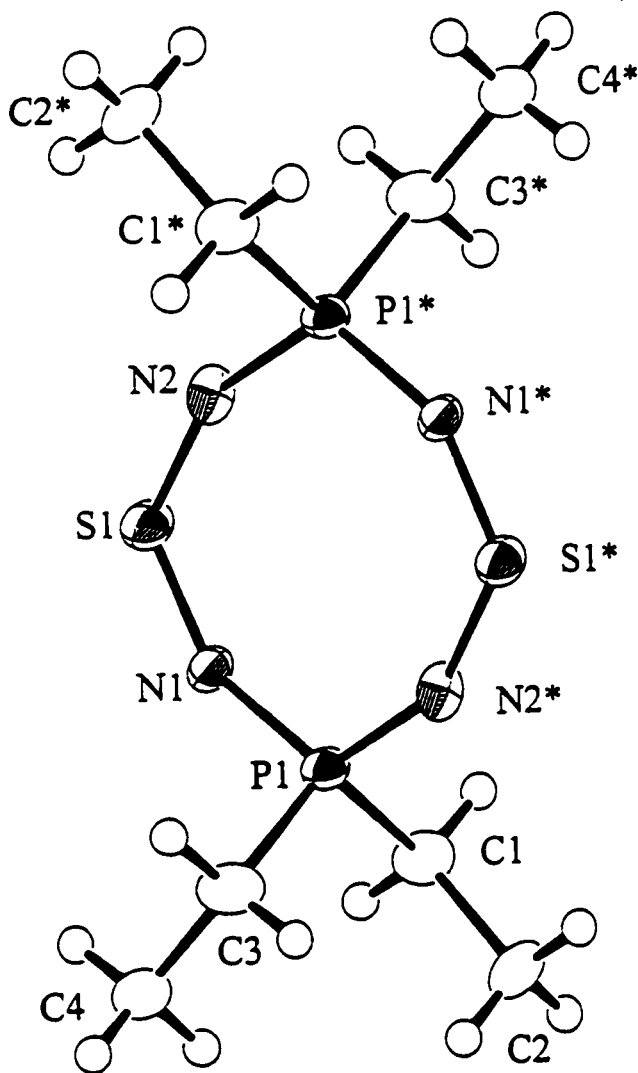
reaction is easily monitored by  $^{31}\text{P}$  NMR since the resonances of **29a** and **29b** shift  $\sim 5$  ppm downfield in the dications. The counterion  $\text{AlCl}_4^-$  is observed, as its expected singlet, at  $\sim 103$  ppm in the  $^{27}\text{Al}$  NMR spectra of **30a** and **30b**.



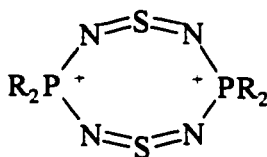
### 2.3.1 X-ray structure of [1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>][AlCl<sub>4</sub>]<sub>2</sub> (**30a**).

The structure of **30a** was obtained by Dr. Vollmerhaus, but it is pertinent to further discussion of the structure of **30b**.<sup>63</sup> The ORTEP diagram of the dication in **30a** is shown in Figure 2.4 and reveals a noninteracting planar 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub><sup>2+</sup> cation. Bond distances and bond angles are summarized in Table 2.5. The mean P-N bond distance 1.645(7) Å is somewhat longer than those found in the parent ring system 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> (**13c**) [ $d(\text{P-N}) = 1.616(8)$  Å].<sup>41</sup> The mean S-N bond lengths of 1.510(7) Å are in the expected range for localized Z,Z sulfur diimide groups,<sup>68</sup> but significantly shorter than the

value 1.55 Å found in the delocalized,  $10\pi$  electron dication  $S_4N_4^{2+}$ .<sup>69</sup> The bonding can be represented as two *Z,Z* sulfur diimides bridged by two  $R_2P^+$  groups (Figure 2.5).



**Figure 2.4.** ORTEP diagram of  $Et_4P_2N_4S_2^{2+}$ .<sup>63</sup>



**Figure 2.5.** Valence bond representation of  $1,5\text{-R}_4\text{P}_2\text{N}_4\text{S}_2^{2+}$ .

### 2.3.2 X-ray structure of $[1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2][\text{AlCl}_4]_2$ (**30b**).

The structure of  $[1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2][\text{AlCl}_4]_2$  (**30b**) was solved but the errors in the structural parameters are significantly greater than those found for the structure of  $[1,5\text{-Et}_4\text{P}_2\text{N}_4\text{S}_2][\text{AlCl}_4]_2$  (**30a**). The crystallographic parameters for **30b** are summarized in Table 2.4. The ORTEP diagram of the dication in **30b** is shown in Figure 2.6. Bond distances, bond angles and torsion angles can be found in Tables 2.5 and 2.6. The large esd's (estimated standard deviations) are the result of the small crystal size and large number of atoms in the unit cell giving a low reflection to parameter ratio of 4.22. The geometrical data for  $[1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2][\text{AlCl}_4]_2$  (**30b**) are similar to those of  $[1,5\text{-Et}_4\text{P}_2\text{N}_4\text{S}_2^{2+}][\text{AlCl}_4]_2$  (**30a**) (Table 2.5). The major difference between the two structures is the number of molecules in the unit cell. In **30b** there are two molecules in the unit cell, which differ by the relative orientation of the two phenyl groups on P (see molecules (i) and (ii) in Figure 2.6). This difference is manifested in the torsion angles  $\text{C}(1)\text{-P}(1)\text{-C}(7)\text{-}$

C(8) vs C(13)-P(2)-C(19)-C(20) [96(1)° vs 64(2)° ] and C(6)-C(1)-P(1)-C(7) vs C(18)-  
C(13)-P(2)-C(19) [87(1)° vs 57(2)°].

**Table 2.4.** Crystallographic Parameters for [1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub><sup>2+</sup>][AlCl<sub>4</sub><sup>-</sup>]<sub>2</sub> (**30b**).

<b>30b</b>	
Empirical Formula	C <sub>25</sub> H <sub>22</sub> N <sub>4</sub> P <sub>2</sub> S <sub>2</sub> Cl <sub>10</sub> Al <sub>2</sub>
Formula Weight	913.04
Crystal Color, Habit	yellow, prism
Crystal Dimensions	0.26 X 0.20 X 0.12 mm
Crystal System	triclinic
Lattice Parameters	a = 14.453(5) Å b = 15.320(5) Å c = 9.890(2) Å α = 108.82(2)° β = 93.47(2)° γ = 69.47(2)° V = 1937(1) Å <sup>3</sup>
Space Group	P $\bar{1}$ (#2)
Z value	2
D <sub>calc</sub>	1.565 g/cm <sup>3</sup>
Temperature	-103.0° C
Reflection/Parameter Ratio	4.22
R	0.055
R <sub>w</sub>	0.046

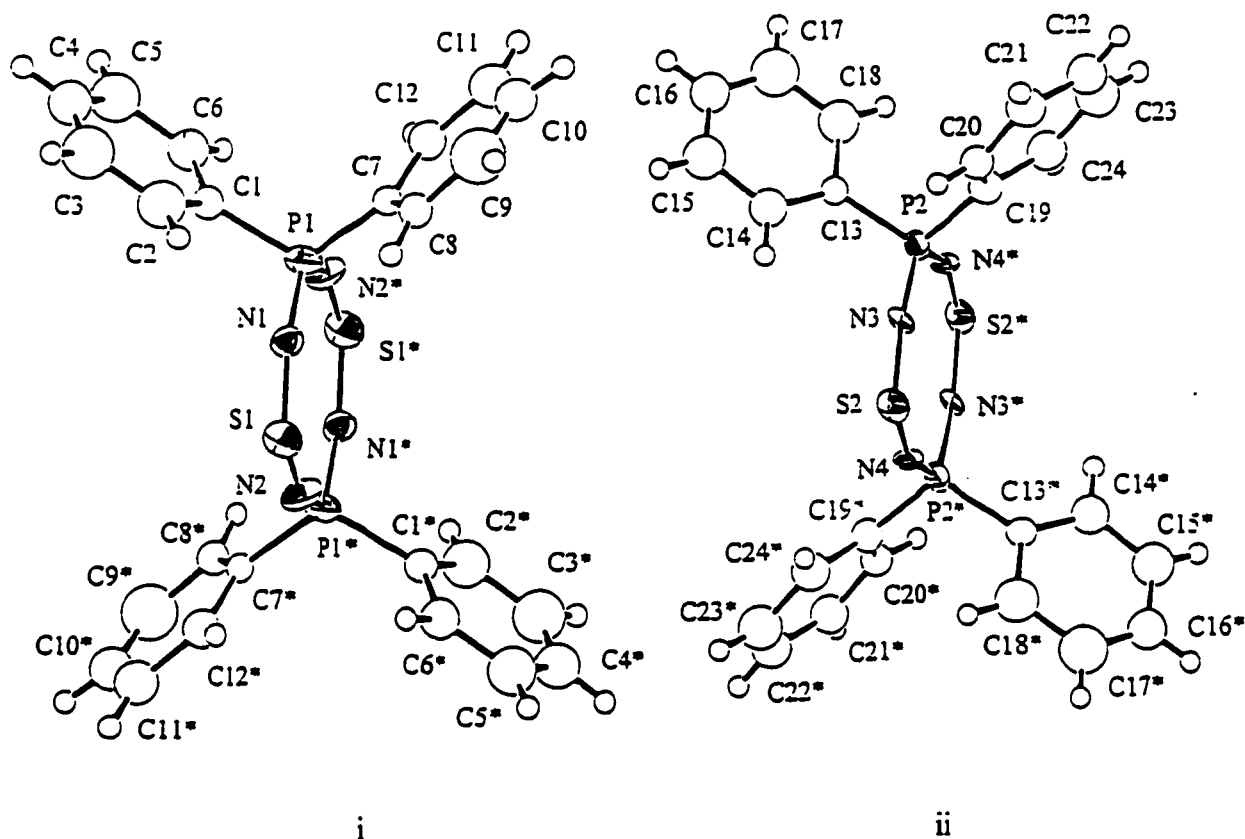


**Table 2.5** Selected Bond Lengths of [1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>][AlCl<sub>4</sub>]<sub>2</sub> (R = Et, **30a**; R = Ph, **30b**).

Atoms	Bond Lengths (Å)	
	<b>30a</b>	<b>30b</b>
S(1)-N(1)	1.509(7)	1.53(2)
S(1)-N(2)	1.511(7)	1.50(2)
S(2)-N(3)		1.48(2)
S(2)-N(4)		1.51(2)
P(1)-N(1)	1.650(7)	1.63(2)
P(1)-N(2)	1.639(7)	1.64(2)
P(2)-N(3)		1.65(2)
P(2)-N(4)		1.64(2)
	Bond Angles (°)	
	<b>30a</b>	<b>30b</b>
N(1)-S(1)-N(2)	121.6(4)	122.0(9)
N(3)-S(2)-N(4)		121.7(10)
S(1)-N(1)-P(1)	149.6(5)	145(1)
S(1)-N(2)-P(1)	151.2(5)	151(1)
S(2)-N(3)-P(2)		147(1)
S(2)-N(4)-P(2)		152(1)
N(1)-P(1)-N(2)	117.6(3)	120.7(8)
N(3)-P(2)-N(4)		117.8(9)

**Table 2.6.** Torsion Angles for the P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> ring of [1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>][AlCl<sub>4</sub>]<sub>2</sub> (**30b**).

Atoms	Torsion Angles (°)
S(1)-N(1)-P(1)-N(2)	-1(2)
S(2)-N(3)-P(2)-N(4)	-9(2)
P(1)-N(1)-S(1)-N(2)	2(2)
P(2)-N(3)-S(2)-N(4)	5(2)
S(1)-N(2)-P(1)-N(1)	1(2)
S(2)-N(4)-P(2)-N(3)	-10(2)
P(1)-N(2)-S(1)-N(1)	3(2)
P(2)-N(4)-S(2)-N(3)	-6(3)



**Figure 2.6.** ORTEP diagram of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub><sup>2+</sup>. Molecules i and ii show the difference in the orientation of the phenyl groups on P for the two molecules in the unit cell.

The 8 $\pi$  electron dications 30a and 30b are the third and fourth examples of planar ring systems involving the eight-membered ring E<sub>2</sub>N<sub>4</sub>S<sub>2</sub>. The heterocycles 1,5-(<sup>t</sup>Bu<sub>2</sub>Si)<sub>2</sub>N<sub>4</sub>S<sub>2</sub> (E = Si<sup>t</sup>Bu<sub>2</sub>)<sup>70</sup> and 1,5-[P(N<sup>i</sup>Pr<sub>2</sub>)(Cr(CO)<sub>5</sub>)]<sub>2</sub>N<sub>4</sub>S<sub>2</sub> (E = P(N<sup>i</sup>Pr<sub>2</sub>)(Cr(CO)<sub>5</sub>))<sup>71</sup> have been structurally characterized and it has been argued that their planarity is due to the steric bulk of the substituents on E. This argument is further supported by the structures of the isoelectronic rings 1,5-(Me<sub>2</sub>Si)<sub>2</sub>N<sub>4</sub>S<sub>2</sub> (E = Me<sub>2</sub>Si)<sup>72</sup> and

1,5-(RE)<sub>2</sub>N<sub>4</sub>S<sub>2</sub> (E = As, Sb)<sup>68,73</sup> in which the E<sub>2</sub>N<sub>4</sub>S<sub>2</sub> rings adopt a boat structure.

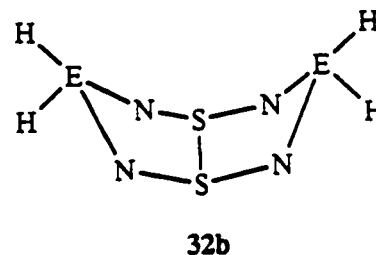
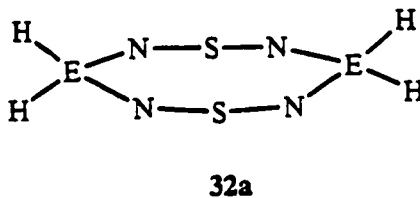
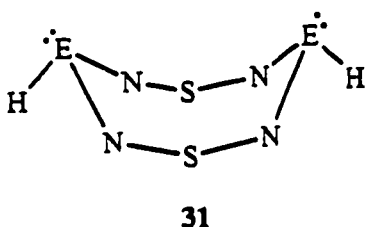
However, when E = Et<sub>2</sub>P<sup>+</sup> (30a) a planar structure is observed even though the ethyl groups are not sterically demanding and do not force the ring into a planar conformation.

In order to understand the factors that influence the conformation of the E<sub>2</sub>N<sub>4</sub>S<sub>2</sub> ring, Dr.

