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The Formation, Structures and Photochemical Isomerization of Dithiatetrazocines

by

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "The Formation, Structures and Photochemical Isomerization of Dithiatetrazocines" submitted by Peter Zoricak in partial fulfillment of the requirements for the degree of Master of Science.

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ABSTRACT

This thesis describes a combination of results focusing around carbon-nitrogen-sulfur (CNS) systems. Initially a systematic study was performed to determine the conditions that favor formation of CNS ring systems from the reaction of $\text{ArCN}_2(\text{SiMe}_3)_3$ with PhSCl . Low temperatures favor the production of rings, whereas at room temperature chalcogen-containing diazenes $Z, E, Z\text{-PhENC}(\text{Ar})\text{N}=\text{NC}(\text{Ar})\text{NEPh}$ are formed in quantitative yields. The structures of the eight-membered rings $(4\text{-XC}_6\text{H}_4)_2\text{C}_2\text{N}_4\text{S}_2(\text{Ph})_2$ ($X = \text{Br}, \text{CF}_3$) were determined by X-ray crystallography. The $\text{C}_2\text{N}_4\text{S}_2$ rings have a boat-boat conformation with the sulfur substituents in equatorial positions. These heterocycles produce a purple color when exposed to UV radiation. A detailed investigation of this process revealed a novel photochemical isomerization of these $\text{C}_2\text{N}_4\text{S}_2$ rings into acyclic diazenes. Kinetic studies have shown the transformation to be an intramolecular process.

A new geometrical isomer of the sulfur-containing diazenes $E, E, E\text{-PhSN}(2\text{-BrC}_6\text{H}_4)\text{CN}=\text{NC}(2\text{-BrC}_6\text{H}_4)\text{NSPh}$ and a Pt complex of this diazene were isolated and structurally characterized.

Finally, the decomposition of $(4\text{-BrC}_6\text{H}_4)\text{C}(\text{NSCCl}_3)[\text{N}(\text{SiMe}_3)_2]$ unexpectedly produced a five membered ring $4\text{-BrC}_6\text{H}_4\overline{\text{CNSC}(\text{Cl})\text{N}}$, which was also structurally characterized.

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LIST OF COMPOUNDS

1. $[\text{N}(\text{PCl}_2)_3]$
2. S_4N_4
3. $1,5\text{-(R)}_4\text{P}_2\text{N}_4\text{S}_2$
 - a. (R = Me)
 - b. (R = Ph)
4. $1,5\text{-(R)}_2\text{C}_2\text{N}_4\text{S}_2$
 - a. (R = Ph)
 - b. (R = Me_2N)
 - c. (R = ^tBu)
5. $(\text{R})_2\text{PN}_3\text{S}_2$
 - a. (R = Me)
 - b. (R = Ph)
6. $1,5\text{-(Ph)}_4\text{P}_2\text{N}_4(\text{SX})_2$
 - a. (X = Br)
 - b. (X = Cl)
7. $1,5\text{-[Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{H][BF}_4]$
8. $1,5\text{-[Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{Me][CF}_3\text{SO}_3]$
9. $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2 \bullet \text{BCl}_3$
10. $1,5\text{-[Ph}_4\text{P}_2\text{N}_4\text{S}_2]_4 \bullet 3\text{SnCl}_4$
11. $\text{Li}[(\text{Ph})_4\text{P}_2\text{N}_4\text{S}_2(\text{R})]$
12. $1,5\text{-(Ph)}_4\text{P}_2\text{N}_4(\text{SR})(\text{SR}')$
 - a. chair conformation
 - b. boat conformation
13. $[\text{Li}_2(\text{Ph})_4\text{P}_2\text{N}_4\text{S}_2]_n$
14. $[1,5\text{-(Ph)}_4\text{P}_2\text{N}_4\text{S}_2][\text{AlCl}_4]_2$
15. $\text{H}_2\text{NC(Ph)=NSN=C(Ph)NH}_2$
16. $[(\text{Me}_2\text{N})_2\text{C}_2\text{N}_4\text{S}_2\text{Cl}]^+[\text{Cl}_3]^-$

17. 1,5-[(Me)₂N]₂C₂N₄S₂(Cl)₂
18. [Me₂N]₂C₂N₄S₂Cl]⁺[PF₆]⁻
19. 1,5-(Me₂N)₂C₂N₄S₂(O)₂[(N(CF₃)₂)]₂
20. 1,5-(Me₂N)C(Ph)CN₄S₂
21. XC₆H₄CN₂(SiMe₃)₃
- (X = 4-H)
 - (X = 4-CH₃)
 - (X = 4-CH₃O)
 - (X = 4-Cl)
 - (X = 4-CF₃)
 - (X = 3-CF₃)
 - (X = 4-NO₂)
22. [XC₆H₄CN₂S₂]⁺Cl⁻
- (X = 4-H)
 - (X = 4-CH₃)
 - (X = 4-CH₃O)
 - (X = 4-Cl)
 - (X = 4-CF₃)
 - (X = 3-CF₃)
 - (X = 4-NO₂)
23. (XC₆H₄CN₂S₂)₂
- (X = 4-H)
 - (X = 4-CH₃)
 - (X = 4-CH₃O)
 - (X = 4-Cl)
 - (X = 4-CF₃)
 - (X = 3-CF₃)
24. 1,5-(XC₆H₄)₂C₂N₄S₂
- (X = 4-H)

- b. (X = 4-CH₃)
- c. (X = 4-CH₃O)
- d. (X = 4-Cl)
- e. (X = 4-CF₃)
- f. (X = 3-CF₃)

25. Z, E, Z-RENC(Ar)N=NC(Ar)NER

- a. (E = Se; Ar = Ph; R = Me)
- b. (E = Se; Ar = Ph; R = Ph)
- c. (E = S; Ar = Ph; R = Ph)
- d. (E = S; Ar = 4-CH₃C₆H₄; R = Ph)
- e. (E = S; Ar = 4-CF₃C₆H₄; R = Ph)
- f. (E = S, Ar = 4-CH₃C₆H₄; R = 4-CH₃C₆H₄)
- g. (E = SO₂; Ar = 4-CH₃C₆H₄; R = Me)
- h. (E = S; Ar = 4-BrC₆H₄; R = Ph)
- i. (E = S; Ar = 3-BrC₆H₄; R = Ph)
- j. (E = Se; Ar = 4-BrC₆H₄; R = Ph)

26. Pt{PhSNC(Ar)N-NC(Ar)NSPh}(PPh₃)

- a. (Ar = 4-CH₃C₆H₄)
- b. (Ar = 2-BrC₆H₄)

27. Ar₂C₂N₄S₂R₂

- a. (Ar = 4-CF₃C₆H₄; R = Ph)
- b. (Ar = Ph; R = CCl₃)
- c. (Ar = Ph, R = 2,4-(NO₂)₂C₆H₃)
- d. (Ar = 4-BrC₆H₄; R = Ph)

28. (4-BrC₆H₄)₄C₄N₈S₄(Ph)₄

29. S(1,2-C₆H₄)SN=C(Ph)C(Ph)=NS(1,2-C₆H₄)SN=C(Ph)C(Ph)=N

30. E, E, E-(Ph)SNC(Ar)N=NC(Ar)NS(Ph)

- a. (Ar = 2-BrC₆H₄)
- b. (Ar = 2-CF₃C₆H₄)

31. *Z, E, Z*-(Ph)SNC(H)N=NC(H)NS(Ph)

32. 4-BrC₆H₄C(NSCCl₃)[N(SiMe₃)₂]

33. 4-BrC₆H₄ $\overline{\text{CNSC(Cl)N}}$

34. 4-BrC₆H₄CN₂(SePh)₃

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LIST OF ABBREVIATIONS AND SYMBOLS

Ar	aryl (aromatic) group
D _{calc.}	calculated density
DMF	dimethyl formamide
DMSO	dimethyl sulfoxide
<i>E</i>	<i>Entgegen</i> = Opposite, with respect to orientation of substituents attached to a double bond
ESD	Estimated Standard Deviation
FAB-MS	Fast Atomic Bombardment Mass Spectrometry
FT-IR	Fourier Transform Infrared Spectroscopy
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
MCPBA	<i>meta</i> -chloroperbenzoic acid
MO	molecular orbital
MS	Mass Spectrometry
NMR	Nuclear Magnetic Resonance
ORTEP	Oakridge Thermal Ellipsoid Plot
Ph	C ₆ H ₅ (phenyl)
ppm	parts per million
THF	tetrahydro furan
TLC	Thin Layer Chromatography
UV	Ultraviolet
Z	Number of molecules in a unit cell
<i>Z</i>	<i>Zusammen</i> = Together, with respect to orientation of substituents attached to a double bond

CHAPTER ONE

Hybrid Inorganic Ring Systems

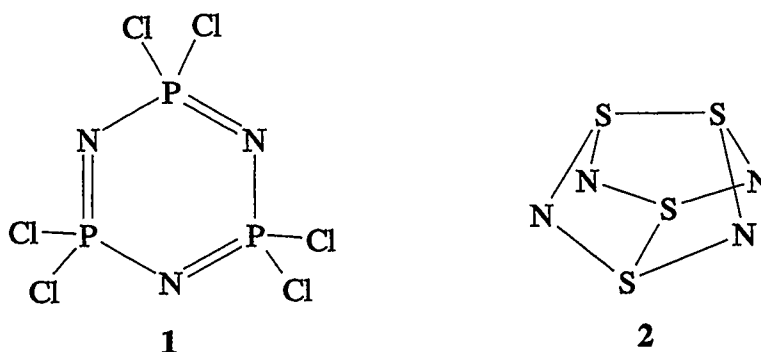
1. Introduction

This thesis is primarily concerned with the synthesis, structures and photochemical isomerization of $C_2N_4S_2$ ring systems (dithiatetrazocines).[†] The purpose of this chapter is to develop an understanding as to the reasons for studying the reaction of trisilylated benzamidines, $ArCN_2(SiMe_3)_3$ (Ar = aryl) with benzenechalcogenyl chlorides, $PhECl$ (E = S, Se) which has been shown to produce both cyclic and acyclic products. The importance of these CNS and CNSe containing compounds will be discussed in terms of potential applications. After a brief account of pertinent inorganic heterocycles, the chemistry of diphosphadithiatetrazocines, $R_4P_2N_4S_2$, will be discussed, and this will be followed by a summary of previous work on dithiatetrazocines, $R_2C_2N_4S_2$. Finally, the known chemistry of chalcogen-containing diazenes, $ArSN=C(Ph)N=NC(Ph)=NSPh$ will be discussed. These intensely colored compounds are the acyclic products referred to above.

[†] The suffix -ocine refers specifically to an unsaturated eight-membered ring containing nitrogen atoms.

1.1 Inorganic Ring Systems

The interest in inorganic heterocycles is mainly due to their fundamental chemistry; however, novel applications have also been discovered. To say that applications are novel does not in any way imply that the chemistry of inorganic heterocycles is a new field. Compounds such as $(\text{NPCl}_2)_3$ (**1**) and S_4N_4 (**2**) date back to the 1830's, but it was not until recently that phosphazene elastomers have been marketed by the Firestone Tire and Rubber Company.¹

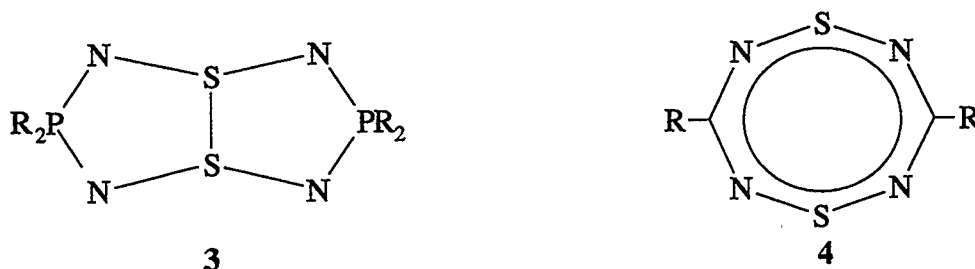


The ring opening polymerization of S_2N_2 , produced by thermolysis of S_4N_4 (**2**), forms poly(sulfur nitride), which also shows interesting properties. It was the first example of a non-metallic superconductor.²

With these two examples, the ring-opening polymerization process has been shown to produce inorganic polymers with unique properties. Although organic polymers have been used for years in numerous household and commercial applications, the ever-

increasing demands on materials and diminishing organic resources point to the need to exploit materials derived from inexhaustible inorganic resources.

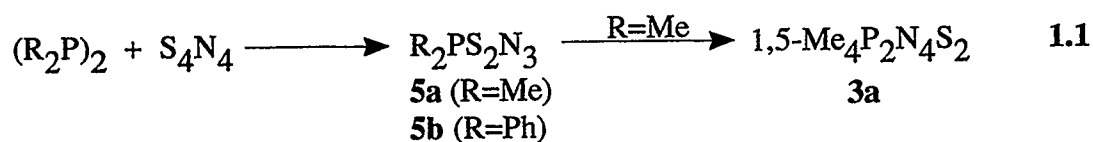
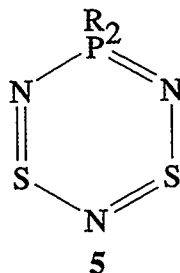
To extend the idea of the binary ring systems to hybrid ring systems involving PNS³ and CNS⁴ we draw attention to 1,5-diphosphadithiatetrazocines (**3**) and 1,5-dithia-2,4,6,8-tetrazocines (**4**), which have been extensively studied over the past decade.



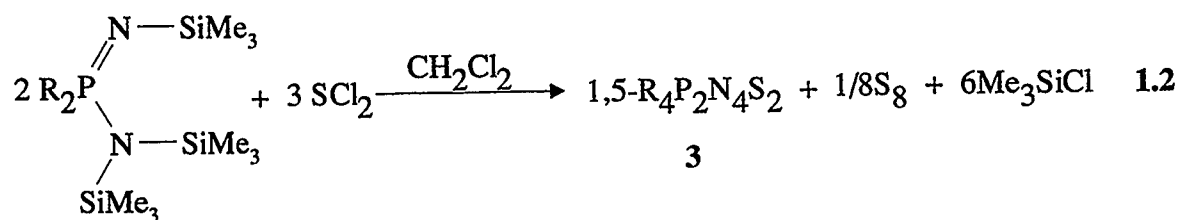
Finally, it should be pointed out that several polymers exist containing the repeating unit PNPNSN⁵ as well as PNPNCN⁶ in the backbone; however, a CNSN polymer has to date eluded isolation which prompts the study of compounds which might act as precursors to some very interesting polymers.

1.2 1,5-Diphosphadithiatetrazocines

The discovery of **3a** ($R = Me$) was accidental. It was obtained from the decomposition of $Me_2PN_3S_2$ (**5a**) in the reaction shown in equation 1.1.³



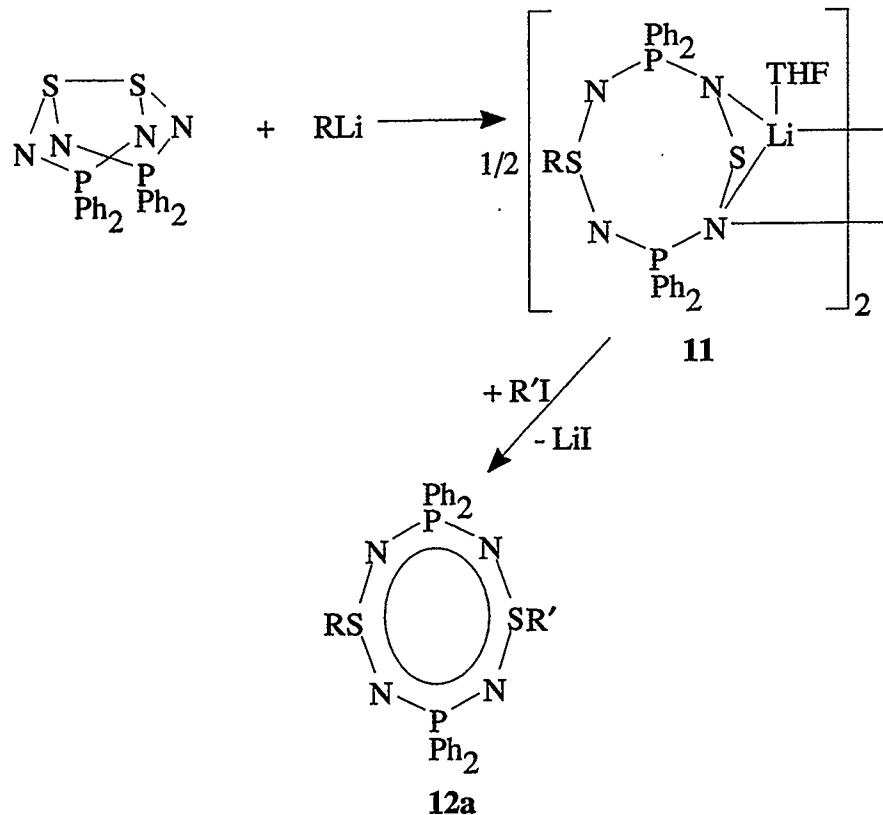
The compound **3a** can be considered as a folded eight-membered ring or two five-membered rings (both S_2N_2 units form a plane) fused together with a weak cross-ring sulfur-sulfur bond, forming an overall butterfly structure. The yields of **3a** and **3b** (R = Ph) from this synthesis (equation 1.1) were very low (ca. 2%) and so a better synthetic route was needed. Equation 1.2 shows a building block approach to the ring utilizing a trisilylated phosphamidine and a sulfur halide.⁷



This approach has increased the yield of **3** to 50%. With the use of SCl_2 , 1,3- $R_4P_2N_4S_2$ is produced in addition to the 1,5-isomer; however, with $SOCl_2$ as the source of S the only product is the 1,5- isomer.⁸ The presence of the sulfur-sulfur bond can be

determined by the characteristic low field ^{31}P -NMR signal in the range 114-136 ppm^{9,10} in contrast to a value of 0-30 ppm for other PN rings without a sulfur-sulfur bond.^{11,12} From an analysis of the frontier orbitals of the folded and planar rings of the type $\text{E}_2\text{N}_4\text{S}_2$ ($\text{E} = \text{CR}, \text{PR}_2, \text{S}^+$) it has been predicted, and shown experimentally, that if the substituent on C is electron-withdrawing (or if $\text{E} = \text{S}^+$) then the planar ($10\pi\text{e}^-$) structure is preferred^{13,14,15}; whereas if the substituents are electron-donating (or $\text{E} = \text{PR}_2$) then the folded ($8\pi\text{e}^-$) structure with a sulfur-sulfur bond is observed.^{3,15,16}

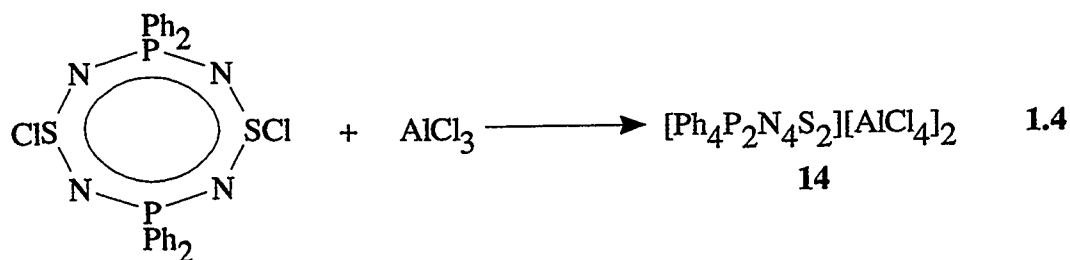
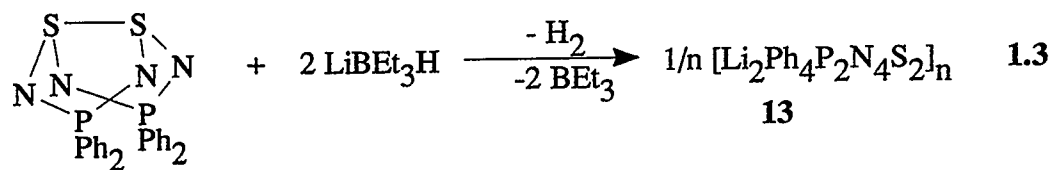
In addition to these interesting structural and electronic properties, the $\text{P}_2\text{N}_4\text{S}_2$ ring also undergoes numerous reactions. Addition of halogens resulted in an electrophilic attack across the S-S bond (*trans* addition) to give 1,5-(Ph) $_4\text{P}_2\text{N}_4\text{S}_2(\text{Br})_2$ (**6a**).¹⁷ Adducts of the ring, with Lewis or Brønsted acids, have been synthesized and characterized, e.g. $[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{H}][\text{BF}_4]$ (**7**), $[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{Me}][\text{CF}_3\text{SO}_3]$ (**8**), $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\bullet\text{BCl}_3$ (**9**) and $[\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2]_4\bullet 3\text{SnCl}_4$ (**10**).¹⁰ The attack of these electrophiles occurs at nitrogen and the S-S bond is retained; however, with the addition of a second equivalent of an electrophile the S-S bond is broken. The eight-membered 1,5- $\text{P}_2\text{N}_4\text{S}_2$ ring also coordinates to transition metals in monodentate and polydentate modes.¹⁸ Reactions of **3b** ($\text{R} = \text{Ph}$) with organolithium reagents give the adducts $\text{Li}[(\text{Ph})_4\text{P}_2\text{N}_4\text{S}_2\text{R}]$ (**11**) which when reacted with an organo-halogen compound yield the S,S' diorgano derivatives 1,5-(Ph) $_4\text{P}_2\text{N}_4(\text{SR})(\text{SR}')$ (**12**), according to **Scheme 1.1**.^{8,19}



Scheme 1.1. Reaction scheme for the formation of 1,5-(Ph)₄P₂N₄(SR)(SR').

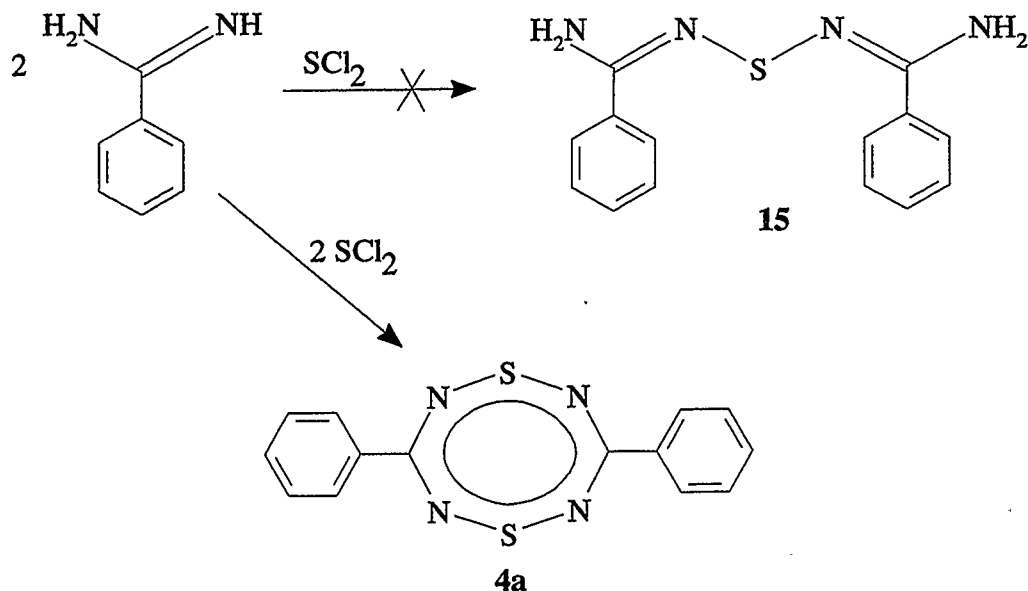
An interesting feature of this reaction is that the 1,5-P₂N₄S₂ ring in the organolithium adduct **11** is initially in a boat conformation, but the product **12a** (after complete workup) is obtained as the chair conformer, indicating a conformational isomerism which can be monitored by ³¹P-NMR.¹⁹ Two intermediates in the conversion of **11** to **12** have been isolated. The first is a LiI adduct of **12** and the second is **12b**, in which the 1,5-P₂N₄S₂ ring is in a boat conformation. It has been shown (by ³¹P-NMR) for several S, S'-diorgano derivatives that heating **12b** (in CH₃CN) produces the thermodynamic product **12a**.^{19,20} In addition to the monoanion 1,5-(Ph)₄P₂N₄S₂R⁻, the dianion 1,5-

$(\text{Ph})_4\text{P}_2\text{N}_4\text{S}_2^{2-}$ ²¹ and the dication $1,5-(\text{Ph})_4\text{P}_2\text{N}_4\text{S}_2^{2+}$ ²² have been prepared according to equations 1.3 and 1.4, respectively.



1.3 1,5-Dithia-2,4,6,8-tetrazocines

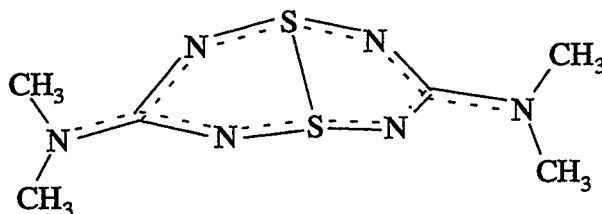
Similar to 1,5-diphosphadithiatetrazocines (3), 1,5-dithia-2,4,6,8-tetrazocines (4) were also discovered by accident; however, in this case the heterocycles were obtained from the reaction of benzamidine with sulfur dichloride in an attempt to make the polymer precursor **15** (see Scheme 1.2).⁴



Scheme 1.2. Attempted polymer synthesis from the reaction of PhCN_2H_3 with SCl_2 .

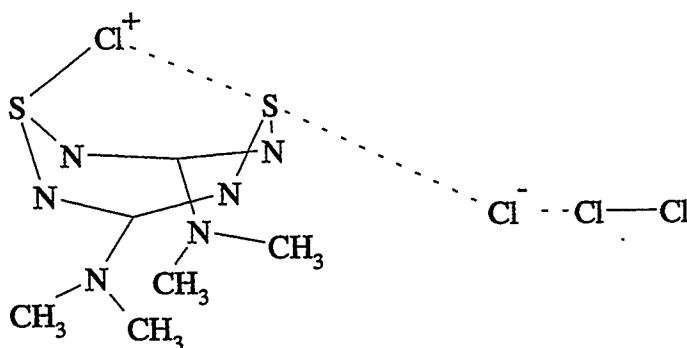
Compound **4a** was obtained in very low yield (ca. 5-10%), and its X-ray structure indicated π -delocalization within the planar ring. This novel ring system is extremely stable to heat, but it decomposes to benzonitrile upon heating to 240°C . Hydrolysis to benzamidine is relatively easy with KOH or HCl in aqueous dioxane; however, **4a** is resistant to other nucleophiles, it is not oxidized by *m*-chloroperbenzoic acid and it is stable to dinitrogen tetroxide, chloroamine-T, diazomethane, norbornadiene, and triphenyl phosphine.²³ A second derivative of the $\text{C}_2\text{N}_4\text{S}_2$ ring system with Me_2N as the exocyclic substituents (**4b**) was obtained in 54% yield.⁴ This new example exhibits a folded structure with partial bonding between the two sulfur atoms [$d(\text{S-S}) = 2.428 \text{ \AA}$]. The derivative **4b** does not appear to possess basic properties, presumably due to the delocalization of the

electron pair of the dimethylamino nitrogens into the ring system, as indicated in the schematic representation below.



4b

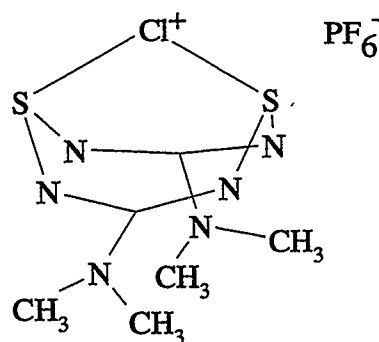
Chlorination of **4b** (Cl_2 gas passed over a saturated acetonitrile solution) produced the ionic compound $[(\text{Me}_2\text{N})_2\text{C}_2\text{N}_4\text{S}_2\text{Cl}]^+[\text{Cl}_3]^-$ (**16**), which was characterized by X-ray crystallography.²⁴ The $\text{C}_2\text{N}_4\text{S}_2$ ring has a boat conformation with an asymmetric $\text{S}-\text{Cl}\cdots\text{S}$ transannular bridge. The S-S separation is 3.491 Å.



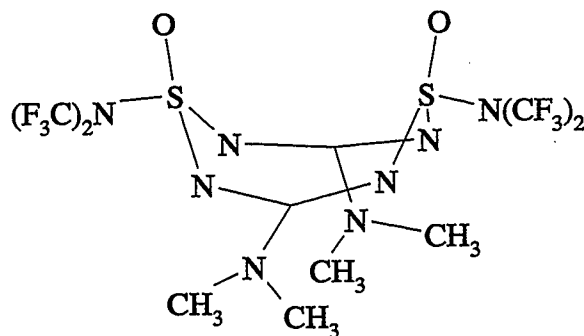
16

The loosely bonded Cl of the anion appears to be approaching the S atom from a direction *trans* to the bridging Cl atom, which is similar to the addition of X_2 across the S-S bond in 1,5-diphosphadithiatetrazocines.¹⁷ The preference for an ionic rather than a covalent structure for **16** has been attributed to the smaller size of the $\text{C}_2\text{N}_4\text{S}_2$ ring

(compared to $P_2N_4S_2$). This size difference results in a strong transannular interaction of the Cl by the two S atoms (in $C_2N_4S_2$ ring) which blocks the final nucleophilic attack of the $[Cl_3]^-$ anion on the cation. However, it is possible to form the covalent species $[(Me)_2N]_2C_2N_4S_2(Cl)_2$ (**17**) by treatment of **4b** with sulfuryl chloride.²⁵ For comparison the recent X-ray structure of 1,5-(Ph) $_4P_2N_4S_2(Cl)_2$ (**6b**) reveals that the two S-Cl bond lengths in **6b** are significantly different, i.e. 2.235(1) Å and 2.419(1) Å.²² This suggests that *trans* addition of two Cl atoms across the S-S bond is incomplete with some ionic character being retained. Treatment of **16** with $NOPF_6$ results in an anion exchange to give $[Me_2N]_2C_2N_4S_2Cl]^+[PF_6]^-$ (**18**).²⁶ The Cl atom in **18** sits in a symmetric fashion between the two S atoms due to loss of secondary interaction with the anion.

**18**

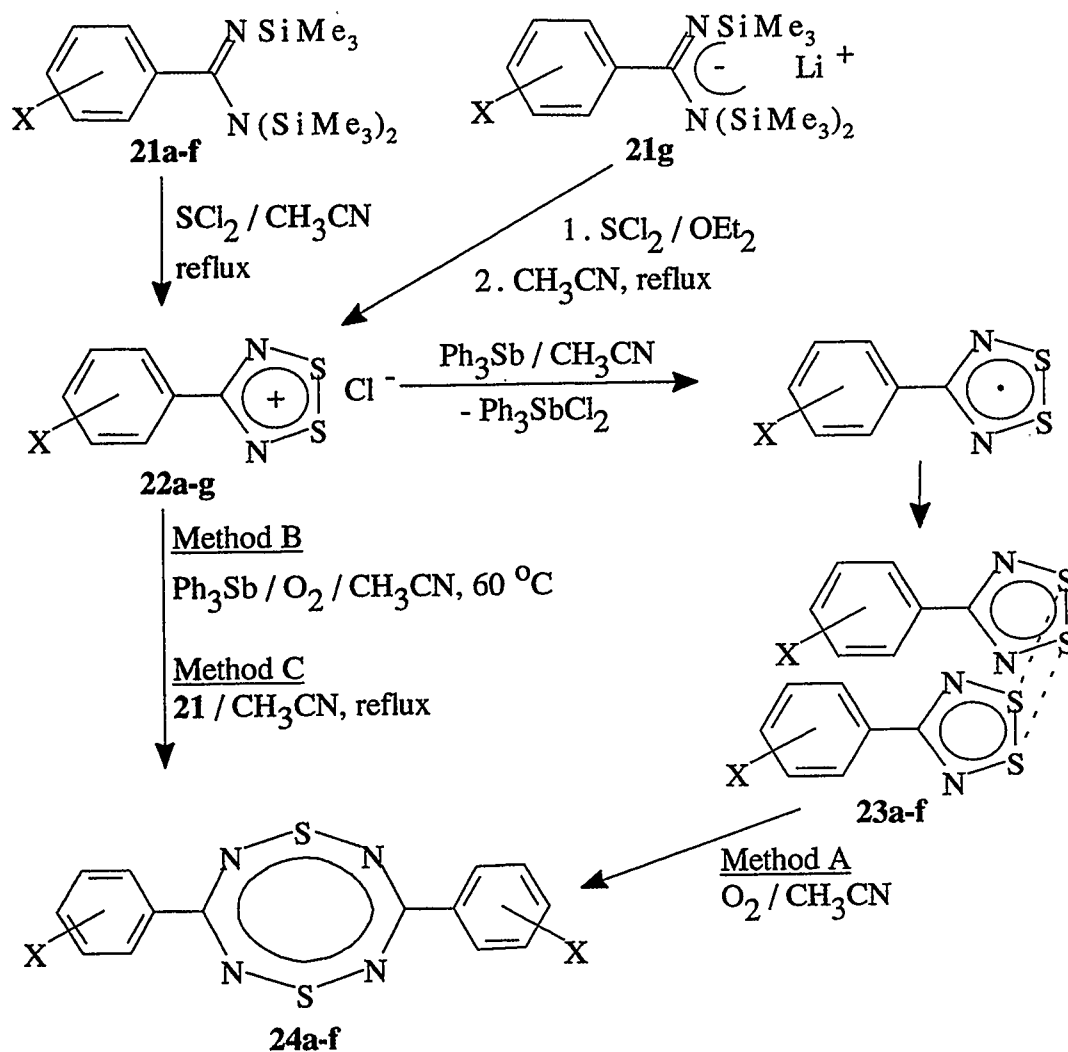
Reaction of **4b** with the nucleophilic radical $(CF_3)_2NO$ resulted in an unexpected rearranged product **19**.²⁶



19

So far the reactions discussed have been limited to symmetrically substituted dithiatetrazocines such as **4a** and **4b**. A route to unsymmetrically substituted $C_2N_4S_2$ rings involves the treatment of a mixture of benzamidine and *N,N*-dimethylguanidine with SCl_2 , which gives a mixture of **4a** (10%), **4b** (5%) and 3-dimethylamino-7-phenyl-dithiatetrazocine (**20**).²³

The synthesis of compounds **4a** and **4b** has been limited to the route developed by Woodward *et al.*⁴ However, with increasing interest in these unusual compounds a versatile, high yield synthesis for heterocycles of type **4** is desirable. With this in mind three synthetic approaches were developed (see **Scheme 1.3**).²⁷

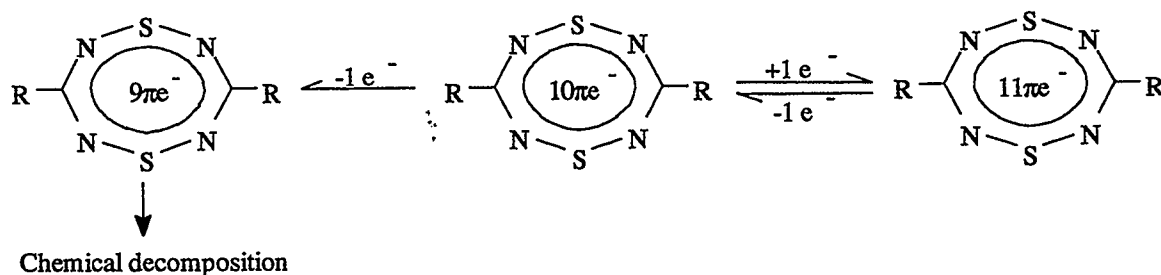


Scheme 1.3. Alternative routes to dithiatetrazocines.

a X=4-H, **b** X=4-CH₃, **c** X=4-CH₃O, **d** X=4-Cl, **e** X=4-CF₃, **f** X=3-CF₃, **g** X=4-NO₂

Of the three synthetic routes, method B seemed consistently to give the highest yields (30-55%). The availability of a series of planar C₂N₄S₂ rings allows a systematic study of their properties. The seven derivatives **24a-f** have very similar NMR and electronic absorption spectra. All the compounds undergo a fully reversible one electron electrochemical

reduction which is essentially independent of the nature of the substituent on C. This can be explained in terms of the frontier orbitals of the $C_2N_4S_2$ ring. The LUMO possesses a node at the C atoms and so substituent effects will be negligible. Another derivative (**4c**, R = t Bu) included in this study did not undergo a reversible one-electron reduction. On the other hand the oxidation step is greatly influenced by substituent effects since the HOMO has a large coefficient at the C atoms. The results for the seven compounds indicate that π -donating substituents lead to lowering of the oxidation potential while inductively withdrawing substituents have a smaller effect in raising the potential. It is important to note that none of the oxidation steps were reversible at ambient temperature (see **Scheme 1.4**).



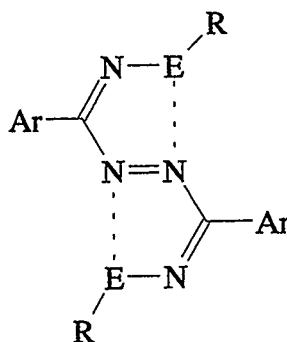
Scheme 1.4. Principle electrode processes of the $10\pi e^-$ ring system 1,5-(R) $_2$ C $_2$ N $_4$ S $_2$.

1.4 Chalcogen-Containing Diazenes

1.4.1 Synthesis

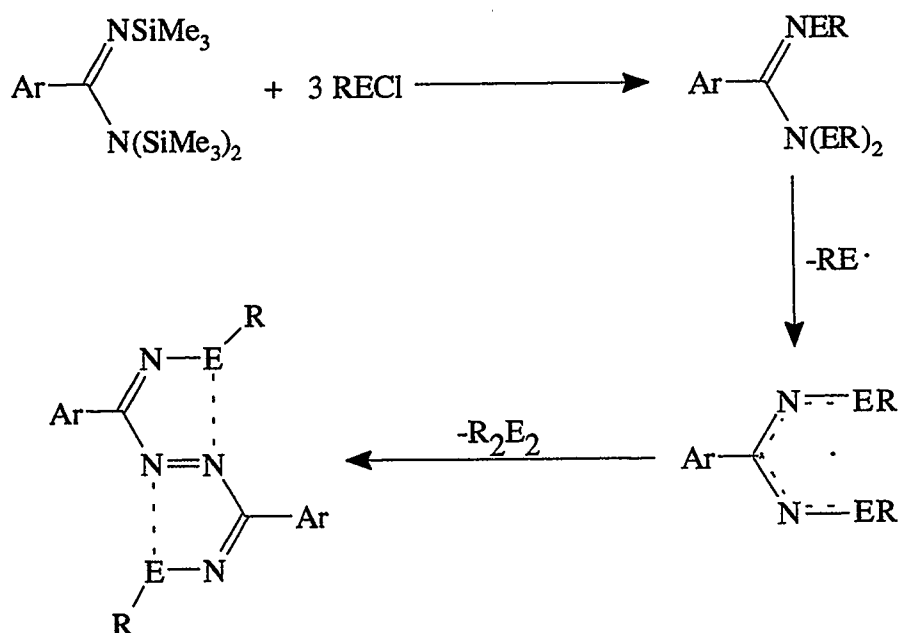
In an attempt to prepare the unknown $C_2N_4Se_2$ ring from a cyclocondensation reaction of $PhCN_2(SiMe_3)_3$ with $RSeCl_3$ (R = Me, Ph), according to the analogous synthesis

of $(\text{Ph})_4\text{P}_2\text{N}_4(\text{SeR})_2$ ($\text{R} = \text{Me}, \text{Et}, \text{Ph}$)²⁸, a new class of compounds was isolated and identified as the chalcogen-containing diazenes *Z, E, Z*- $\text{RENC}(\text{Ar})\text{N}=\text{NC}(\text{Ar})\text{NER}$ (**25**).²⁹



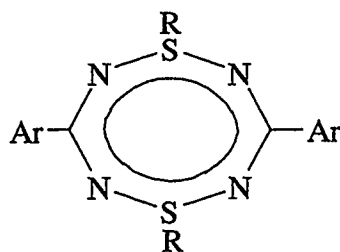
25

Subsequently, it was shown that these diazenes can also be prepared by the reaction of $\text{ArCN}_2(\text{SiMe}_3)_3$ ($\text{Ar} = \text{Ph}, 4\text{-CH}_3\text{C}_6\text{H}_4, 4\text{-CF}_3\text{C}_6\text{H}_4$) with PhECl ($\text{E} = \text{S}, \text{Se}$) in a 1:3 molar ratio. The formation of these diazenes has been studied by ESR spectroscopy which indicates a radical intermediate is involved.³⁰ The initial step of the synthesis involves a metathetical reaction producing the $\text{ArCN}_2(\text{EPh})_3$ ($\text{E} = \text{S}, \text{Se}$) and trimethylsilyl chloride. The tri-substituted benzamidine then undergoes a homolytic E-N cleavage to give the $\text{ArCN}_2(\text{EPh})_2\bullet$ radical, which exhibits a five line (1:2:3:2:1) ESR signal consistent with spin delocalization over two N (^{14}N , $I = 1$, 99.6%) atoms. The final step involves the dimerization of the radical to give the diazene **25** with subsequent elimination of R_2E_2 . The overall reaction is shown in **Scheme 1.5**. In addition it has recently been observed that the diazenes are also formed in the reaction of $\text{PhC}[\text{NH}_2]\text{NBr}$ with REER ($\text{E} = \text{S}, \text{Se}$; $\text{R} = \text{Me}, \text{Ph}$).³¹



Scheme 1.5. Reaction scheme for the formation of *Z*, *E*, *Z*-RENC(Ar)N=NC(Ar)NER.

Another interesting observation in the synthesis of the diazenes is the formation of an eight-membered ring as a side-product.³⁰ The cyclic products, which are of the type $\text{Ar}_2\text{C}_2\text{N}_4\text{S}_2\text{R}_2$ (**27**) ($\text{R} = \text{CCl}_3$, Ph, 2,4-(NO_2) $_2\text{C}_6\text{H}_3$; $\text{Ar} = 4\text{-CF}_3\text{C}_6\text{H}_4$, Ph), are isomers of the diazene **25** ($\text{E} = \text{S}$). These heterocycles are formed when electronegative substituents are attached to either the chalcogen or the C atom; diazenes are also produced. Another route to the 8-membered rings is through a decomposition of $\text{PhCN}_2(\text{SR})(\text{SePh})_2$ ($\text{R} = \text{CCl}_3$, 2,4-(NO_2) $_2\text{C}_6\text{H}_3$).³⁰ It is important to note that an X-ray structure of these $\text{Ar}_2\text{C}_2\text{N}_4\text{S}_2\text{R}_2$ rings has not yet been determined, in contrast to their P analogues (see Section 1.2 and Scheme 1.1).¹⁹



27

1.4.2 Structures

The structure of one of these diazenes, **25a** (E = Se; Ar = Ph; R = Me) shown in **Figure 1.1**, indicates a planar geometry with short, intramolecular contacts between the selenium atoms and one of the nitrogen atoms of the azo group, i.e. Se(1)-N(4) and Se(2)-N(3), of ca. 2.65 Å²⁹ (cf. 3.5 Å for the sum of van der Waals radii for Se and N).³²

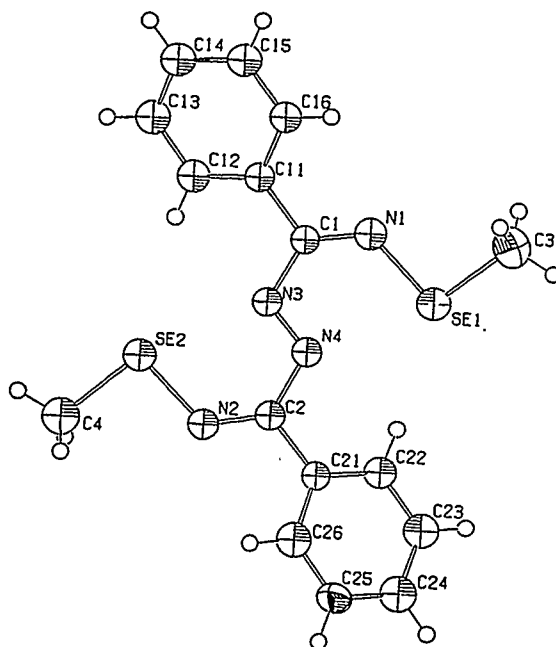


Figure 1.1. ORTEP diagram of *Z, E, Z*-MeSeNC(Ph)N=NC(Ph)NSeMe.

In addition X-ray structures of the sulfur (II) diazene **25f** ($E = S$; $Ar = R = 4\text{-CH}_3\text{C}_6\text{H}_4$) and the sulfur (VI) diazene **25g** ($E = \text{SO}_2$, $R = \text{Me}$, $Ar = 4\text{-CH}_3\text{C}_6\text{H}_4$) have been determined.³³ The latter does not exhibit a $\text{S}\cdots\text{N}$ interaction involving the azo nitrogen.³³ The three structurally characterized diazenes all have the same geometry with respect to the various double bonds, i.e. the substituents around the two $\text{C}=\text{N}$ bonds are in a *Z* orientation and those around the $\text{N}=\text{N}$ bond are in an *E* orientation. The diazenes containing divalent chalcogens are also planar, possessing an inversion center with an overall C_{2h} symmetry.

The $\text{Se/S}\cdots\text{N}$ (**Figure 1.2**) interaction has been attributed to a π type donation of a lone pair of the Se/S into the π^* antibonding orbital of the $\text{N}=\text{N}$ linkage.³⁴ Such donation is expected to cause a small increase in the $\text{N}=\text{N}$ bond length; however, the structural data for the diazene **25a** do not fully support this prediction. For the heavier chalcogen Te MO calculations predict a greater donation and so a greater lengthening of the $\text{N}=\text{N}$ bond is expected.

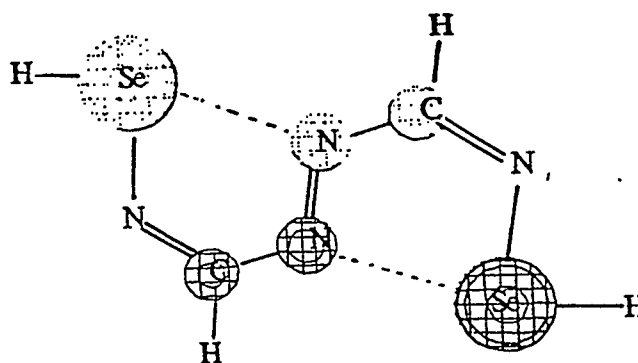
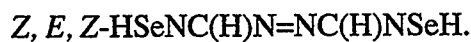


Figure 1.2. Molecular orbital (π^* ($\text{N}=\text{N}$)) of a model diazene

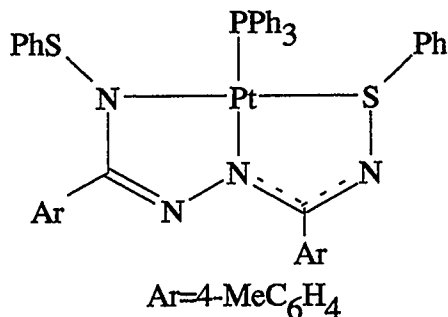


1.4.3 Spectroscopic Properties

Apart from interesting structural features these diazenes are also intensely colored and so are sometimes referred to as “azo dyes”. The electronic spectra of these red and purple diazenes exhibit intense ($\epsilon = 1\text{-}3 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) absorption bands in the region 500-550 nm. This intense visible absorption band has been assigned to the HOMO-1 (π) $\rightarrow$ LUMO (π^*) transition in which the HOMO-1 involves the Se($4p\pi$)-N($2p\pi$) interactions.³⁰

1.4.4 Ligand Behavior

Another interesting feature of these chalcogen-containing diazenes is their potentially rich coordination chemistry due to the ligand properties of N and Se/S. With this in mind several complexes with Pt and Pd have been made.³⁵ The diazenes bind to the metal in a tridentate fashion through N, N and S/Se. The X-ray structures of these complexes, e.g. Pt{PhSNC(4-MeC₆H₄)N-NC(4-MeC₆H₄)NSPh}(PPh₃) (**26a**), show considerable conformation changes from that of the original diazene. The Se/S $\cdots$ N interaction no longer exists, hence the complexes are not intensely colored. There is also a rearrangement of the π bonding in the complex. One major change is the reduction of the N=N bond in the diazene (1.263(4) Å) to a N-N single bond (1.41(1) Å).

**26**

1.5 C₄N₈S₄ Ring

As mentioned in Section 1.4.1 the substituents on C and S are important in determining the type of compounds which are formed in the reaction shown in **Scheme 1.5**. In one reaction, when the aryl substituent on C was 4-BrC₆H₄, the diazene **25h** was isolated (in 98% yield); however, a novel sixteen-membered ring (4-BrC₆H₄)₄C₄N₈S₄(Ph)₄ (**28**) was also isolated (<1% yield).³⁶ Compound **28** was characterized by X-ray crystallography (**Figure 1.3**). The heterocycle **28** is a unique 16-membered ring with alternating CN and SN groups. The molecular symmetry of this compound is S₄ and it has a cradle-like shape. Some interesting structural parameters for **28** include: (a) S-N (1.667(7) Å, cf. 1.77 Å for single bond) and C-N (1.359(9) Å, cf. 1.46 Å for single bond) bonds are somewhat shorter than single bonds, (b) endocyclic bond angles at C (119.5°), at S (108.7°), at N1 (119.4°), and at N2 (111.7°), (c) the N(1)-C(1)-N(2)-S(1*) unit is almost planar whereas C(1)-N(2)-S(1*)-N(1*) has a torsion angle of 79° and (d) the cavity of the ring indicates suitable size

for tetradentate coordination of certain metal ions. The four N(2) nitrogens of the ring are essentially co-planar forming a square-planar orientation.

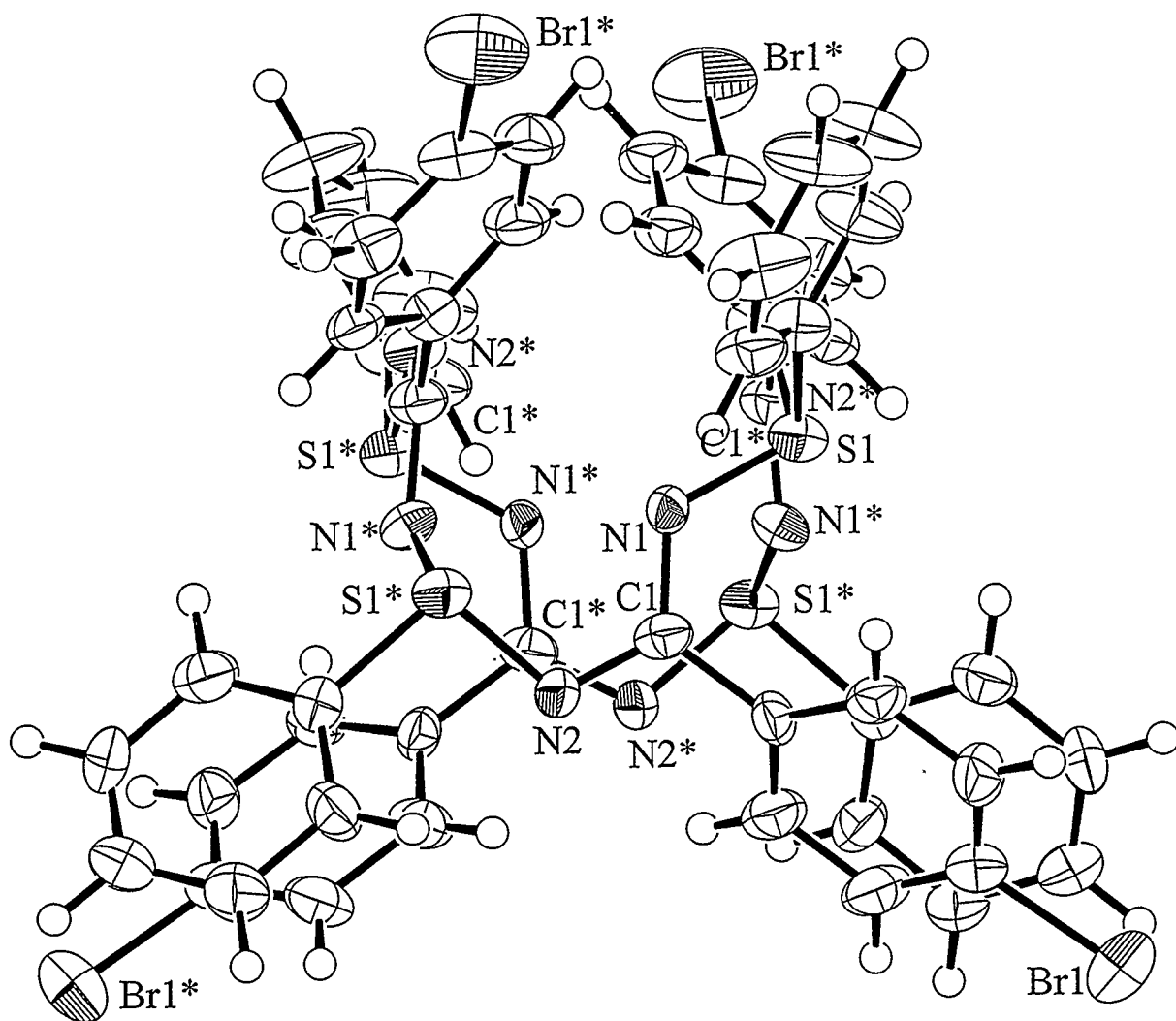
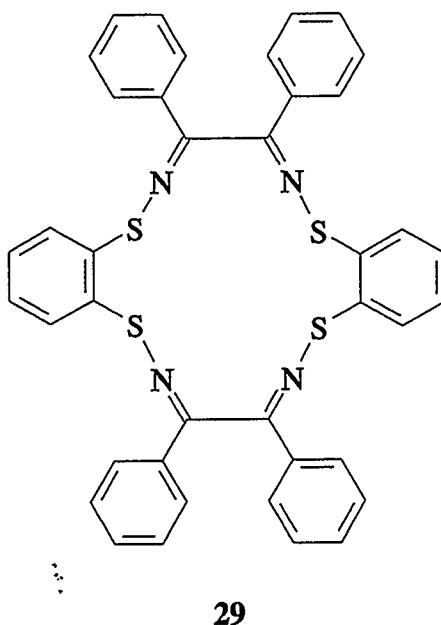


Figure 1.3. ORTEP diagram of $(4\text{-BrC}_6\text{H}_4)_4\text{C}_4\text{N}_8\text{S}_4(\text{Ph})_4$.

A search of other structurally characterized 16-membered heterocycles containing C, N and S revealed only one other compound. However, in that example the compound has a $C_8N_4S_4$ (**29**) molecular skeleton with alternating CC and NS units.³⁷



1.6 Thesis Objectives

From the brief introduction to the chemistry of diphosphadithiatetrazocines and dithiatetrazocines it is apparent that these two classes of compounds have similarities and, at the same time, significant differences so that each system needs to be studied carefully and separately. The chemistry of diphosphadithiatetrazocines has been investigated more extensively than that of dithiatetrazocines; however, with new interest in these CNS rings it is important to gain more insight into the properties of these unusual systems.

It is the objective of this thesis to investigate more fully the reaction of $\text{ArCN}_2(\text{SiMe}_3)_3$ with PhECI ($\text{E} = \text{S}, \text{Se}$) in order to determine how substituent effects and reaction conditions determine the outcome of the reaction. In this way it is hoped that a better understanding of the formation of the eight-membered rings **27** and the corresponding diazenes will be obtained. A structural determination of these novel heterocycles is also desirable prior to detailed studies of their reactions.

The isolation of the novel sixteen-membered heterocycle **28** introduces a new puzzle to the system. It indicates that the reaction of $\text{ArCN}_2(\text{SiMe}_3)_3$ with PhSCl is not as simple as previously thought and suggests the possible formation of larger macrocycles. Before attempts to separate other products are made, it is important to determine the conditions which optimize the formation of the sixteen-membered ring. Clearly, the yield must be increased considerably before any investigations of its ligand behavior can be undertaken. It is this second objective which will be the initial focus of this thesis.

CHAPTER TWO

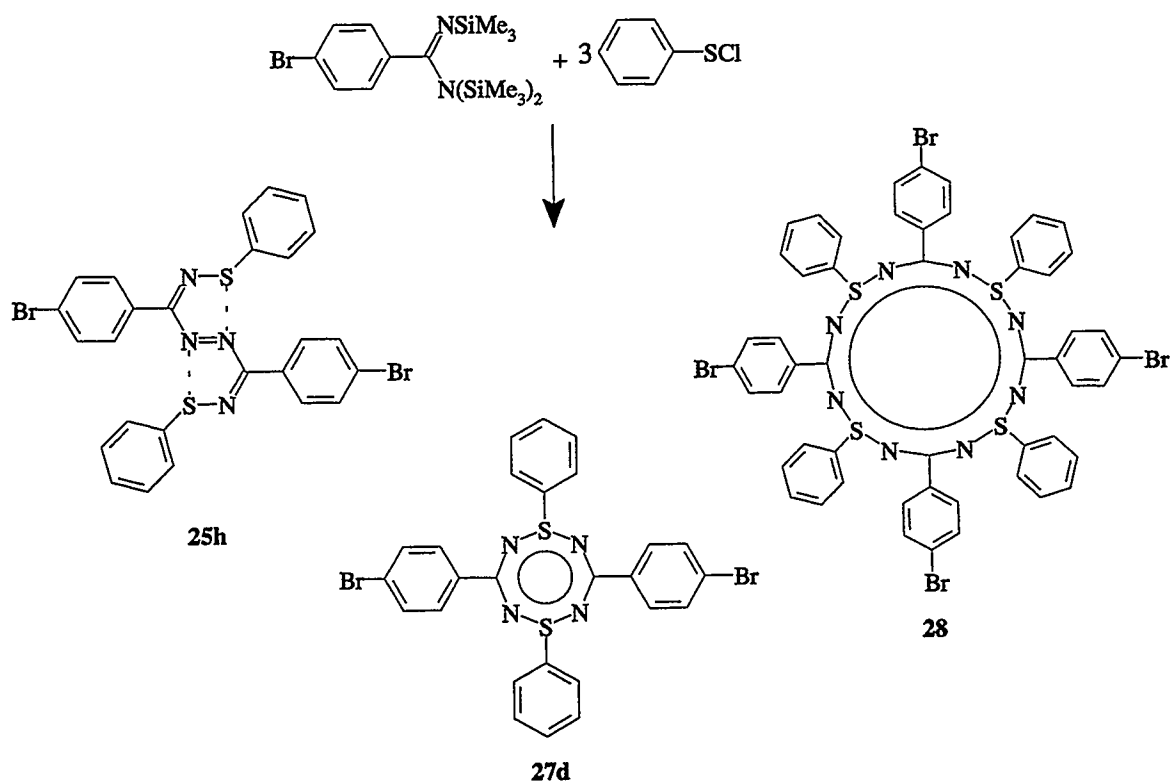
Study of the Products Derived from the Reactions of Trisilylated Benzamidines with Benzenesulphenyl Chloride

2.1 INTRODUCTION

One of the objectives of this thesis was to optimize the synthesis of new CNS rings from the reaction of $\text{ArCN}_2(\text{SiMe}_3)_3$ with benzenesulphenyl chloride. To this end several different aryl substituents have been used including: $\text{Ar} = 2\text{-BrC}_6\text{H}_4$, $3\text{-BrC}_6\text{H}_4$, $4\text{-BrC}_6\text{H}_4$, $2\text{-F}_3\text{CC}_6\text{H}_4$ and $4\text{-F}_3\text{CC}_6\text{H}_4$. All of these different benzamidines were prepared from ArCN and $\text{Li}[\text{N}(\text{SiMe}_3)]_2$ by the method developed by Oakley *et al.*³⁸ The aryl substituents were chosen for their availability from Aldrich as well as characteristic ^1H -NMR signals. Of the various substituents, $4\text{-BrC}_6\text{H}_4$ has been shown to produce the largest number and the most interesting compounds, most of which have been characterized by X-ray diffraction. The substituent $2\text{-BrC}_6\text{H}_4$ has also generated unexpected products, which have been characterized by X-ray crystallography.

2.2 Reaction of 4-BrC₆H₄CN₂(SiMe₃)₃ with 3 PhSCl

The reaction of 4-BrC₆H₄CN₂(SiMe₃)₃ with three molar equivalents of PhSCl is a rich source of cyclic and acyclic products, three of which have been identified as (Ph)SN(4-BrC₆H₄)CN=NC(4-BrC₆H₄)NS(Ph) (**25h**), (4-BrC₆H₄)₂C₂N₄S₂(Ph)₂ (**27d**), and (4-BrC₆H₄)₄C₄N₈S₄(Ph)₄ (**28**). The reactants and their products are shown in **Scheme 2.1**.



Scheme 2.1. Isolated products from reaction of 4-BrC₆H₄CN₂(SiMe₃)₃ with PhSCl.

The formation of diazenes of the type **25** was known from earlier experiments and eight-membered rings of the type **27** were tentatively identified (based on mass spectrometry data),³⁰ but the sixteen-membered ring **28** was unknown. The sixteen-membered ring **28**

was initially discovered by accident during a recrystallization of **25h**.³⁶ The next step involved the determination of the number of compounds present and some of their properties (i.e. relative solubilities and stability to silica) which might facilitate their separation. One characteristic of these compounds which makes them easy to work with is their relative stability towards oxygen and moisture. Consequently, a thin layer chromatogram (TLC) on silica plates was attempted in order to determine the product distribution. The experiment was done by dissolving the reaction mixture in a minimum amount of CH_2Cl_2 and then spotting a small sample on a silica plate. The best eluent was determined to be a mixture of CH_2Cl_2 :hexanes in a 1:3 ratio and a 400mL beaker was used with an aluminum foil cover to produce a solvent-rich atmosphere. The TLC was then removed and allowed to dry for several minutes and examined under UV light. A typical TLC with some spot assignments is shown in **Figure 2.1**. The spots on the TLC were assigned according to color (**25h** is deep purple, **27d** is pale yellow and **28** is colorless) and by use of pure compounds as references (after the mode of separation was determined). The unassigned spot was red and readily changed to the purple color of the diazene **27h**; consequently, it was not isolated as a pure fraction. The possible identity of this red compound will be discussed in detail in Section 2.3. Two vital pieces of information are evident from the TLC. First the order of elution is **25h**→**27d**→**28**. Second, the compounds seem to be stable on silica gel and so a preparative scale separation on a silica gel column seemed feasible.

2.2.1 Separation of Products

Based on the conditions determined for the TLC, a silica gel column was used with CH_2Cl_2 :hexane as eluent. This separation was ineffective because excess diazene **25h** tails on the silica gel which leaves a purple stain on the entire column. It is necessary, therefore, to remove the diazene (as much as possible) from the mixture of products prior to the chromatography step.