Vargas-Baca performed DFT (Density Functional Theory) calculations on the model

systems 1,5-(HE)<sub>2</sub>N<sub>4</sub>S<sub>2</sub> (31) and 1,5-(H<sub>2</sub>E)<sub>2</sub>N<sub>4</sub>S<sub>2</sub><sup>n+</sup> (E = P, As; n = 0, 2) in both planar

(32a) and boat (32b) conformations.<sup>74</sup>

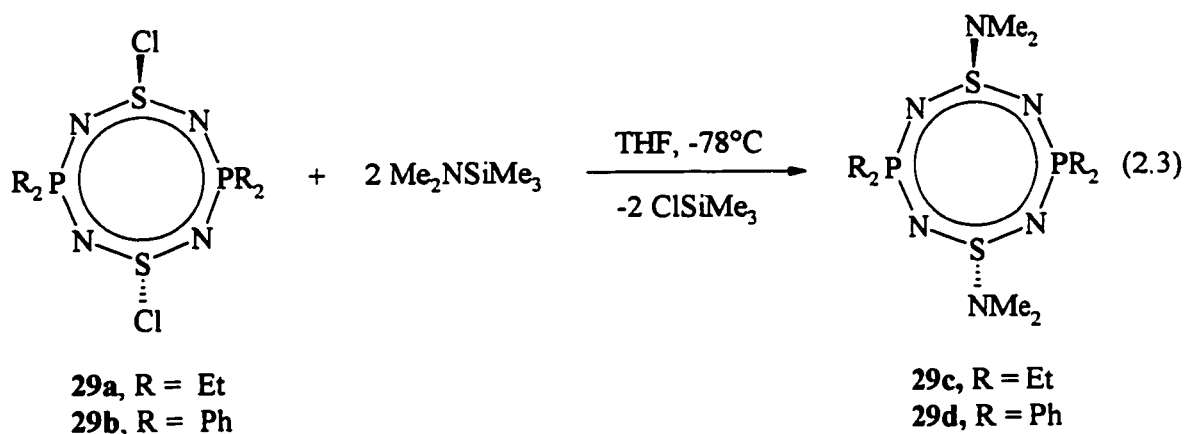


It was found that the heterocycles 1,5-(HE)<sub>2</sub>N<sub>4</sub>S<sub>2</sub> (31) and 1,5-(H<sub>2</sub>E)<sub>2</sub>N<sub>4</sub>S<sub>2</sub><sup>n+</sup> (E = P, As; n = 0, 2) (32) cannot be considered isoelectronic. The boat conformation in 1,5-(HE)<sub>2</sub>N<sub>4</sub>S<sub>2</sub> (E = P, As) (31) is the result of a repulsive interaction between the lone pair on the pnictogen and the sulfur diimide π system, which prevents the formation of a planar ring system. However, the planar ring 1,5-(H<sub>2</sub>E)<sub>2</sub>N<sub>4</sub>S<sub>2</sub><sup>n+</sup> (E = P, As; n = 2) (32a) does

not have lone pairs on the pnictogen and, as a result, the planar conformation is more stable because it allows for maximum P-N overlap. In the  $10\pi$  electron neutral heterocycle 1,5-(H<sub>2</sub>E)<sub>2</sub>N<sub>2</sub>S<sub>2</sub> (E = P, As) (**32b**) the boat conformation is due a distortion that results in the formation of a S-S transannular interaction and lowers the energy of the HOMO; this distortion is absent in the  $8\pi$  electron system because it does not possess the two  $\pi$  electrons necessary for the formation of the S-S interaction.

#### 2.4 Synthesis of 1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (R = Et, **29c**; R = Ph, **29d**).

The S,S-dimethylamino derivative 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (**29c**) was prepared by treating the S,S-dichloro derivative 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29a**) with a slight excess of Me<sub>2</sub>NSiMe<sub>3</sub> (Equation 2.3). The reaction is readily monitored by <sup>31</sup>P NMR with the disappearance of the signal of **29a** at +27.4 ppm and the appearance of a new resonance at +39.4 ppm. A second species ( $\delta^{31}\text{P} = +34.7$  ppm) is also formed in the reaction in about 3% yield by integration of the <sup>31</sup>P NMR signals. The reaction is performed at -78° C and the solvent is removed while keeping the mixture cold (*ca.* -20° C). The colorless, thermally unstable product is stored in the freezer to prevent decomposition. Upon decomposition the product turns from colorless to pale pink and finally a deep red color. The nature of the red species is not known, but the thermolysis of this ring was investigated (see Section 2.4.2).



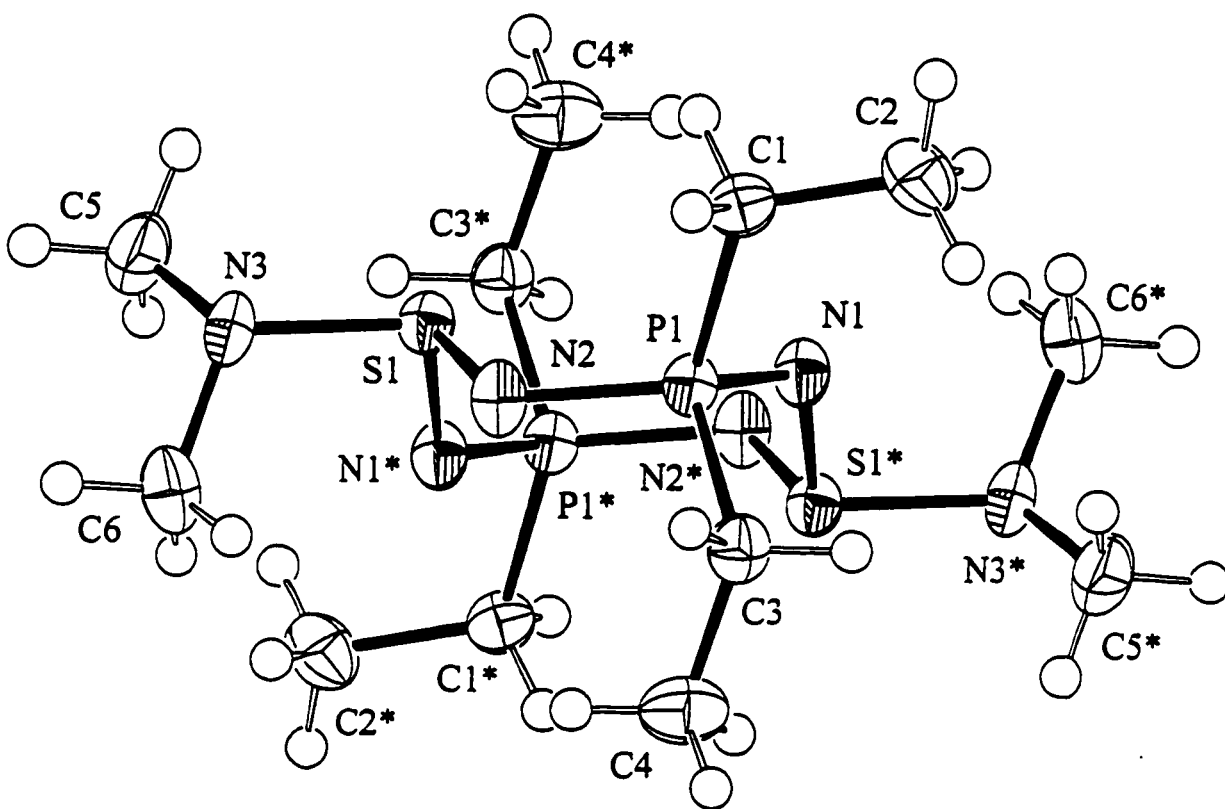
The tetraphenyl derivative 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (**29d**) is prepared in a manner similar to that used for 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (**29c**) (Equation 2.3). The S,S-dichloro derivative 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29b**) reacts with a slight excess of Me<sub>2</sub>NSiMe<sub>3</sub> to give **29d** as the major product. The <sup>31</sup>P NMR resonance of the dichloride (+2.6 ppm) disappears after the addition and two new resonances (+14.7 ppm and +6 ppm) appear in a ratio of 1:0.13. The minor product is very difficult to remove from **29d** because it has similar solubility properties. A small amount of pure **29d** was isolated by recrystallization of the mixture from a mixture of CH<sub>2</sub>Cl<sub>2</sub> and Et<sub>2</sub>O.

#### 2.4.1 X-ray structures of 1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (R = Et, **29c**; R = Ph, **29d**).

Crystals of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (**29c**) were obtained by layering a solution of **29c** in ether with pentanes. Crystallographic parameters for **29c** and **29d** are given in Table

2.7. The ORTEP diagram of **29c** is shown in Figure 2.7. Pertinent bond distances, bond angles and torsion angles can be found in Tables 2.8 and 2.9. The ring conformation is a chair with a maximum deviation of 0.094 Å from the P<sub>2</sub>N<sub>4</sub> plane and the S atoms are 0.906 Å out and on opposite sides of the P<sub>2</sub>N<sub>4</sub> plane. The dimethylamino groups attached to sulfur adopt equatorial positions. The mean P-N bond distance 1.619(3) Å does not deviate from the mean P-N distance of 1.627(3) Å<sup>41</sup> found in the parent ring 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29a**). However, the substitution of -NMe<sub>2</sub> for Cl on sulfur causes an increase in the mean endocyclic S-N bond distances from 1.545(3) Å in 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SCl)<sub>2</sub> (**29a**) to 1.603(3) Å in 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (**29c**) and they are comparable to those of those of the twelve-membered ring Ph<sub>8</sub>P<sub>4</sub>N<sub>6</sub>(SNMe<sub>2</sub>)<sub>2</sub> (**9**) [d(S-N) = 1.590(5) Å].<sup>31</sup> The mean exocyclic S-N bond lengths [d(S-N) = 1.704(3) Å] are significantly longer than the endocyclic S-N bond distances in **29c** [cf. d(S-N) = 1.703(3) Å for the exocyclic S-N bonds of Ph<sub>8</sub>P<sub>4</sub>N<sub>6</sub>(SNMe<sub>2</sub>)<sub>2</sub> (**9**)].<sup>31</sup>

The structure of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (**29c**) is quite different from that of the related molecule 1,5-(Me<sub>2</sub>N)<sub>2</sub>S<sub>4</sub>N<sub>4</sub>, which has a significant interaction of a dimethylamino nitrogen with the opposing sulfur atom [d(S<sup>⋯</sup>N) = 2.760 Å].<sup>9</sup> The chair conformation of **29c** does not allow this type of interaction to occur.



**Figure 2.7.** ORTEP diagram of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (**29c**).

**Table 2.7** Crystallographic Parameters for 1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (R = Et, **29c**; R = Ph, **29d**).

	<b>29c</b>	<b>29d</b>
Empirical Formula	C <sub>12</sub> H <sub>32</sub> N <sub>6</sub> P <sub>2</sub> S <sub>2</sub>	C <sub>28</sub> H <sub>32</sub> N <sub>6</sub> P <sub>2</sub> S <sub>2</sub>
Formula Weight	386.49	578.67
Crystal Color, Habit	colorless, prism	colorless, prism
Crystal Dimensions	0.65 X 0.55 X 0.45 mm	0.70 X 0.45 X 0.30 mm
Crystal System	monoclinic	triclinic
Lattice Parameters	a = 8.144(2) Å b = 15.548(3) Å c = 8.250(2) Å  β = 109.24(2)°	a = 9.981(4) Å b = 10.123(6) Å c = 8.759(4) Å  α = 113.12(3)° β = 111.82(3)° γ = 64.28(4)°
Space Group	P2 <sub>1</sub> /c (#14)	P $\bar{1}$ (#2)
Z value	2	1
D <sub>calc</sub>	1.301 g/cm <sup>3</sup>	1.363 g/cm <sup>3</sup>
Temperature	-103.0° C	-103.0° C
Reflection/Parameter Ratio	14.29	11.66
R	0.038	0.032
R <sub>w</sub>	0.040	0.031



**Table 2.8.** Selected Bond Lengths and Angles of 1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (R = Et, **29c**; R = Ph, **29d**).

Atoms	Bond Lengths (Å)	
	<b>29c</b>	<b>29d</b>
S(1)-N(1)	1.599(3)	1.595(2)
S(1)-N(2)	1.607(3)	1.622(2)
S(1)-N(3)	1.704(3)	1.675(2)
P(1)-N(1)	1.617(3)	1.604(2)
P(1)-N(2)	1.620(3)	1.610(2)
Atoms	Bond Angles (°)	
	<b>29c</b>	<b>29d</b>
N(1)-S(1)-N(2)	107.9(2)	109.6(1)
N(2)-S(2)-N(3)	98.0(2)	105.2(1)
S(1)-N(1)-P(1)	125.7(2)	125.2(1)
S(1)-N(2)-P(1)	117.1(2)	123.3(1)
N(1)-P(1)-N(2)	117.6(2)	116.6(1)

**Table 2.9.** Selected Torsion Angles of 1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (R = Et, **29c**; R = Ph, **29d**).

Atoms	Torsion Angles (°)	
	<b>29c</b>	<b>29d</b>
S(1)-N(1)-P(1)-N(2)	61.1(3)	-28.9(2)
P(1)-N(1)-S(1)-N(2)	114.0(2)	33.2(2)
P(1)-N(2)-S(1)-N(1)	85.8(2)	104.5(1)
S(1)-N(2)-P(1)-N(1)	-26.7(3)	-105.9(1)
P(1)-N(1)-S(1)-N(3)	-142.9(2)	143.0(2)
P(1)-N(2)-S(1)-N(3)	-167.2(2)	-150.0(1)

Crystals of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (**29d**) were grown from a mixture of CH<sub>2</sub>Cl<sub>2</sub> and Et<sub>2</sub>O at -20°C. An ORTEP diagram of **29d** is shown in Figure 2.9. Tables 2.8 and 2.9 contain bond distances, bond angles, and torsion angles. The structure of **29d** is quite different from that of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (**29c**) (Figure 2.8) as the conformation of the

ring is a distorted chair and there are variations in the endocyclic S-N bond distances. However, the mean S-N bond distance of 1.608(2) Å in **29d** is similar to the value of 1.603(3) Å found in 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (**29c**). The exocyclic S-N bond distance in **29d** is 1.675(2) Å, which is shorter than the corresponding bond distance for 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (**29c**) [d(S-N) = 1.704(3) Å]. The differences in S-N bond distances follow a similar trend to those found in the six-membered heterocycle Ph<sub>4</sub>P<sub>2</sub>N<sub>3</sub>SNMe<sub>2</sub> (**8f**) where the endocyclic bond distances are 1.586(3) Å and 1.603(2) Å and the exocyclic S-N bond length is 1.685(3) Å.<sup>64</sup> In S-diisopropylamino substituted thiatriazines R<sub>2</sub>C<sub>2</sub>N<sub>3</sub>SNiPr<sub>2</sub> the endocyclic S-N bonds are longer than the exocyclic S-N bonds and the dialkylamino N is suggested to be involved in π bonding to S.<sup>75</sup> The distorted boat structure and trends in S-N bond lengths in 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (**29d**) may result from π-electron donation from the dialkylamino groups to the P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> ring combined with the presence of the electron-withdrawing phenyl groups on P that facilitate the donation from N. In the tetraethyl substituted derivative 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (**29c**) the electron-donating ethyl groups do not encourage an interaction between S and the dialkylamino N. Consequently, an undistorted boat conformation with S-N bond distances consistent with a delocalized π system in the ring and an exocyclic S(VI)-N single bond [d(S-N) = 1.704(3) Å, cf. Ph<sub>8</sub>P<sub>4</sub>N<sub>6</sub>(SNMe<sub>2</sub>)<sub>2</sub> d(S-N) = 1.703(3) Å] is observed.<sup>31</sup> The mean P-N bond distance 1.607(2) Å in **29d** is not significantly different from the value of 1.600(2) Å found in Ph<sub>4</sub>P<sub>2</sub>N<sub>3</sub>SNMe<sub>2</sub> (**8f**).<sup>64</sup> Given the structural similarities of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (**29d**) and **8f** it is predicted that **29d** will ring open to give larger rings as observed for **8f**.

This process could account for the minor product, perhaps a larger ring, formed in the reaction of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> and Me<sub>2</sub>NSiMe<sub>3</sub> and for the difficulties experienced in the purification of 29d.

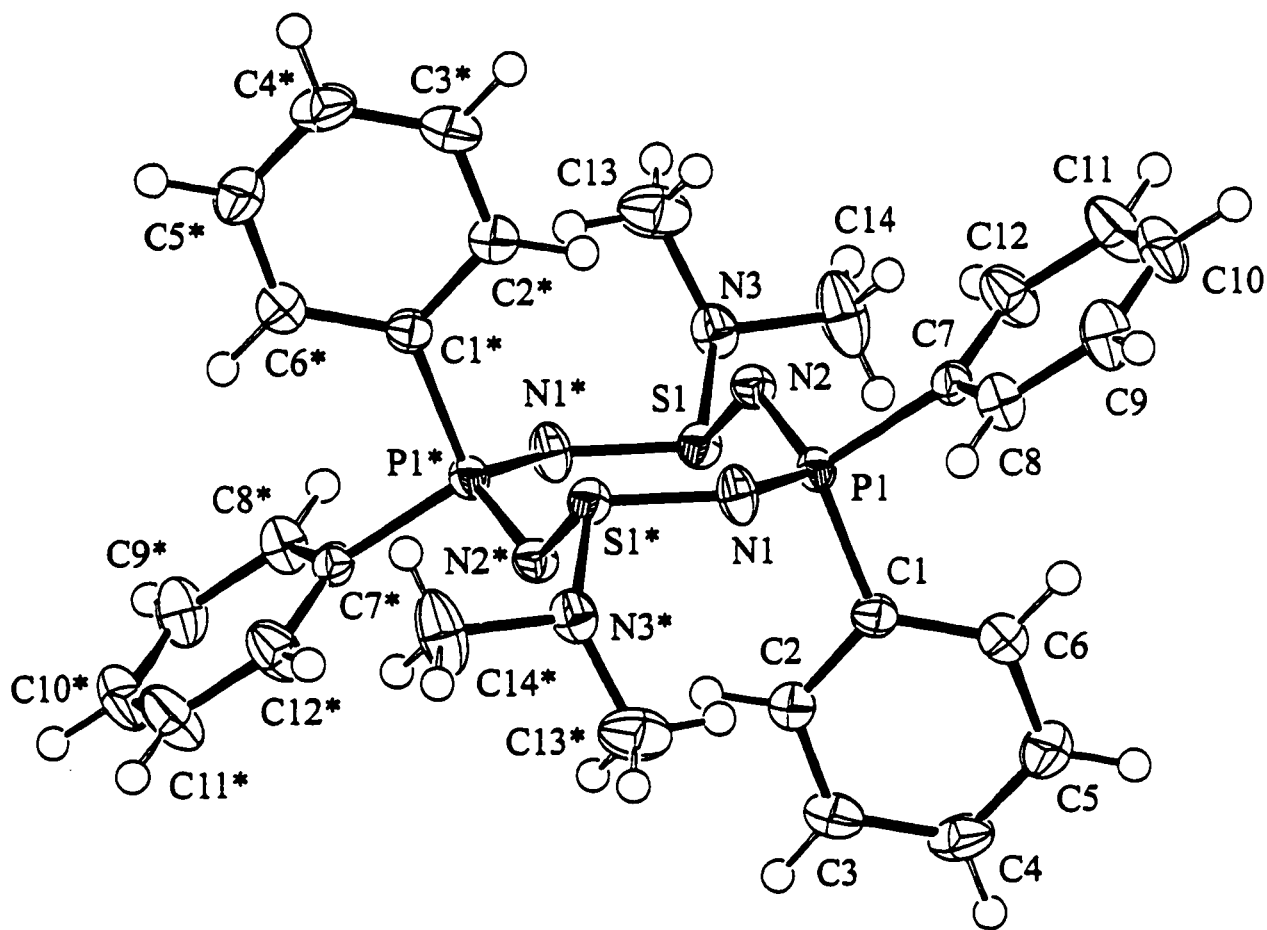


Figure 2.8. ORTEP diagram of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (29d).

### 2.4.2 Thermolysis of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub>.

The thermolysis of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (**29c**) was investigated by heating a sample under vacuum in a temperature controlled furnace. The first investigation was performed at 80°C and monitored by <sup>31</sup>P NMR. After two hours the starting material ( $\delta = +39.4$  ppm) had been partially converted to a red species with a <sup>31</sup>P NMR chemical shift of +38.3 ppm. The thermolysis was continued and after 33 hours the resonance of the starting material had decreased while the signal of the species at +38.3 ppm had increased. After 87 hours a broad peak appeared between +21 and +23 ppm and a signal due to 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> (**13c**) was observed at +134 ppm. Upon subsequent heating this resonance became larger while the resonance of **29c** and that of the intermediate species at +38.3 ppm decreased. The experiment was performed at higher temperatures (ca 120° C) and for a shorter length of time, but this resulted in decomposition of the initial products to Et<sub>2</sub>PN<sub>2</sub>H<sub>3</sub><sup>+</sup> and 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> (**13c**). The mass spectra of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> and 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> show an immediate loss of both dimethylgroups as the M<sup>+</sup> peak 44 m/z (a dimethylamino group) less than what would be expected for **29c** and **29d**, therefore it is likely that the decomposition of **29c** involves the loss of the dimethylamino groups which would result in the formation of the ring 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> (see Figures 2.9 and 2.10). The loss of the dimethylamino groups implies the formation of a radical species in which case ESR could be used to monitor the thermolysis of these heterocycles. Preliminary investigations into the thermolysis of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (**29d**) have shown that **29d** does not form 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> which indicates it does not lose dimethylamino groups upon

heating. The increased stability of **29d** is most likely a result of  $\pi$ -donation from the N of the exocyclic dimethylamino group which is absent in the 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> [d(S-N) = 1.675(2) Å for **29d** vs. d(S-N) = 1.704(3) Å for **29c**] (see Section 2.4.1).

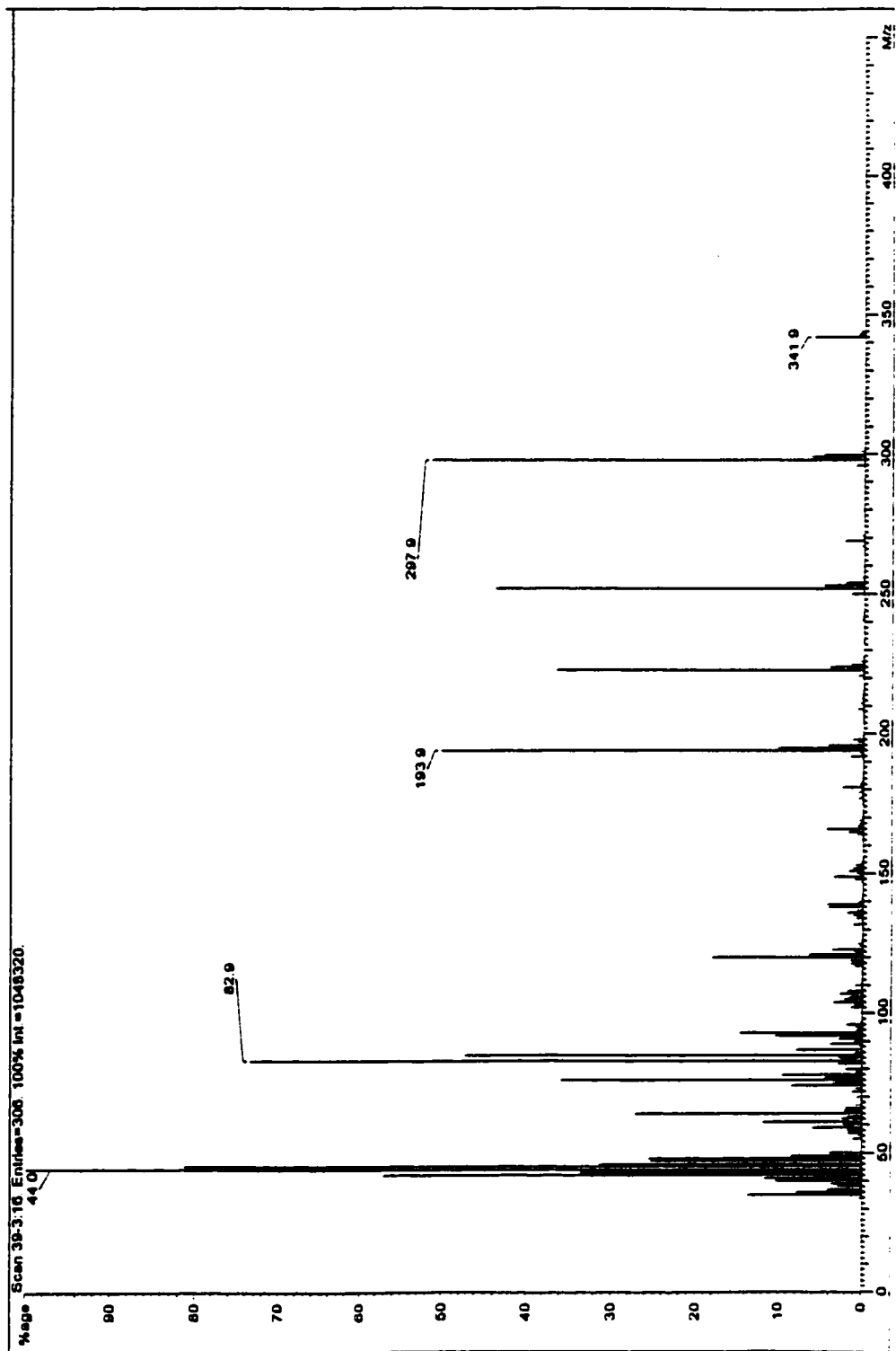


Figure 2.9. Mass spectra of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (29c).

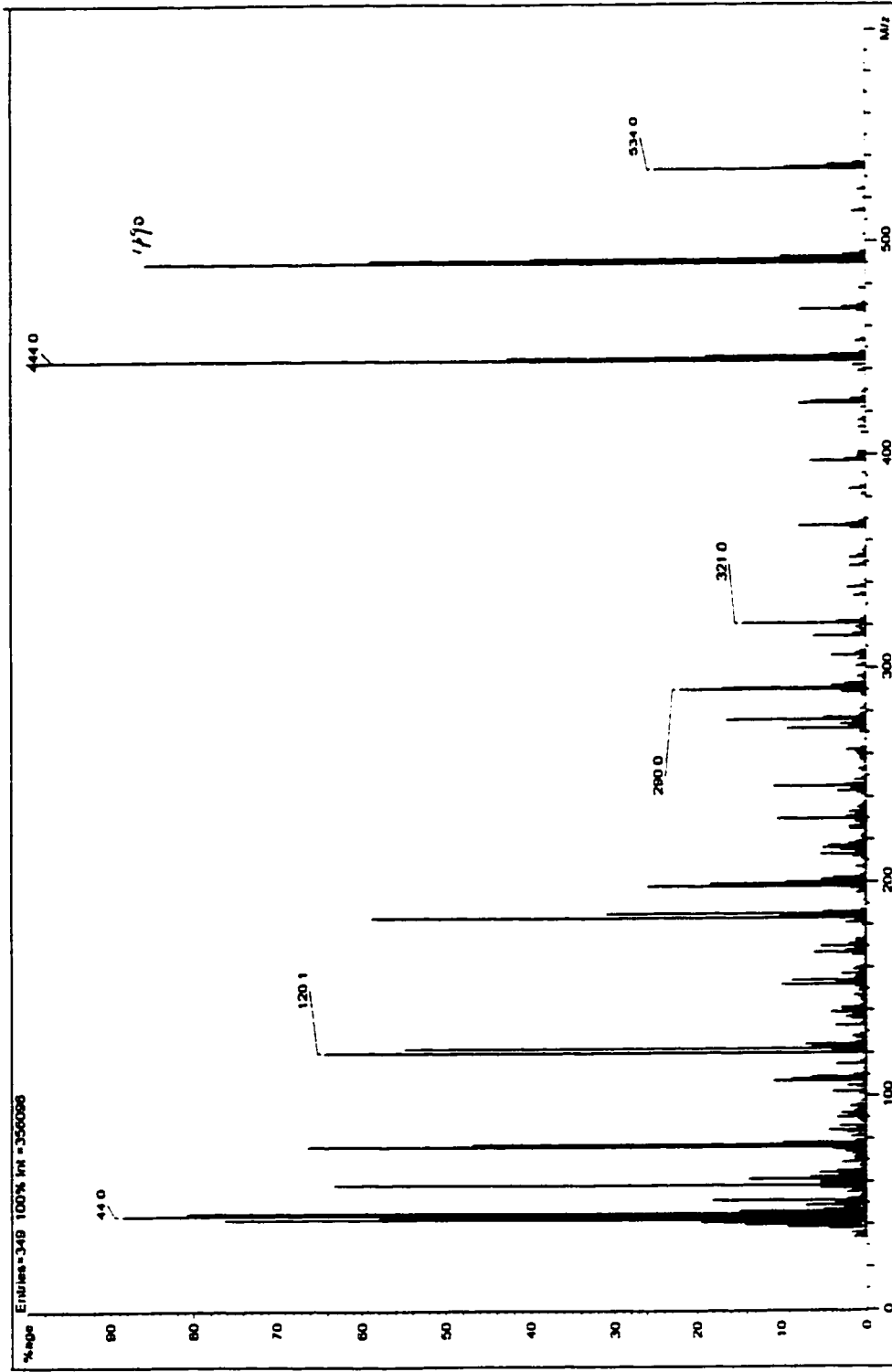


Figure 2.10. Mass spectra of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (29d).

## 2.5 Conclusions.

The synthesis of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> was achieved by the reaction 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> with SO<sub>2</sub>Cl<sub>2</sub>. The X-ray structure of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> shows inequivalent S-Cl bond distances and is consistent with the proposed mechanism of oxidative addition of halogens across the S-S transannular bond of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> (See Figure 1.4). The reaction of the dichlorides 1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (R = Et, Ph) with AlCl<sub>3</sub> gives the dicationic species 1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub><sup>2+</sup> whose ring structure was shown to have a planar conformation.

The heterocycles 1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe)<sub>2</sub> are the first examples of S,S dialkylamino substituted diphosphadithiatetrazocines. Their preparation involves the treatment of 1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> with Me<sub>2</sub>NSiMe<sub>3</sub> and this method could be used to prepare a variety of other S,S dialkylamino substituted derivatives. The six-membered ring Ph<sub>4</sub>P<sub>2</sub>N<sub>3</sub>SNMe<sub>2</sub> ring opens to give the corresponding twelve-membered ring Ph<sub>8</sub>P<sub>4</sub>N<sub>6</sub>(SNMe<sub>2</sub>)<sub>2</sub> so investigations into the ring opening of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> may lead to larger rings or, perhaps, polymers. The thermolysis of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>) leads to decomposition of the ring to an unidentified red species and, subsequently, to 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>.

## 2.6 Experimental Section.

### 2.6.1 Reagents and General Procedures.

All solvents were dried and distilled before use: diethyl ether, tetrahydrofuran and toluene (all with Na/benzophenone), pentanes (Na), acetonitrile and methylene chloride (P<sub>4</sub>O<sub>10</sub> and CaH<sub>2</sub>). SO<sub>2</sub>Cl<sub>2</sub> and Al<sub>2</sub>Cl<sub>6</sub> were obtained from Aldrich and distilled or sublimed



prior to use. Other reagents were used as received from Aldrich:  $\text{PCl}_3$ ,  $\text{Ph}_2\text{PCl}$ ,  $\text{EtMgBr}$ ,  $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ ,  $\text{SOCl}_2$ ,  $\text{Me}_3\text{SiN}_3$  and  $\text{Me}_2\text{NSiMe}_3$ . The manipulation of all the moisture-sensitive products was carried out under an atmosphere of nitrogen or argon using Schlenk techniques or a nitrogen-filled glove box.  $1,5\text{-Et}_4\text{P}_2\text{N}_4\text{S}_2$ ,<sup>41</sup>  $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2$ <sup>50</sup> and  $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{Cl}_2$ <sup>42</sup> were prepared by literature methods.

### 2.6.2 Instrumentation.

$^{31}\text{P}$  and  $^{27}\text{Al}$  NMR spectra were recorded on a Varian XL-200 spectrometer or a Bruker AM-400 spectrometer. The chemical shifts are relative to external standards, 85%  $\text{H}_3\text{PO}_4$  with a  $\text{CDCl}_3$  or  $\text{D}_2\text{O}$  lock., and  $\text{Al}(\text{NO}_3)_3$  in  $\text{D}_2\text{O}$ , respectively.  $^1\text{H}$  NMR spectra were collected on a Bruker AM-200 spectrometer. Infrared spectra were obtained on a Mattson 4030 FTIR spectrophotometer and mass spectra were obtained using a VG 7070F Micromass instrument at 70eV. Elemental analyses and mass spectra were provided by the Analytical Services Laboratory of the Department of Chemistry, The University of Calgary. X-ray data were collected on a Rigaku AFC6S diffractometer using the  $\omega$ - $2\theta$  technique and Mo  $\text{K}\alpha$  radiation. The solution and refinement of the structures were carried out by Dr. M. Parvez.