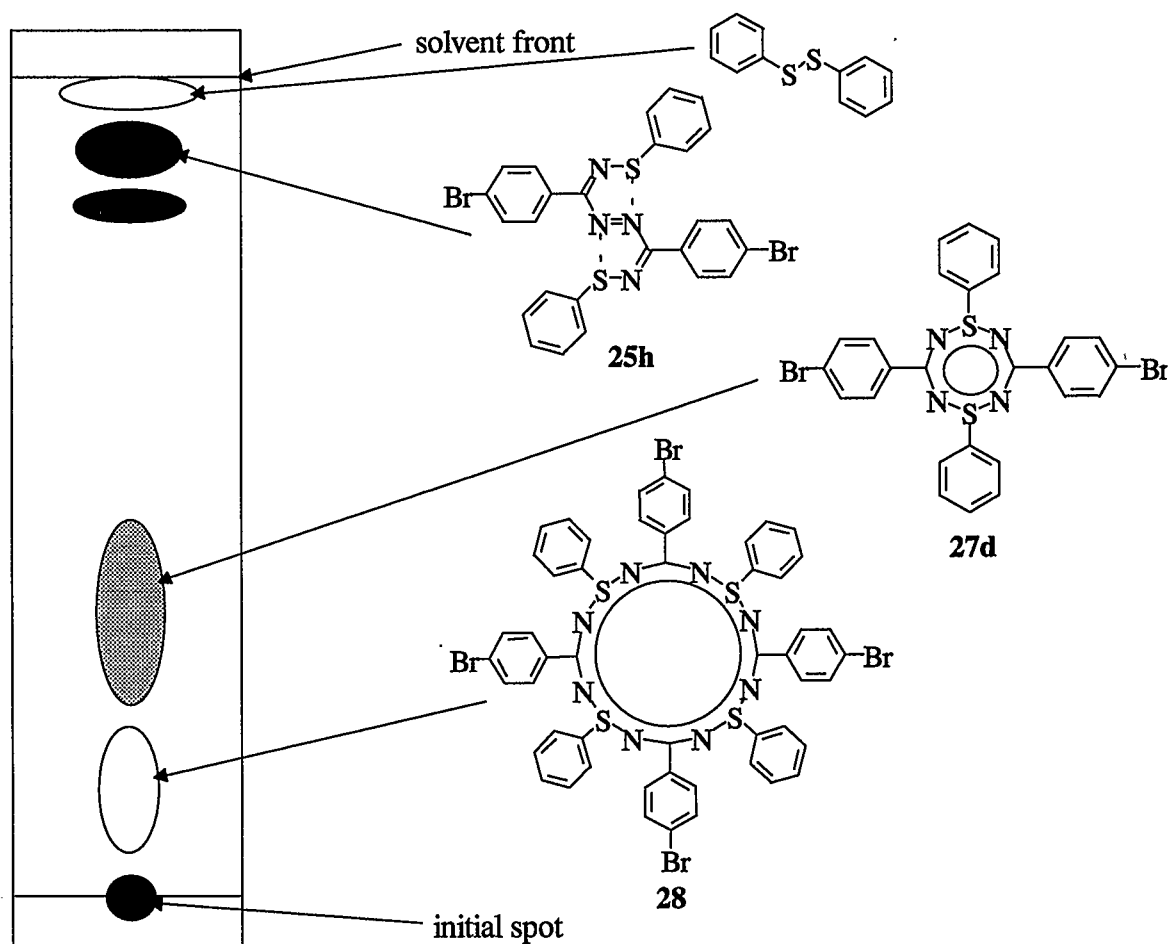


Figure 2.1. Typical TLC of products isolated from the reaction of $4\text{-BrC}_6\text{H}_4\text{CN}_2(\text{SiMe}_3)_3$ with PhSCl .

The by-product Ph_2S_2 can be removed from the reaction mixture by washing with pentane, which leaves compounds **25h**, **27d** and **28** in the insoluble fraction. The diazene **25h** is partially removed by dissolving this mixture in a large amount of CH_2Cl_2 and then layering the solution with ether. This mixture is then left overnight to precipitate the diazene which is then separated by filtration. The remaining mixture of **25h**, **27d**, and **28** is placed on the silica gel column as a CH_2Cl_2 solution and eluted first with hexanes to remove the diazene and then with CH_2Cl_2 to separate the eight-membered ring **27d** and the sixteen-membered ring **28**. It is important to note that elution with hexanes should not be started until all the CH_2Cl_2 solution has gone onto the column and a band of clean silica appears; otherwise the hexanes will precipitate the compounds and no separation will be achieved. The last two fractions are monitored by periodic spotting of a small sample on a TLC plate and viewing with a UV light. This separation may be performed several times depending on the purity of the initial fractions. The volume of each fraction is then reduced to a minimum and layered with diethyl ether to crystallize each compound. The diazene **25h** crystallizes as violet needles, the eight-membered ring **27d** as yellow needles and the sixteen-membered ring **28** as colorless rectangular prisms. It is important to note that the mode of separation has to be modified slightly depending on the major product and also on the product distribution which will be discussed in section 2.2.2. As a general rule the compound which is present in excess of 50% yield must be initially removed by precipitation or recrystallization prior to chromatography. **Figure 2.2** shows a flow chart for a typical separation of a mixture consisting of 55% **25h**, 40% **27d** and 5% **28**.

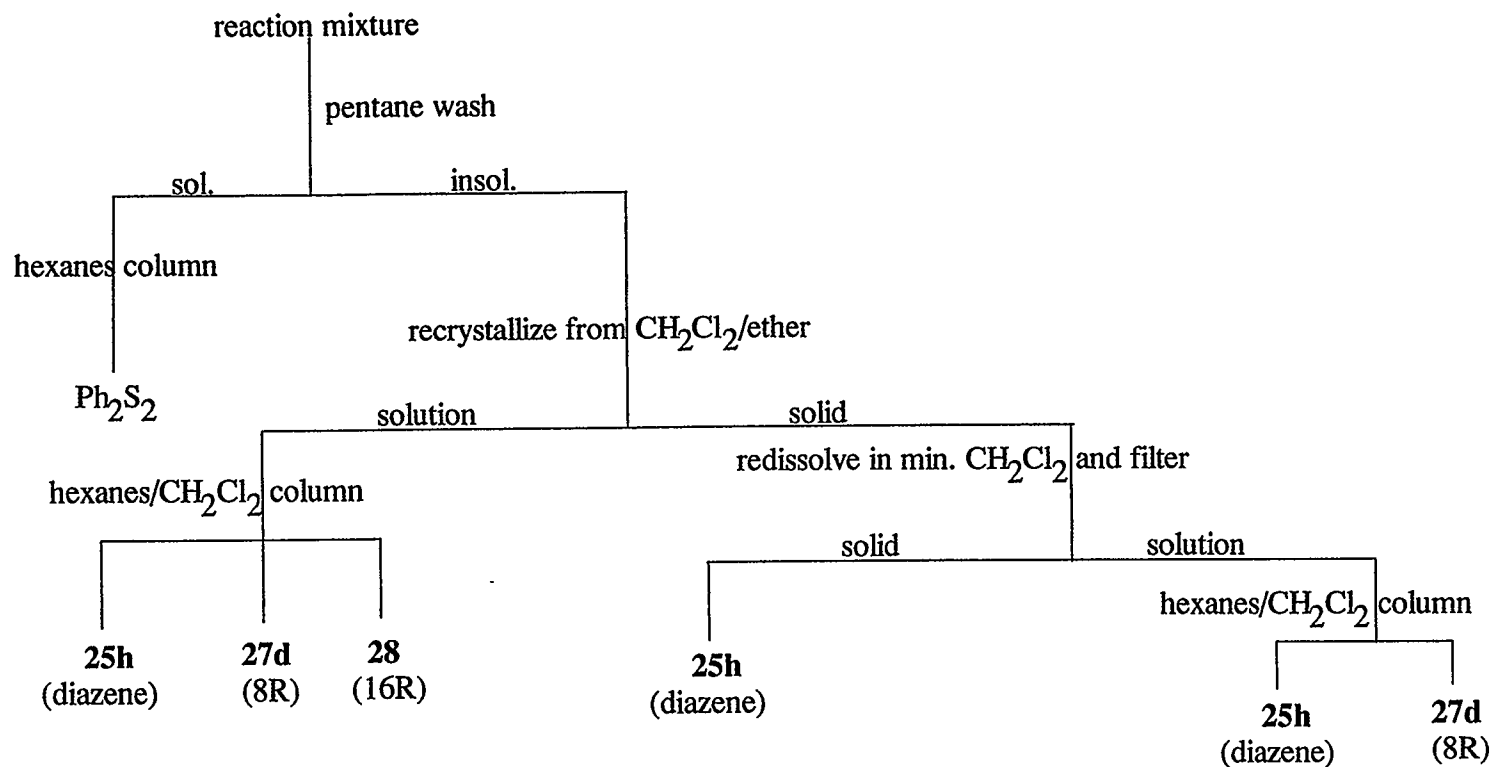
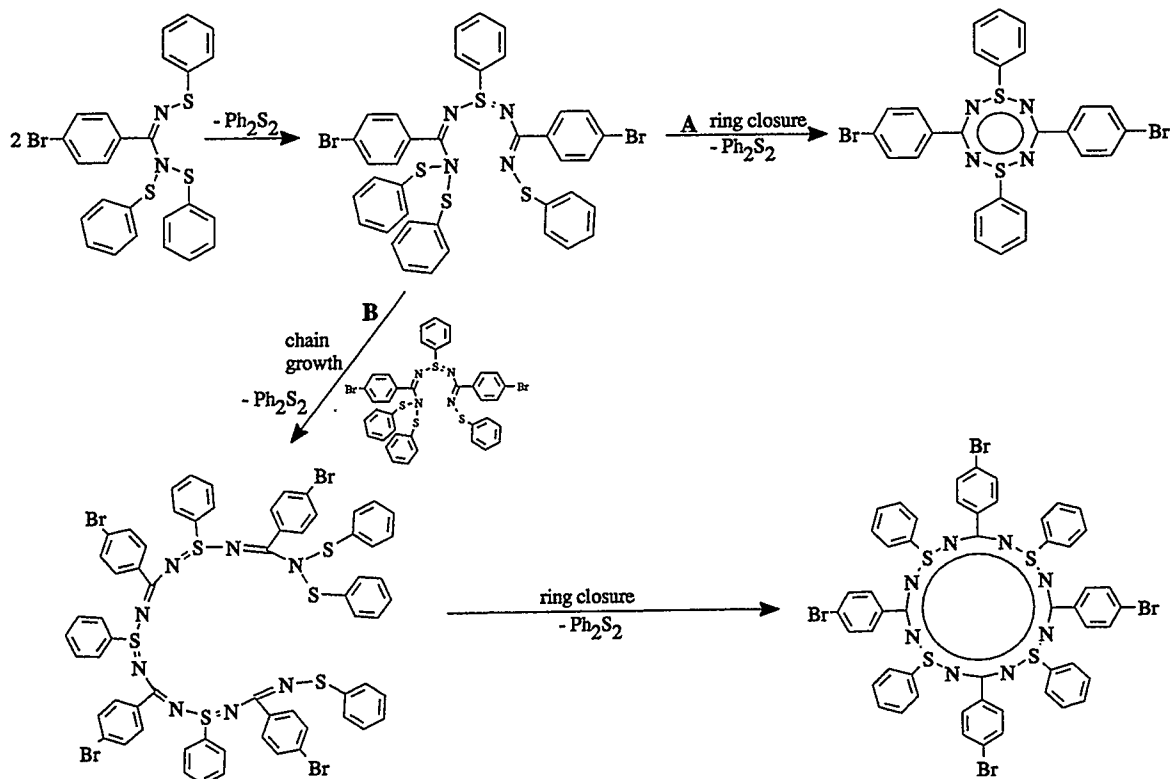


Figure 2.2. Flow chart for separation of *Z*, *E*, *Z*-(Ph)SN(4-BrC₆H₄)CN=NC(4-BrC₆H₄)NS(Ph), (4-BrC₆H₄)₂C₂N₄S₂(Ph)₂ and (4-BrC₆H₄)₄C₄N₈S₄(Ph)₄. (8R = eight-membered ring; 16R = sixteen-membered ring)

2.2.2 Optimization of Yield of Cyclic Products

When first isolated, the yield of the sixteen-membered ring **28** was less than 1%³⁶ and so changes in the reaction conditions were attempted in order to improve the yield. The three variables that were investigated were (a) concentration, (b) temperature and (c) time. The effect of each of these variables on reaction conditions will be discussed in detail. It should be noted that all the initial reactions (i.e. addition of reagents at -78°C followed by 16h at room temperature for the completion of the reaction) yielded mainly the diazenes in close to quantitative yields and so all changes in conditions were relative to these reactions. Although the mechanism of formation of the cyclic products **27d** and **28** is unknown, it is assumed that the radicals $\text{ArC(NSPh)}_2\bullet$ are not involved, i.e. the condensation of two trithiolated molecules to give an acyclic intermediate with the elimination of Ph_2S_2 (see **Scheme 2.2**) is less endothermic than the homolytic cleavage of two S-N bonds (to give 2 $\text{ArC(NSPh)}_2\bullet$). The acyclic intermediate may then undergo ring closure to form an eight-membered ring (route **A**) or react with itself to form a larger acyclic chain which, subsequently, undergoes ring closure to give a sixteen-membered ring (route **B**). The intramolecular process depicted by route **A** should be favored under dilute conditions whereas chain growth (route **B**) would be preferred at higher concentrations. In the absence of evidence for the formation of other ring sizes, alternate pathways for chain growth, e.g. the formation of precursors to twelve-membered rings, are not considered in **Scheme 2.2**.



Scheme 2.2. Proposed pathways for the formation of rings.

Consequently, concentration was the first variable to be investigated. The first reaction was carried out at a concentration of 0.24M [of 4- $\text{BrC}_6\text{H}_4\text{CN}_2(\text{SiMe}_3)_3$]. This reaction yielded primarily the diazene **25h** and less than 1% of sixteen-membered ring **28**. When the concentration of 4- $\text{BrC}_6\text{H}_4\text{CN}_2(\text{SiMe}_3)_3$ was reduced to 0.016M the yield of diazene **25h** was again almost quantitative with less than 1% of the eight-membered ring **27d**. Since the yield of the cyclic products was so low it is difficult to say whether other rings were formed under these conditions.

The second variable investigated was temperature. Since the previous reactions were performed at -78°C , the next step was to attempt a reaction at higher temperatures. The typical reaction procedure involves adding the reagents together at -78°C and then allowing the reaction mixture to reach room temperature (over 16 h). A reaction was performed in which the reagents were added at 30°C (carefully monitored water bath) and then allowed to reach room temperature (25°C). In this reaction the yield of diazene **25h** was quantitative and there was no evidence of any cyclic products. A similar reaction was carried out in which the reagents were added to boiling carbon tetrachloride (at 77°C). This reaction also gave a quantitative yield of diazene **25h** with no cyclic products. The only conclusion that can be drawn for these two reactions is that elevated temperatures favor the formation of the diazene **25h**, which is the thermodynamic product.³⁴

Since higher temperatures did not give the desired products, the next obvious choice is lower temperatures. A reasonable lower temperature would be -100°C (acetone/ $\text{N}_2\text{(l)}$). In addition to temperature, the effect of reaction time was also investigated. As mentioned in Section 1.4 the reaction proceeds through a trisubstituted species ($\text{ArCN}_2(\text{SPh})_3$), which decomposes to a radical intermediate that, in turn, dimerizes to form the diazene. The aim is to slow down or prevent the formation of the radical intermediate, in order to allow the cyclization reaction to proceed. A reaction in which the reactants were added at -100°C and then kept at -30°C for 16h. gave a product distribution of 54.5% **25h**, 40% **27d** and 5.5% **28**, and an overall yield of 100%. Two other reactions were performed in which the reaction mixture was kept at -78°C after the addition at -100°C . The product distributions

from these reactions are listed in **Table 2.1**. From these results one can conclude that prolonged low temperatures favor the formation of cyclic products, whereas elevated temperatures lead to the diazene **25h** in quantitative yields. Also, the longer the reaction mixture is kept at low temperature the better the yield of the sixteen-membered ring **28**.

Table 2.1. Reaction conditions and relative product distribution of *Z*, *E*, *Z*-(Ph)SN(4-BrC₆H₄)CN=NC(4-BrC₆H₄)NS(Ph), (4-BrC₆H₄)₂C₂N₄S₂(Ph)₂ and (4-BrC₆H₄)₄C₄N₈S₄(Ph)₄.

	25h	27d	28
A	99%		<1%
B	99%	<1%	
C	100%		
D	100%		
E	54.5%	40%	5.5%
F	10%	80%	10%
G	22%	46%	32%

A) 0.24M at -78°C to RT

B) 0.016M at -78°C to RT

C) 0.325M at 30°C to RT

D) 0.287M at 77°C to RT

E) 0.036M at -100°C to -30°C for 16h.

F) 0.079M at -100°C to -78°C for 16h.

G) 0.034M at -100°C to -78°C for 40h.

25h = (Ph)SN(4-BrC₆H₄)CN=NC(4-BrC₆H₄)NS(Ph)

27d = (4-BrC₆H₄)₂C₂N₄S₂(Ph)₂

28 = (4-BrC₆H₄)₄C₄N₈S₄(Ph)₄

2.2.3 Spectroscopic Characterization of *Z*, *E*, *Z*-(Ph)SN(4-BrC₆H₄)CN=NC(4-BrC₆H₄)NS(Ph), (4-BrC₆H₄)₂C₂N₄S₂(Ph)₂ and (4-BrC₆H₄)₄C₄N₈S₄(Ph)₄.

The three products **25h**, **27d** and **28** can readily be distinguished by their ¹H-NMR spectra. The *para*-substituted aryl substituents on C give a characteristic AA'XX' spin system resulting in a doublet of doublets pattern in the aromatic region with some further fine structure. The phenyl groups on S give a multiplet, which can be assigned on

the basis of integration ratios. All ^1H -NMR data are listed in **Table 2.2**, and the spectra are shown in **Figure 2.3**.

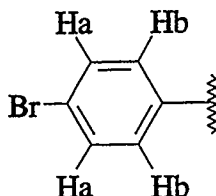


Table 2.2. ^1H -NMR data for *Z*, *E*, *Z*-(Ph)SN(4-BrC₆H₄)CN=NC(4-BrC₆H₄)NS(Ph) (**25h**), (4-BrC₆H₄)₂C₂N₄S₂(Ph)₂ (**27d**) and (4-BrC₆H₄)₄C₄N₈S₄(Ph)₄ (**28**).

	<u>δ (ppm)</u>	<u>Integration</u>	<u>Assignment</u>
25h	8.3 (doublet)	2	4-BrC ₆ (Ha) ₂ (Hb) ₂ -
	7.72 (doublet)	2	4-BrC ₆ (Ha) ₂ (Hb) ₂ -
	7.75 (multiplet)		
	7.52 (multiplet)	5	C ₆ H ₅ -
	7.38 (multiplet)		
	<u>δ (ppm)</u>	<u>Integration</u>	<u>Assignment</u>
27d	8.16 (multiplet)	5	C ₆ H ₅ -
	7.68 (multiplet)		
	8.05 (doublet)	2	4-BrC ₆ (Ha) ₂ (Hb) ₂ -
	7.47 (doublet)	2	4-BrC ₆ (Ha) ₂ (Hb) ₂ -
	<u>δ (ppm)</u>	<u>Integration</u>	<u>Assignment</u>
28	7.65-7.4 (multiplet)	7	C ₆ H ₅ -, 4-BrC ₆ (Ha) ₂ (Hb) ₂ -
	6.95 (doublet)	2	4-BrC ₆ (Ha) ₂ (Hb) ₂ -
Internal reference CDCl ₃			

Figure 2.3 shows the characteristic ^1H -NMR patterns for each compound. It is evident that a quick inspection of the ^1H -NMR spectra provides a good indication of the purity and identity of the compounds, which is important for verifying the separation of these products on a silica gel column. Also this information is vital for bulk sample characterization since the elemental analyses of these three compounds are identical.

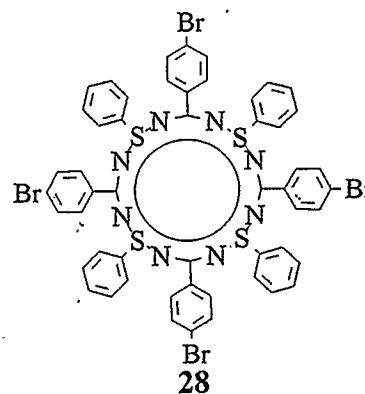
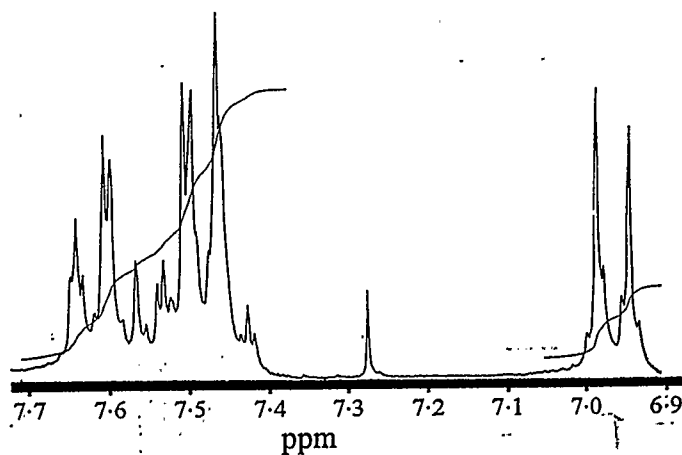
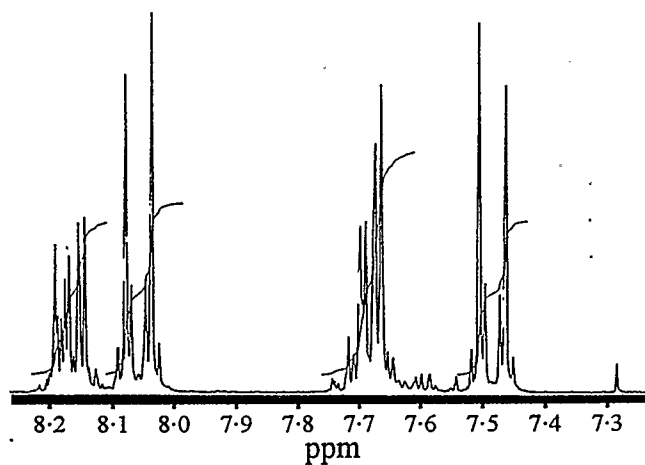
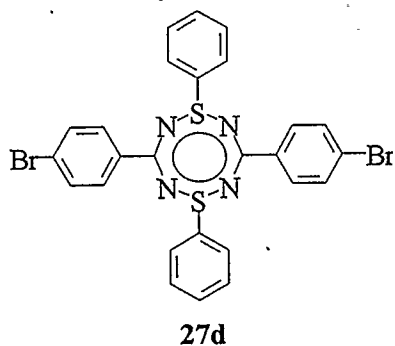
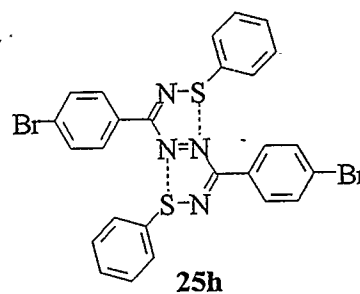
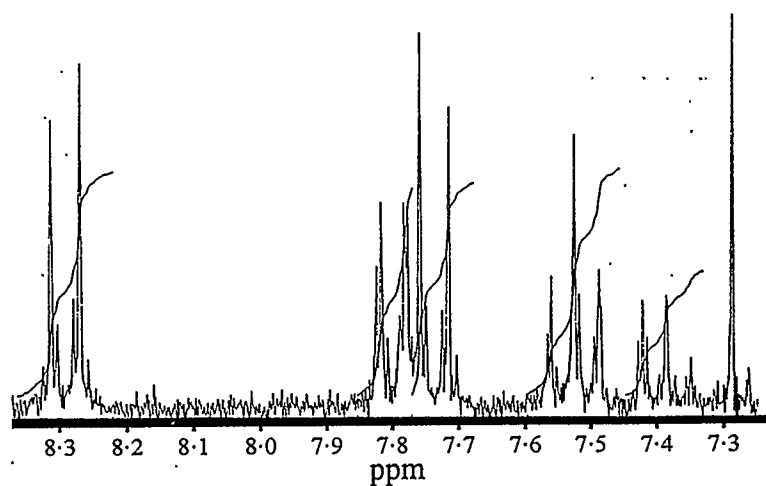


Figure 2.3. ^1H -NMR Spectra for *Z*, *E*, *Z*-(Ph)SN(4-BrC₆H₄)CN=NC(4-BrC₆H₄)NS(Ph), (4-BrC₆H₄)₂C₂N₄S₂(Ph)₂ and (4-BrC₆H₄)₄C₄N₈S₄(Ph)₄.

2.2.4 X-ray Structure of (4-BrC₆H₄)₂C₂N₄S₂(Ph)₂.

As mentioned in Chapter 1, Section 1.5 the identity of **28** was previously determined by X-ray crystallography, by Dr. M. Parvez.³⁶

In this work, the structure of **27d** was also determined by X-ray crystallography by Dr. M. Parvez. The crystals were carefully grown from a CH₂Cl₂/diethyl ether mixture for several weeks giving clusters of rectangular prisms suitable for X-ray analysis. The crystallographic data are summarized in **Table 2.3** and selected bond lengths, bond angles and torsional angles are given in **Table 2.4**. **Figure 2.4** illustrates an ORTEP drawing of the structure. Full details of the X-ray structure are available from Dr. M. Parvez.

Table 2.3. Crystallographic Parameters for (4-BrC₆H₄)₂C₂N₄S₂(Ph)₂.

Empirical Formula	C ₂₆ H ₁₈ N ₄ S ₂ Br ₂
Formula Weight	610.38
Crystal Color, Habit	yellow, prism
Crystal Dimensions	0.50 x 0.30 x 0.20 mm
Crystal System	monoclinic
Lattice Type	C-centered
Lattice Parameters	a=25.383(9) Å b=4.080(2) Å c=23.181(3) Å β=95.31(2)° V=2390(1) Å ³
Space Group	C2/c (# 15)
Z value	4
D _{calc}	1.696 g/cm ³
Temperature	-103°C
R	0.045
R _w	0.043

Compound **27d** is light sensitive (see Chapter 3) and so the data collection was performed in the dark (as much as possible). Low temperature was utilized in order to further reduce decomposition and thermal motion within the molecule. The space group $C2/c$ suggests internal symmetry in the molecule, namely a 2-fold rotation axis, which enables quicker data collection. Because of this internal symmetry, bond lengths and angles are only reported for half the molecule.

Table 2.4. Selected Bond Lengths (Å), Bond Angles (°) and Torsional Angles (°) for (4-BrC₆H₄)₂C₂N₄S₂(Ph)₂.

Atoms	(Å)	Atoms	(°)
S(1)-N(2)	1.650(7)	N(1)*-S(1)-N(2)	110.8(4)
N(1)-C(1)	1.328(9)	N(1)-S(1)-C(8)	98.4(4)
S(1)-N(1)	1.661(7)	N(2)-S(1)-C(8)	99.2(4)
N(2)-C(1)	1.339(10)	S(1)-N(1)-C(1)	118.0(6)
		S(1)-N(2)-C(1)	118.6(6)
		N(1)-C(1)-C(2)	112.7(7)
		N(1)-C(1)-N(2)	135.1(7)
		N(2)-C(1)-C(2)	112.1(7)
		S(1)*-N(1)-C(1)-N(2)	7(1)
		N(1)*-S(1)-N(2)-C(1)	87.7(7)
		S(1)-N(2)-C(1)-N(1)	-11(1)
		N(2)-S(1)-N(1)*-C(1)*	-81.6(7)

There are several important structural features of this heterocycle which need to be pointed out and explained. The eight-membered ring has a boat-boat conformation (C_{2v} symmetry).³⁹ The exocyclic substituents on S are equatorial and appear to be at an angle of approximately 90° with respect to one another. The bond lengths; S(1)-N(2) 1.650(7) Å, S(1)-N(1) 1.661(7) Å (cf. 1.710 Å for single S-N bond)⁴⁰, N(1)-C(1) 1.328(9) Å and N(2)-

C(1) 1.339(10) Å (cf. 1.46 Å for single N-C bond)⁴¹, indicate some π -bond delocalization within the ring. The torsional angles for one half of the ring, consisting of S(1)*-N(1)-C(1)-N(2) and S(1)-N(2)-C(1)-N(1) are 7(1)° and 11(1)° respectively, indicating virtual planarity for the SNCNS* units. The endocyclic angle S (i.e. N(1)*-S(1)-N(2)) is approximately 110°.

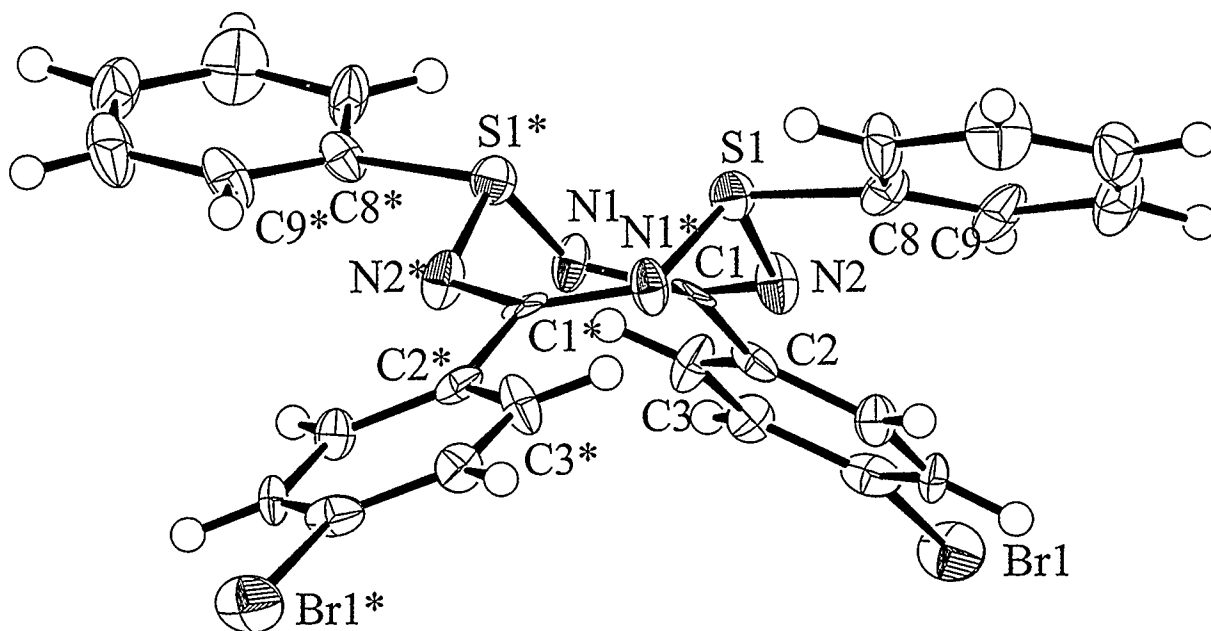
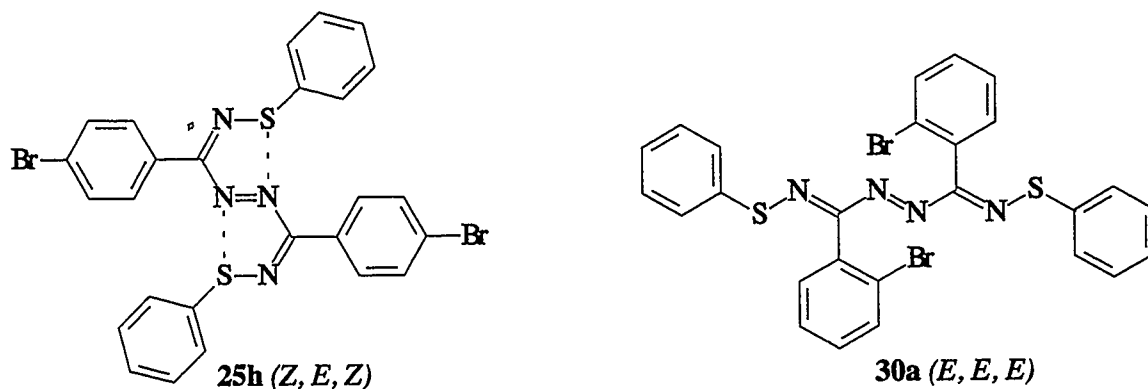


Figure 2.4. ORTEP diagram of (4-BrC₆H₄)₂C₂N₄S₂(Ph)₂.