### 2.6.3 Preparation of $1,5\text{-Et}_4\text{P}_2\text{N}_4\text{S}_2\text{Cl}_2$ (29a).

$\text{SO}_2\text{Cl}_2$  (0.202g, 1.50 mmol) was added dropwise, by syringe, to a stirred solution of  $1,5\text{-Et}_4\text{P}_2\text{N}_4\text{S}_2$  (0.449g, 1.50 mmol) in  $\text{CH}_2\text{Cl}_2$  (ca. 20 mL) at 23°C. During the

addition the solution turns from pale yellow to orange to red then to a vibrant yellow when one equivalent of  $\text{SO}_2\text{Cl}_2$  has been added. The solvent and volatile products were removed by vacuum to give a yellow solid. The yellow solid was recrystallized from acetonitrile (*ca.* 10 mL) to give pale yellow crystals (0.325g, 0.880 mmol, 59%). Anal. Calcd for  $\text{C}_8\text{H}_{20}\text{N}_4\text{P}_2\text{S}_2\text{Cl}_2$ : C, 26.02; H, 5.46; N, 15.17. Found C, 25.71; H, 5.63; N, 14.74. IR (Nujol,  $\text{cm}^{-1}$ ): 1274 w, 1217 s, 1172 s, 1019 m, 999 w, 777 s, 742 m, 742 m, 727 w, 666 w, 459 m, 406 m, 383 w, 365 w, 358 w, 341 w, 313 w, 279 m, 246 m, 225 m, 206 s. NMR spectra ( $\delta$ , ppm) ( $\text{CD}_2\text{Cl}_2$ ):  $^{31}\text{P}$  27.4.  $^1\text{H}$  1.25 [d of t,  $^2\text{J}(^1\text{H}-^{31}\text{P}) = 20.9$  Hz,  $^3\text{J}(^1\text{H}-^1\text{H}) = 7.6$  Hz], 2.26 [d of q,  $^3\text{J}(^1\text{H}-^{31}\text{P}) = 14.8$  Hz,  $^3\text{J}(^1\text{H}-^1\text{H}) = 7.4$  Hz]

#### 2.6.4 Preparation of [1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ ][ $\text{AlCl}_4$ ]<sub>2</sub> (30b).

Solid  $\text{AlCl}_3$  (0.069g, 0.520 mmol) was added to a stirred solution of 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{Cl}_2$  (0.146g, 0.260 mmol) in  $\text{CH}_2\text{Cl}_2$  (*ca.* 20 mL). An orange precipitate was formed which was filtered to give [1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2$ ][ $\text{AlCl}_4$ ]<sub>2</sub> (0.063 g, 0.754 mmol, 29%). Anal. Calcd for  $\text{C}_{24}\text{H}_{20}\text{N}_4\text{P}_2\text{Al}_2\text{Cl}_8\text{S}_2$ : C, 34.81; H, 2.43; N, 6.77. Found: C, 34.85; H, 3.46; 6.47. IR (Nujol,  $\text{cm}^{-1}$ ): 1260 vs, 1120 m, 1101 m, 899 w, 796 m, 619 m, 504 m.  $\{^1\text{H}\}^{31}\text{P}$  NMR ( $\text{CH}_2\text{Cl}_2$ ):  $\delta$  (ppm) 7.3.  $^{27}\text{Al}$  NMR ( $\text{CH}_2\text{Cl}_2$ ):  $\delta$  (ppm) 102.8.

#### 2.6.5 Preparation of 1,5- $\text{Et}_4\text{P}_2\text{N}_4(\text{SNMe}_2)_2$ (29c).

A solution of  $\text{Me}_2\text{NSiMe}_3$  (0.203 g, 1.73 mmol) in THF (*ca.* 25 mL) was added dropwise to a stirring slurry of 1,5- $\text{Et}_4\text{P}_2\text{N}_4\text{S}_2\text{Cl}_2$  (0.269g, 0.788 mmol) in THF (*ca.*

25mL) at  $-78^{\circ}\text{C}$ . After one hour the colorless solution was warmed to  $-30^{\circ}\text{C}$  and the solvent was removed by vacuum to give a pale pink solid. The product was recrystallized from a  $\text{Et}_2\text{O}$ /pentane solution to give colorless crystals of  $1,5\text{-Et}_4\text{P}_2\text{N}_4(\text{NMe}_2)_2$  (0.256 g, 0.662 mmol, 84%). mp  $55\text{-}57^{\circ}\text{C}$ . Anal. Calcd for  $\text{C}_{12}\text{H}_{32}\text{N}_6\text{P}_2\text{S}_2$ : C, 37.29; H, 8.35; N, 21.74. Found: C, 37.61; H, 8.45; N, 21.28. IR (Nujol,  $\text{cm}^{-1}$ ) 1456 s, 1377 s, 1260 w, 1177 m, 1147 s, 1127 s, 1114 s, 1101 s, 1064 s, 1033 s, 994 m, 910 m, 797 m, 786 m, 751 m, 723 m, 701 m, 648 m, 629 s, 501 w, 443 w, 426 w, 398 w, 329 w, 281 w. NMR spectra ( $\delta$ , ppm) ( $\text{CDCl}_3$ ):  $\{^1\text{H}\}^{31}\text{P}$  39.4.  $^1\text{H}$  2.39 [s,  $\text{NCH}_3$ , 3H], 1.77 [d of q,  $^2\text{J}(^1\text{H}\text{-}^{31}\text{P}) = 17.6$  Hz,  $^3\text{J}(^1\text{H}\text{-}^1\text{H}) = 7.6$  Hz,  $\text{CH}_2\text{CH}_3$ , 2H], 1.10 [d of t,  $^3\text{J}(^1\text{H}\text{-}^{31}\text{P}) = 14.6$  Hz,  $^3\text{J}(^1\text{H}\text{-}^1\text{H}) = 7.6$  Hz  $\text{CH}_2\text{CH}_3$ , 3H]. MS:  $m/e$ : 342 (4,  $\text{M}^+ \text{-NMe}_2$ ), 298 (25,  $\text{M}^+ \text{-2NMe}_2$ ).

#### 2.6.6 Thermolysis of $1,5\text{-Et}_4\text{P}_2\text{N}_4(\text{SNMe}_2)_2$ .

A sample of  $1,5\text{-Et}_4\text{P}_2\text{N}_4(\text{SNMe}_2)_2$  was placed in a thick-walled tube fitted with a J. Young valve. The tube was evacuated, heated to  $80^{\circ}\text{C}$  and the thermolysis was monitored by  $^{31}\text{P}$  NMR. After 16 hours the red product was dissolved in  $\text{CDCl}_3$  and transferred to an NMR tube. Initially the starting material at +39.4 ppm partially converts to a new species at 38.3 ppm. The solution was returned to the tube, the solvent was removed by vacuum and the sample was heated to  $80^{\circ}\text{C}$ . The  $^{31}\text{P}$  NMR spectrum was recorded at 22, 33, 87, 106, and 202 hours. (See Section 2.4.2)

### 2.6.7 Preparation of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> (29d).

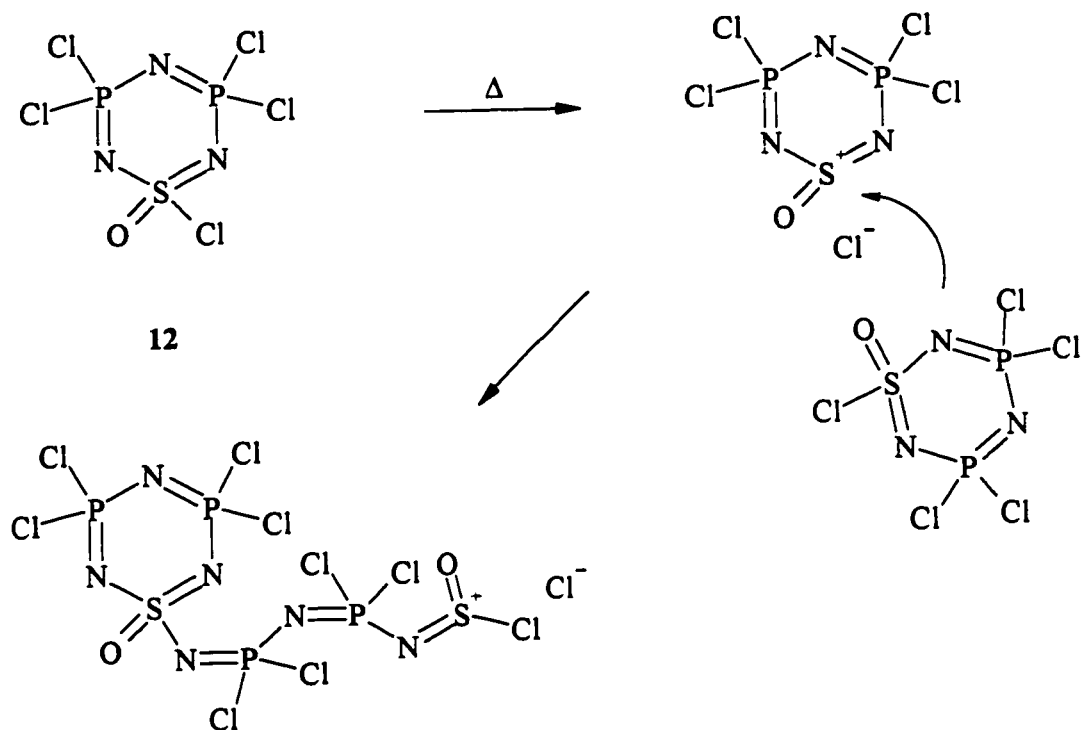
A solution of Me<sub>2</sub>NSiMe<sub>3</sub> (0.083g, 0.705 mmol) in THF (*ca.* 25 mL) was added dropwise to a stirring slurry of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (0.180g, 0.320 mmol) in THF (*ca.* 25mL) at -78° C. A white precipitate formed and the supernatant was decanted giving the crude product (0.183g). 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(NMe<sub>2</sub>)<sub>2</sub> (0.046g, 29.4 %) was recrystallized from a solution of CH<sub>2</sub>Cl<sub>2</sub> and Et<sub>2</sub>O cooled to -20° C. mp 165-166 °C. Anal. Calcd. for C<sub>28</sub>H<sub>32</sub>N<sub>6</sub>P<sub>2</sub>S<sub>2</sub>: C, 58.12 ; H, 5.57 ; N, 14.52. Found: C, 57.22 ; H, 6.51 ; N, 12.47. IR (Nujol, cm<sup>-1</sup>) 1462 s, 1435 s, 1377 s, 1260 w, 1183 w, 1157 m, 1137 s, 1112 s, 1075 s, 1042 m, 1023 m, 996 m, 909 m, 807 m, 766 w, 752 w, 718 m, 694 s, 640 w, 630 w, 536 s, 517 w, 502 m, 444 w, 427 w. NMR spectra (δ, ppm) (CDCl<sub>3</sub>): {<sup>1</sup>H}<sup>31</sup>P 14.7. <sup>1</sup>H 2.61 [s, NCH<sub>3</sub>, 3H], 7.8-8.0, 7.2-7.4[m, C<sub>6</sub>H<sub>5</sub>, 5H]. m/e: 534 (25, M<sup>+</sup>-NMe<sub>2</sub>), 490 (86, M<sup>+</sup>-2NMe<sub>2</sub>).

## CHAPTER 3

### Synthesis, Spectroscopic Characterization and X-ray Structures of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)R]<sub>2</sub>.

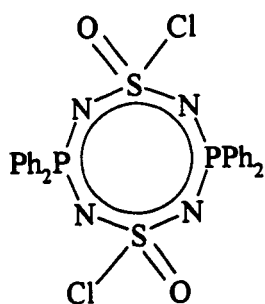
#### 3.1 Introduction.

The polymer  $[-\text{PCl}_2=\text{N}-\text{PCl}_2=\text{N}-\text{S}(\text{O})\text{Cl}=\text{N}-]_n$  (**26**) has been shown to be more stable than its S(IV) analog (see Section 1.6).<sup>38</sup> In the S(IV) derivative polythiophosphazene,  $[-\text{PCl}_2=\text{N}-\text{PCl}_2=\text{N}-\text{S}(\text{Cl})=\text{N}-]_n$  (**25**), the replacement of one out of every three phosphorus atoms with one S(IV) center in the repeat chain of polyphosphazene  $[-\text{PCl}_2=\text{N}-\text{PCl}_2=\text{N}-\text{PCl}_2=\text{N}-]_n$  has significantly decreased the stability of the polymer backbone. In the polymer  $[-\text{R}_2\text{P}=\text{N}-\text{S}(\text{R})=\text{N}-]_n$  half of the phosphorus atoms would be replaced with S(IV) atoms so it is predicted that  $[-\text{R}_2\text{P}=\text{N}-\text{S}(\text{R})=\text{N}-]_n$  will be less stable than polythiophosphazene (**25**). The S(VI) polymer **26**, on the other hand, is more stable than the S(IV) polymer **25** so a S(VI)-containing PNSN polymer would be expected to be stable.

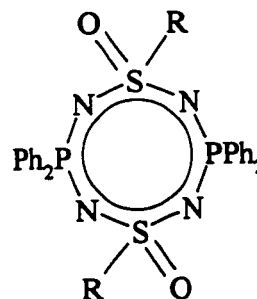


**Figure 3.1.** Proposed mechanism for ring opening polymerization of  $\text{Cl}_4\text{P}_2\text{N}_3\text{S}(\text{O})\text{Cl}$  (12).

The six-membered ring  $\text{Cl}_4\text{P}_2\text{N}_3\text{S}(\text{O})\text{Cl}$  (12) opens to give polymer 26 (Equation 1.7).<sup>59</sup> The polymerization is thought to be initiated by an S-Cl bond heterolysis which creates a cationic S center.<sup>58</sup> A nitrogen atom from another  $\text{Cl}_4\text{P}_2\text{N}_3\text{S}(\text{O})\text{Cl}$  (12) molecule acts as a nucleophile and attacks the  $\text{S}^+$  center causing the ring to open (Figure 3.1). The mechanism is similar to that of the ring opening proposed for cyclophosphazenes (Figure 1.6), but ionization occurs at the S(VI)-Cl bond rather than the P-Cl bond. The eight-membered ring  $1,5\text{-R}_4\text{P}_2\text{N}_4(\text{S}(\text{O})\text{Cl})_2$  (33) would have two S(VI)-Cl bonds like that which is responsible for the ring opening of  $\text{Cl}_4\text{P}_2\text{N}_3\text{S}(\text{O})\text{Cl}$  (12).



33



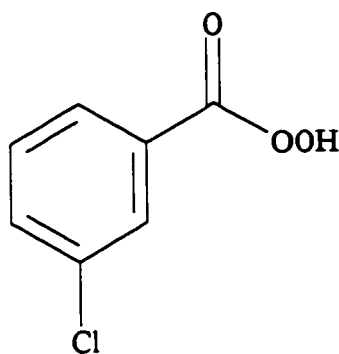
34a, R = Ph

34b, R = Me

Since the polymer  $[-R_2P=N-S(O)R'=N-]_n$  (**28**) is predicted to be a stable PNS(VI)N polymer it is of interest to investigate the synthesis of the corresponding eight-membered rings  $1,5\text{-Ph}_4\text{P}_2\text{N}_4[\text{S(O)R}]_2$  (**34**) as precursors to **28**. This chapter describes the synthesis of **34** by oxidation of the known S(IV) heterocycles  $1,5\text{-Ph}_4\text{P}_2\text{N}_4(\text{SR})_2$  (**21**) with *m*-chloroperbenzoic acid (*m*CPBA). The derivatives **21** were chosen for the initial investigation into the oxidation of S(IV) to S(VI) in this type of heterocycle because they are sufficiently stable to moisture and air. It is anticipated that this method of preparation of  $1,5\text{-Ph}_4\text{P}_2\text{N}_4[\text{S(O)R}]_2$  (R = Ph, Me) will be applicable to other  $1,5\text{-R}_4\text{P}_2\text{N}_4(\text{SR}')_2$  derivatives, which are more suitable precursors for the PNS(VI)N polymer  $[-R_2P=N-S(O)R'=N-]_n$  (**28**).

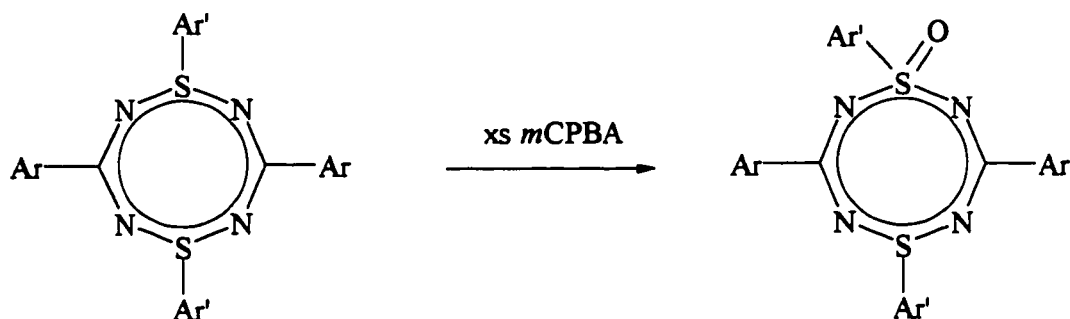
### 3.2 Synthesis of *trans*-1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)R]<sub>2</sub> (34a, R = Ph; 34b, R = Me).