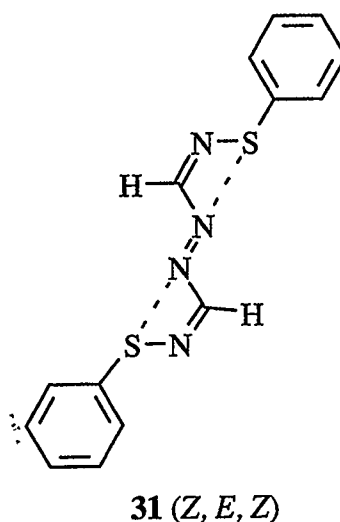
2.3 Reaction of 2-BrC₆H₄CN₂(SiMe₃)₃ with 3 PhSCl.

After the accidental discovery of the sixteen-membered ring **28**, it was considered of interest to see whether other aryl substituents would lead to the formation of additional sixteen-membered rings or, perhaps, larger macrocycles. To this end the reaction of 2-BrC₆H₄CN₂(SiMe₃)₃ with three molar equivalents of PhSCl was investigated. To our surprise the 2-BrC₆H₄- substituent behaves quite differently from the 4-BrC₆H₄- group. In contrast to the *Z, E, Z* geometry of **25h**, the 2-BrC₆H₄- substituent gives rise to the formation of **30a**, a new geometrical isomer of **25** (ignoring the different substituents on carbon). The *E, E, E* isomer **30a** (obtained in 50% yield) is red in color and appears to be just as stable as **25h**, and so it can be purified by column chromatography. The structure of **30a** was established by X-ray crystallography (see Section 2.3.2).



In addition to **30a** there is another product **W** in this reaction which, on the basis of C, H, N analysis has the same elemental composition as **30a**. However, compound **W** is white and has different properties from those of **30a**. For example, whereas **30a** is readily

soluble in CH_2Cl_2 , **W** is completely insoluble. The unknown compound **W** is insoluble in solvents such as DMSO, DMF and has poor solubility in nitrobenzene. However **W** can be recrystallized from nitrobenzene giving tiny white needles. In addition to the new diazene **30a**, there is another structurally characterized diazene **31** which is also a *Z, E, Z* isomer, but has a different orientation about the C-N single bonds compared to **25**. This compound was synthesized by Ignacio Vargas-Baca.³⁴



DFT calculations for the model diazene $(\text{H})\text{SNC}(\text{H})\text{N}=\text{NC}(\text{H})\text{NS}(\text{H})$ have been carried out to determine the relative stabilities of various geometrical isomers. **Figure 2.5** shows the potential energy diagram for model diazenes and the isomeric eight-membered ring. From the potential energy plot, several trends can be seen. First of all, the presence of the sulphur-nitrogen interaction seems to stabilize the system so that the classic closed diazene **25** is the thermodynamic product. To date analogues of compounds **I**, **II**, **III** and the eight-membered ring have been isolated and structurally characterized. There is also

some evidence for the presence of isomers **IV** and **V** on the basis of variable temperature

^1H -NMR studies of $(\text{Ph})\text{SNC}(\text{H})\text{N}=\text{NC}(\text{H})\text{NS}(\text{Ph})$.⁴²

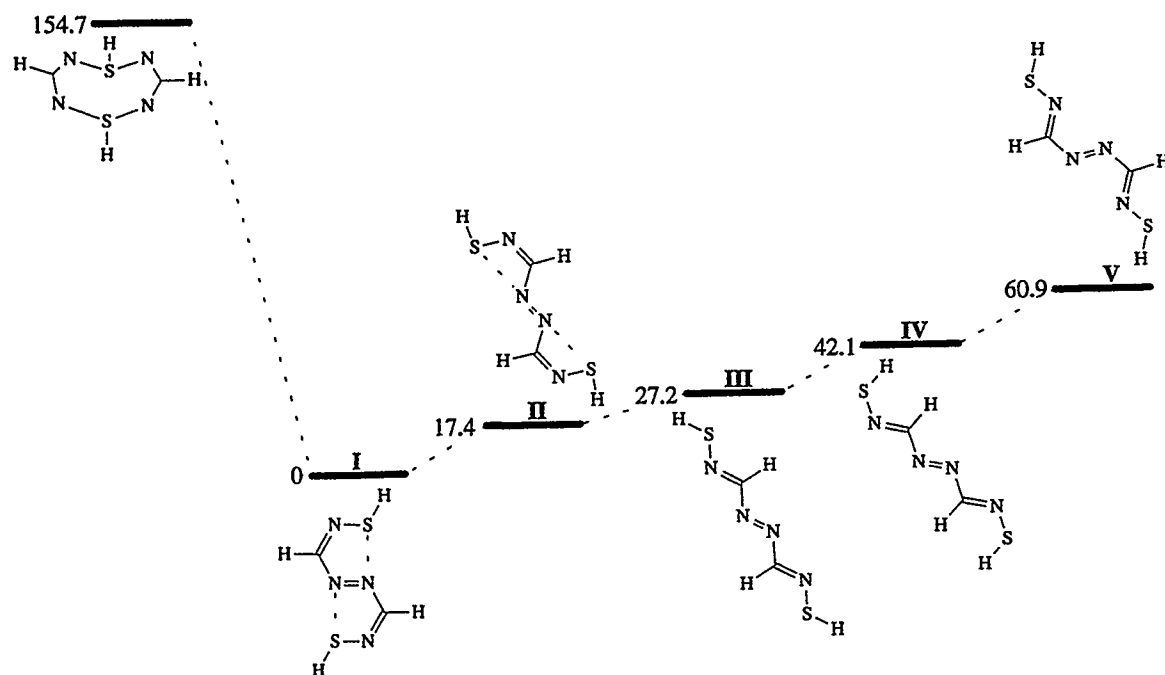


Figure 2.5. Calculated relative energies (kJ/mol) of $(\text{H})\text{SNC}(\text{H})\text{N}=\text{NC}(\text{H})\text{NS}(\text{H})$ isomers and the eight-membered ring $(\text{H})_2\text{C}_2\text{N}_4\text{S}_2(\text{H})_2$.³⁴

From **Figure 2.5** it can be seen that the linear diazene **III** (cf. **30a**) appears to be less stable by 27.2 kJ/mol than the thermodynamic diazene **I** (cf. **25**). Attempts to isomerize **30a** into the diazene **25**, in boiling toluene (2h.), were unsuccessful. A possible explanation for this could be the steric effects of the *ortho* substituted phenyl groups attached to carbon. This is not completely unreasonable since the X-ray structure (see **Figure 2.6**) shows the Br substituted phenyl to be twisted nearly 90° out of the plane of the rest of the molecule,

whereas diazene **25f** (the only other structurally characterized *Z, E, Z* S(II) diazene with aryl substituents on C and S) is essentially planar.

2.3.1 Spectroscopic Characterization of *E, E, E*-(Ph)SNC(2-BrC₆H₄)N=NC(2-BrC₆H₄)NS(Ph).

Unlike the 4-BrC₆H₄ derivative, ¹H-NMR is not a convenient probe for the 2-BrC₆H₄ substituent (because of the complex resonances). Consequently, characterization is based on elemental analysis, mass spectra and an X-ray structure.

2.3.2 X-ray Structure of *E, E, E*-(Ph)SNC(2-BrC₆H₄)N=NC(2-BrC₆H₄)NS(Ph).

Cubic crystals of **30a** were grown from a concentrated CH₂Cl₂ solution at -20°C. At higher temperatures, the compound crystallizes as very thin plates. The crystallographic data are summarized in **Table 2.5** and selected bond lengths, bond angles and torsional angles are given in **Table 2.6**. **Figure 2.6** illustrates an ORTEP drawing of the structure. Full details of the X-ray structure are available from Dr. M. Parvez.

Table 2.5. Crystallographic Parameters for *E, E, E*-(Ph)SNC(2-BrC₆H₄)N=NC(2-BrC₆H₄)NS(Ph).

Empirical Formula	C ₂₆ H ₁₈ N ₄ S ₂ Br ₂
Formula Weight	610.38
Crystal Color, Habit	red, prism
Crystal Dimensions	0.55 x 0.45 x 0.40 mm
Crystal System	orthorhombic
Lattice Parameters	a=13.884(5) Å
	b=24.763(7) Å
	c=14.500(3) Å

	V=4985(2) Å ³
Space Group	Ccca (# 68)
Z value	8
D _{calc}	1.626 g/cm ³
Temperature	-123°C
R	0.043
R _w	0.044

Table 2.6. Selected Bond Lengths (Å), Bond Angles (°) and Torsional Angles (°) for *E,E,E*-(Ph)SNC(2-BrC₆H₄)N=NC(2-BrC₆H₄)NS(Ph).

Atoms	(Å)	Atoms	(°)
N(1)-N(1)*	1.26(1)	N(2)-S(1)-C(8)	100.9(5)
N(1)-C(1)	1.41(1)	S(1)-N(2)-C(1)	118.5(6)
N(2)-C(1)	1.32(1)	N(1)-C(1)-N(2)	114.7(8)
N(2)-S(1)	1.627(8)	N(1)-C(1)-C(2)	120.5(9)
		N(1)*-N(1)-C(1)	113.5(9)
		N(2)-C(1)-C(2)	124.9(8)
		S(1)-N(2)-C(1)-N(1)	179.3(7)
		N(1)-C(1)-C(2)-C(3)	-94(1)
		N(1)*-N(1)-C(1)-N(2)	173.8(7)
		N(2)-S(1)-C(8)-C(9)	7(1)

The main feature of this compound is its unique geometry with respect to the C=N bonds. All previous diazenes isolated from the reaction of trisilylated benzamidines with benzenechalcogenyl chlorides are believed to exhibit the *Z, E, Z* structure analogous to **25f**.⁴² In this case, however, there is no S...N interaction, but rather a zig-zag chain consisting of S-N=C-N=N-C=N-S in an *E, E, E* conformation. The bond lengths indicate a tendency towards localization of single and double bonds, in contrast to the eight-membered ring **27d**, in which delocalization is evident (see Section 2.2.4). The C(1)-N(1) bond distance is 1.41 Å (cf. 1.46 Å for a single C-N bond) and the C(1)-N(2) bond distance is 1.26 Å (cf. 1.28 Å for a double C=N bond)⁴¹. The torsional angles show the chain and

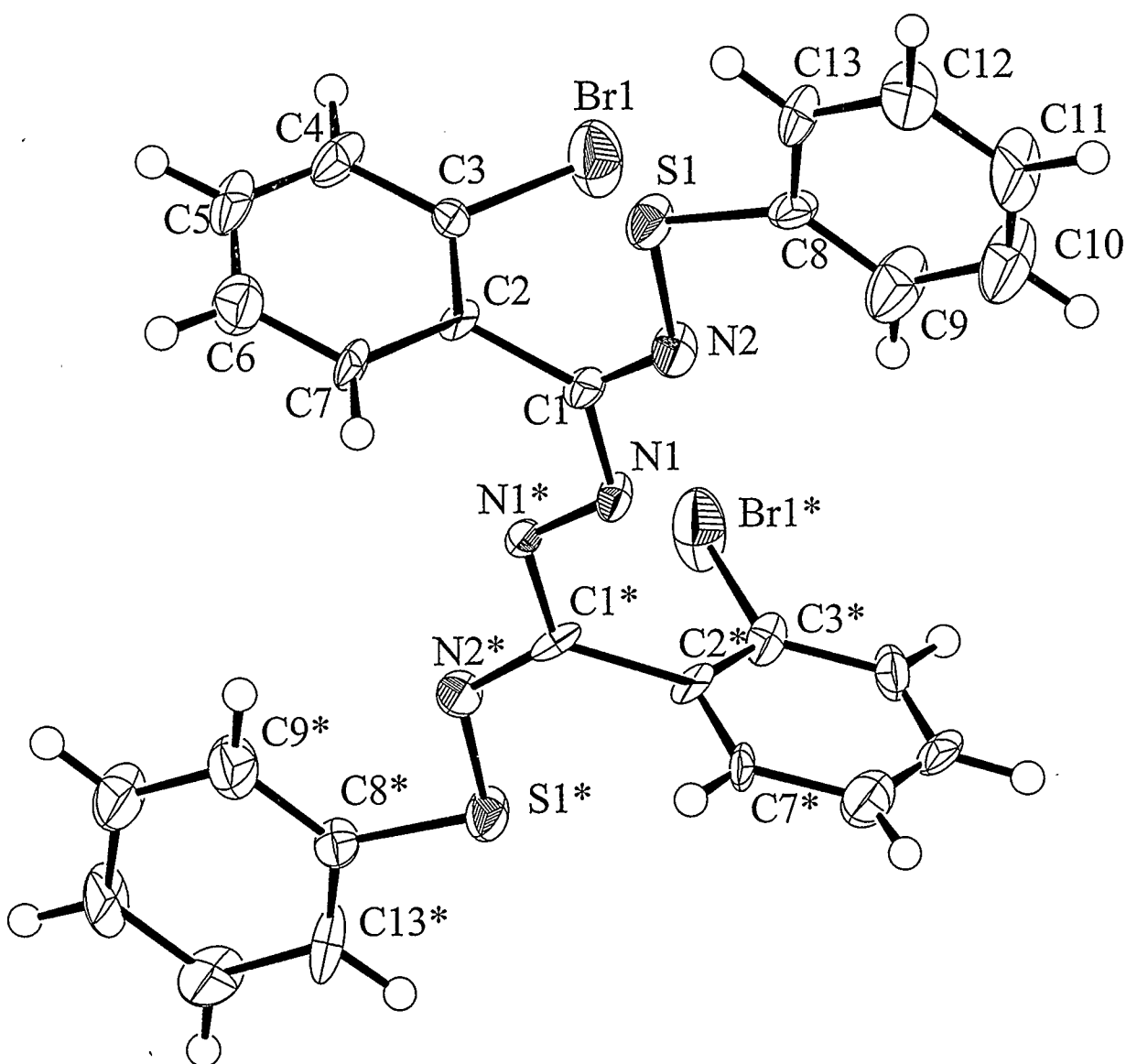


Figure 2.6. ORTEP diagram of *E, E, E*-(Ph)SN=C(2-BrC₆H₄)N=NC(2-BrC₆H₄)=NS(Ph).

the phenyl groups on S are almost coplanar with deviation of less than 10° from the plane consisting of C(9)*-C(8)*-S(1)*-N(2)*-C(1)*-N(1)*-N(1)-C(1)-N(2)-S(1)-C(8)-C(9). The 2-BrC₆H₄- group on C is essentially perpendicular to the rest of the molecule with a torsional angle of $-94(1)^\circ$ for N(1)-C(1)-C(2)-C(3).

2.4 Reaction of *E, E, E*-(Ph)SN=C(2-BrC₆H₄)N=NC(2-BrC₆H₄)=NS(Ph) with (Ph₃P)₂Pt(H₂C=CH₂)

To further explore the possibility of isomerization of **30a** to **25** a Pt complex of **30a** was synthesized by reaction with Pt(PPh₃)₂(H₂C=CH₂) (see Section 2.11.7) for comparison with the X-ray structure of **26a**, which was made using the *Z, E, Z* diazene **25d**.³⁵ The new Pt complex **26b**, is yellow like **26a**.

2.4.1 Spectroscopic Characterization of Pt{PhSNC(2-BrC₆H₄)N-NC(2-BrC₆H₄)NSPh}(PPh₃)

Table 2.7. ³¹P-NMR data for Pt{PhSNC(2-BrC₆H₄)N-NC(2-BrC₆H₄)NSPh}(PPh₃) (**26b**)

	<u>δ (ppm)</u>		
26b	16.5 (singlet)	¹ J _{195Pt,31P} 3609Hz	in CDCl ₃

2.4.2 X-ray Structure of Pt{PhSNC(2-BrC₆H₄)N-NC(2-BrC₆H₄)NSPh}(PPh₃)

Rectangular prism crystals of **26b** were grown from a CH₂Cl₂/diethyl ether solution at room temperature. The asymmetric unit contains two molecules (designated by **a** and **b** in the X-ray data) which resulted in a lengthy data collection. The crystallographic data are

summarized in **Table 2.8** and selected bond lengths and bond angles are given in **Table 2.9**.

The fractional subscripts in the empirical formula account for a cocrystallized diethyl ether molecule which is present for every four molecules of $\text{Pt}\{\text{PhSNC}(2\text{-BrC}_6\text{H}_4)\text{N-NC}(2\text{-BrC}_6\text{H}_4)\text{NSPh}\}(\text{PPh}_3)$. **Figure 2.7** illustrates an ORTEP drawing of the structure. Full details of the X-ray structure are available from Dr. M. Parvez.

Table 2.8. Crystallographic Parameters for $\text{Pt}\{\text{PhSNC}(2\text{-BrC}_6\text{H}_4)\text{N-NC}(2\text{-BrC}_6\text{H}_4)\text{NSPh}\}(\text{PPh}_3)$

Empirical Formula	$\text{C}_{45}\text{H}_{35.50}\text{N}_4\text{S}_2\text{PBr}_2\text{PtO}_{0.25}$
Formula Weight	1086.29
Crystal Color, Habit	yellow, prism
Crystal Dimensions	0.25 x 0.20 x 0.16 mm
Crystal System	triclinic
Lattice Parameters	$a=18.497(5) \text{ \AA}$ $b=18.769(6) \text{ \AA}$ $c=14.005(4) \text{ \AA}$ $\alpha=103.86(2)^\circ$ $\beta=95.55(2)^\circ$ $\gamma=73.23(2)^\circ$ $V=4517(2) \text{ \AA}^3$
Space Group	$P\bar{1} \text{ (#2)}$
Z value	4
D_{calc}	1.597 g/cm^3
Temperature	-73.0°C
R	0.062
R_w	0.063

Table 2.9. Selected Bond Lengths (Å) and Bond Angles (°) for Pt{PhSNC(2-BrC₆H₄)N-NC(2-BrC₆H₄)NSPh}(PPh₃) (a).

Atoms	(Å)	Atoms	(°)
S(1a)-Pt(1a)	2.24(1)	P(1a)-Pt(1a)-S(1a)	97.7(3)
P(1a)-Pt(1a)	2.27(1)	N(2a)-Pt(1a)-S(1a)	82.6(8)
N(2a)-Pt(1a)	1.95(2)	N(2a)-Pt(1a)-P(1a)	171.9(8)
N(4a)-Pt(1a)	2.03(2)	N(4a)-Pt(1a)-S(1a)	159.3(7)
N(1a)-S(1a)	1.69(3)	N(4a)-Pt(1a)-P(1a)	102.8(7)
N(4a)-S(2a)	1.70(3)	N(4a)-Pt(1a)-N(2a)	76.7(10)
C(1a)-N(1a)	1.33(4)	N(1a)-S(1a)-Pt(1a)	103.0(10)
N(3a)-N(2a)	1.35(3)	C(1a)-N(1a)-S(1a)	111(2)
C(1a)-N(2a)	1.36(4)	N(3a)-N(2a)-Pt(1a)	125(2)
C(2a)-N(3a)	1.28(4)	C(1a)-N(2a)-Pt(1a)	117(2)
C(2a)-N(4a)	1.47(4)	C(1a)-N(2a)-N(3a)	118(3)
		C(2a)-N(3a)-N(2a)	107(2)
		S(2a)-N(4a)-Pt(1a)	128(1)
		C(2a)-N(4a)-Pt(1a)	109(2)
		C(2a)-N(4a)-S(2a)	120(2)
		N(2a)-C(1a)-N(1a)	126(3)
		N(4a)-C(2a)-N(3a)	123(3)

Table 2.9. Cont. Selected Bond Lengths (Å) and Bond Angles (°) for Pt{PhSNC(2-BrC₆H₄)N-NC(2-BrC₆H₄)NSPh}(PPh₃) (b).

Atoms	(Å)	Atoms	(°)
S(1b)-Pt(1b)	2.27(1)	P(1b)-Pt(1b)-S(1b)	101.3(3)
P(1b)-Pt(1b)	2.27(1)	N(2b)-Pt(1b)-S(1b)	79.8(8)
N(2b)-Pt(1b)	1.96(3)	N(2b)-Pt(1b)-P(1b)	173.9(8)
N(4b)-Pt(1b)	2.03(3)	N(4b)-Pt(1b)-S(1b)	158.1(8)
N(1b)-S(1b)	1.69(3)	N(4b)-Pt(1b)-P(1b)	100.6(8)
N(4b)-S(2b)	1.72(3)	N(4b)-Pt(1b)-N(2b)	78.4(11)
C(1b)-N(1b)	1.32(3)	N(1b)-S(1b)-Pt(1b)	100.9(9)
N(3b)-N(2b)	1.43(3)	C(1b)-N(1b)-S(1b)	117(2)
C(1b)-N(2b)	1.32(4)	N(3b)-N(2b)-Pt(1b)	116(2)
C(2b)-N(3b)	1.23(4)	C(1b)-N(2b)-Pt(1b)	124(2)
C(2b)-N(4b)	1.42(4)	C(1b)-N(2b)-N(3b)	120(3)
		C(2b)-N(3b)-N(2b)	114(3)
		S(2b)-N(4b)-Pt(1b)	125(2)
		C(2b)-N(4b)-Pt(1b)	111(2)
		C(2b)-N(4b)-S(2b)	116(2)
		N(2b)-C(1b)-N(1b)	118(3)
		N(4b)-C(2b)-N(3b)	120(3)

The ESDs on the structural data are quite large due to refinement of certain atoms isotropically instead of anisotropically and also the poor reflection:parameter ratio; however, certain trends can be pointed out. The two independent molecules in the asymmetric unit (designated by **a** and **b**) are nearly superimposable mirror images apart from some slight differences in the orientation of the phenyl substituents and so the data will only be discussed for molecule **a**. The diazene **30a** has undergone significant transformation upon coordination to platinum. Compound **30a** is attached to platinum through S(1a), N(2a) and N(4a) in a tridentate fashion forming two five-membered rings. One main feature of this complex is that the N(3a)-N(2a) bond distance of 1.35(3) Å (cf. N=N of 1.26(1) Å in **30a**) indicates a partial reduction to a single N-N bond. Also the C(2a)-N(3a) bond distance of 1.28(4) Å (cf. C-N of 1.41(1) Å in **30a**) now suggests the presence of a C=N double bond. In the second five-membered ring the C(1a)-N(1a) and C(1a)-N(2a) bond distances of 1.33(4) Å and 1.36(4) Å, respectively, indicate delocalization in the NCN segment. All of these structural features are comparable to the previously structurally characterized complex **26a**.³⁵

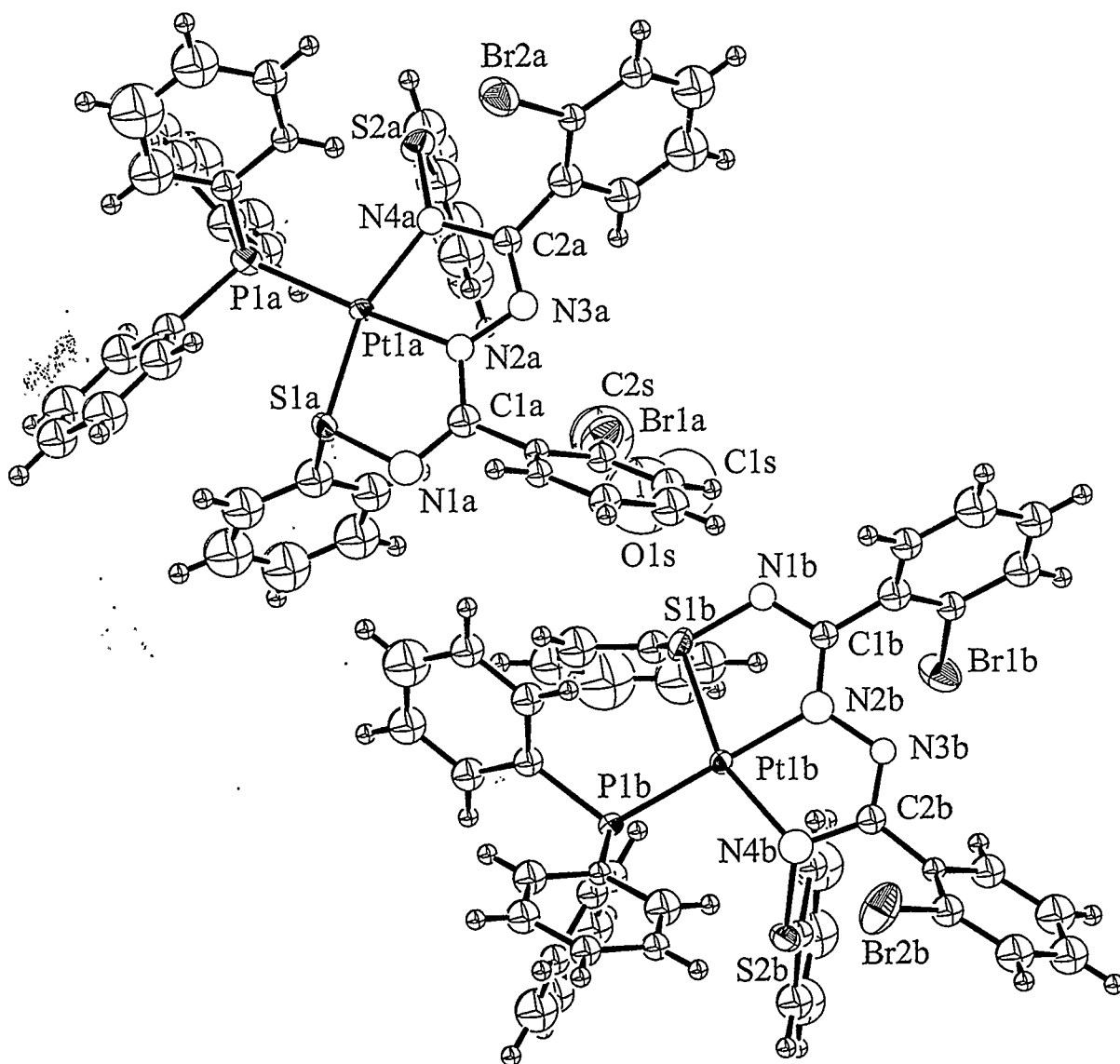


Figure 2.7. ORTEP diagram of $\text{Pt}\{\text{PhSNC}(\text{2-BrC}_6\text{H}_4)\text{N-NC}(\text{2-BrC}_6\text{H}_4)\text{NSPh}\}(\text{PPh}_3)$.

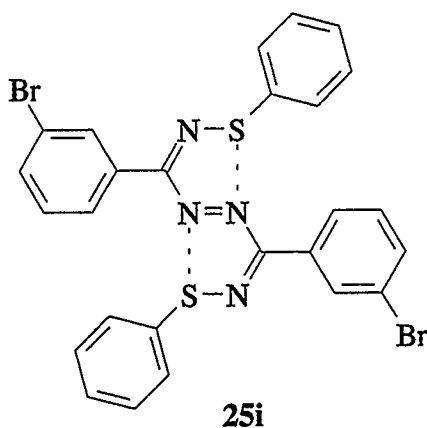
2.5 Reaction of 2-CF₃C₆H₄CN₂(SiMe₃)₃ with 3 PhSCL.

To test the hypothesis that steric effects are the predominant factor favoring the *E, E* geometry of the novel diazene **30a**, a reaction was attempted utilizing the 2-CF₃C₆H₄ group on C. In this reaction the diazene *E, E, E*-(Ph)SNC(2-CF₃C₆H₄)N=NC(2-CF₃C₆H₄)NS(Ph) (**30b**), which exhibits striking similarities to **30a**, was isolated in 25% yield. These linear diazenes exhibit characteristic absorption maxima in the UV-visible spectrum. Unlike the diazenes of the type **25**, which have $\lambda_{\text{max.}} = 500\text{-}550\text{ nm}$, the two linear diazenes **30a** and **30b** both have $\lambda_{\text{max.}} = 469\text{ nm}$. In addition to identical $\lambda_{\text{max.}}$ values, these diazenes appear to have similar solubilities in pentane and CH₂Cl₂, as well as similar EI-MS and ¹H-NMR spectra. Owing to the numerous similarities between **30a** and **30b** an X-ray structural analysis was not attempted. In addition to **30b**, a second product **X** was isolated in about three times the yield of **30b** (by mass). This product has similar properties to those of the unidentified compound **W**.

2.6 Reaction of 3-BrC₆H₄CN₂(SiMe₃)₃ with 3 PhSCL.

With the isolation of the new compounds **27d**, **28**, and **30**, and with little understanding as to the effects that determine their formation, it was of interest to investigate the effects of a 3-BrC₆H₄- substituent on the carbon of ArCN₂(SiMe₃)₃. In contrast to the previous reactions this particular experiment did not yield any unusual compounds but, as with the previous two experiments, the reactions were not simple in that more than one major product was formed. In this reaction the closed diazene **25i**

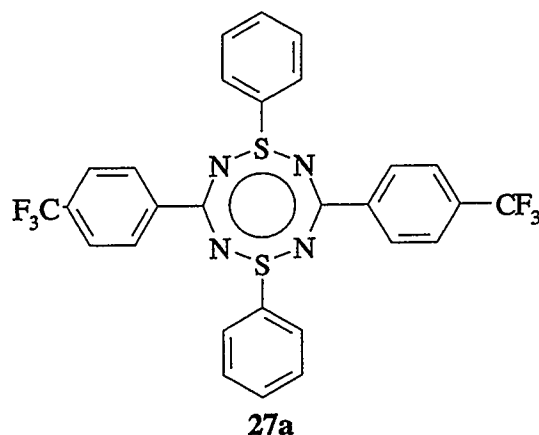
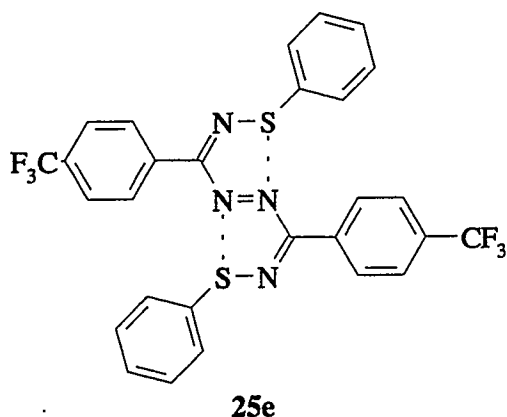
(analogous to **25h**) was formed in 75% yield and a second product **Y** was isolated as colorless rectangular-prism crystals in approximately 22% yield. The identity of this new compound **Y** is a little puzzling, due to some conflicting data (see Section 2.11.9), and further discussion would not be useful.



2.7 Reaction of 4-CF₃C₆H₄CN₂(SiMe₃)₃ with 3 PhSCL.

The effect of a more electronegative substituent than Br in the *para* position, i.e. CF₃, in the aryl group of ArCN₂(SiMe₃)₃ was investigated to determine how the electronic properties of the substituent on C will influence the nature of the products formed. The reaction conditions which favor the formation of cyclic products (addition of reagents at -100°C and then allowing the reaction to stand at -78°C for 16h.) were employed. However, in this reaction no evidence for the formation of a sixteen-membered ring was evident from the TLC. The three products that were observed were: the closed diazene **25e** (19%), the eight-membered ring **27a** (81%) and a burgundy compound which readily changed color to

the purple diazene **25e**. Due to the instability of the burgundy compound, it was not isolated, but only observed on the TLC.



2.7.1 Spectroscopic Characterization of *Z*, *E*, *Z*-(Ph)SN(4-CF₃C₆H₄)CN=NC(4-CF₃C₆H₄)NS(Ph) and (4-CF₃C₆H₄)₂C₂N₄S₂(Ph)₂.

The 4-CF₃C₆H₄- substituent, like 4-BrC₆H₄-, gives rise to simple AA'XX' (doublet of doublet) pattern in the ¹H-NMR spectra that can be used to quickly determine the identity and purity of compounds. This is very useful when dealing with mixtures of products which either have to be separated by chromatography or fractional crystallization.

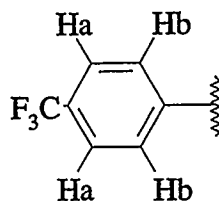


Table 2.10. ¹H-NMR data for *Z*, *E*, *Z*-(Ph)SN(4-CF₃C₆H₄)CN=NC(4-CF₃C₆H₄)NS(Ph) (**25e**) and (4-CF₃C₆H₄)₂C₂N₄S₂(Ph)₂ (**27a**).

	<u>δ (ppm)</u>	<u>Integration</u>	<u>Assignment</u>
25e	8.5 (doublet)	2	4-CF ₃ C ₆ (Hb) ₂ (Ha) ₂ -
	7.5 (doublet)	2	4-CF ₃ C ₆ (Hb) ₂ (Ha) ₂ -
	7.8 (multiplet)		

	7.55	(multiplet)	5	C ₆ H ₅ -
	7.38	(multiplet)		
	<u>δ (ppm)</u>		<u>Integration</u>	<u>Assignment</u>
27a	8.2	(multiplet)	5	C ₆ H ₅ -
	7.7	(multiplet)		
	8.3	(doublet)	2	4-CF ₃ C ₆ (Hb) ₂ (Ha) ₂ -
	7.62	(doublet)	2	4-CF ₃ C ₆ (Hb) ₂ (Ha) ₂ -

Internal reference CDCl₃

2.7.2 X-ray Structure of (4-CF₃C₆H₄)₂C₂N₄S₂(Ph)₂.

Crystals of compound **27a** were grown as long rectangular prisms by slow evaporation of a CH₂Cl₂ solution. The crystals were cut to an appropriate size. This proved somewhat difficult owing to cocrystallized solvent (identified by ¹H-NMR and subsequent X-ray structural determination) within the crystal and upon attempting to cut them they shattered. Eventually a suitable crystal was obtained and a good data set was collected. Like the other eight-membered ring **27d**, this heterocycle is also sensitive to light and so similar precautions were employed (see Section 2.2.4). The crystallographic data are summarized in **Table 2.11** and selected bond lengths, bond angles and torsional angles are given in **Table 2.12**. **Figure 2.8** illustrates an ORTEP drawing of the structure. Full details of the X-ray structure are available from Dr. M. Parvez. The structure was solved by N. Sandblom as part of a Chemistry 681 class project.

Table 2.11. Crystallographic Parameters for (4-CF₃C₆H₄)₂C₂N₄S₂(Ph)₂.

Empirical Formula	C ₂₈ H ₁₈ N ₄ S ₂ F ₆ •0.5CH ₂ Cl ₂
Formula Weight	631.05
Crystal Color, Habit	yellow, prism
Crystal Dimensions	0.45 x 0.30 x 0.15 mm
Crystal System	monoclinic

Lattice Parameters	a=27.417(6) Å
	b=7.933(4) Å
	c=26.772(7) Å
	β =111.07(3)°
	V=5433(3) Å ³
Space Group	C2/c (# 15)
Z value	8
D _{calc}	1.543 g/cm ³
Temperature	-73.0°
R	0.055
R _w	0.055

In comparison to the structure of the eight-membered ring **27d** there are several key differences which need to be pointed out. Similar to **27d**, the heterocycle **27a** also crystallizes in the C2/c space group, but there is no longer a twofold rotation axis within the molecule. As a result the asymmetric unit now consists of an entire molecule giving rise to eight molecules in the unit cell.

Table 2.12. Selected Bond Lengths (Å), Bond Angles (°) and Torsional Angles (°) for (4-CF₃C₆H₄)₂C₂N₄S₂(Ph)₂.

Atoms	(Å)	Atoms	(°)
S(1)-N(1)	1.651(6)	N(1)-S(1)-N(4)	112.5(3)
S(1)-N(4)	1.634(6)	N(2)-S(2)-N(3)	114.1(3)
S(2)-N(2)	1.623(5)	S(1)-N(1)-C(13)	118.6(5)
S(2)-N(3)	1.652(5)	S(2)-N(2)-C(13)	125.5(5)
N(2)-C(13)	1.330(7)	S(2)-N(3)-C(21)	124.0(4)
N(1)-C(13)	1.319(7)	S(1)-N(4)-C(21)	118.1(5)
N(4)-C(21)	1.348(7)	N(1)-C(13)-N(2)	132.9(6)
N(3)-C(21)	1.312(7)	N(3)-C(21)-N(4)	133.6(6)
		S(1)-N(1)-C(13)-N(2)	6(1)
		S(1)-N(4)-C(21)-N(3)	-17(1)
		S(2)-N(2)-C(13)-N(1)	-15(1)
		S(2)-N(3)-C(21)-N(4)	3(1)
		N(1)-S(1)-N(4)-C(21)	93.3(6)
		N(2)-S(2)-N(3)-C(21)	-66.2(7)
		N(3)-S(2)-N(2)-C(13)	82.4(6)
		N(4)-S(1)-N(1)-C(13)	-78.6(6)

The C₂N₄S₂ ring still has a boat-boat conformation, but the two halves of the ring are slightly different, thus resulting in no symmetry within the molecule. The exocyclic substituents on sulfur are equatorial and appear to be at an angle of approximately 90° with respect to one another. The bond lengths; S(1)-N(1) 1.651(6) Å, S(1)-N(4) 1.634(6) Å, S(2)-N(2) 1.623(5) Å, S(2)-N(3) 1.652(5) Å, (cf. 1.710 Å for single S-N bond)⁴⁰, N(2)-C(13) 1.330(7) Å, N(1)-C(13) 1.319(7) Å, N(4)-C(21) 1.348(7) Å, N(3)-C(21) 1.312(7) Å (cf. 1.46 Å for single N-C bond)⁴¹, indicate some π -bond delocalization within the ring. Torsional angles indicate the two halves of the ring, consisting of S(1)-N(1)-C(13)-N(2) and S(2)-N(3)-C(21)-N(4), are essentially planar with deviation of 6(1)° and 3(1)° on the two halves. The angle between the two halves is different at each S, which makes this compound slightly different from **27d**. At S(1) the bond angle for N(1)-S(1)-N(4) is 112.5(3)° and at S(2) the bond angle for N(2)-S(2)-N(3) is 114.1(3)°.

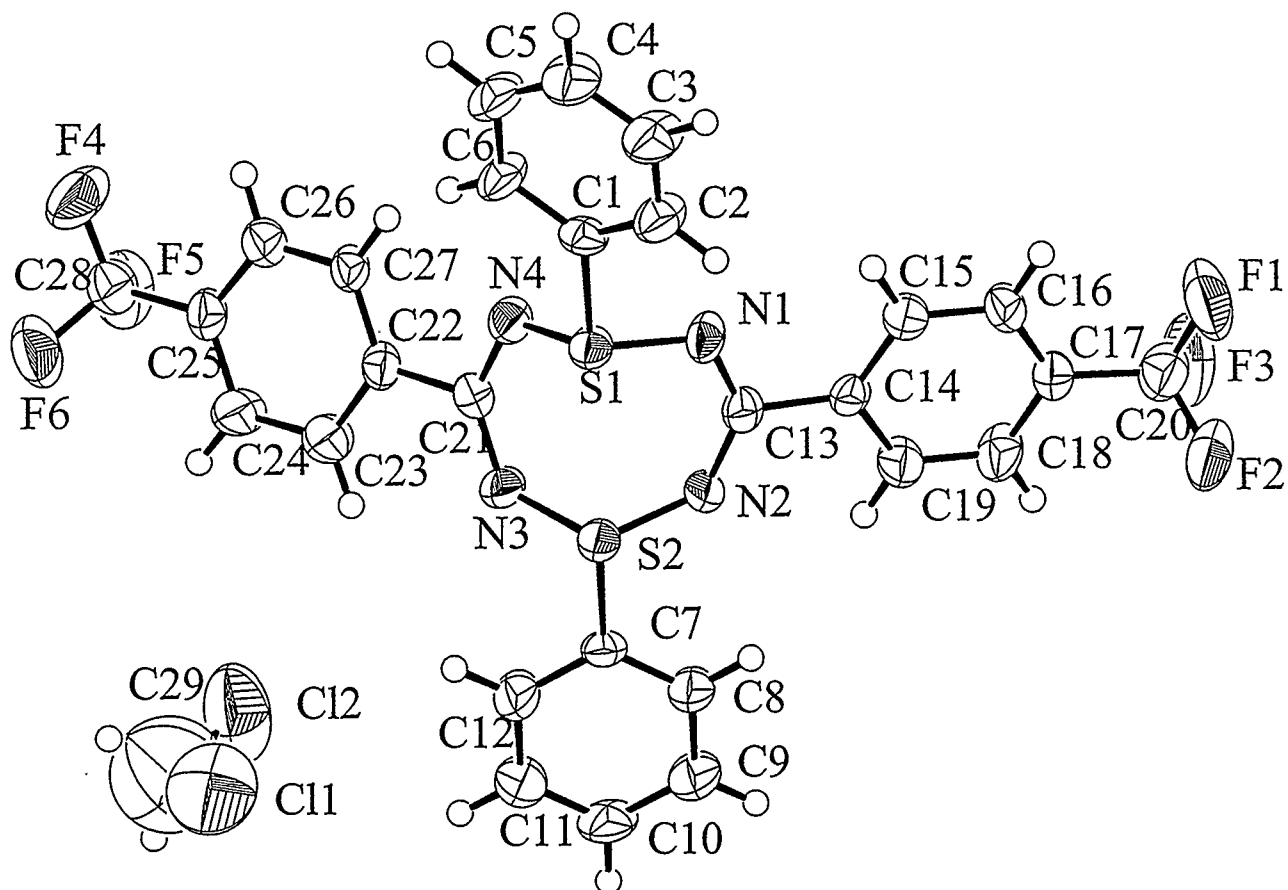
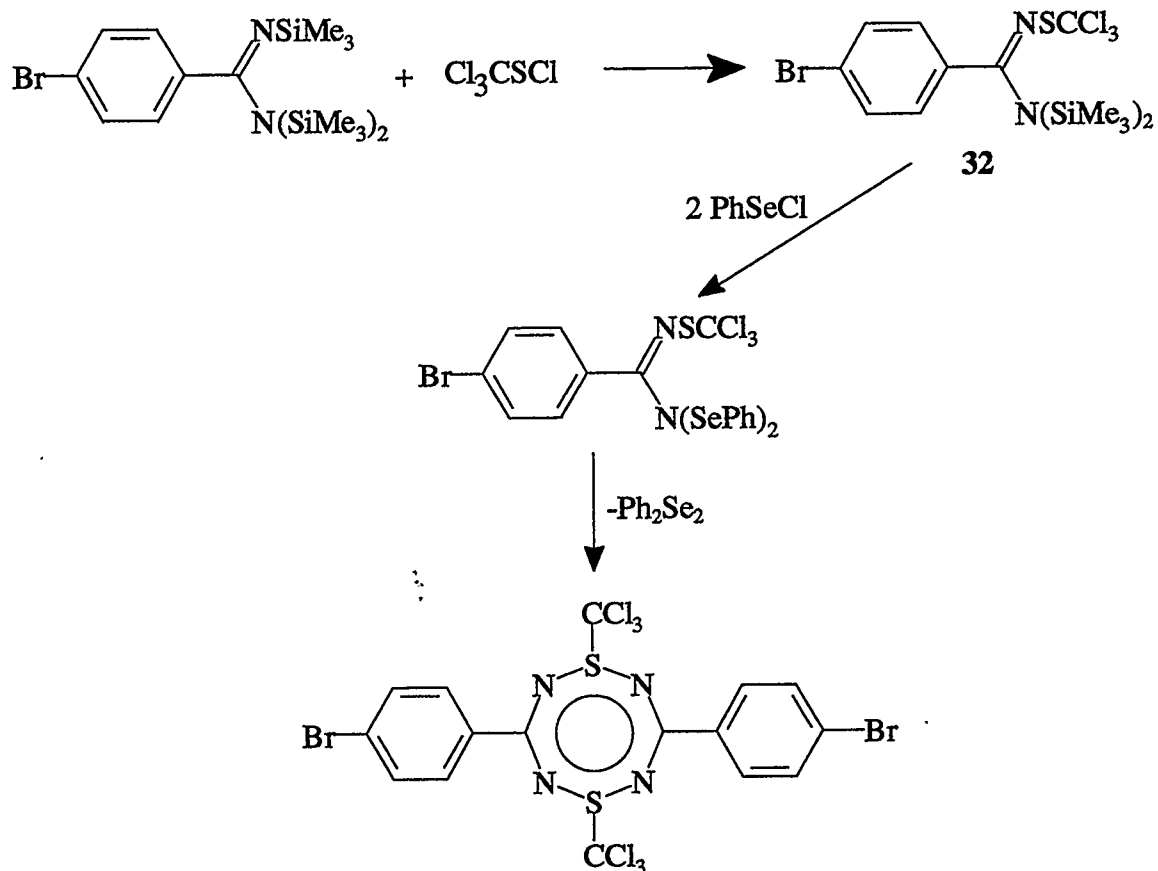


Figure 2.8. ORTEP diagram of $(4\text{-CF}_3\text{C}_6\text{H}_4)_2\text{C}_2\text{N}_4\text{S}_2(\text{Ph})_2$.

2.8 Reaction of 4-BrC₆H₄CN₂(SiMe₃)₃ with Cl₃CSCl.

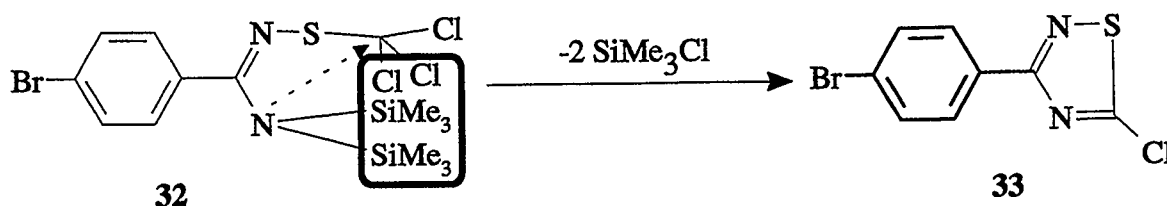
In an attempt to devise a synthetic route that would primarily produce the eight-membered ring, the following scheme was considered.



Scheme 2.3. Attempted synthesis of the eight-membered ring (4-BrC₆H₄)₂C₂N₄S₂(CCl₃)₂.

The first step of this synthesis was the preparation of the mono-substituted derivative 4-BrC₆H₄C(NSCCl₃)[N(SiMe₃)₂] **32**. This reaction proved successful based on ¹H-NMR data, but there was also some evidence for the formation of a five-membered ring system 4-

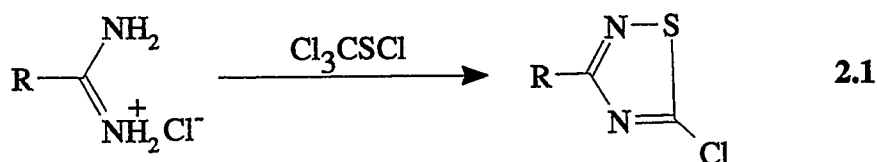
$\text{BrC}_6\text{H}_4\text{CNSC}(\text{Cl})\text{N}$ (**33**). In light of the formation of this five-membered heterocycle the subsequent reaction of **32** with benzeneselenenyl chloride was not explored. The five-membered ring **33** was obtained (in 82% yield) as pale beige rectangular crystals after slow evaporation of a diethyl ether solution. The reaction that gave compound **33** seems to have been a nucleophilic attack of the amino N (with the two SiMe_3 groups) on the electron poor C (with three Cls), resulting in a thermodynamically favourable ring closure with elimination of two ClSiMe_3 molecules (see Scheme 2.4).



Scheme 2.4. Proposed route to $4\text{-BrC}_6\text{H}_4\text{CNSC}(\text{Cl})\text{N}$.

The heterocyclic ring system exemplified by **33** i.e. a 1,2,4-thiadiazole is well known.

Numerous synthetic approaches exist to these compounds with varying substituents present on C, N or S.⁴³⁻⁴⁷ The closest analogy to the synthesis described above involves the reaction of $\text{RC}(\text{NH}_2)[\text{NH}_2^+]\text{Cl}^-$ with Cl_3CSCl , see equation 2.1.⁴⁷



2.8.1 Spectroscopic Characterization of 4-BrC₆H₄C(NSCCl₃)[N(SiMe₃)₂],

4-BrC₆H₄CNSC(Cl)N.

The three products can readily be distinguished by their ¹H-NMR spectra. All ¹H-NMR data are listed in **Table 2.13**.

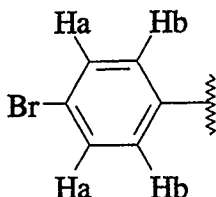


Table 2.13. ¹H-NMR data for 4-BrC₆H₄C(NSCCl₃)[N(SiMe₃)₂] (**32**), 4-BrC₆H₄CNSC(Cl)N (**33**).

	<u>δ (ppm)</u>		<u>Integration</u>	<u>Assignment</u>
32	8.8	(doublet)	2	4-BrC ₆ (<u>Ha</u>) ₂ (Hb) ₂ -
	7.56	(doublet)	2	4-BrC ₆ (Ha) ₂ (<u>Hb</u>) ₂ -
	0.3	(singlet)	18	N(Si(<u>CH</u> ₃) ₃) ₂
33	8.15	(doublet)	2	4-BrC ₆ (<u>Ha</u>) ₂ (Hb) ₂ -
	7.65	(doublet)	2	4-BrC ₆ (Ha) ₂ (<u>Hb</u>) ₂ -

Internal reference CDCl₃

2.8.2 X-ray Structure of 4-BrC₆H₄CNSC(Cl)N.

Crystals of compound **33** were grown by slow evaporation of a diethyl ether solution to give long rectangular plate crystals. The crystallographic data are summarized in **Table 2.14** and selected bond lengths, bond angles and torsional angles are given in **Table 2.15**. **Figure 2.9** illustrates an ORTEP drawing of the structure. Full details of the X-ray structure are available from Dr. M. Parvez.

Table 2.14. Crystallographic Parameters for 4-BrC₆H₄CNSC(Cl)N.

Empirical Formula	C ₈ H ₄ N ₂ SBrCl
Formula Weight	275.55
Crystal Color, Habit	pale beige, plate
Crystal Dimensions	0.50 x 0.40 x 0.20 mm
Crystal System	triclinic
Lattice Parameters	a=7.957(3) Å
	b=10.864(5) Å
	c=5.625(1) Å
	α=95.94(3)°
	β=111.07(3)°
	γ=100.72(3)°
	V=469.2(3) Å ³
Space Group	P $\bar{1}$ (# 2)
Z value	2
D _{calc}	1.950 g/cm ³
Temperature	-103.0°
R	0.042
R _w	0.041

Table 2.15. Selected Bond Lengths (Å), Bond Angles (°) and Torsional Angles (°) for 4-BrC₆H₄CNSC(Cl)N.

Atoms	(Å)	Atoms	(°)
S-N(2)	1.650(6)	N(2)-S-C(1)	91.8(3)
S-C(1)	1.709(7)	C(1)-N(1)-C(2)	107.9(5)
N(1)-C(1)	1.302(7)	S-N(2)-C(2)	108.4(5)
C(2)-N(1)	1.380(8)	Cl-C(1)-S	122.8(4)
N(2)-C(2)	1.331(7)	Cl-C(1)-N(1)	123.5(5)
Cl-C(1)	1.706(7)	S-C(1)-N(1)	113.6(5)
		N(1)-C(2)-N(2)	118.3(6)
		Cl-C(1)-S-N(2)	-178.8(4)
		Cl-C(1)-N(1)-C(2)	178.8(4)
		S-N(2)-C(2)-N(1)	0.0(7)
		S-N(2)-C(2)-C(3)	179.8(4)
		S-C(1)-N(1)-C(2)	-0.6(6)
		C(1)-S-N(2)-C(2)	-0.3(5)

Numerous structurally characterized examples of 1,2,4-thiadiazoles exist with N, C and S bound substituents on the two cyclic C atoms.⁴³⁻⁴⁷ A common structural feature of these rings is their planarity. In **33** the planarity of the five-membered-ring is evident from the various torsional angles listed in **Table 2.15**. Bond lengths indicate partial π -bond delocalization within the five-membered ring: C(1)-N(1) 1.302(7) Å, C(2)-N(1) 1.38 Å, C(2)-N(2) 1.331(7) Å (cf. 1.28 Å for C=N double bond and 1.46 Å for C-N single bond)⁴¹, N(2)-S 1.650(6) Å (cf. 1.78 Å for N-S single bond and 1.60 Å for N=S double bond)⁴⁰ and finally C(1)-S 1.709(7) Å (cf. 1.81 Å for C-S single bond and 1.62 Å for C=S double bond). Bond angles S-C(1)-N(1) and N(1)-C(2)-N(2) are 113.6(5)° and 118.3(6)°, respectively, for the two C centers. Endocyclic bond angles at N(1), N(2) and S are 107.9(5)°, 108.4(5)° and 91.8(3)°, respectively.

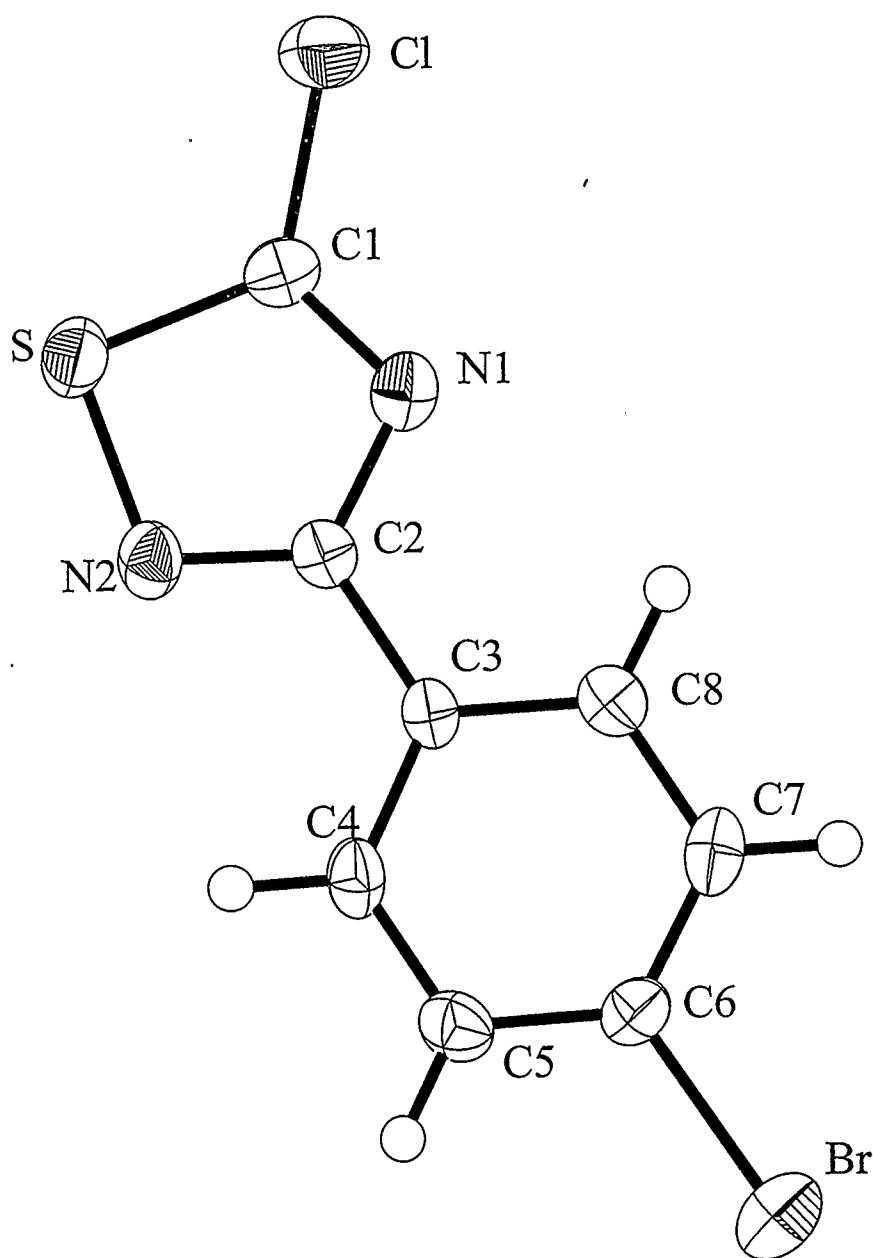
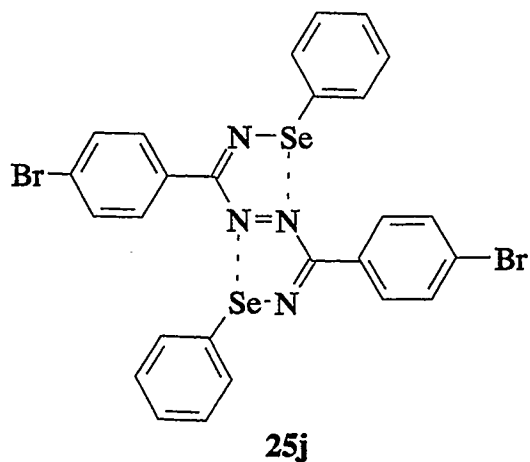
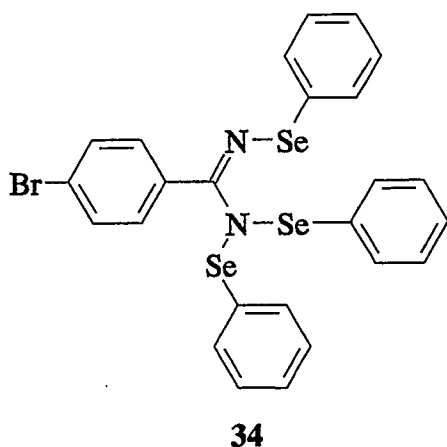


Figure 2.9. ORTEP diagram of 4-BrC₆H₄CNSC(Cl)N.

2.9 Reaction of 4-BrC₆H₄CN₂(SiMe₃)₃ with 3 PhSeCl.

In addition to the experiments discussed in Sections 2.1 - 2.8, several other reactions were attempted in order to isolate a selenium-containing eight-membered or sixteen-membered ring. In contrast to the reaction of 4-BrC₆H₄CN₂(SiMe₃)₃ with PhSeCl, the corresponding reaction with PhSeCl seems to favor the formation of diazenes of type **25**. The selenium compounds are extremely sensitive to moisture and air and so the usual detection method (TLC) and separation technique (column chromatography) could not be utilized. Since the reaction of various benzamidines with PhSeCl give similar products, the characterization data for only one reaction, 4-BrC₆H₄CN₂(SiMe₃)₃ and PhSeCl will be given. The conditions that favored the formation of the ring systems **27d** and **28** were used giving only one new observation. When the reaction is kept at -78°C for 16h the solution becomes red for S, but for Se the solution remains yellow and a lot of yellow precipitate is formed. This yellow precipitate, possibly the trisubstituted derivative **34**, was not isolated since it decomposes upon warming (quantitatively) to the diazene **25j**.



2.9.1 Spectroscopic Characterization of *Z, E*, *Z*-PhSeNC(4-BrC₆H₄)N=NC(4-BrC₆H₄)NSePh.

The ¹H-NMR spectra for **25h** (E = S) and **25j** (E = Se) are similar. All ¹H-NMR data are listed in **Table 2.16**.

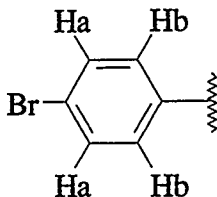


Table 2.16. ¹H-NMR data for *Z, E*, *Z*-PhSeNC(4-BrC₆H₄)N=NC(4-BrC₆H₄)NSePh.

	<u>δ (ppm)</u>	<u>Integration</u>	<u>Assignment</u>
25j	8.27 (doublet)	2	4-BrC ₆ (<u>Ha</u>) ₂ (Hb) ₂ -
	7.72 (doublet)	2	4-BrC ₆ (Ha) ₂ (<u>Hb</u>) ₂ -
	7.82 (multiplet)	5	C ₆ <u>H</u> ₅ -
	7.37-7.55 (multiplet)		

Internal reference CDCl₃

2.10 CONCLUSIONS

The aim of this part of the research was to develop synthetic routes or conditions that would favor formation of CNS macrocycles. To date a sixteen-membered ring **28** has been isolated and structurally characterized. It was determined through systematic trials that prolonged low temperature reaction conditions favor the formation of rings, whereas room temperature and elevated temperatures clearly result in quantitative yields of the diazene **25**. Although larger rings were not isolated, eight and sixteen-membered rings were obtained in optimized yields of 80% and 30%, respectively. In addition to the X-ray structure of the sixteen-membered ring determined previously,³⁶ two eight-membered C₂N₄S₂ rings, (4-BrC₆H₄)₂C₂N₄S₂(Ph)₂ (**27d**) and (4-CF₃C₆H₄)₂C₂N₄S₂(Ph)₂ (**27a**), were

isolated and structurally characterized. The structures of these two heterocycles show several similarities: both crystallize in the same space group ($C2/c$ #15), both have a boat-boat conformation, there is extensive delocalization in the $C_2N_4S_2$ rings, and they produce a purple color when exposed to UV radiation or heated (see Chapter 3).

In addition, a new geometrical isomer of the diazene of type **25** was isolated. This new isomer $\text{PhSN}(2\text{-BrC}_6\text{H}_4)\text{CN}=\text{NC}(2\text{-BrC}_6\text{H}_4)\text{NSPh}$ **30a** is predominantly formed when the aryl group attached to C has an *ortho* substituent. It is red and adopts an *E, E, E* geometry. As well, a Pt complex of **30a** was synthesized to determine if interconversion between **30** and **25** was possible. The metal complex $\text{Pt}\{\text{PhSNC}(2\text{-BrC}_6\text{H}_4)\text{N}-\text{NC}(2\text{-BrC}_6\text{H}_4)\text{NSPh}\}(\text{PPh}_3)$ (**26b**) exhibits the same structural features as were found previously for an analogous Pt complex of the diazene **25d**.³⁵ This suggests that interconversion between these diazene isomers is possible.

To further explore the factors affecting formation of eight-membered rings, an alternative synthetic route was considered. However, the reaction of $4\text{-BrC}_6\text{H}_4\text{N}_2(\text{SiMe}_3)_3$ with Cl_3CSCl produced a five-membered ring $4\text{-BrC}_6\text{H}_4\overline{\text{CNSC}(\text{Cl})\text{N}}$ (**33**) through an interesting reaction which is best seen in Scheme 2.4. The X-ray analysis of this five-membered ring showed it to be planar with some indication of π -bond delocalization.

Finally several attempts to make the selenium analogs of the heterocycles **27a**, **27d** and **28** were carried out, but the exclusive product was a selenium-containing diazene of type **25** (based on UV-vis. data) regardless of the substituent on C.

2.11 EXPERIMENTAL

2.11.1 General

All reactions and distillations were performed under an atmosphere of nitrogen gas. Separation of products on silica gel columns and TLC were performed under a solvent-rich atmosphere and exposure to air was minimized. Nitrogen was dried by passing through a column of phosphorus pentoxide and Sicapent (E. Merck Darmstedt), a commercial drying agent of phosphorus pentoxide and a moisture indicator. Manipulations of solids, both reagents and products, were carried out under an atmosphere of nitrogen gas, either under a cone of flowing gas or in a Innovative Technology glove box. All solutions were transferred via syringes or transfer needle, flushed with nitrogen.

2.11.2 Instrumentation

All ^1H -NMR spectra were recorded on a Bruker ACE 200 Spectrometer. The references for the spectra were internal deuterated solvents. Chemical shifts are quoted relative to tetramethylsilane (0 ppm).

Ultraviolet spectra were obtained by using a Cary 219 spectrometer. Infrared spectra were obtained as Nujol mulls on KBr plates with a Mattson 4030 FT-IR spectrometer. Crystal structures were determined from data collected on a Rigaku AFCS diffractometer, at low temperatures. Computer programs for data processing were part of teXsan installed on a Silicon Graphics Personal Iris 4D/35 computer. The structures were solved and refined using the appropriate programs contained in the teXsan⁴⁸ package and

plotted using ORTEP⁴⁹. All chemical analyses were carried out by the Analytical Services division of the Department of Chemistry, University of Calgary.