The heterocycle 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)R]<sub>2</sub> (34) can be prepared by oxidizing 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SR)<sub>2</sub> with *m*-chloroperbenzoic acid (*m*CPBA) (35). The synthesis of 34a is performed at room temperature in THF. A solution of *m*CPBA in THF is added to a stirring slurry of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SR)<sub>2</sub> in THF. As the reaction proceeds the slurry turns from pale yellow to white. The product is soluble in THF so upon completion the reaction mixture becomes a colorless solution. The solvent is removed and the remaining solid is dissolved in CH<sub>2</sub>Cl<sub>2</sub>, washed with an aqueous NaHCO<sub>3</sub> solution to remove benzoic acid which is a byproduct of the reaction. Recrystallization of the product from hot CH<sub>3</sub>CN gives colorless crystals. The product has a <sup>31</sup>P NMR resonance at δ = +5.1 ppm and the IR spectrum reveals a S=O stretch at 1148 cm<sup>-1</sup>. The mass spectrum has a M<sup>+</sup> peak at *m/e* = 676 corresponding to the eight-membered ring 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)Ph]<sub>2</sub>. The crystals are thermally stable [mp = 233-235 °C] and are not sensitive to air or moisture.





The reaction between 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SPh)<sub>2</sub> (**21b**) and *m*CPBA can be monitored by <sup>31</sup>P NMR as **21b** has a chemical shift of δ = +30 ppm. The oxidation of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SPh)<sub>2</sub> (**21b**) requires four equivalents of *m*CPBA for complete conversion to 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)Ph]<sub>2</sub>. As the reaction proceeds three singlets appear at δ = +12.1, +10.5, +5.1 ppm and upon completion a major resonance at δ = +5.1 ppm remains. This resonance is due to the final product 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)Ph]<sub>2</sub> (**34a**). The other two are likely due to intermediates as excess *m*CPBA consumes the products with chemical shifts at +12.1 and +10.5 ppm and the reaction goes to completion. The nature of the intermediates is unknown, however it is likely that one is a monoxidized species since the oxidation of the related heterocycle 1,5-(*p*-Br-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C<sub>2</sub>N<sub>4</sub>[S(*p*-tolyl)]<sub>2</sub> only gives the mono-oxidized species 1,5-(*p*-Br-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C<sub>2</sub>N<sub>4</sub>S(O)(*p*-tolyl)S(*p*-tolyl) (Figure 3.2).<sup>76</sup> The white slurry observed during the reaction may be the mono-oxidized product 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)Ph][SPh]. It should also be noted that the conformation of the ring changes from a chair in **21b** to a twist boat structure in **34a**. Consequently, one of the intermediates may involve an oxidized product in which the P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> ring is in a conformation different from that of **34a**.



**Figure 3.2.** Synthesis of 1,5-(Ar)<sub>2</sub>C<sub>2</sub>N<sub>4</sub>S(O)(Ar')S(Ar') [Ar = *p*-Br-C<sub>6</sub>H<sub>4</sub>, Ar' = *p*-tolyl].

### 3.3 Synthesis of *trans*-1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)Me]<sub>2</sub> (34b).

The oxidation of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SMe)<sub>2</sub> with *m*CPBA (35) gives 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)Me]<sub>2</sub> (34b). The *m*CPBA is added to a stirring solution of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SMe)<sub>2</sub> in THF. Upon the addition the pale yellow solution turns a vibrant pink color which fades over a two hour period. The pink color may be due to a radical species as PNS rings are known to form radicals and *m*CPBA oxidizes via a radical process.<sup>77</sup> The pink species is undetectable by <sup>31</sup>P NMR. The reaction is readily monitored by <sup>31</sup>P NMR as the starting material peak at δ = +27 ppm disappears and a new resonance appears at δ = +4.2 ppm. The solvent is removed and an aqueous work-up similar to that described for 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)Ph]<sub>2</sub> (See Section 3.2) is used. The crude product can be recrystallized from a supersaturated solution of CH<sub>3</sub>Cl or hot CH<sub>3</sub>CN to give colorless crystals. The mass spectrum has an M<sup>+</sup> peak at *m/e* = 551 consistent with the formula 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)Me]<sub>2</sub>. The <sup>1</sup>H NMR exhibits a triplet at δ = 2.8 ppm corresponding to a

methyl group coupling to two equivalent phosphorus atoms. The IR spectrum shows a S=O stretch at  $1139\text{ cm}^{-1}$ . The product is stable to air and moisture. It melts with decomposition at  $256\text{-}257\text{ }^{\circ}\text{C}$ .

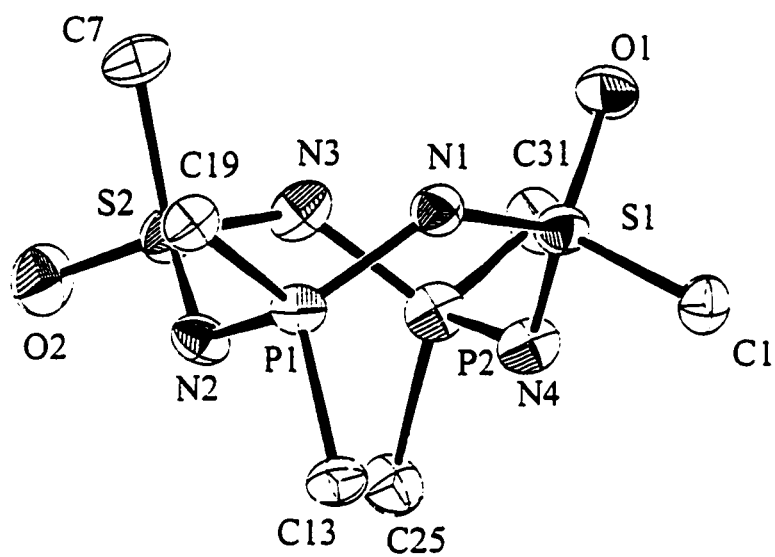
In contrast to the oxidation of  $1,5\text{-Ph}_4\text{P}_2\text{N}_4(\text{SPh})_2$ ,  $1,5\text{-Ph}_4\text{P}_2\text{N}_4(\text{SMe})_2$  requires only two equivalents of *m*CPBA to give the oxidized product  $1,5\text{-Ph}_4\text{P}_2\text{N}_4[\text{S(O)Me}]_2$  (**34b**). The difference in reactivity could arise from two different factors. The bulky phenyl groups attached to S in  $1,5\text{-Ph}_4\text{P}_2\text{N}_4(\text{SPh})_2$  may lead to longer reaction times which allows the *m*CPBA to decompose slowly in solution. A second contributing factor could be the type of organic group bonded to S and its electronic contribution to the oxidation of S(IV) to S(VI). In the case of  $1,5\text{-Ph}_4\text{P}_2\text{N}_4[\text{S(O)Me}]_2$  (**34b**) the electron-donating Me group may facilitate the oxidation at S while the electron-withdrawing phenyl groups bonded to S in  $1,5\text{-Ph}_4\text{P}_2\text{N}_4[\text{S(O)Ph}]_2$  (**34a**) could make the oxidation more difficult.

### 3.4 X-ray Structure of *trans* $1,5\text{-Ph}_4\text{P}_2\text{N}_4[\text{S(O)R}]_2$ (**34a**, R = Ph; **34b**, R = Me).

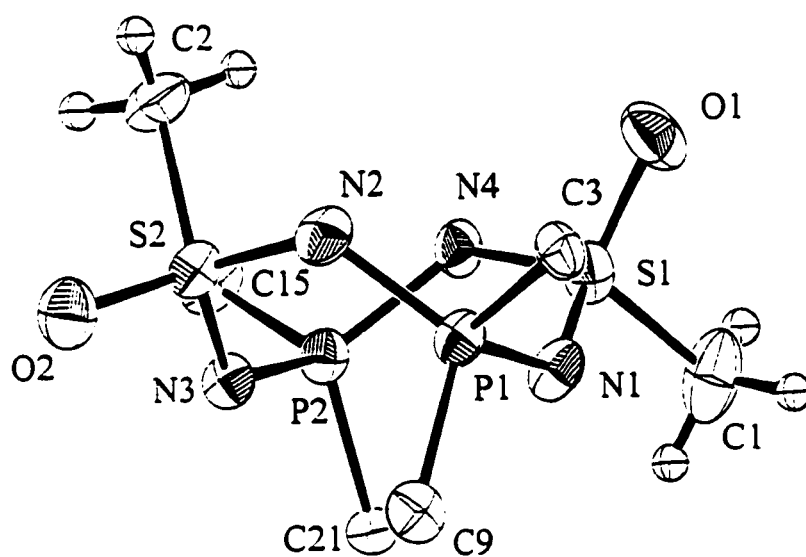
Crystals of  $1,5\text{-Ph}_4\text{P}_2\text{N}_4[\text{S(O)Ph}]_2$  (**34a**) were obtained by slow evaporation of a supersaturated solution of **34a** in  $\text{CHCl}_3$  and  $1,5\text{-Ph}_4\text{P}_2\text{N}_4[\text{S(O)Me}]_2$  (**34b**) was recrystallized from  $\text{CH}_3\text{CN}$  at  $-20^{\circ}\text{C}$ . The ORTEP drawings of  $1,5\text{-Ph}_4\text{P}_2\text{N}_4[\text{S(O)Ph}]_2$  (**34a**) and  $1,5\text{-Ph}_4\text{P}_2\text{N}_4[\text{S(O)Me}]_2$  (**34b**) are shown in Figure 3.3. The crystallographic parameters are listed in Table 3.1 and selected bond distances, bond angles and torsion angles can be found in Tables 3.2, 3.3 and 3.6, respectively. The structures of **34a** and **34b** have similar bond distances and bond angles and the  $\text{P}_2\text{N}_4\text{S}_2$  rings adopt twist boat structures. Further discussion on the ring

conformations is given in Section 3.5.1. The S-bonded oxygen atoms are in *trans* orientations with respect to each other in both **34a** and **34b**. The S-O bond distances [ $d(\text{S-O}) = 1.442(3)$  Å (**34a**) and  $1.443(5)$  Å (**34b**)] are consistent with a S(VI)=O bond [*cf.*  $d(\text{S-O}) = 1.417(3)$  Å in  $1,5\text{-(Me}_2\text{N)}_2\text{C}_2\text{N}_4[\text{S(O)N(CF}_3)_2]_2$ <sup>65</sup> and  $1.422(3)$  Å in  $\text{Cl}_4\text{P}_2\text{N}_3\text{S(O)Cl}^{35}$ ]

The structure of the starting material  $1,5\text{-Ph}_4\text{P}_2\text{N}_4(\text{SPh})_2$  (**21b**) is known and can be compared to that of the product  $1,5\text{-Ph}_4\text{P}_2\text{N}_4(\text{S(O)Ph})_2$  (**34a**).<sup>45</sup> No change is observed in the mean P-N bond distance, but there is a contraction in the mean S-N bond distance from  $1.622(5)$  Å in **21b** to  $1.564(4)$  Å in **34a** upon oxidation of the S atoms. There is an increase in the mean NSN bond angle from  $108.8(2)^\circ$  in **21b** to  $113.0(2)^\circ$  as the ring structure changes from chair to twist-boat and there is increased coordination at S. There is an increase in the SNP bond angle from  $117.4(3)^\circ$  for  $1,5\text{-Ph}_4\text{P}_2\text{N}_4(\text{SPh})_2$  to  $123.9(3)^\circ$  in  $1,5\text{-Ph}_4\text{P}_2\text{N}_4[\text{S(O)Ph}]_2$ .



34a



34b

**Figure 3.3.** ORTEP drawings of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(S(O)R)<sub>2</sub> (34a R = Ph, 34b R = Me) [For clarity only  $\alpha$  carbons on P are shown].

**Table 3.1.** Crystallographic Parameters for 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)R]<sub>2</sub> (**34a**, R = Ph; **34b**, R = Me).

	<b>34a</b>	<b>34b</b>
Empirical Formula	C <sub>36</sub> H <sub>30</sub> O <sub>2</sub> N <sub>4</sub> P <sub>2</sub> S <sub>2</sub>	C <sub>26</sub> H <sub>26</sub> O <sub>2</sub> N <sub>4</sub> P <sub>2</sub> S <sub>2</sub>
Formula Weight	676.73	552.58
Crystal Color, Habit	colorless, prism	colorless, plate
Crystal Dimensions	0.60 X 0.40 X 0.37 mm	0.60 X 0.30 X 0.09 mm
Crystal System	monoclinic	monoclinic
Lattice Parameters	a = 10.173(3) Å b = 18.030(3) Å c = 17.920(2) Å β = 91.47° (1) V = 3285(1) Å <sup>3</sup>	a = 10.616(2) Å b = 17.883(3) Å c = 14.133(5) Å β = 97.00 (3)° V = 2655(1) Å <sup>3</sup>
Space Group	P2 <sub>1</sub> /n (#14)	P2 <sub>1</sub> /n (#14)
Z value	4	4
D <sub>calc</sub>	1.368 g/cm <sup>3</sup>	1.382 g/cm <sup>3</sup>
Temperature	-73.0° C	-73.0° C
R	0.045	0.049
R <sub>w</sub>	0.043	0.049

**Table 3.2** Selected Bond Lengths of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)R]<sub>2</sub> (**34a**, R = Ph; **34b**, R = Me).

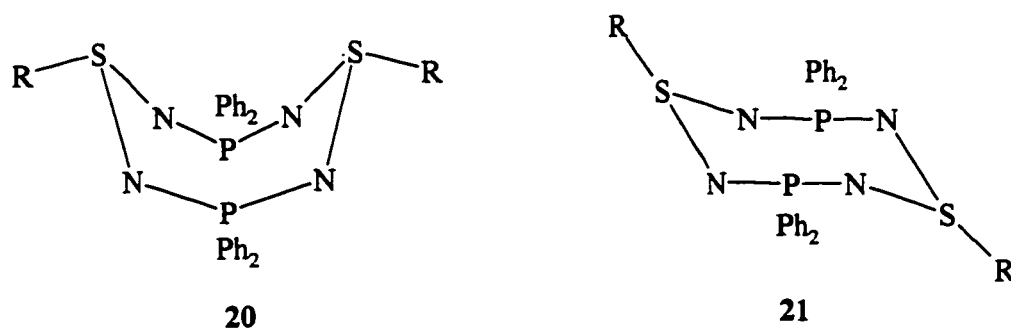
Atoms	Bond Lengths (Å)	
	<b>34a</b>	<b>34b</b>
S(1)-O(1)	1.445(3)	1.442(5)
S(2)-O(2)	1.439(3)	1.444(5)
S(1)-N(1)	1.561(4)	1.560(6)
S(1)-N(4)	1.567(4)	1.574(5)
S(2)-N(2)	1.572(4)	1.559(5)
S(2)-N(3)	1.555(4)	1.552(5)
P(1)-N(1)	1.618(4)	1.608(5)
P(1)-N(2)	1.616(4)	1.616(5)
P(2)-N(3)	1.604(4)	1.621(5)
P(2)-N(4)	1.618(4)	1.625(5)
S(1)-C(1)	1.782(5)	1.763(8)
S(1)-C(7)	1.777(5)	
S(1)-C(2)		1.757(7)

**Table 3.3.** Selected Bond Angles of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)R]<sub>2</sub> (**34a**, R = Ph; **34b**, R = Me).