2.11.3 Solvents

All solvents used for reactions and crystallizations were of reagent grade and refluxed over the appropriate drying agent, under an inert atmosphere of nitrogen or argon. Solvents (and drying agents) used include: chloroform (phosphorus pentoxide); dichloromethane (first distilled over phosphorus pentoxide and then calcium hydride (BDH)); diethyl ether (sodium wire/benzophenone, both from Aldrich); hexanes (sodium wire/benzophenone); pentane (sodium wire) and toluene (sodium wire/benzophenone). Chloroform- d_3 and dichloromethane- d_2 (Aldrich) were not distilled, but used after drying over freshly heated (400°C) Davison Molecular sieves (4 Å, purchased from Fisher).

2.11.4 Reagents

The starting materials: *p*-bromobenzonitrile, *m*-bromobenzonitrile, *o*-bromobenzonitrile, *p*-trifluorotolunitrile, *o*-trifluorotolunitrile, diphenyl disulphide, trichloromethanethiol, benzeneselenenyl chloride, potassium tetrachloroplatinate(II), cyclooctadiene, triphenylphosphine, sulphuryl chloride and trimethylsilyl chloride were obtained from Aldrich and used as received. Celite 545 for the purpose of filtration was obtained from Fisher Scientific and dried in an oven (110°C) prior to use. Silica gel (170-250 mesh) for column chromatography and silica plates for thin layer chromatography were

also obtained from Aldrich and used as received. Lithium hexamethyldisilylamide (from Aldrich) was dissolved in hexanes and 1.1 equivalents of diethyl ether was added. The lithium hexamethyldisilylamide etherate adduct then precipitated out of solution and was washed twice with hexanes prior to storage in a dry box. Sulphuryl chloride and trichloromethanethiol were freshly distilled prior to use.

The synthesis of benzenesulphenyl chloride involved the oxidative addition of Cl_2 across the S-S bond in diphenyl disulphide.⁵⁰ $(\text{PPh}_3)_2\text{Pt}(\text{H}_2\text{C}=\text{CH}_2)$ was made according to a literature preparation.⁵¹ 4- $\text{BrC}_6\text{H}_4\text{CN}_2(\text{SiMe}_3)_3$, 3- $\text{BrC}_6\text{H}_4\text{CN}_2(\text{SiMe}_3)_3$, 2- $\text{BrC}_6\text{H}_4\text{CN}_2(\text{SiMe}_3)_3$, 4- $\text{CF}_3\text{C}_6\text{H}_4\text{CN}_2(\text{SiMe}_3)_3$ and 2- $\text{CF}_3\text{C}_6\text{H}_4\text{CN}_2(\text{SiMe}_3)_3$ were prepared by the same general route according to the method of Oakley *et al.*³⁸ All these compounds have similar ^1H -NMR spectra with an aromatic signal between 7-8 ppm (either an AA'XX' doublet of doublets for *p*-substituted compounds or a multiplet from the *m* and *o*-substituted compounds with an integrated area of 4) and a singlet at ~0.1 ppm (three SiMe_3 groups with an integrated area of 27).

2.11.5 Reaction of 4- $\text{BrC}_6\text{H}_4\text{CN}_2(\text{SiMe}_3)_3$ with 3 PhSCl.

A solution of PhSCl (0.77 g, 5.4 mmol) in 30 mL of CH_2Cl_2 was added dropwise to 4- $\text{BrC}_6\text{H}_4\text{CN}_2(\text{SiMe}_3)_3$ (0.744 g, 1.79 mmol) in 50 mL of CH_2Cl_2 at -100°C (acetone/ N_2 (l)) under an N_2 atmosphere. Near the end of the addition (~30 min.) the solution changed from pale yellow to an orange color. After the addition the solution was kept at -30°C for 16h., during which time the color changed to purple. The following day the solvent was reduced

to 10 mL and a TLC was conducted to determine the number of products present in the reaction mixture (see Section 2.2.1). The remaining solvent was pumped off and the solid was washed with pentane (4 x 20 mL) to remove Ph_2S_2 (0.37 g, 94.7%). The pentane-insoluble solid was separated into $(\text{Ph})\text{SN}(4\text{-BrC}_6\text{H}_4)\text{CN}=\text{NC}(4\text{-BrC}_6\text{H}_4)\text{NS}(\text{Ph})$ (**25h**) (0.30 g, 55%), $(4\text{-BrC}_6\text{H}_4)_2\text{C}_2\text{N}_4\text{S}_2(\text{Ph})_2$ (**27d**) (0.22 g, 40%), and $(4\text{-BrC}_6\text{H}_4)_4\text{C}_4\text{N}_8\text{S}_4(\text{Ph})_4$ (**28**) (0.03 g, 5.5%) according to the scheme depicted in Figure 2.2. The details of the ^1H -NMR characterization and crystallographic data for compounds **25h**, **27d** and **28** are found in Section 2.2.3. The remaining characterization data are listed in Table 2.17.

Table 2.17. Elemental Analysis, Mass Spectra, Melting Points and UV-visible data for *Z*, *E*, *Z*-(Ph) $\text{SN}(4\text{-BrC}_6\text{H}_4)\text{CN}=\text{NC}(4\text{-BrC}_6\text{H}_4)\text{NS}(\text{Ph})$ (**25h**), $(4\text{-BrC}_6\text{H}_4)_2\text{C}_2\text{N}_4\text{S}_2(\text{Ph})_2$ (**27d**) and $(4\text{-BrC}_6\text{H}_4)_4\text{C}_4\text{N}_8\text{S}_4(\text{Ph})_4$ (**28**).

25h		
Elemental Analysis	Calculated (%)	Experimental (%)
Carbon	51.16	49.95
Hydrogen	2.97	2.87
Nitrogen	9.18	9.07
Mass Spectrum		
Electron Impact	610 (M^+)	
Melting Point		
193°C decomposes to a pale yellow liquid		
UV-visible Spectra		
$\lambda_{\text{max.}} = 543 \text{ nm in CH}_2\text{Cl}_2, 547 \text{ nm in toluene, } \epsilon = 1.7 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$		
27d		
Elemental Analysis	Calculated (%)	Experimental (%)
Carbon	51.16	50.86
Hydrogen	2.97	2.60
Nitrogen	9.18	8.95
Mass Spectrum		
Electron Impact	610 (M^+)	
Melting Point		
199°C decomposes to a purple colored liquid		

UV-visible Spectra $\lambda_{\text{max.}} = 288 \text{ nm}$, $\epsilon = 3.8 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$, in toluene**28**

Elemental Analysis	Calculated (%)	Experimental (%)
Carbon	51.16	50.66
Hydrogen	2.97	2.71
Nitrogen	9.18	8.95

Mass SpectrumFast Atomic Bombardment 1220 (M^+)**Melting Point**

211°C decomposes and gets a little darker; continues to get darker up to 263°C and then it melts giving a brown liquid

UV-visible Spectra

absorbs below 230nm

2.11.6 Reaction of 2-BrC₆H₄CN₂(SiMe₃)₃ with 3 PhSCl.

A solution of PhSCl (1.89 g, 13.3 mmol) in 70 mL of CH₂Cl₂ was added dropwise to 2-BrC₆H₄CN₂(SiMe₃)₃ (1.85 g, 4.46 mmol) in 90 mL of CH₂Cl₂ at -100°C under an N₂ atmosphere. The addition took about 45 min. after which the solution was kept at -78°C in a large Dewar flask. The following day the solvent was pumped off and the remaining solid was washed with pentane (5 x 20 mL). The pentane soluble fraction was separated on a silica column (hexane eluent; 130-270 mesh; column size: 2.5 cm x 40 cm) to give Ph₂S₂ (0.72 g, 75%) and a red compound (Ph)SN(2-BrC₆H₄)CN=NC(2-BrC₆H₄)NS(Ph) (**30a**). The diazene **30a** was recrystallized from a concentrated CH₂Cl₂ solution in the freezer (-20°C) to give cubic crystals (0.68 g, 50%). The pentane-insoluble fraction was dissolved in CH₂Cl₂ and filtered to remove some white powder **W** (0.16 g). The crystallographic data

for compound **30a** is found in Section 2.3.2. The remaining characterization data is listed in Table 2.18.

Table 2.18. Elemental Analysis, Mass Spectra, Melting Points, UV-visible and ^1H -NMR data for *E, E, E*-(Ph)SNC(2-BrC₆H₄)N=NC(2-BrC₆H₄)NS(Ph) (**30a**) and **W**.

30a		
Elemental Analysis	<u>Calculated (%)</u>	<u>Experimental (%)</u>
Carbon	51.16	50.88
Hydrogen	2.97	2.96
Nitrogen	9.18	9.03
Mass Spectrum		
Fast Atomic Bombardment 613 ($\text{M}^+ + 3$)		
Melting Point		
178-179°C sharp		
UV-visible Spectra		
$\lambda_{\text{max.}} = 469 \text{ nm}$, $\epsilon = 1.75 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, in CH_2Cl_2		
^1H-NMR (CDCl_3)		
7.2-7.9 ppm (m, aromatic H's)		
W		
Elemental Analysis	<u>Calculated (%)</u>	<u>Experimental (%)</u>
Carbon	51.16	50.86
Hydrogen	2.97	2.60
Nitrogen	9.18	8.95
Mass Spectrum		
Electron Impact 198/200 (two equal peaks indicating a single Br)		
Melting Point		
293°C decomposes to a brown liquid		
IR		
No evidence of N-H		

2.11.7 Reaction of *E, E, E*-(Ph)SN=C(2-BrC₆H₄)N=NC(2-BrC₆H₄)=NS(Ph) with (Ph₃P)₂Pt(H₂C=CH₂)

A solution of *E, E, E*-(Ph)SN=C(2-BrC₆H₄)N=NC(2-BrC₆H₄)=NS(Ph) (**30a**) (67.6 mg, 0.111 mmol) in 20 mL of toluene was placed over molecular sieves (4 Å, flamed and pumped on for 1h.) for 1h. A solution of (Ph₃P)₂Pt(H₂C=CH₂) (84.7 mg, 0.113 mmol) was also dried over molecular sieves and transferred to a Schlenk vessel and cooled to -78°C. The diazene solution was then added dropwise to the (Ph₃P)₂Pt(H₂C=CH₂) solution and the mixture was allowed to reach room temperature. After 3 days the solvent was pumped off the dark red solution. Recrystallization from CH₂Cl₂/diethyl ether gave some red plates of **30a** (8 mg) and also yellow rectangular prisms of Pt{PhSNC(2-BrC₆H₄)N-NC(2-BrC₆H₄)NSPh}(PPh₃) (**26b**) (35 mg, 30%). The ³¹P-NMR and crystallographic data for compound **26b** are found in Section 2.4.1 and 2.4.2 respectively. The other characterization data are listed in Table 2.19.

Table 2.19. Elemental Analysis, Melting Points and UV-visible data for Pt{PhSNC(2-BrC₆H₄)N-NC(2-BrC₆H₄)NSPh}(PPh₃) (**26b**).

26b		
Elemental Analysis	Calculated (%)	Experimental (%)
Carbon	49.49	44.12
Hydrogen	3.12	1.26
Nitrogen	5.25	4.48
Melting Point		
225°C decomposes		
UV-visible Spectra		
$\lambda_{\text{max.}}$ = 240 nm, 266 nm, 320 nm, 366 nm, in CH ₂ Cl ₂		

2.11.8 Reaction of 2-CF₃C₆H₄CN₂(SiMe₃)₃ with 3 PhSCl.

A solution of PhSCl (1.80 g, 12.5 mmol) in 60 mL of CH₂Cl₂ was added dropwise to 2-CF₃C₆H₄CN₂(SiMe₃)₃ (1.61 g, 3.99 mmol) in 100 mL of CH₂Cl₂ at -100°C under an N₂ atmosphere. The addition took about 45 min. after which the solution was kept at -78°C in a large dewar. The following day the solvent was pumped off and the remaining solid was washed with pentane (5 x 20 mL). The pentane soluble fraction was passed on a silica column (hexane eluent; 130-270 mesh; column: 2.5 cm x 40 cm) to separate Ph₂S₂ (0.85 g, 98%) and a red compound (Ph)SN(2-CF₃C₆H₄)CN=NC(2-CF₃C₆H₄)NS(Ph) (**30b**) (0.29 g, 25%). The pentane-insoluble fraction was dissolved in CH₂Cl₂ and filtered to remove some white powder X (0.84 g). The characterization data for **30b** are listed in Table 2.20.

Table 2.20. Elemental Analysis, Mass Spectra, Melting Points, UV-visible and ¹H-NMR data for *E, E, E*-(Ph)SNC(2-CF₃C₆H₄)N=NC(2-CF₃C₆H₄)NS(Ph) (**30b**) and X.

30b

Elemental Analysis	Calculated (%)	Experimental (%)
Carbon	57.14	56.75
Hydrogen	3.08	2.87
Nitrogen	9.52	9.11
Mass Spectrum		
Fast Atomic Bombardment	591 (M ⁺ +3)	
Melting Point		
134°C, sharp		
UV-visible Spectra		
$\lambda_{\text{max.}} = 469 \text{ nm}, \epsilon = 1.57 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, in CH ₂ Cl ₂		
¹ H-NMR (CDCl ₃)		
7.3-7.9 ppm (m, aromatic H's)		

X

Elemental Analysis	Calculated (%)	Experimental (%)
Carbon		3.35, 4.33
Hydrogen		4.30, 4.25
Nitrogen		2.03, 2.28

Mass Spectrum

Electron Impact 188

Melting Point

285°C, decomposes to black solid

2.11.9 Reaction of 3-BrC₆H₄CN₂(SiMe₃)₃ with 3 PhSCl.

A solution of PhSCl (1.71 g, 12.0 mmol) in 50 mL of CH₂Cl₂ was added dropwise to 3-BrC₆H₄CN₂(SiMe₃)₃ (1.852 g, 4.46 mmol) in 70 mL of CH₂Cl₂ at -100°C under an N₂ atmosphere. During the addition the solution remained yellow. The solution was kept at -78°C in a large Dewar flask for 16h., during which time it became purple. The following day the solvent was pumped off and the solid residue was washed with pentane (4 x 20 mL) to remove Ph₂S₂ (0.66 g, 78.5%). The remaining solid was dissolved in CH₂Cl₂ and filtered to remove some *Z*, *E*, *Z*-(Ph)SNC(3-BrC₆H₄)N=NC(3-BrC₆H₄)NS(Ph) (**25i**). Pentane was added to the CH₂Cl₂ solution and the solution was placed in the freezer (-30°C) to give a second crop of **25i** (0.88 g, 75%). The remaining solution was pumped down and the solid residue was recrystallized from CH₂Cl₂/diethyl ether to give a white crystalline powder **Y** (0.26 g). There was also some evidence of a red colored species ($\lambda_{\text{max}} = 509 \text{ nm}$) which readily transformed into **25i**. The characterization data for **25i** and **Y** are listed in Table 2.21.

Table 2.21. Elemental Analysis, Mass Spectra, Melting Points, UV-visible and ^1H -NMR data for *Z*, *E*, *Z*-(Ph)SNC(3-BrC₆H₄)N=NC(3-BrC₆H₄)NS(Ph) (**25i**) and **Y**.

25i

Elemental Analysis		
	<u>Calculated (%)</u>	<u>Experimental (%)</u>
Carbon	51.16	51.00
Hydrogen	2.97	2.84
Nitrogen	9.18	9.08
Mass Spectrum		
Electron Impact	487 (M ⁺ -NSPh)	
Melting Point		
200°C sharp		
UV-visible Spectra		
$\lambda_{\text{max.}} = 544 \text{ nm}$, $\epsilon = 2.0 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$, in CH ₂ Cl ₂		
¹H-NMR (CDCl₃)		
7.4-8.6 ppm (m, aromatic H's)		

Y

Elemental Analysis	Calculated (%)	Experimental (%)
Carbon		61.3
Hydrogen		4.17
Nitrogen		5.14
Mass Spectrum		
Fast Atomic Bombardment	611	
Melting Point		
220°C decomposes to a orange-red solid		
UV-visible Spectra		
absorbs below 230 nm		
¹H-NMR (CDCl₃)		
6.97-8.32 ppm (m, aromatic H's)		

2.11.10 Reaction of 4-CF₃C₆H₄CN₂(SiMe₃)₃ with 3 PhSCl.

A solution of PhSCl (1.3 g, 9.1 mmol) in 50 mL of CH_2Cl_2 was added dropwise to 4-CF₃C₆H₄CN₂(SiMe₃)₃ (1.16 g, 2.87 mmol) in 80 mL of CH_2Cl_2 at -100°C under an N_2 atmosphere. During the addition the solution remained yellow. The solution was kept at -78°C in a large Dewar flask, during which time it became purple. The following day the

solvent was pumped off and the solid residue was washed with pentane (4 x 15 mL) to remove Ph_2S_2 (0.6 g, 96%). A TLC of both the solid (in CH_2Cl_2) and the pentane solution indicated the presence of Ph_2S_2 , the diazene *Z, E, Z*-(Ph) $\text{SNC}(4\text{-CF}_3\text{C}_6\text{H}_4)\text{N}=\text{NC}(4\text{-CF}_3\text{C}_6\text{H}_4)\text{NS}(\text{Ph})$ (**25e**), a burgundy compound (which readily transformed to **25e**), and some eight-membered ring $(4\text{-CF}_3\text{C}_6\text{H}_4)_2\text{C}_2\text{N}_4\text{S}_2(\text{Ph})_2$ (**27a**). The remaining solid (after pentane wash) was dissolved in CH_2Cl_2 and filtered to remove **25e** (0.26 g, 19%). The filtrate mainly contained the eight-membered ring **27a** (1.13 g, 80%), which was purified by several recrystallizations from CH_2Cl_2 /diethyl ether. The details of the spectroscopic characterization are found in Section 2.7.1. The other characterization data are listed in Table 2.22.

Table 2.22. Elemental Analysis, Mass Spectra, Melting Points and UV-visible data for *Z, E, Z*-(Ph) $\text{SNC}(4\text{-CF}_3\text{C}_6\text{H}_4)\text{N}=\text{NC}(4\text{-CF}_3\text{C}_6\text{H}_4)\text{NS}(\text{Ph})$ (**25i**) and $(4\text{-CF}_3\text{C}_6\text{H}_4)_2\text{C}_2\text{N}_4\text{S}_2(\text{Ph})_2$ (**27a**).

25i		
Elemental Analysis	Calculated (%)	Experimental (%)
Carbon	57.14	56.23
Hydrogen	3.08	2.58
Nitrogen	9.52	9.14
Mass Spectrum		
Electron Impact	588 (M^+)	
Melting Point		
205°C, sharp with some dec. to red liquid		
UV-visible Spectra		
$\lambda_{\text{max.}} = 541 \text{ nm}$, $\epsilon = 2.2 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$, in CH_2Cl_2		
27a		
Elemental Analysis	Calculated (%)	Experimental (%)
Carbon	57.14	57.56
Hydrogen	3.08	2.15
Nitrogen	9.52	9.23

Mass SpectrumElectron Impact 588 (M^+)**Melting Point**

178°C begins to turn purple and melts at 204°C giving purple liquid

UV-visible Spectra $\lambda_{\text{max.}} = 252 \text{ nm}$, $\epsilon = 3.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, in CHCl_3 **2.11.11 Reaction of 4-BrC₆H₄CN₂(SiMe₃)₃ with Cl₃CSCl.**

A solution of Cl₃CSCl (0.60 g, 3.22 mmol) in 25 mL of CH₂Cl₂ was added dropwise to 4-BrC₆H₄CN₂(SiMe₃)₃, (1.37 g, 3.30 mmol) in 25 mL of CH₂Cl₂ at 23°C under an N₂ atmosphere. The solution was then stirred for 72 h during which time no color changes were observed. ¹H-NMR spectra were recorded periodically to monitor the disappearance of 4-BrC₆H₄C(NSCCl₃)[N(SiMe₃)₂] (**32**). After 3 days the solvent was pumped off, leaving a viscous yellow oil with some white powder. The mixture was separated by precipitation of the white powder from a CH₂Cl₂:diethyl ether mixture. The white powder was identified as the hydrolyzed carbamidine 4-BrC₆H₄CN₂H₃ (0.10 g, 16%) by EI-MS. The remaining solution was recrystallized by a slow evaporation of a diethyl ether solution giving pale beige rectangular crystals of the five membered ring 4-BrC₆H₄CNSC(Cl)N (**33**) (0.73 g, 82%).

Table 2.23. Elemental Analysis, Mass Spectrum and Melting Point data for 4-BrC₆H₄CNSC(Cl)N (**33**).

33		
Elemental Analysis	Calculated (%)	Experimental (%)
Carbon	34.87	35.39
Hydrogen	1.46	1.50
Nitrogen	10.17	9.33

Mass SpectrumElectron Impact 275 (M^+)**Melting Point**

85°C sharp

2.11.12 Reaction of 4-BrC₆H₄CN₂(SiMe₃)₃ with PhSeCl.

A solution of PhSeCl (0.987 g, 5.15 mmol) in 40 mL of CH₂Cl₂ was added dropwise to 4-BrC₆H₄CN₂(SiMe₃)₃ (0.738 g, 1.78 mmol) in 65 mL of CH₂Cl₂ at -100°C (acetone/N₂(l)) under an N₂ atmosphere. During the addition the solution went to a pale yellow color. The solution was kept at -78°C in a large Dewar flask, during which time it remained yellow and a lot of yellow precipitate formed. The following day the solution was allowed to reach 23°C, during which time the precipitate dissolved and the solution became an intense violet color. The solvent was pumped off and the solid residue was washed with pentane (5 x 10 mL) to remove Ph₂Se₂ leaving the diazene *Z, E, Z*-PhSeNC(4-BrC₆H₄)N=NC(4-BrC₆H₄)NSePh (**25j**) (0.63 g, 100%). The details of the spectroscopic characterization are found in Section 2.9.1. The other characterization data are listed in Table 2.24.

Table 2.24. Elemental Analysis, Melting Point and UV-visible data for *Z, E, Z*-PhSeNC(4-BrC₆H₄)N=NC(4-BrC₆H₄)NSePh (**25j**).

25j

Elemental Analysis	<u>Calculated (%)</u>	<u>Experimental (%)</u>
Carbon	44.35	44.21
Hydrogen	2.58	2.09
Nitrogen	7.96	7.76

Melting Point

166°C decomposes to yellow liquid

UV-visible Spectra

$\lambda_{\text{max.}} = 555 \text{ nm}$, $\epsilon = 1.3 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$, in CH_2Cl_2

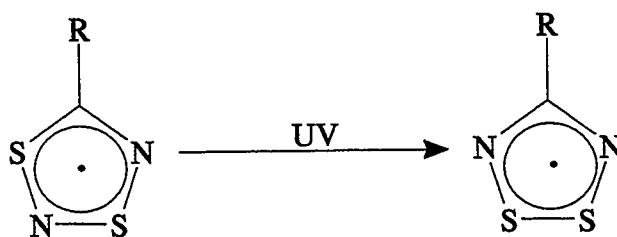
CHAPTER THREE

Photochemical Investigation of the Isomerization of Eight-membered Rings

$(\text{Ar})_2\text{C}_2\text{N}_4\text{S}_2(\text{Ph})_2$ to the Diazenes $(\text{Ph})\text{SNC}(\text{Ar})\text{N}=\text{NC}(\text{Ar})\text{NS}(\text{Ph})$

3.1 Introduction

The photochemistry of inorganic ring systems is a relatively unexplored area of research. To date only a few reports of the photolysis of sulfur-nitrogen ring systems have appeared in literature.^{52,53} Usually these photochemical processes involve the expulsion of small molecules, e.g. S_8 , S_4N_2 , and S_7NH . However, only one article has been reported that describes a photochemical isomerization. This involves the transformation of 1,3,2,4-dithiadiazolyl radicals to the 1,2,3,5-dithiadiazolyl isomer (see **Scheme 3.1**).⁵³



Scheme 3.1. Photochemical rearrangement of 1,3,2,4-dithiadiazolyl to 1,2,3,5-dithiadiazolyl radicals.

The above process involves an unstable $\pi^*-\pi^*$ dimer intermediate. The overall reaction proceeds by second order kinetics and is essentially quantitative.

3.2 Qualitative Experiments

In this work it was observed during a standard melting point determination of the two eight-membered rings $(\text{Ar})_2\text{C}_2\text{N}_4\text{S}_2(\text{Ph})_2$, ($\text{Ar} = 4\text{-BrC}_6\text{H}_4$ (**27d**), $4\text{-CF}_3\text{C}_6\text{H}_4$ (**27a**)), that the compounds seemed to decompose at approx. 195°C to give a dark colored melt. In addition, it was noticed that a pure (solid) samples of **27d** and **27a** developed a purple stain when left in a sample vial for several days on the bench. It was postulated that the unexpected purple coloration could be a result of the formation of the corresponding diazene **25**. In order to determine the source of the purple color a sample of **27d** was melted in a 5 mm. NMR tube. A ^1H -NMR spectrum of **27d** was obtained prior to melting to verify the absence of the diazene. A second ^1H -NMR spectrum was recorded after melting the sample. In addition to the resonances for **27d**, new signals for the corresponding diazene **25h** were observed. Details of the ^1H -NMR spectra of **27d** and **25h** can be found in Section 2.2.3. The entire mixture was then quickly washed with CH_2Cl_2 to remove trace amounts of **27d** and concentrate the diazene (by ^1H -NMR). At this point it was apparent that the product of this unusual transformation was the diazene **25h**. However, the conditions under which this interconversion could be studied needed to be established. A sample of **27d** was dissolved in toluene and refluxed for 10h under an atmosphere of N_2 . Under these conditions no purple coloration was observed. A second

test was done by taking a sample of this toluene solution and placing it in a quartz cuvette. The sample was then irradiated with UV light using a handheld UV lamp (METRILIGHT, UVS-11), and within several minutes the solution began to appear slightly purple in color. Several solvents were tested and it was observed that **27d** was most stable in toluene. Therefore, based on these qualitative tests, it was determined that the photochemical transformation should be studied in toluene solution.

3.3 Experimental Setup

Various UV reactors were tested. However, most were too powerful resulting in rapid transformation and poor data. The set-up which proved to be satisfactory involved the use of a single xenon light source with a 313 nm cutoff filter and various interference filters (**Figure 3.1**). A water filter was placed between the light source and interference filter in order to absorb any heat generated. The entire set-up was then covered by dark plastic and the room was kept dark at all times. The various toluene solutions of **27d** were placed in a stoppered flame-sealed quartz cuvette which contained a micro stirring bar for maintaining homogeneity. Absorption spectra were periodically recorded giving the evolution of the UV-vis spectra shown in **Figure 3.2**. This procedure was performed for various light intensities (by use of interference filters) and also for different concentrations of **27d**.

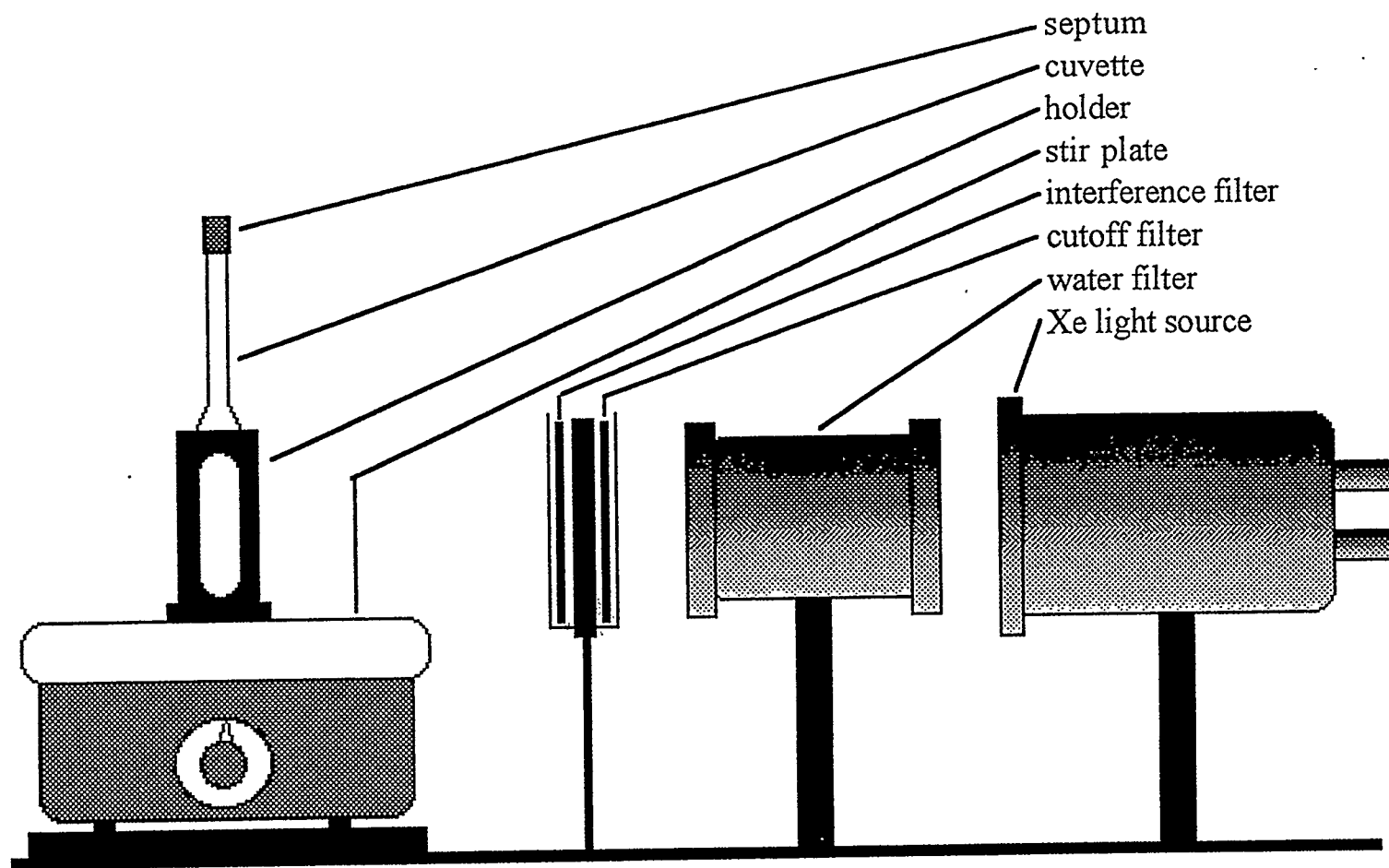


Figure 3.1. Experimental setup for studying the kinetics of the rearrangement of an eight-membered $C_2N_4S_2$ ring to the corresponding diazene.