Atoms	Bond Angles (°)	
	<b>34a</b>	<b>34b</b>
N(1)-S(1)-N(4)	113.5(2)	113.8(3)
N(2)-S(2)-N(3)	112.6(2)	113.3(3)
S(1)-N(1)-P(1)	126.6(3)	128.7(4)
S(1)-N(4)-P(2)	122.1(3)	123.3(3)
S(2)-N(2)-P(1)	127.4(2)	124.1(3)
S(2)-N(3)-P(2)	127.3(3)	126.6(4)
N(1)-P(1)-N(2)	118.9(2)	119.0(3)
N(3)-P(2)-N(4)	118.5(2)	119.1(3)

### 3.5 Synthesis of *cis*-1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)Me]<sub>2</sub> (**34b'**).

Various routes can be used to prepare 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SR)<sub>2</sub> (see Section 1.4.3). The reaction of Li[Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Me] with MeI allows for the isolation of boat (**20**) and chair (**21**) conformations of the ring as shown in Figure 3.4.<sup>48</sup> The boat conformation of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SMe)<sub>2</sub> has been isolated, however it readily converts to the chair form with slight warming in CH<sub>2</sub>Cl<sub>2</sub> (Figure 1.5). The synthesis of *trans*-1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)Me]<sub>2</sub> (**34b**), described in Section 3.3, was performed using the chair conformation of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SMe)<sub>2</sub> (**21**, R = Me). The orientation of the S atoms in the chair form of **21** allows for attack by *m*CPBA to occur in a *trans* manner, whereas in the boat conformation oxidation at S will give rise to O atoms which are in *cis* (or *endo*) positions with respect to the P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> ring.



**Figure 3.4.** Boat (**20**) and chair (**21**) conformations of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SR)<sub>2</sub>



One of the byproducts of the synthesis of **20** and **21** is LiI which is normally removed by washing the product with toluene or CH<sub>2</sub>Cl<sub>2</sub>. The boat conformation is thermally unstable so the oxidation with *m*CPBA was performed *in situ*, i.e. without removing LiI. An extra two equivalents of *m*CPBA was added in order to convert LiI to I<sub>2</sub> and prevent any interference with the reaction between *m*CPBA and the boat form of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SMe)<sub>2</sub>. The reaction of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SMe)<sub>2</sub> (**20a**, R = Me) with *m*CPBA is readily monitored by <sup>31</sup>P NMR. The resonance for **20a** (δ = +14 ppm) disappears and a major product is observed at δ = +3.4 ppm along with a minor product (20% by integration) at δ = +4.2 ppm, which on the basis of its chemical shift, is *trans*-1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)Me]<sub>2</sub>. The solvent is removed from the reaction mixture and the remaining solid is subjected to an aqueous work-up like that described for 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)Ph]<sub>2</sub> (see Section 3.2). The <sup>1</sup>H NMR spectrum of the crude product exhibits a methyl resonance for the *trans* isomer at δ = 2.8 ppm and a larger overlapping triplet at δ = 2.9 ppm with a similar coupling constant [<sup>4</sup>J(<sup>1</sup>H-<sup>31</sup>P) = 1.7 Hz] to that found for the *trans* product 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)Me]<sub>2</sub> [<sup>4</sup>J(<sup>1</sup>H-<sup>31</sup>P) = 1.7 Hz].

The product with the δ(<sup>31</sup>P) = 3.4 ppm is isolated by recrystallization from hot toluene to give a white powder. The mass spectrum of the white powder shows a M<sup>+</sup> peak at m/e = 551 consistent with the composition of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)Me]<sub>2</sub> and the <sup>1</sup>H NMR spectrum has a triplet at δ = 2.9 ppm corresponding to the S bonded methyl group coupling to two equivalent P atoms. The melting point of the white powder is 222°C (with decomposition) while the melting point of *trans*-1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)Ph]<sub>2</sub> is 256°C

(with decomposition). The IR spectrum has an S=O stretch at  $1128\text{ cm}^{-1}$ . In summary, the combined spectroscopic data suggest that this product is an isomer of *trans*-1,5- $\text{Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Me}]_2$ . Consequently, an X-ray structural determination was carried out.

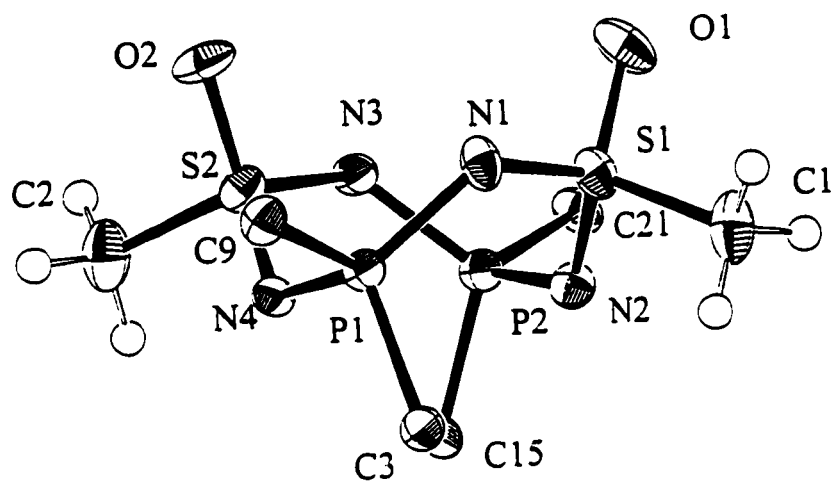
### 3.5.1 X-ray structure of *cis*-1,5- $\text{Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Me}]_2$ (**34b'**).

Crystals of *cis*-1,5- $\text{Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Me}]_2$  (**34b'**) were grown in a solution of  $\text{CH}_2\text{Cl}_2$  and hexane at room temperature. The crystal was mounted in a capillary with a small amount of the mother liquor as previous crystals had turned to powder due to a loss of solvent. Interestingly, no solvent was found in the crystal lattice of **34b'**. The product was revealed to be *cis*-1,5- $\text{Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Me}]_2$ . For comparison, the ORTEP drawings of both *cis* and *trans* isomers of 1,5- $\text{Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Me}]_2$  are shown in Figure 3.5. The crystallographic parameters are listed in Table 3.4 and selected bond distances, bond angles and torsion angles can be found in Tables 3.5 and 3.6, respectively.

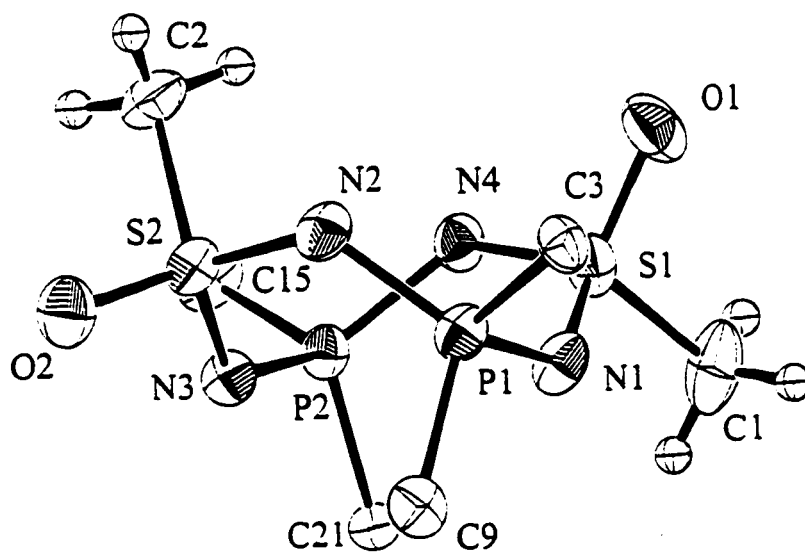
The structure of *cis*-1,5- $\text{Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Me}]_2$  (**34b'**) has similar bond distances and bond angles to those of *trans*-1,5- $\text{Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Me}]_2$  (**34b**). The mean S=O bond distance for **34b'** is  $1.443(3)\text{ \AA}$  [cf  $d(\text{S}-\text{O}) = 1.443(5)\text{ \AA}$  for **34b**]. The mean S-N bond lengths are  $1.566(4)\text{ \AA}$  in the *cis* isomer (**34b'**) and  $1.561(6)\text{ \AA}$  in the *trans* isomer (**34b**) while the mean P-N bond distances are  $1.618(4)\text{ \AA}$  for **34b'** and  $1.618(5)\text{ \AA}$  in **34b**. The mean NPN bond angle in **34b'** is  $118.6(2)^\circ$  which is equal within error to the mean NPN bond angle found in **34b** ( $\angle\text{NPN} = 118.7(2)^\circ$ ). The mean SNP and NSN bond angles for *cis*-1,5-

$\text{Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Me}]_2$  (**34b'**) are  $123.2(6)^\circ$  and  $112.6(2)^\circ$ , respectively [cf.  $\angle\text{SNP} = 125.7(4)^\circ$  and  $\angle\text{NSN} = 113.6(3)^\circ$  for *trans*-1,5- $\text{Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Me}]_2$  (**34b**)].

The torsion angles for *trans*-1,5- $\text{Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Ph}]_2$  (**34a**), *trans*-1,5- $\text{Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Me}]_2$  (**34b**) and *cis*-1,5- $\text{Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Me}]_2$  (**34b'**) are given in Table 3.6. All three structures have a twist boat ring conformation however, the twist boat ring conformation of *trans*-1,5- $\text{Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Me}]_2$  differs significantly from those of **34a** and **34b'**. This difference is evident in the torsion angles, for example, the torsion angle for S(1)-N(1)-P(1)-N(2) is  $-53.0(4)^\circ$  for *trans*-1,5- $\text{Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Ph}]_2$  (**34a**) and  $-57.5(4)^\circ$  for *cis*-1,5- $\text{Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Me}]_2$  (**34b'**), but this torsion angle in *trans*-1,5- $\text{Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Me}]_2$  (**34b**) is  $31.6(6)^\circ$ . Many eight-membered cyclophosphazenes have been structurally characterized and it has been found that the  $\text{P}_4\text{N}_4$  ring adopts various types of ring conformations. The different ring conformation in each structure arises from both inter- and intra-molecular forces including steric factors, crystal packing, and orientation and polarity of substituents therefore, the difference in ring conformations found for **34a**, **34b** and **34b'** could be due to a combination of these factors.<sup>5</sup>



34b'



34b

**Figure 3.5.** ORTEP diagrams of *cis*-1,5- $\text{Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Me}]_2$  (34b') and *trans*-1,5- $\text{Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Me}]_2$  (34b) [For clarity only the  $\alpha$  carbon atoms on P are shown].

**Table 3.4.** Crystallographic Parameters for *cis*-1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)Me]<sub>2</sub> (**34b'**).

	<b>34b'</b>
Empirical Formula	C <sub>26</sub> H <sub>26</sub> O <sub>2</sub> N <sub>4</sub> P <sub>2</sub> S <sub>2</sub>
Formula Weight	552.58
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.70 X 0.40 X 0.30 mm
Crystal System	monoclinic
Lattice Parameters	a = 10.536(3) Å b = 17.219(2) Å c = 15.085(3) Å β = 109.45 (2)° V = 2580.5(9) Å <sup>3</sup>
Space Group	P2 <sub>1</sub> /n (#14)
Z value	4
D <sub>calc</sub>	1.422 g/cm <sup>3</sup>
Temperature	-73.0° C
R	0.045
R <sub>w</sub>	0.042

**Table 3.5.** Selected Bond Lengths and Bond Angles of *cis*-1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)Me]<sub>2</sub> (**34b'**).

Atoms	Bond Lengths (Å)	Atoms	Bond Angles (°)
S(1)-O(1)	1.438(3)	N(1)-S(1)-N(2)	112.5(2)
S(2)-O(2)	1.448(3)	N(3)-S(2)-N(4)	112.7(2)
S(1)-N(1)	1.577(3)	S(1)-N(1)-P(1)	122.5(2)
S(1)-N(2)	1.562(4)	S(1)-N(2)-P(2)	123.8(2)
S(2)-N(3)	1.570(3)	S(2)-N(3)-P(2)	123.2(2)
S(2)-N(4)	1.555(4)	S(2)-N(4)-P(1)	123.4(2)
P(1)-N(1)	1.609(4)	N(1)-P(1)-N(4)	118.8(2)
P(1)-N(4)	1.621(4)	N(2)-P(2)-N(3)	118.4(2)
P(2)-N(2)	1.620(4)		
P(2)-N(4)	1.620(4)		
S(1)-C(1)	1.765(5)		
S(2)-C(2)	1.758(5)		

**Table 3.6.** Selected Torsion Angles of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)R]<sub>2</sub> (R = Ph, **34a**; R = Me, *trans* **34b**; R = Me *cis*, **34b'**).

Atoms	Torsion Angles (°)		
	<b>34a</b>	<b>34b</b>	<b>34b'</b> *
S(1)-N(1)-P(1)-N(2)	-53.0(4)	31.6(6)	-57.5(4)
S(2)-N(3)-P(2)-N(4)	-57.7(4)	34.3(5)	-55.2(3)
S(1)-N(4)-P(2)-N(3)	-38.9(4)	61.5(5)	-32.7(4)
S(2)-N(2)-P(1)-N(1)	-35.6(4)	61.8(5)	-30.9(3)
P(2)-N(4)-S(1)-N(1)	82.0(3)	-22.2(5)	83.6(3)
P(1)-N(2)-S(2)-N(3)	73.1(4)	-19.3(5)	83.9(3)
P(1)-N(1)-S(1)-N(4)	8.9(4)	-69.6(5)	7.1(4)
P(2)-N(3)-S(2)-N(2)	19.8(4)	-73.8(5)	5.2(4)

\* N(2) in **34a** and **34b** is N4 in **34b'**

### 3.6 Conclusions.

The synthesis of the novel eight-membered S(VI) heterocycle *trans*-1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)R]<sub>2</sub> (R = Ph, Me) was achieved by treating 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SR)<sub>2</sub> with the oxidizing agent *m*CPBA. The ring conformation of the starting material allows for control over stereochemistry in the synthesis of these S(VI) eight-membered heterocycles with the formula 1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)R']<sub>2</sub>. When the chair form of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SR)<sub>2</sub> was reacted with *m*CPBA the products obtained were structurally characterized and found to have the O atoms in a *trans* orientation with respect to each other. Subsequently, it was shown that the treatment of the boat conformation of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SMe)<sub>2</sub> results in the *cis* isomer of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)Me]<sub>2</sub>. The only other known PNS(VI)N eight-membered ring is (NPCl<sub>2</sub>)<sub>3</sub>NS(O)Cl which has one S(VI) center.<sup>51</sup> Therefore these are the first structurally characterized eight-membered PNS heterocycles that contain two S(VI) centers.

The investigation into the preparation of eight-membered PNS(VI)N rings could be extended to 1,5-R<sub>4</sub>P<sub>4</sub>N<sub>4</sub>[S(O)Cl]<sub>2</sub> (**33**) which can act as a precursor to S(VI) polymers of the type [-R<sub>2</sub>P=N-S(O)R'=N-] (**28**). One pathway to **33** would involve the preparation of the heterocycle 1,5-R<sub>4</sub>P<sub>4</sub>N<sub>4</sub>[S(O)NMe<sub>2</sub>]<sub>2</sub> (**36**) via the oxidation of 1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SMe<sub>2</sub>)<sub>2</sub>. Subsequently, **36** could be treated with a chlorinating agent like HCl to give the desired product 1,5-R<sub>4</sub>P<sub>4</sub>N<sub>4</sub>[S(O)Cl]<sub>2</sub> (**33**) (Figure 3.6). It has been shown that *m*CPBA oxidizes the eight-membered S(IV) heterocycles 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SR)<sub>2</sub> (R = Ph, Me) to their S(VI)

counterparts. Perhaps other S(VI) eight-membered rings can be prepared leading to the PNS(VI)N polymer system  $[-R_2P=N-S(O)R'=N-]_n$  (28).

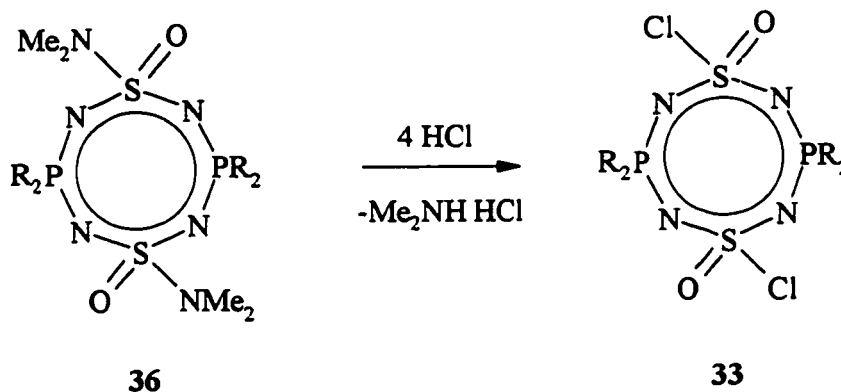


Figure 3.6. Proposed synthetic route to 1,5- $R_4P_2N_4[S(O)Cl]_2$ .