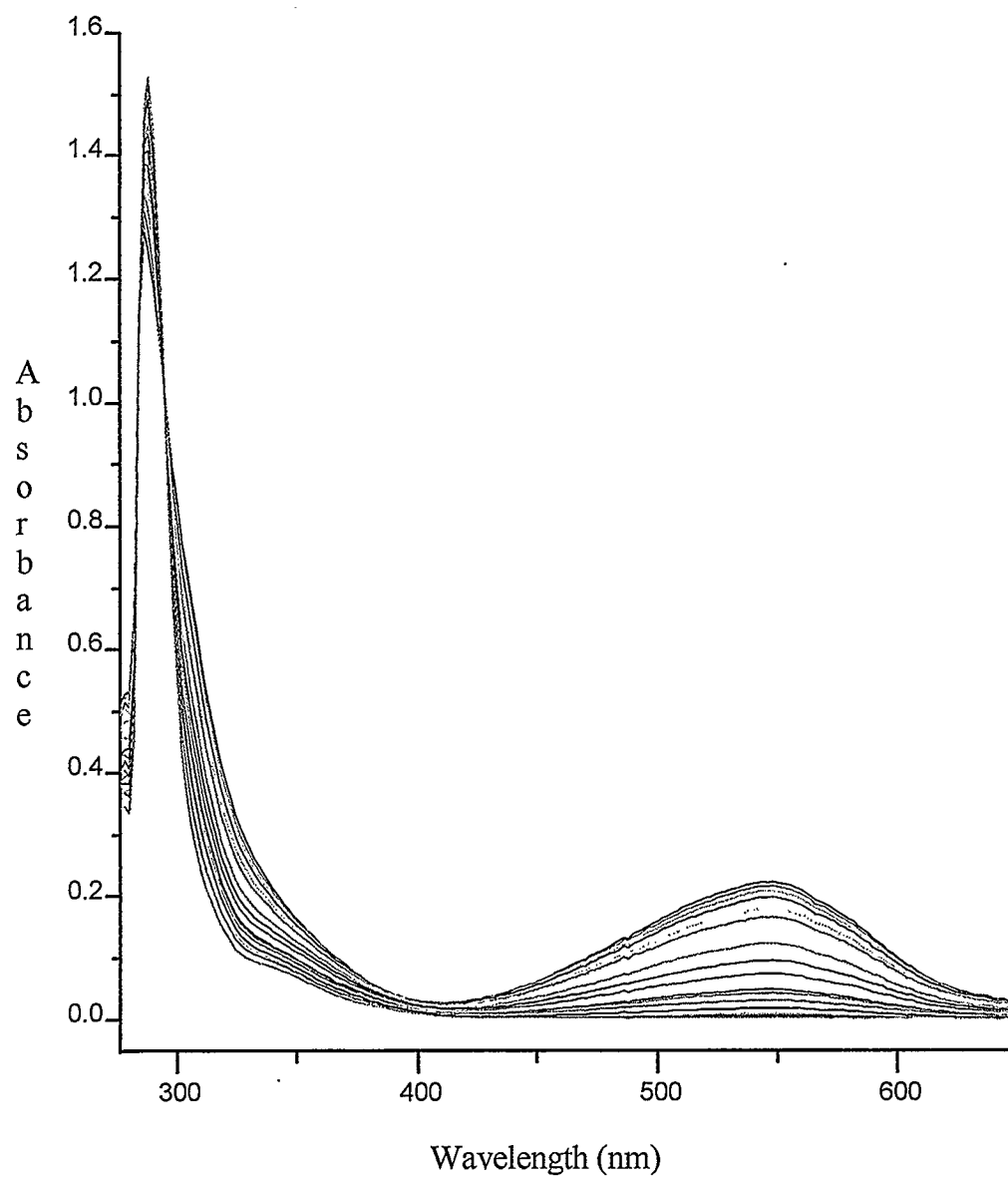


Figure 3.2. Absorbance vs. wavelength (nm) for a typical kinetic run.

3.4 Determination of Order of Reaction

For comparison of the accuracy of the data two different concentrations were used for the determination of order of reaction. Run 1 employed a $3.15 \times 10^{-5} \text{ M}$ toluene solution and Run 2 used a $3.98 \times 10^{-5} \text{ M}$ toluene solution. Three interference filters (82.2%, 63.8% and 41.9% of incident radiation transmitted) were used to obtain data at four intensities (one without any filters). The various runs took approximately 100 min to complete. The data were obtained in the form of absorbance (at 547 nm) versus time (min) as shown in **Tables A.1 and A.3** (see **Appendix A**). **Figures 3.3 and 3.4** show the linear plots, with slopes indicated, of absorbance at 547 nm vs. time for Run 1 and **Figures 3.6 and 3.7** display the same data for Run 2. From these plots one can obtain the rate of the reaction from the slopes, using $\epsilon = 1.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (for the diazene **25h**) and the volume of cell equal to 3.665 mL (see **Tables A.2 and A.4; Appendix A**). The final two plots (**Figures 3.5 and 3.8**) are required to determine the relation between rate and intensity. From these two figures, showing data for Run 1 and Run 2, we can see a linear relation between rate and intensity which indicates a first order reaction. Therefore the rate law would be in the form shown below:

$$\vartheta = \Phi I_{\text{abs.}}$$

where ϑ is the rate of the reaction, Φ is the quantum yield and $I_{\text{abs.}}$ is the amount of incident radiation which is absorbed. From the order it can be inferred that the reaction is unimolecular and hence the transformation is most likely intramolecular.

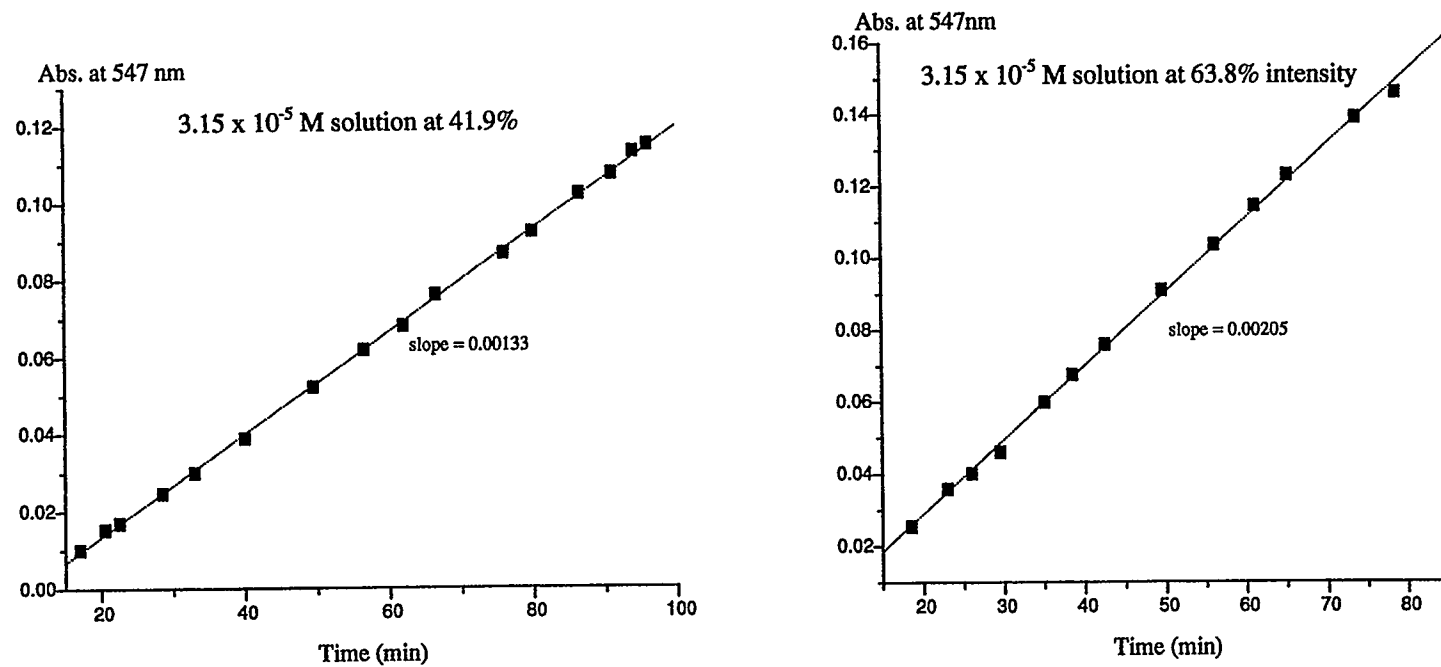


Figure 3.3. Plots of absorbance at 547 nm vs. time for 3.15×10^{-5} M solution of 27d in toluene at intensities of 41.9% and 63.8%.

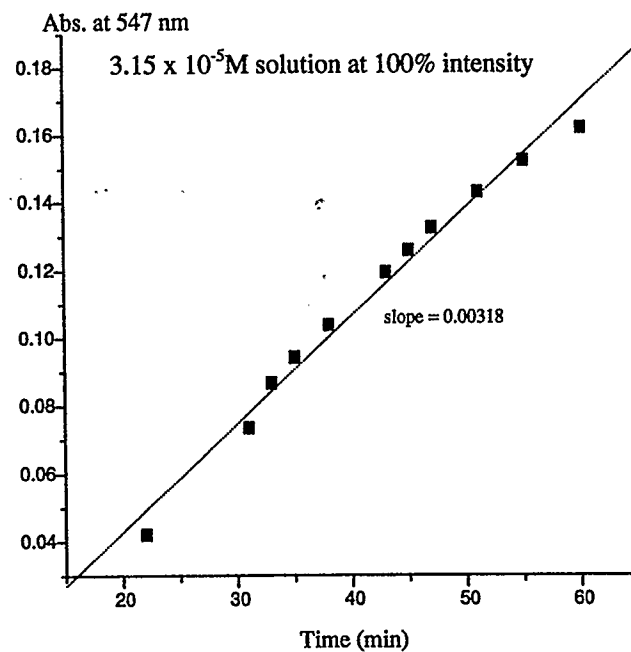
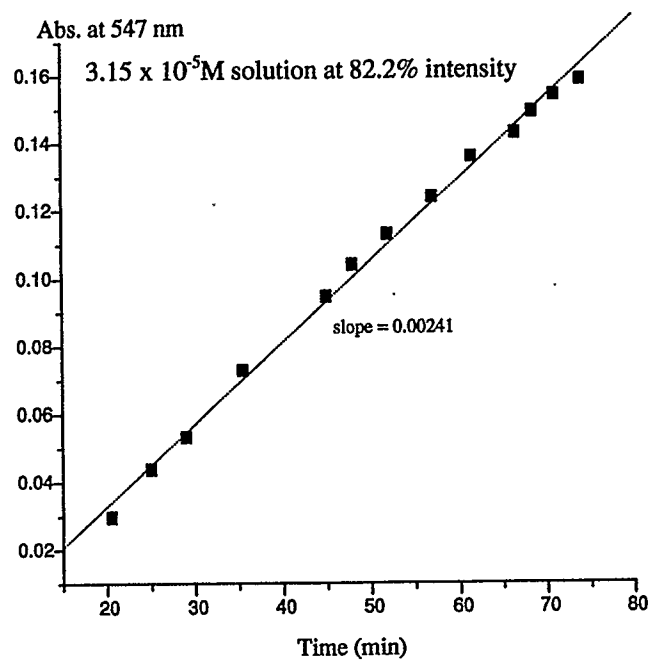


Figure 3.4. Plots of absorbance at 547 nm vs. time for 3.15×10^{-5} M solution of **27d** in toluene at intensities of 82.2% and 100%.

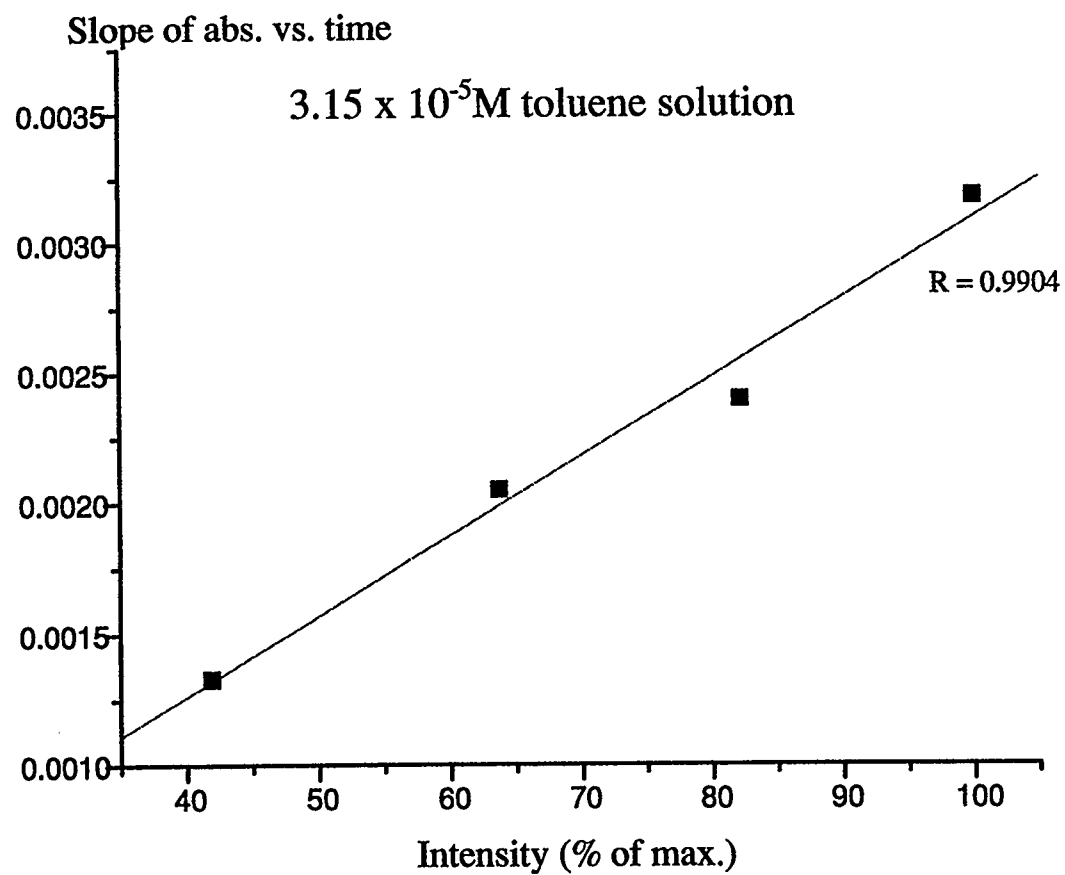


Figure 3.5. Slope of absorbance vs. time vs. intensity plot for $3.15 \times 10^{-5} \text{ M}$ toluene solution of **27d**.

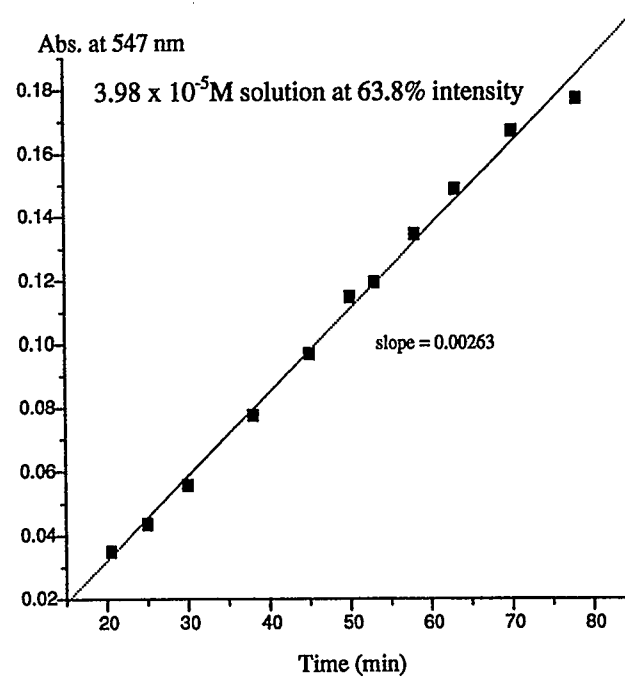
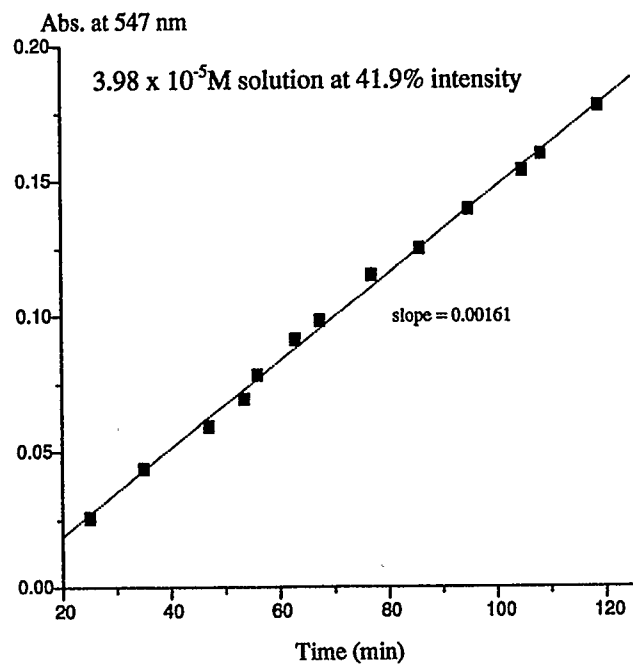


Figure 3.6. Plots of absorbance at 547 nm vs. time for $3.98 \times 10^{-5} \text{ M}$ solution of **27d** in toluene at intensities of 41.9% and 63.8%.

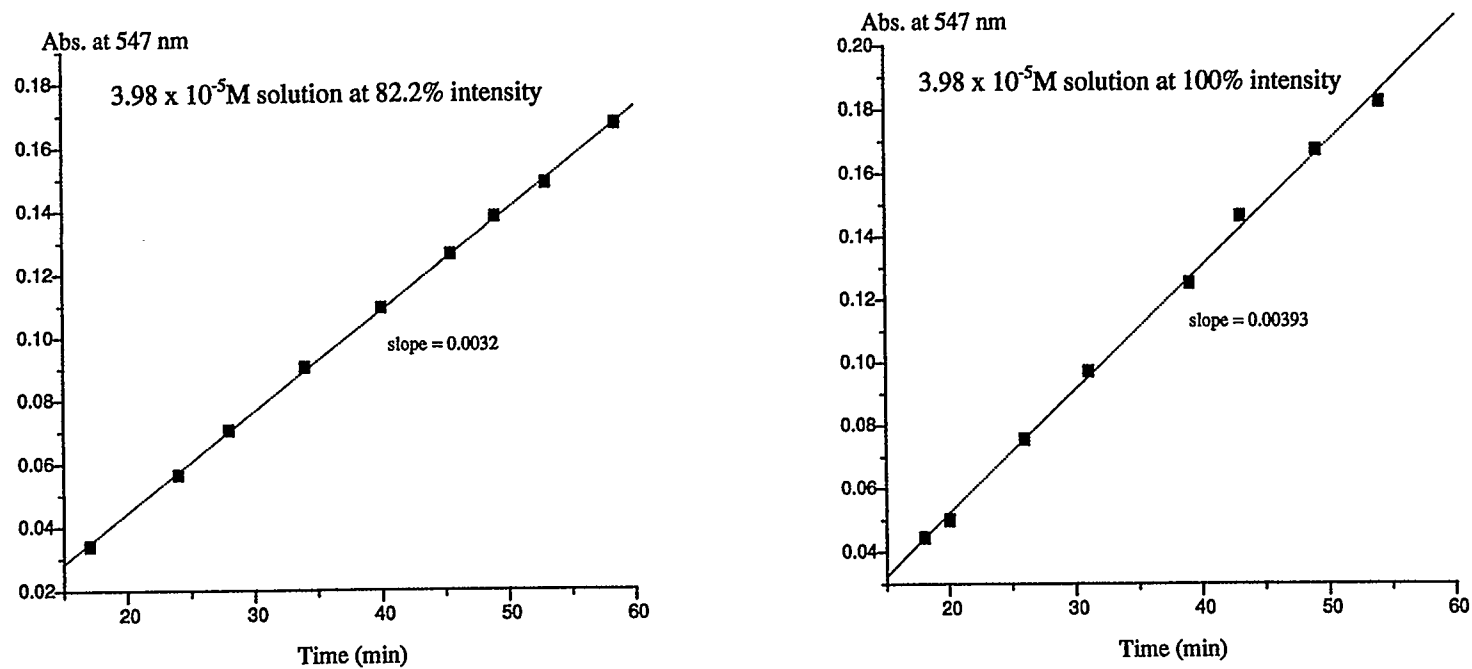


Figure 3.7. Plots of absorbance at 547 nm vs. time for 3.98×10^{-5} M solution of **27d** in toluene at intensities of 82.2% and 100%.

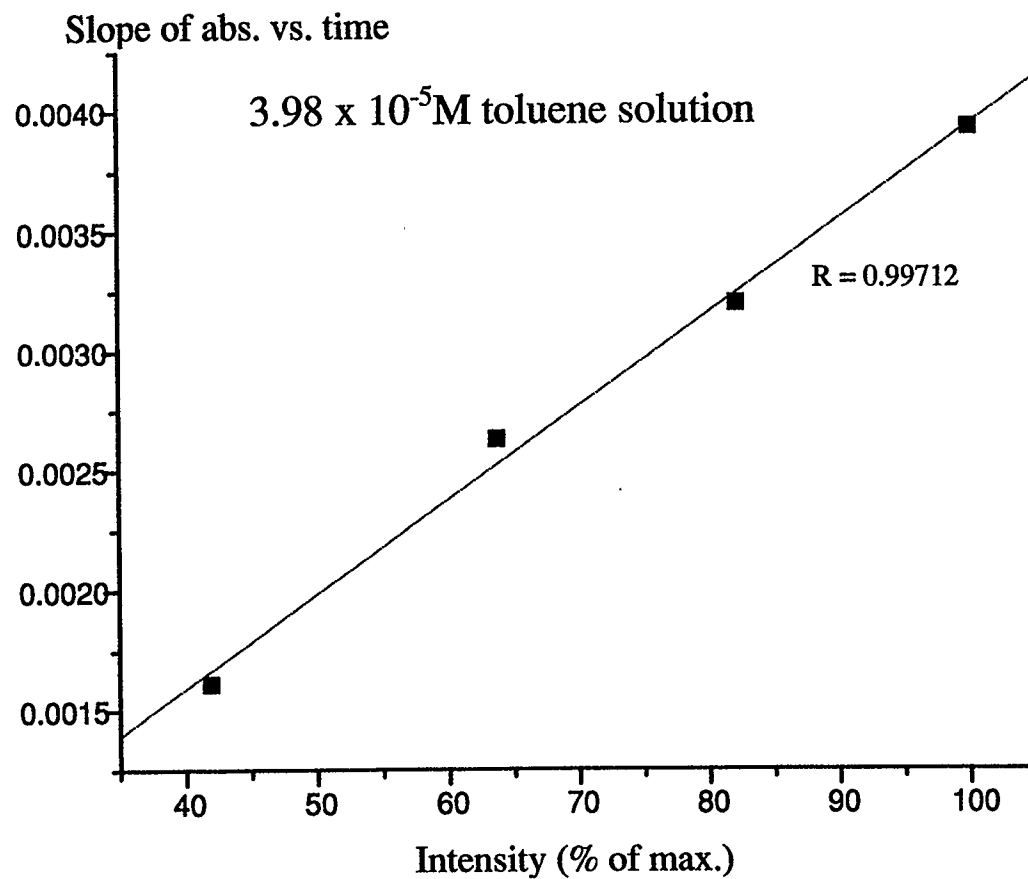
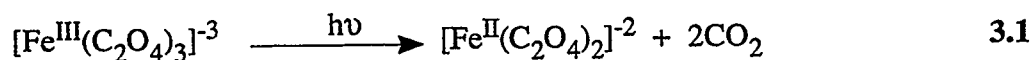


Figure 3.8. Slope of absorbance vs. time vs. intensity plot for $3.98 \times 10^{-5} \text{M}$ toluene solution of **27d**.

3.5 Determination of Quantum Yield

A third run was performed in order to determine the quantum yield and an accurate rate for the reaction. In this particular experiment the concentration of the solution of **27d** was increased by 25 times from that of Run 2 in order to ensure that the heterocycle **27d** is absorbing 100% of the incident radiation with minimal absorption by the diazene and solvent. Also, only data from the first 5% of the transformation was used for determination of the quantum yield and rate in order to maximize absorption of radiation by **27d**. Incident radiation intensity was determined by standard actinometry techniques⁵⁴ using potassium tris(oxalato)ferrate (III) which undergoes a reduction of Fe^{III} to Fe^{II}, according to equation **3.1**, when irradiated at 313 nm.



The amount of Fe^{II} produced is then measured at 510 nm after reacting with a developer solution (0.05% 1,10-phenanthroline/ 0.25M sodium acetate/ 0.1M H₂SO₄). Radiation intensity can then be calculated knowing $\epsilon = 1.11 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ and $\Phi = 1.24$ for the Fe^{II}-phenanthroline complex. The actinometry data are listed in **Table A.5** and the data from Run 3 are listed in **Table A.6** (see **Appendix A**). The slope from the plot of absorbance at 510 nm vs. time is shown in **Figure 3.9**, from which the light intensity can be readily calculated, using equations **3.2** and **3.3**.

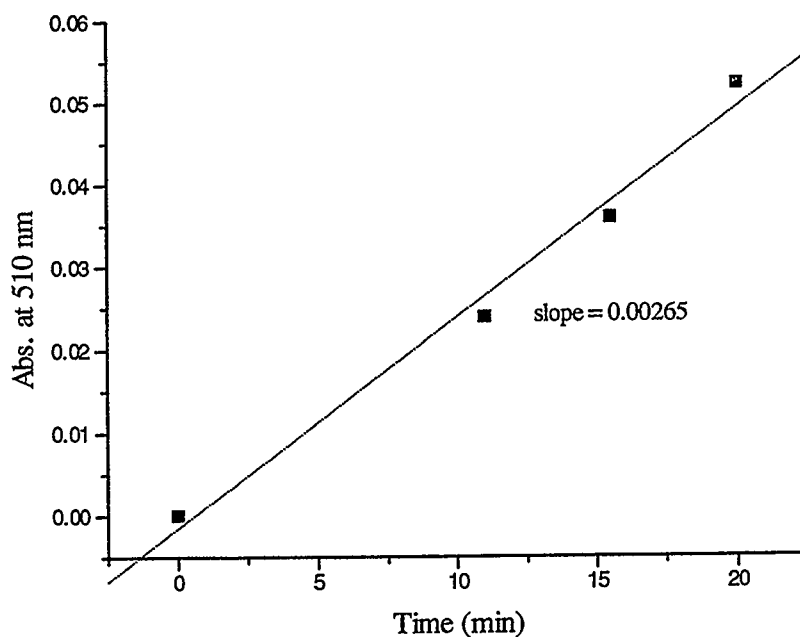


Figure 3.9. Plot of absorbance at 510 nm vs. time for actinometry experiment.

$$n(\text{Fe}^{\text{II}})/\text{sec} = ((A_{510}/\text{min})(V))/((\epsilon_{\text{Fe}})60) \quad 3.2$$

$$I_{\text{abs.}}/\text{sec} = (n(\text{Fe}^{\text{II}})/\text{sec})/(\Phi_{\text{Fe}}) \quad 3.3$$

Where:

$n(\text{Fe}^{\text{II}})/\text{sec}$ = moles of Fe^{II} produced per second

A_{510}/min = slope of abs. at 510 nm vs. time plot (**Figure 3.9**)

V = total volume (50 mL)

ϵ_{Fe} = molar absorptivity of Fe^{II} -phenanthroline at 510 nm
($1.11 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$)

$I_{\text{abs.}}/\text{sec}$ = number of photons per second

Φ_{Fe} = quantum yield for formation of Fe^{II} (1.24 at 313 nm)

Therefore, the two calculated values are:

$$n(\text{Fe}^{\text{II}})/\text{sec} = 1.99 \times 10^{-10} \text{ mol/sec}$$

$$I_{\text{abs.}}/\text{sec} = 1.60 \times 10^{-10} \text{ einsteins/sec}$$

At this point we can again use equations 3.2 and 3.3 to determine $n(\text{diazene})/\text{sec}$ and $\Phi_{27\text{d}}$ (quantum yield for the interconversion of **27d** to the diazene **25h**) using the calculated $I_{\text{abs.}}/\text{sec}$ from above; however, this time total volume $V = 3.665 \text{ mL}$ and $\epsilon_{25\text{h}} = 1.7 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$. For this we require the plot of abs. at 547 nm vs. time for Run 3, shown in **Figure 3.10**. The final results are summarized in **Table 3.1**.

Table 3.1. Rate and quantum yield results for isomerization of an eight-membered ring **27d** to the diazene **25h**.

RUN 3: $9.62 \times 10^{-4} \text{ M}$ Toluene Solution.			
	Trial 1	Trial 2	Average
Rate (mol/sec.)	1.42E-11	1.39E-11	1.41E-11
Φ	0.089	0.087	0.088

3.6 Mechanism of Isomerization

Having determined the quantum yield and order of the reaction we can begin to make some inferences as to the mechanism of the isomerization. First, an order of one suggests the transformation is intramolecular. To support this conclusion, the photolysis of the sixteen-membered ring was also investigated;

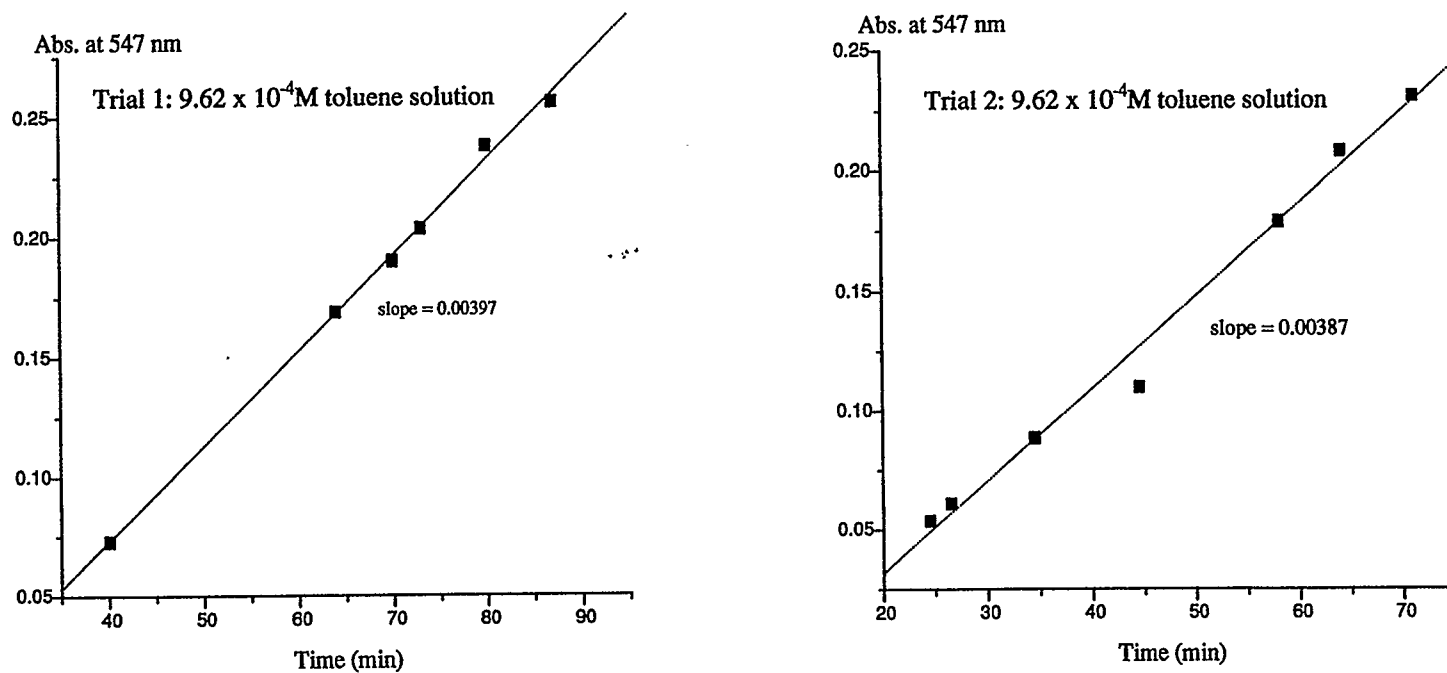


Figure 3.10. Plots of absorbance at 547 nm vs. time for $9.62 \times 10^{-4} \text{ M}$ solution of **27d** in toluene for Run 3 (trials 1 and 2).

however, no color change was observed even after 3 hours of irradiation. Second, the quantum yield was determined to be 0.09, which indicates that a radical chain process is unlikely. Usually radical chain processes have quantum yields in excess of 1.⁵⁵ In addition, Ignacio Vargas-Baca has performed DFT calculations to identify the molecular orbitals involved in the rearrangement and to determine the correlation diagram for the isomerization process (see **Figure 3.11**).^{34,56} These calculations indicate that the isomerization is symmetry-forbidden; however, if an electron is photoexcited to the LUMO (in the UV region) the process is allowed. The calculations also suggest that the pseudo transition state would involve considerable change in the geometry of **27d**, including flattening and compression of the ring, which brings two antipodal N atoms closer to each other. The proposed mechanism is shown in **Scheme 3.2** and **Figure 3.12**, which depicts the formation of a N=N bond at the expense of the elongation of two N-S bonds. It should be noted that the S-N bonds are not fully broken since there are weak S...N interactions in the diazene. The bicyclic transition state is only a proposed intermediate and has not been isolated.