### 3.7 Experimental Section.

#### 3.7.1 Reagents and General Procedures.

Solvents were dried and distilled before use: tetrahydrofuran, diethyl ether, toluene, hexane (Na/benzophenone), acetonitrile and methylene chloride ( $P_4O_{10}$  and  $CaH_2$ ).  $SO_2Cl_2$  was distilled prior to use.  $CH_3I$  was purified by passing it through a column of alumina. The purification of *m*CPBA was performed by using literature procedures.<sup>78</sup> Other reagents were used as received:  $PCl_3$ ,  $Ph_2PCl$ ,  $Me_3SiN_3$ ,  $SOCl_2$ ,  $MeLi$ ,  $Li[N(SiMe_3)]_2$ ,  $PhSSPh$ ,  $Me_3SiNMe_2$ . The compounds 1,5- $Ph_4P_2N_4S_2$ ,<sup>50</sup> 1,5- $Ph_4P_2N_4(SPh)_2$ ,<sup>46</sup> 1,5- $Ph_4P_2N_4(SMe)_2$ <sup>49</sup> and  $PhSCl$ <sup>79</sup> were prepared by literature methods.



The handling of air and moisture sensitive reagents was performed under an atmosphere of argon or nitrogen.

### 3.7.2 Instrumentation.

$^{31}\text{P}$  NMR spectra were recorded on a Varian XL-200 instrument and the chemical shifts are relative to external standards, 85%  $\text{H}_3\text{PO}_4$  in  $\text{CDCl}_3$ .  $^1\text{H}$  NMR spectra were collected on a Bruker AM-200 spectrometer. Infrared spectra were obtained on a Mattson 4030 FTIR spectrophotometer. Elemental analyses and electron impact (70eV) mass spectra were provided by the Analytical Services Laboratory of the Department of Chemistry, The University of Calgary. X-ray data were collected on a Rigaku AFC6S diffractometer using the  $\omega$ -2 $\theta$  technique and Mo  $\text{K}\alpha$  radiation. The solution and refinement of structures were performed by Dr. M. Parvez.

### 3.7.3 Synthesis of *trans*-1,5- $\text{Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Ph}]_2$ (34a).

A solution of *m*CPBA (0.146g, 0.844 mmol) in THF (*ca.* 25 mL) was added dropwise to a stirred slurry of 1,5- $\text{Ph}_4\text{P}_2\text{N}_4(\text{SPh})_2$  (0.136g, 0.211 mmol) in THF (*ca.* 25 mL) at 25°C. The pale yellow slurry changed to a white slurry then to a colorless solution over one hour. The solvent was removed by vacuum, leaving a white solid. The solid was dissolved in  $\text{CH}_2\text{Cl}_2$  (*ca.* 75 mL) and treated with an aqueous solution of  $\text{NaHCO}_3$  (0.7 g, 8.4 mmol). The organic layer was isolated, dried with anhydrous  $\text{MgSO}_4$  and purified by passing through a column of silica. The solvent was removed under vacuum leaving an

off-white solid. The product was recrystallized by slow evaporation of  $\text{CHCl}_3$  from a saturated solution to give 1,5- $\text{Ph}_4\text{P}_2\text{N}_4(\text{S}(\text{O})\text{Ph})_2$  (0.153 mmol, 0.104 g, 73%). Anal. Calcd. (still need to obtain) IR (Nujol,  $\text{cm}^{-1}$ ) 1458 s, 1374 a, 1240 s, 1218 s, 1148 vs, 1117 vs, 1023 m, 996 m, 870 m, 790 w, 747 m, 690 s, 558 m, 517 w, 449 w. NMR spectra ( $\delta$ , ppm) ( $\text{CDCl}_3$ ):  $^{31}\text{P}\{^1\text{H}\}$  +5.1,  $^1\text{H}$  7.6-7.9, 7.0-7.4 (m,  $\text{C}_6\text{H}_5$ ). MS ( $m/e$ ): 676 (100%,  $\text{M}^+$ ). mp: 233-235°C.

#### 3.7.4 Synthesis of *trans*-1,5- $\text{Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Me}]_2$ (34b).

A solution of *m*CPBA (0.052g, 0.300 mmol) in THF (*ca.* 25 mL) was added dropwise to a stirred slurry of the chair isomer of 1,5- $\text{Ph}_4\text{P}_2\text{N}_4(\text{SMe})_2$  (0.078g, 0.150 mmol) in THF (*ca.* 25 mL) at 25°C. The pale yellow solution turned pink during the addition. After stirring for two hours the solution turned to a pale yellow color and the solvent was removed by vacuum leaving a yellow solid. The solid was dissolved in  $\text{CH}_2\text{Cl}_2$  (*ca.* 50 mL) and treated with an aqueous solution of  $\text{NaHCO}_3$  (0.252g, 3.00 mmol). The organic layer was isolated, dried with anhydrous  $\text{MgSO}_4$  and filtered. The  $\text{CH}_2\text{Cl}_2$  was removed under vacuum leaving a yellow solid. The product was recrystallized from  $\text{CH}_3\text{CN}$  at -20°C to give colorless needles of 1,5- $\text{Ph}_4\text{P}_2\text{N}_4[\text{S}(\text{O})\text{Me}]_2$  (0.0272g, 0.049 mmol, 35%). Anal. Calcd. for  $\text{C}_{26}\text{H}_{26}\text{P}_2\text{N}_4\text{S}_2\text{O}_2$ : C, 56.51; H, 4.74; N, 10.14. Found: C, 56.29; H, 4.74; N, 10.14. IR (Nujol,  $\text{cm}^{-1}$ ) 1462 vs, 1376 vs, 1226 m, 1193 m, 1171 m, 1156 s, 1139 s, 1112 s, 1077 w, 1025 w, 977 w, 954 w, 845 w, 747 w, 725 w, 693 m, 686 w. NMR spectra ( $\delta$ , ppm) ( $\text{CDCl}_3$ ):  $^{31}\text{P}\{^1\text{H}\}$  +4.2.  $^1\text{H}$  7.8-8.0, 7.4-7.6 (m,  $\text{C}_6\text{H}_5$ ) 2.8 [t,

$^4J(^1\text{H}-^{31}\text{P}) = 1.7 \text{ Hz, SCH}_3]$ . MS ( $m/e$ ): 551 (100%,  $M^+$ ). mp: 256-257 °C with decomposition.

### 3.7.5 Synthesis of *cis*-1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SMe)<sub>2</sub> (21).

The boat isomer of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SMe)<sub>2</sub> (0.175 mmol) was prepared in THF (*ca.* 25 mL) by the reaction of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> with MeLi to give [1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Me][Li] which was subsequently reacted with MeI. The reaction mixture was then treated, *in situ*, with *m*CPBA (0.061g, 0.350 mmol) in THF (*ca.* 25 mL). The reaction mixture turned orange during the addition of *m*CPBA with the color becoming less intense upon completion. The solvent was removed by vacuum and the yellow solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (*ca.* 50 mL) and treated with aqueous NaHCO<sub>3</sub> (0.287g, 3.50 mmol). The organic layer was collected, dried with anhydrous MgSO<sub>4</sub> and filtered. The solvent was removed and the yellow solid was recrystallized from hot toluene to give a colorless crystalline solid (0.060g, 0.108 mmol, 62%). Anal. Calcd. for C<sub>26</sub>H<sub>26</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>O<sub>2</sub>: C, 56.51; H, 4.74; N, 10.14. Found: C, 55.70; H, 4.62; N, 9.78. IR (Nujol, cm<sup>-1</sup>) 1461 vs, 1378 s, 1260 w, 1225 m, 1128 s, 1171 m, 1024 m, 978 w, 841 w, 809 w, 752 w, 720 m, 696 m, 564 w, 543 m. NMR spectra (δ, ppm) (CDCl<sub>3</sub>): <sup>31</sup>P{<sup>1</sup>H} +3.4, <sup>1</sup>H 7.4-8.3 (m, C<sub>6</sub>H<sub>5</sub>) 2.9 [t, <sup>4</sup>J(<sup>1</sup>H-<sup>31</sup>P) = 1.7 Hz, SCH<sub>3</sub>]. MS ( $m/e$ ): 551 (100%,  $M^+$ ). mp: 222 °C with decomposition.

## CHAPTER 4

### Conclusions and Future Work

#### 4.1 Conclusions

The main objective of this thesis was to synthesize new S(IV) and S(VI) containing eight-membered PN heterocycles as potential precursors to hybrid PNSN polymers. In order to prepare new S,S-disubstituted S(IV) rings, 1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (R = Et, Ph) was used as it possesses two reactive S-Cl bonds which can undergo nucleophilic substitution. The derivative 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> is known and the new compound 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29a**) was prepared by a similar route, i.e. the oxidation of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> with SO<sub>2</sub>Cl<sub>2</sub>. Structural data were obtained on the product 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29a**), which was found to have a distorted chair conformation with S-Cl bond distances that differ by 0.18 Å. The structure of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29a**) is similar to that of the ionic compound [1,5-(Me<sub>2</sub>N)<sub>2</sub>C<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl][Cl<sub>3</sub>] suggesting that **29a** consists of an incipient cation, 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sup>+</sup>, ionically bonded to a chloride anion (see Figure 2.3). The mechanism of oxidative addition of X<sub>2</sub> (X = Cl, Br) across the S-S transannular bond of 1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> is proposed to occur by trans oxidative addition (see Figure 1.4) and the structure of Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29a**) offers further support for this mechanism.

The reaction of 1,5- $R_4P_2N_4S_2Cl_2$  ( $R = Et, Ph$ ) with  $AlCl_3$  gives the dicationic species 1,5- $R_4P_2N_4S_2^{2+}$  whose ring structure was shown to have a planar conformation and bond distances consistent with two sulfur diimides bridged by two  $R_2P^+$  groups (see Figure 2.6). In the isoelectronic rings 1,5- $(Me_2Si)_2N_4S_2^{72}$  and 1,5- $(RE)_2N_4S_2$  ( $E = As, Sb$ )<sup>68,73</sup> the rings adopt a boat conformation. In the neutral ring systems 1,5- $(tBu_2Si)_2N_4S_2$  ( $E = Si, R = tBu$ )<sup>70</sup> and 1,5- $[P(N^iPr_2)(Cr(CO)_5)]_2N_4S_2$  [ $E = P, R = N^iPr_2, R' = Cr(CO)_5$ ]<sup>71</sup> planar ring conformations are found to occur when  $R_2E$  is sterically demanding. However, in the case of 1,5- $Et_4P_2N_4S_2^{2+}$ , the ethyl group on phosphorus is not sterically demanding and this argument is no longer valid.

The monofunctional six-membered ring  $Ph_4P_2N_3SNMe_2$  ring opens to give the corresponding twelve-membered ring  $Ph_8P_4N_6(SNMe_2)_2$ <sup>24</sup> so it was of interest to prepare the eight-membered heterocycles 1,5- $R_4P_2N_4(SNMe_2)_2$  in order to determine if this difunctional system undergoes ring opening to give macrocycles or polymers. The heterocycles 1,5- $R_4P_2N_4(SNMe_2)_2$  ( $R = Et, Ph$ ) were prepared by reacting 1,5- $R_4P_2N_4S_2Cl_2$  with  $Me_2NSiMe_3$ . Structural characterization of both 1,5- $Et_4P_2N_4(SNMe_2)_2$  and 1,5- $R_4P_2N_4(SNMe_2)_2$  was performed and these rings are the first examples of S,S-dialkylamino-substituted diphosphadithiatetrazocines.

The heterocycle 1,5- $Et_4P_2N_4(SNMe_2)_2$  was found to have a chair conformation with normal bond distances and bond angles. However, the structure of 1,5- $Ph_4P_2N_4(SNMe_2)_2$  has a distorted chair conformation with a short mean exocyclic S-N bond distance of 1.675(2) Å and endocyclic S-N bond distances of 1.586(3) Å and

1.603(2) Å. It was suggested that the distorted boat structure and the varying S-N bond distances could be a result of  $\pi$  donation of the lone pair from the exocyclic N atoms into the  $P_2N_4S_2$   $\pi$  system, which is facilitated by the electron-withdrawing phenyl groups bonded to P. The electron-donating ethyl groups in 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> do not encourage this type of  $\pi$  interaction and as a result there are no observed distortions in S-N bond distances or the P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> ring.

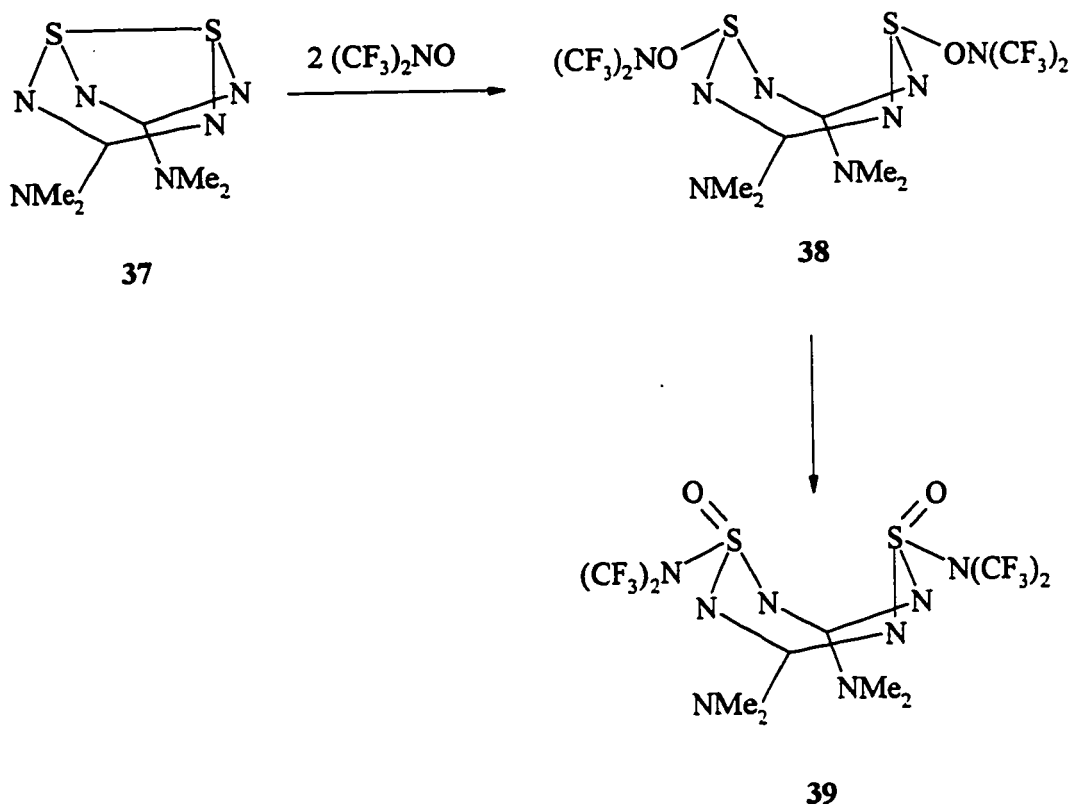
The S(VI) polymer [-PCl<sub>2</sub>=N-PCl<sub>2</sub>=N-S(O)Cl=N-]<sub>n</sub> (**26**) is stable<sup>58</sup> and it has been predicted that the polymer [-R<sub>2</sub>P=N-S(O)R'=N-]<sub>n</sub> (**28**) will also be a stable PNS(VI)N polymer. Consequently, the investigation of the synthesis of the corresponding eight-membered rings 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)R]<sub>2</sub> (**34**) as precursors to **28** was pursued. The novel eight-membered S(VI) heterocycles 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)R]<sub>2</sub> (R = Ph, Me) were prepared by oxidizing the corresponding S(IV) heterocycles 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SR)<sub>2</sub> (R = Ph, Me) with the oxidizing agent *m*CPBA. The products were structurally characterized and it was found that the oxidation of the chair forms of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SR)<sub>2</sub> (R = Ph, Me) gave *trans*-1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)R]<sub>2</sub> (R = Ph, Me) with respect to the orientation of the oxygen atoms on S. The oxidation of the boat form of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SMe)<sub>2</sub> gave, on the basis of spectroscopic characterization, an isomer of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)Me]<sub>2</sub>, and upon structural characterization it was shown that the product is *cis*-1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)Me]<sub>2</sub>. All three structures had similar bond lengths and bond angles and twist boat ring conformations, however the degree and direction of twisting of the ring varies between the structures. The only other known PNS(VI)N eight-membered ring is (NPCI<sub>2</sub>)<sub>3</sub>NS(O)Cl which has one S(VI)

center.<sup>51</sup> Therefore these are the first structurally characterized eight-membered PNS heterocycles that contain two S(VI) centers.

## 4.2 Future Work

### 4.2.1. Alkoxy Derivatives of $P_2N_4S(IV)_2$ Rings

It has been shown that 1,5- $R_4P_2N_4S_2Cl_2$  (**29a** and **29b**) undergoes nucleophilic substitution with  $Me_2NSiMe_3$  so it would be of interest to investigate the reaction of the dichlorides with other nucleophiles. Several alkoxy derivatives of phosphazenes, thiophosphazenes and thionylphosphazenes have been prepared by reacting the P-Cl or S-Cl bonds with metal alkoxides. Preliminary investigations of the reaction of 1,5- $Ph_4P_2N_4S_2Cl_2$  (**29b**) with  $KO^tBu$  show the formation of two products in the  $^{31}P$  NMR at  $\delta = +1.6$  ppm and  $\delta = -1.4$  ppm in a ratio of 1:2, respectively. Similar results were observed in the reaction of **29b** with  $NaOCH_2CF_3$  where two products with  $\delta(^{31}P) = +3.7$  ppm and  $+2.3$  ppm were formed in a ratio of approximately 2:1. The addition of excess  $KO^tBu$  or  $NaOCH_2CF_3$  does not alter this ratio, therefore it is unlikely that one of the products is a monosubstituted and the second a disubstituted derivative. In both cases the products decomposed over a 24 hour period at 23°C giving very complex  $^{31}P$  NMR spectra.



**Figure 4.1.** The synthesis and rearrangement of 1,5-(Me<sub>2</sub>N)<sub>2</sub>C<sub>2</sub>N<sub>4</sub>[SON(CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (**38**) to 1,5-(Me<sub>2</sub>N)<sub>2</sub>C<sub>2</sub>N<sub>4</sub>[S(O)N(CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (**39**).

In previous work the heterocycle 1,5-(Me<sub>2</sub>N)<sub>2</sub>C<sub>2</sub>N<sub>4</sub>S<sub>2</sub> (**37**) was treated with (CF<sub>3</sub>)<sub>2</sub>NO with the intention of preparing the S(IV) containing 1,5-(Me<sub>2</sub>N)<sub>2</sub>C<sub>2</sub>N<sub>4</sub>[SON(CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (**38**) however, this surprisingly rearranged to make the S(VI) containing ring 1,5-(Me<sub>2</sub>N)<sub>2</sub>C<sub>2</sub>N<sub>4</sub>[S(O)N(CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (**39**) as determined by X-ray crystallography (Figure 4.1).<sup>65</sup> In light of these results the products of the reaction of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (**29b**) with KO<sup>t</sup>Bu (**40a**) or NaOCH<sub>2</sub>CF<sub>2</sub> (**40b**) could be a mixture of the S(IV) and S(VI) derivatives (Figure 4.2). Further investigations into these reactions are required to isolated and characterize the products formed.



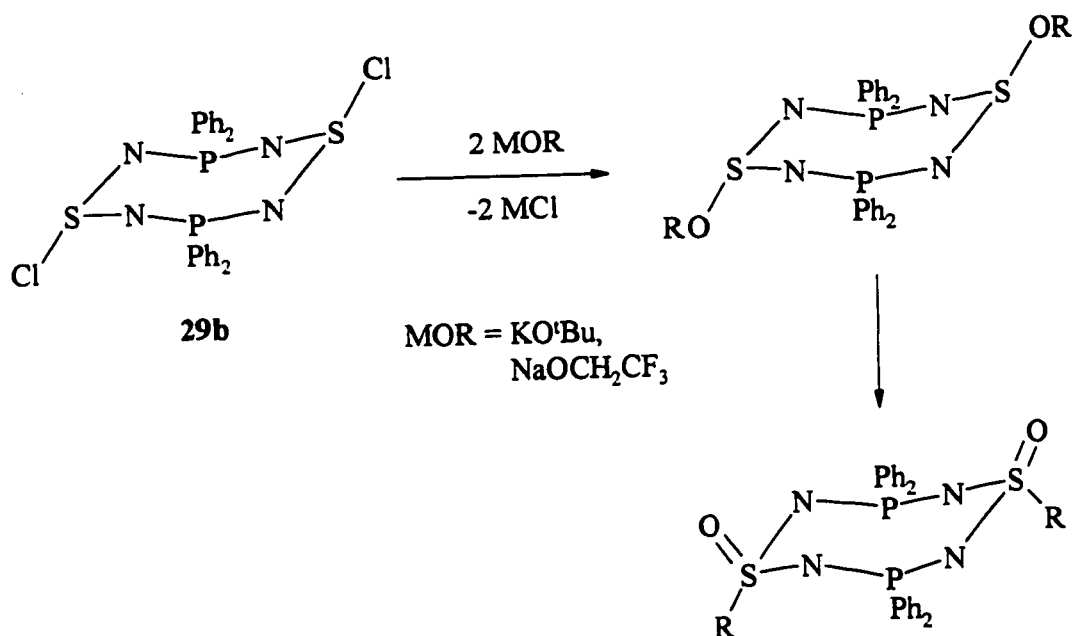


Figure 4.2. Reaction of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> with MOR.

#### 4.2.2 Thermolysis of R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SR)<sub>2</sub> (R = Cl, NMe<sub>2</sub>)

Preliminary investigations into the thermolysis of the heterocycles 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SR)<sub>2</sub> (R = Cl, NMe<sub>2</sub>) and 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> have been performed. The thermolysis of the dichloride, 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub>, at 120°C for 4 hours results in the formation of two new species with  $\delta$  (<sup>31</sup>P) = +73.3 ppm and +34.3 ppm in a ratio of 1:3. The product mixture was dissolved in CH<sub>3</sub>CN and small crystals began to grow from the solution, but they decomposed before they were sufficiently large for X-ray analysis. More thermolysis investigations of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> are required in order to identify the

two products. In addition the effect of the duration and temperature of the thermolysis on the product ratio should be investigated.

Preliminary studies of the thermolysis of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> at 170°C, using <sup>31</sup>P NMR, show that several products are formed. After heating a sample of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> for 5.5 hours major resonances are observed at  $\delta$  (<sup>31</sup>P) = +15.2 ppm, +18.2 ppm, +21.1 ppm, +43.3 ppm, +54.9 ppm and +61.0 ppm. After heating for 22 hours the resonances at  $\delta$  (<sup>31</sup>P) = +18.2 ppm and +54.9 ppm increase in intensity while the other major peaks observed after 5.5 hours of heating decrease in intensity and a broad peak between  $\delta$  = +8 ppm and 0 ppm is observed. The new broad resonance observed is possibly due to polymer formation as it begins to grow as the heating time is increased. The effect of longer thermolysis times needs to be investigated further and the major products of the thermolysis should be isolated and characterized.

#### 4.2.3. Eight-membered S(VI) Rings

The ROP of polythionylphosphazenes is proposed to initiate by ionization of a S(VI)-Cl bond, therefore a S(VI)-Cl bond is desirable for polymerization of P<sub>2</sub>N<sub>4</sub>S(VI)<sub>2</sub> ring systems. Several attempts were made to oxidize 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> to give 1,5-R<sub>4</sub>P<sub>4</sub>N<sub>4</sub>[S(O)Cl]<sub>2</sub> (**33**), however the reactions either resulted in hydrolysis or no reaction occurred. In the case of *m*CPBA as the oxidant, decomposition and hydrolysis to R<sub>2</sub>PN<sub>2</sub>H<sub>4</sub><sup>+</sup> occurred. It may be possible to make **33** by an indirect method that involves the preparation of the heterocycle 1,5-R<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)NMe<sub>2</sub>]<sub>2</sub> (**36**) via the oxidation of 1,5-

$R_4P_2N_4(SNMe_2)_2$ . The treatment of **36** with a chlorinating agent like HCl could give 1,5- $R_2P_2N_4[S(O)Cl]_2$  (**33**) (Figure 3.6). The oxidation of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> with *m*CPBA has been attempted, but it appears like protonation occurs at the dimethylamino nitrogens. After 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub> was treated with 2 equivalents of *m*CPBA three resonances appeared at  $\delta$  (<sup>31</sup>P) = +53.8 ppm, +42.6 ppm and +36.4 ppm. When excess *m*CPBA was added only one resonance remained at  $\delta$  = +42.6 ppm, and after stirring this mixture over K<sub>2</sub>CO<sub>3</sub> the resonances at  $\delta$  = +36.4 ppm and +53.8 ppm reappeared, while the resonance at  $\delta$  = +42.6 disappeared. The <sup>1</sup>H NMR of the mixture exhibited two broad resonances for the methyl groups of NMe<sub>2</sub>, and some peaks between  $\delta$  = 7.5 and 8.2 ppm which are most likely due to protons attached to N. Unfortunately, prolonged stirring over K<sub>2</sub>CO<sub>3</sub> could not completely deprotonate the product however, the reaction could be performed in the presence of an amine which may prevent protonation of 1,5-Et<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SNMe<sub>2</sub>)<sub>2</sub>, or the protonated product could be treated with a stronger base, like *n*BuLi, after the oxidation is performed.

In light of the attempted oxidation of 1,5-(*p*-Br-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C<sub>2</sub>N<sub>4</sub>[S(*p*-tolyl)]<sub>2</sub>, which gives only the mono-oxidized product of 1,5-(*p*-Br-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C<sub>2</sub>N<sub>4</sub>[S(O)(*p*-tolyl)][S(*p*-tolyl)],<sup>76</sup> it may be possible to isolate the mono-oxidized heterocycle 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)R]SR which could lead to the synthesis of mixed PNS(IV)N and PNS(VI)N polymers. During the synthesis of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>[S(O)Ph]<sub>2</sub> a white precipitate is formed, this could be the mono-oxidized derivative 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>N<sub>4</sub>[S(O)Ph]SPh. The oxidation of the chair form of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SMe)<sub>2</sub> is quantitative as it only requires two equivalents

of *m*CPBA, so it should be possible to react one equivalent of *m*CPBA with the chair form of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>(SMe)<sub>2</sub> and isolate the product (Figure 4.3). The product should be readily identified using <sup>31</sup>P NMR, <sup>1</sup>H NMR and mass spectrometry.

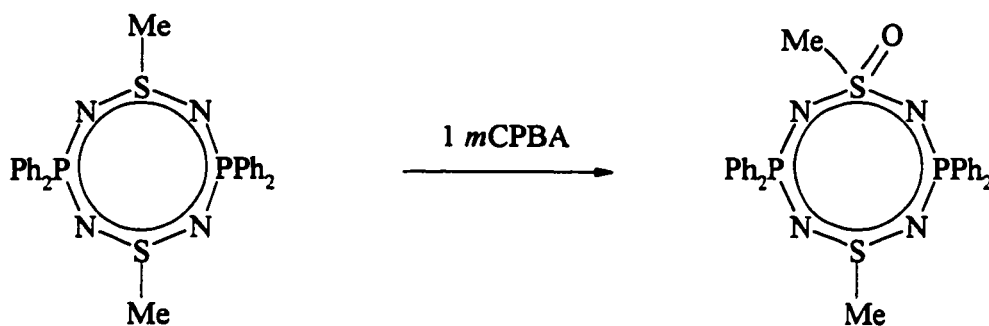


Figure 4.3. Proposed synthesis of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>N<sub>4</sub>[S(O)Me]SMe.

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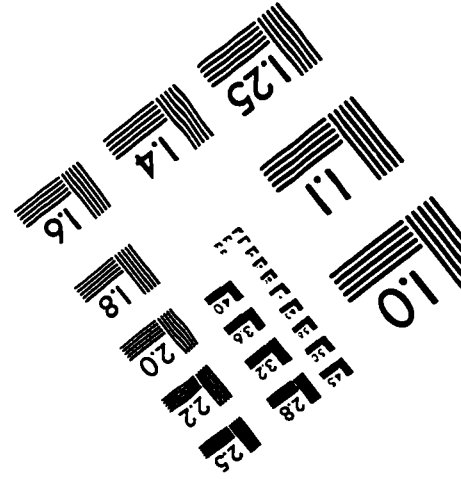
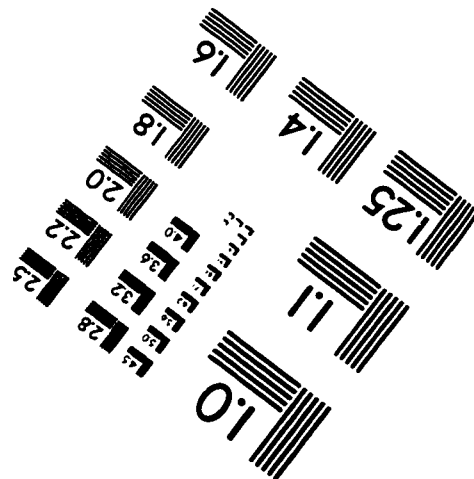
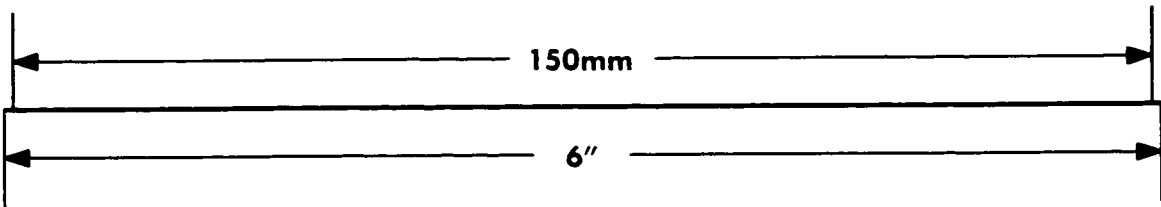
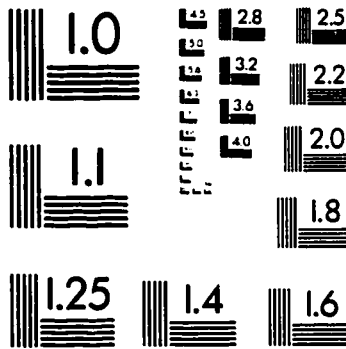
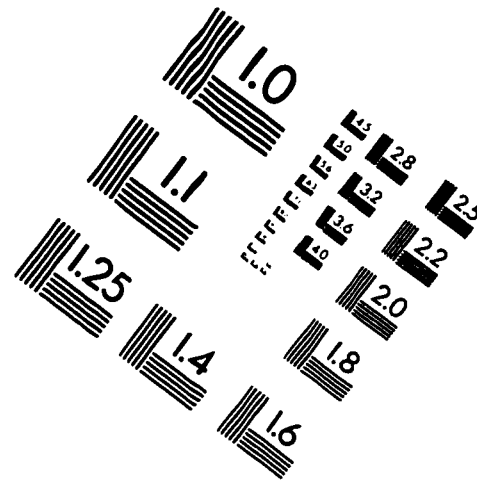
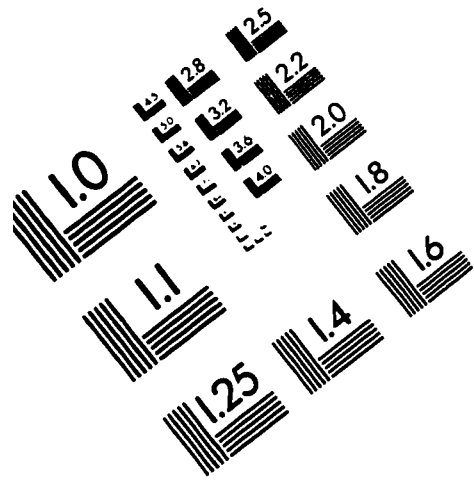


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