Another interesting feature of this isomerization is that it also proceeds in visible light when the eight-membered rings are heated to the melting point. When **27d** is heated it presumably begins to vibrate faster. Two of the vibrational modes, i.e. those involved in compressing and flattening of the ring, bring it closer to the pseudo transition state (point A on **Figure 3.11**). In this way as the ring is distorted its frontier orbitals will also change in energy (point B on **Figure 3.11**) resulting in a lower HOMO-LUMO gap, which will allow

the excitation of an electron by lower energy visible light. This is qualitatively supported by an observed color change (from faint yellow to orange) of the ring as it is heated to approx. 170°C (m.p. = 196°C). In addition a melting point was performed in the dark which resulted in a decomposition of the eight-membered ring **27d** with no formation of the diazene **25h** (by $^1\text{H-NMR}$).

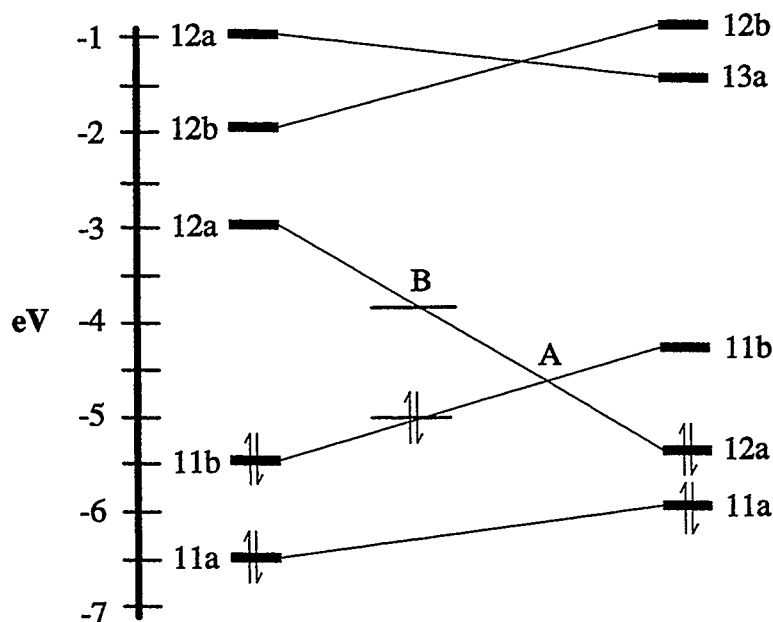
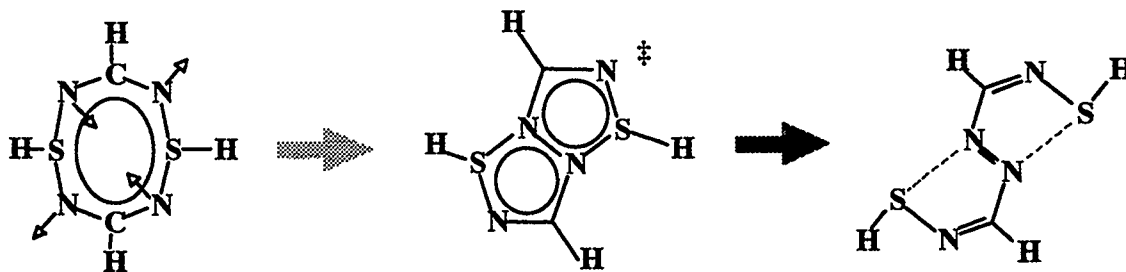


Figure 3.11. Correlation diagram for the photoisomerization of $(\text{H})_2\text{C}_2\text{N}_4\text{S}_2(\text{H})_2$ into $(\text{H})\text{SN}=\text{C}(\text{H})\text{N}=\text{NC}(\text{H})=\text{NS}(\text{H})$.³⁴



Scheme 3.2. Proposed mechanism for the photoisomerization.

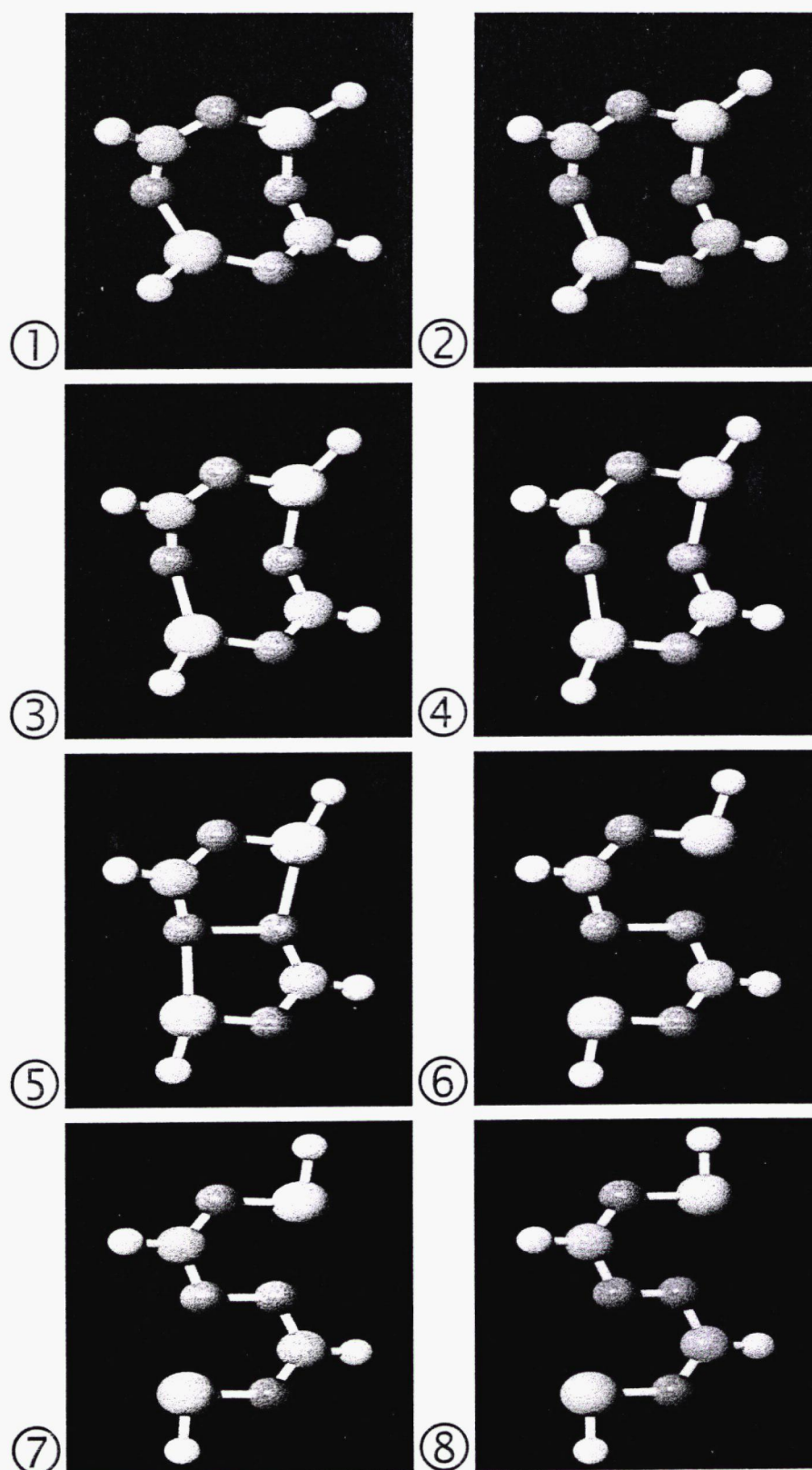


Figure 3.12. Sequence showing photoisomerization of $(\text{H})_2\text{C}_2\text{N}_4\text{S}_2(\text{H})_2$ into $(\text{H})\text{SN}=\text{C}(\text{H})\text{N}=\text{NC}(\text{H})=\text{NS}(\text{H})$.

3.7 Conclusions

The photoisomerization described here represents an interesting and novel conversion of an inorganic ring system to an acyclic diazene. Kinetic studies have shown the reaction to be an intramolecular process which does not involve ring opening. The calculated quantum yield also excludes the possibility of a radical chain process. In addition, DFT calculations have revealed the process to be symmetry-forbidden; however, it is photochemically allowed. In view of the ease of this rearrangement, it is likely to be the forerunner of other unexpected molecular transformations of S-N heterocycles (see Chapter 4 for suggestions).

CHAPTER FOUR

Conclusions and Suggestions for Future Work

4.1 Conclusions

As stated in Chapter 1 the initial focus of this thesis was the elucidation of the conditions that would aid in increasing the yield of the novel sixteen-membered ring (4-BrC₆H₄)₄C₄N₈S₄(Ph)₄ (**28**) from the reaction of 4-BrC₆H₄CN₂(SiMe₃)₃ with PhSCl.³⁶ To do this a series of reactions were performed in which the tested variables were: concentration, temperature and time. These experiments indicated that prolonged low temperature reaction conditions favor the formation of rings with the final optimized yield of **28** being 30%. Elevated temperatures clearly favored the formation of the diazene *Z, E, Z*-PhSNC(4-BrC₆H₄)N=NC(4-BrC₆H₄)NSPh (**25h**) in quantitative yield.

In addition to the sixteen-membered ring, an eight-membered ring (4-BrC₆H₄)₂C₂N₄S₂(Ph)₂ (**27d**) was also isolated with an optimized yield of 80%. The X-ray structure revealed the C₂N₄S₂ ring (ie. **27d**) to be in a boat-boat conformation with extensive π -bond delocalization. A routine melting point determination on this eight-membered ring revealed an unexpected formation of a purple stain which was attributed to the diazene **25h**. This observation led to an extensive kinetic study into this unusual

isomerization of an inorganic heterocycle to an acyclic diazene. These studies have shown the reaction to be an intramolecular process which does not involve ring opening. The calculated quantum yield also eliminated the possibility of a radical chain process. In addition, DFT calculations indicated the process to be symmetry-forbidden, but photochemically allowed, which was further supported by the observation that thermal isomerization does not occur in the dark. An investigation of a more electronegative substituent than Br (ie. CF₃) on the phenyl ring attached to C resulted in the formation of another eight-membered ring (4-CF₃C₆H₄)₂C₂N₄S₂(Ph)₂ (**27a**) as the major product in addition to the diazene *Z, E, Z*-PhSNC(4-CF₃C₆H₄)N=NC(4-CF₃C₆H₄)NSPh (**25h**). The X-ray structure of this heterocycle indicated structural features analogous to those found for **27d**, as well as the similar formation of a purple stain when **27a** is exposed to UV radiation. The study of these S,S-diorgano dithiatetrazocines eventually became the main focus of this thesis.

The effect of changing the position of the substituent attached to the aryl group on the nature and distribution of products was also investigated. A reaction of 2-XC₆H₄CN₂(SiMe₃)₃ (X = Br) with PhSCl resulted in the isolation of a new geometrical isomer of the diazene of type **25**, namely *E, E, E*-PhSN(2-BrC₆H₄)CN=NC(2-BrC₆H₄)NSPh (**30a**), whose geometry was established by X-ray crystallography. A similar reaction with X = CF₃ resulted in an analogous red *E, E, E* diazene **30b**, which indicates that these new diazenes are predominantly formed when the aryl group attached to C has an *ortho* substituent.

The possible isomerization of the geometrical isomers of the diazenes was also considered. To test this a platinum complex of **30a** was synthesized. The metal complex $\text{Pt}\{\text{PhSNC}(\text{2-BrC}_6\text{H}_4)\text{N-NC}(\text{2-BrC}_6\text{H}_4)\text{NSPh}\}(\text{PPh}_3)$ (**26b**) exhibits the same structural features as were found previously for an analogous platinum complex of the diazene **25d**.³⁵ This suggests that interconversion between these diazene isomers is possible in the presence of a metal template; however, this transformation does not occur in boiling toluene in the absence of a metal centre.

To further explore the factors affecting the formation of eight-membered rings, an alternative synthetic route was considered. The outcome of the reaction of 4- $\text{BrC}_6\text{H}_4\text{CN}_2(\text{SiMe}_3)_3$ with Cl_3CSCl did not lead to the eight-membered ring; however, it did produce a five membered ring 4- $\text{BrC}_6\text{H}_4\overline{\text{CNSC}(\text{Cl})\text{N}}$ (**33**) through an interesting reaction which resulted in the loss of two Cl atoms from CCl_3 . The X-ray analysis of this five-membered ring showed it to be planar with some indication of π -bond delocalization.

Finally several attempts to make the selenium analogs of the heterocycles **27a**, **27d** and **28** were carried out, but the exclusive product was a selenium-containing diazene of type **25** (based on UV-vis. data) regardless of the aryl substituent on C.

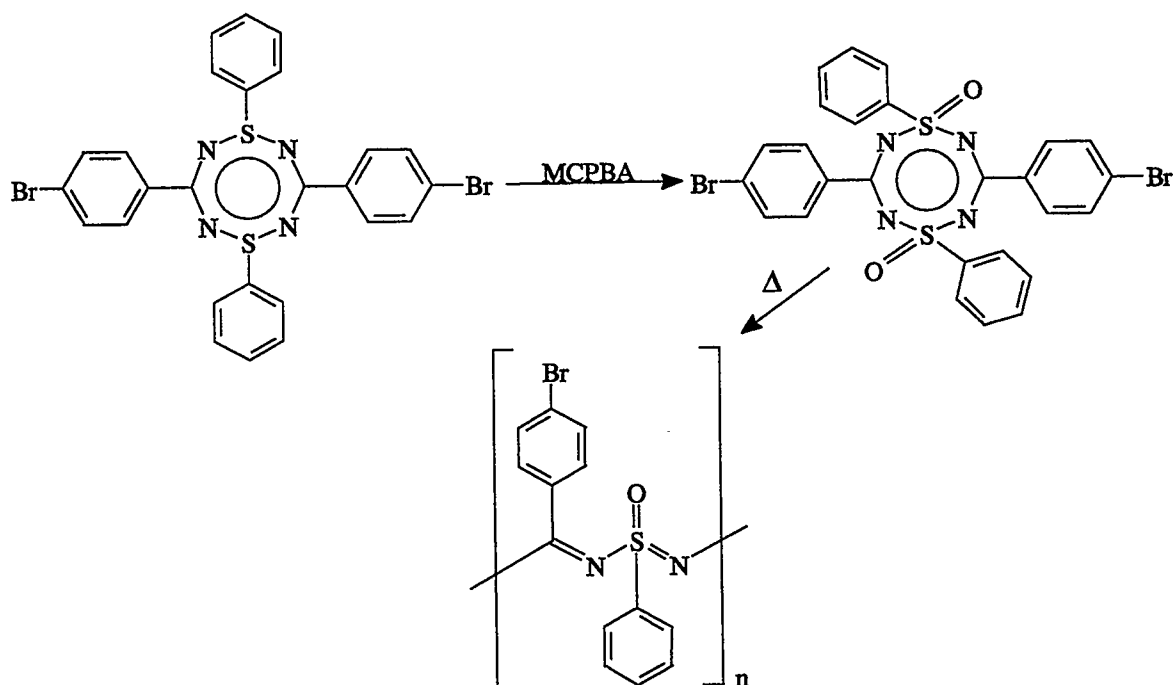
4.2 Future Work

In light of these results several suggestions for future work come to mind. In particular it would be of interest to elucidate the mechanism for the formation of the eight and sixteen-membered rings in order to be able to design a better synthetic route to these

interesting compounds. As was suggested in **Scheme 2.2** the formation of these rings could proceed through a chain growth process. It should be possible to monitor the formation and disappearance of these acyclic intermediates by ^1H -NMR at low temperatures since the terminal aryl substituents would be in a different environment from the substituents in the middle of the chain. The reaction would have to be performed in the NMR tube in order to prevent temperature fluctuations during transfer. The mixture could then be monitored by low temperature ^1H -NMR at various time intervals (up to 3 days) for presence of chain species. An advantage of this particular experiment (when the aryl substituent on C is 4- BrC_6H_4 -) is that all the products (total yield 100%, with no unidentified side products) from the reaction have been identified and they all exhibit characteristic ^1H -NMR spectra. This would enable a quick detection of new or transient species. In addition it was shown that when the aryl substituent on C is 4- $\text{CF}_3\text{C}_6\text{H}_4$ - the predominant product is the eight membered ring **27a**. The presence of the CF_3 group introduces a new NMR active nucleus (^{19}F , $I = 1/2$, 100%) with a larger chemical shift window which might make it easier to detect very similar chain species.

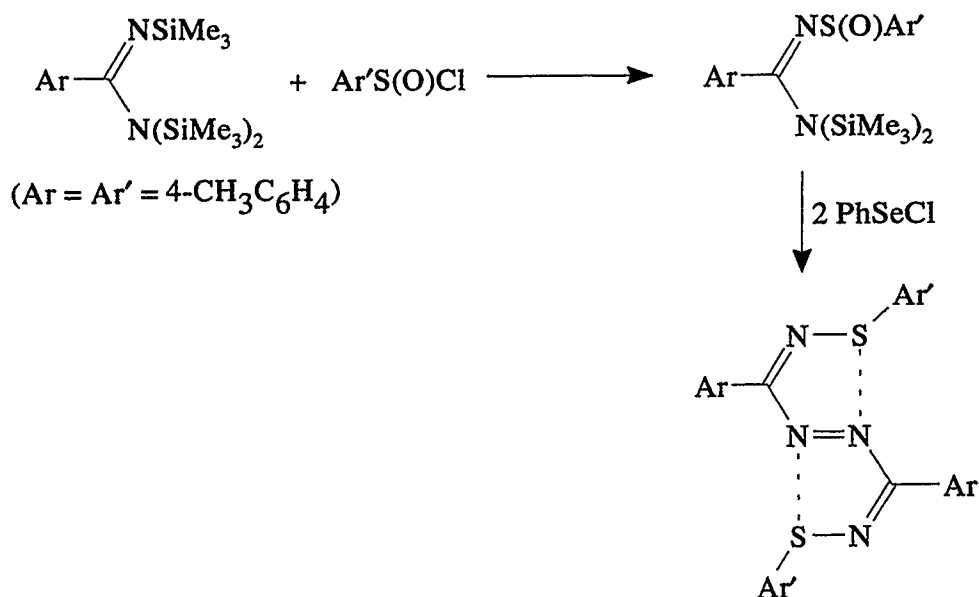
A second possibility, which relates to the statement made in the introduction regarding polymerization of these CNS containing rings, brings us to another interesting experiment. It was shown that the eight-membered rings (**27a**, **27d**) are readily converted to the diazenes (**25e**, **25h**) either photochemically or upon melting; in addition the rings and the diazenes both decompose at temperatures above 200°C and so polymerization via ring opening of S(IV)-containing heterocycles is not feasible. However, oxidation of the S(IV)

center in the ring to S(VI) may provide more thermally stable rings, whose ring-opening polymerization properties could be studied (see **Scheme 4.1**). Ideally the S(VI) centre should have a halogen substituted (e.g. S(O)Cl) since ring-opening polymerization usually proceeds by a cationic intermediate.⁵



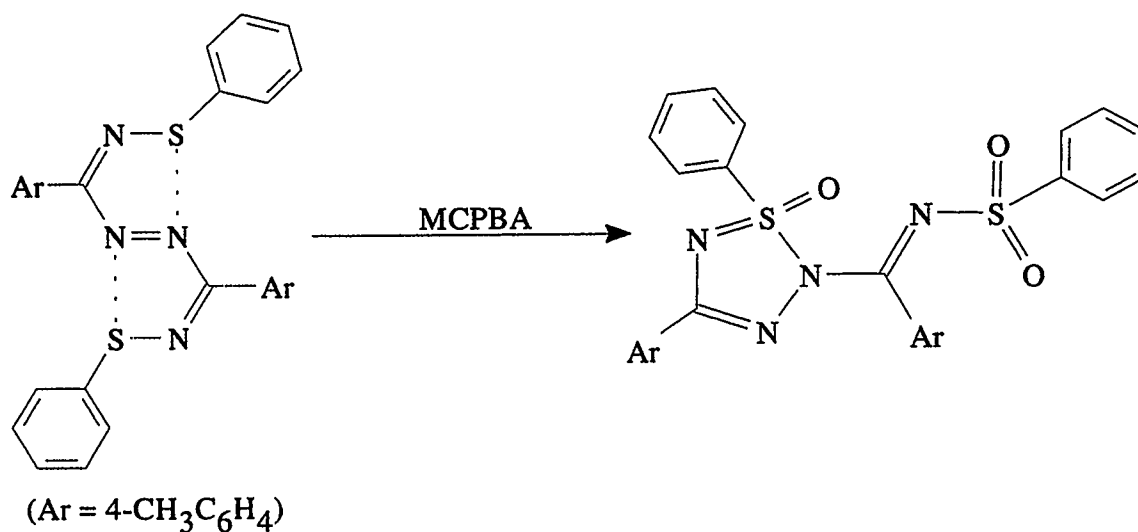
Scheme 4.1. Proposed scheme for the formation of CNSN polymers.

Two recent attempts to make an S(IV) diazene of the type $\text{Ar}'\text{S}(\text{O})\text{NC}(\text{Ar})\text{N}=\text{NC}(\text{Ar})\text{NS}(\text{O})\text{Ar}'$ have resulted in unexpected products. As indicated in **Scheme 4.2** the introduction of a sulfinyl substituent into a trisilylated benzamidine followed by reaction with two equivalents of PhSCl produced S(II) diazene.³³



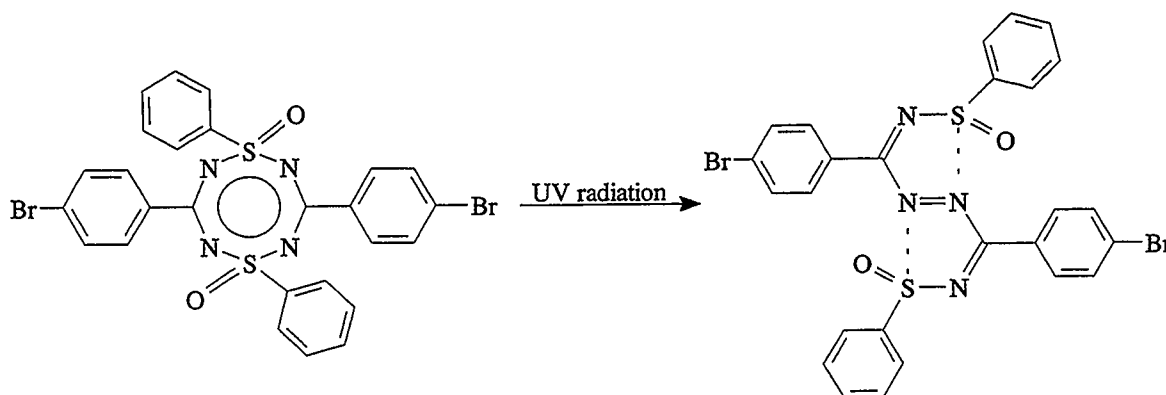
Scheme 4.2. Attempted synthesis of a S(IV) diazene.

In a different approach, the attempted oxidation of the S(II) diazene to the corresponding S(IV) diazene results in an intramolecular redox cyclization to give the 1-thia-2,3,5-triazolene shown in **Scheme 4.3**.⁵⁷



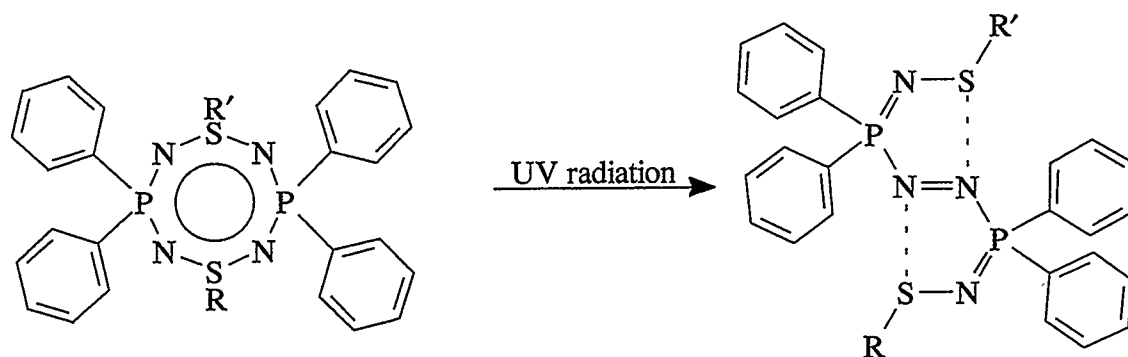
Scheme 4.3. Attempted oxidation of a S(II) diazene to a S(IV) diazene.

The discovery of the isomerization of the eight-membered $C_2N_4S_2$ rings to the corresponding diazenes might provide an interesting route to the S(IV) diazenes. It should be pointed out that, in addition to significant structural rearrangement during the isomerization, the S(IV) centers in the rings (ie. **27a** and **27d**) are reduced to S(II) in the diazenes (**25e** and **25h**) while the formation of a N=N double bond occurs. By analogy, the photolysis of a S(VI) might provide a convenient route to a S(IV) diazene (see **Scheme 4.4**).



Scheme 4.4. Proposed photochemical route to S(IV) diazenes.

Furthermore it would be of interest to attempt the isomerization of the phosphorus analogues of the $C_2N_4S_2$ eight-membered rings (ie. the S, S'-diorgano 1,5-(Ph)₄P₂N₄(SR)(SR') ring)¹⁹ to determine if diazene formation is possible and if so which isomer is preferred.



Scheme 4.5. Proposed isomerization of the $(\text{Ph})_4\text{P}_2\text{N}_4(\text{SR})(\text{SR}')$ ring to a diazene.

Finally the product distribution, in the reaction of $\text{ArCN}_2(\text{SiMe}_3)_3$ with $\text{Ar}'\text{SCl}$ as a function of the substituent at S has not yet been studied. In view of the variety of products obtained by altering the aryl substituent attached to carbon it seems likely that the nature of the reagent $\text{Ar}'\text{SCl}$ will also have a marked influence on product distribution. As an example of the effect of the aryl substituent on S, it has been shown that $\text{PhCN}_2(\text{SCCl}_3)_3$ is stable to 200°C ; whereas $\text{PhCN}_2(\text{SPh}_3)_3$ decomposes to the diazene below room temperature.³⁰

Clearly the research in this area is not complete, but has only begun especially in view of the new and unexpected chemistry discovered during the isomerization described in this thesis. Practical applications of the photochemical isomerization process are one possibility that should be considered further.

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APPENDIX A

Table A.1. Time and absorbance data for Run 1.**RUN 1: 3.15×10^{-5} M Toluene Solution.**

Intensity at 41.9%		Intensity at 63.8%		Intensity at 82.2%		Intensity at 100%	
Time (min)	Abs. at 547 nm	Time (min)	Abs. at 547 nm	Time (min)	Abs. at 547 nm	Time (min)	Abs. at 547 nm
0	0.00725	0	0.01375	0	-0.00432	0	0.00371
4.5	0.00473	2.5	0.01039	2	0.0016	2	0.00217
10.5	0.01016	5	0.01332	4	0.00586	4	0.0072
15	0.01315	12	0.01741	6	0.0083	6	0.00531
17	0.01006	15	0.01942	9.5	0.01379	8	0.00786
20.5	0.01538	18.5	0.02544	12	0.01505	11	0.01675
22.5	0.01695	23	0.03577	14	0.02179	13	0.01758
28.5	0.02466	26	0.04015	20.5	0.02962	15	0.02237
33	0.02995	29.5	0.04507	25	0.04381	17	0.02696
40	0.0388	35	0.05983	29	0.05328	19	0.03319
49.5	0.05217	38.5	0.06755	35.5	0.07275	22	0.04207
56.5	0.06189	42.5	0.076	45	0.09468	31	0.07365
62	0.06802	49.5	0.09097	48	0.10396	33	0.08664
66.5	0.07603	56	0.10349	52	0.1129	35	0.09425
76	0.08672	61	0.11444	57	0.12378	38	0.10385
80	0.09227	65	0.12552	61.5	0.13583	41	0.11716
86.5	0.10219	73.5	0.13898	66.5	0.14279	43	0.11945
91	0.1073	78.5	0.14767	68.5	0.149	45	0.12488
94	0.11292	81	0.1503	71	0.15385	47	0.13255
96	0.11472	86.5	0.15778	74	0.15852	51	0.14293
97.5	0.11998	91	0.16396	79	0.16454	55	0.15227
		94.5	0.16762	82.5	0.17088	60	0.16394
		97.5	0.17215	84.5	0.17513	64	0.17178
		100	0.17607			67	0.17476
						73	0.18214
						79	0.18736
						82	0.19537
						86	0.19432
						89	0.19551
						92	0.19617

Table A.2. Rate of reaction for Run 1.

RUN 1: 3.15×10^{-5} M Toluene Solution.		
Intensity (% of max.)	Slope of abs. vs. time plots	Rate (mol/sec)
41.9	0.00133 /min.	4.77×10^{-12}
63.8	0.00205 /min.	7.36×10^{-12}
82.2	0.00241 /min.	8.65×10^{-12}
100	0.00318 /min.	1.14×10^{-11}

Table A.3. Time and absorbance data for Run 2.

RUN 2: 3.98×10^{-5} M Toluene Solution.							
Intensity at 41.9%		Intensity at 63.8%		Intensity at 82.2%		Intensity at 100%	
Time (min)	Abs. at 547 nm	Time (min)	Abs. at 547 nm	Time (min)	Abs. at 547 nm	Time (min)	Abs. at 547 nm
0	0.01064	0	-0.00192	0	0.00842	0	0.00356
15	0.01837	5.5	0.0069	4	0.01134	3	0.00778
25	0.02582	11	0.01358	8	0.01633	7	0.01132
35	0.04372	17	0.02757	13	0.02554	10	0.01939
47	0.05919	20.5	0.03506	17	0.0341	14	0.03256
53.5	0.0694	25	0.04356	24	0.05653	18	0.04446
56	0.07825	30	0.05563	28	0.07057	20	0.05003
63	0.09143	38	0.07762	34	0.09052	26	0.07565
67.5	0.09819	45	0.09703	40	0.10924	31	0.09715
77	0.11507	50	0.11478	45.5	0.12621	39	0.12508
86	0.12498	53	0.11946	49	0.13802	43	0.14636
95	0.13927	58	0.13422	53	0.1487	49	0.16718
105	0.15373	63	0.14859	58.5	0.16722	54	0.18234
108.5	0.15996	70	0.16693	64.5	0.17857	60.5	0.19943
119	0.17868	78	0.17905	70	0.19301	65.5	0.20969
		88	0.19812	73	0.20264	68	0.21815
		96.5	0.21719	76.5	0.20743	72.5	0.22507
		101	0.22302	79	0.21515		

Table A.4. Rate of reaction for Run 2.

RUN 2: 3.98×10^{-5} M Toluene Solution.		
Intensity (% of max.)	Slope of abs. vs. time plots	Rate (mol/sec)
41.9	0.00161 /min.	5.78×10^{-12}
63.8	0.00263 /min.	9.44×10^{-12}
82.2	0.0032 /min.	1.15×10^{-11}
100	0.00393 /min.	1.41×10^{-11}

Table A.5. Actinometry data for
Fe^{II}-phenanthroline complex.

Actinometer Data	
Time (min)	Abs. at 510 nm
0	0.000076
11	0.02354
15.5	0.03526
20	0.0553

Table A.6. Time and absorbance data for Run 3.

RUN 3: 9.62e-4M Toluene Solution.			
Trial 1		Trial 2	
Intensity at 100%		Intensity at 100%	
Time (min)	Abs. at 547 nm	Time (min)	Abs. at 547 nm
0	0.00288	0	0.01749
17	0.02014	18.5	0.04129
25	0.03331	22.5	0.05078
40	0.07265	24.5	0.05373
64	0.16896	26.5	0.06096
70	0.19006	34.5	0.08852
73	0.20349	44.5	0.10979
80	0.23775	58	0.17854
87	0.25722	64	0.20795
		71	0.22993