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Synthetic Methods and Structure–Reactivity Relationships in Electron-Rich Sulfur–Nitrogen Rings and Cages

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I. Introduction

During the last 15 years the study of sulfur–nitrogen (S–N) compounds has progressed from relative obscurity to a position in the vanguard of main-group chemistry. In part, this rise to prominence originated with the discovery of the unusual properties of the conducting polymer $(SN)_x$.[1] Concurrently, the variety of chemical transformations and structures found for

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sulfur–nitrogen heterocycles have attracted both experimental and theoretical interest. In a recent book[2] Heal stated "...the reaction chemistry of these substances (S–N rings) deserves to rank with that of boranes for novelty and interest." Investigations of the chemistry of boron hydrides continue to play a leading role in the development of our understanding of electron-deficient compounds and their influence has been extended to an appreciation of the structures of other cluster systems and organometallic complexes.[3] The purpose of the present review is to demonstrate that studies of cyclothiazenes have similarly provided a framework for comprehending the behavior of π-electron-rich inorganic systems. This point will be emphasized by comparing their structures and properties with those of π-electron-precise rings, e.g., cyclophosphazenes and aromatic hydrocarbons. [In an electron-rich S–N ring the number of π-electrons exceeds the number of atomic centers in the ring. It follows that the number of π-electrons is equal to the number of atomic centers in an electron-precise ring. Strictly speaking, this definition cannot be applied to cages since the distinction between σ- and π-electrons is not clear-cut for nonplanar molecules.]

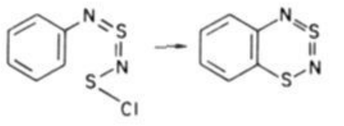
Of the numerous reviews devoted to various aspects of sulfur–nitrogen chemistry, those on cyclic S–N compounds by Banister[4] and Roesky[5] are the most comprehensive. The latter covers the literature to the end of 1977 and is organized according to (a) ring size and (b) coordination number at sulfur and nitrogen. The wide variety of sulfur–nitrogen compounds can be attributed to the range of oxidation states (0–6) and coordination numbers (2–4) available to sulfur in combination with nitrogen (or other sulfur atoms).[5] In addition nitrogen may be two-coordinate (unsaturated) or three-coordinate (saturated). This article will focus on *π-electron-rich rings, i.e., those containing two-coordinate sulfur and two-coordinate nitrogen*, and related bicyclic and cage molecules.

The survey begins with a discussion of general synthetic approaches to both binary S–N rings and heterocyclothiazenes in which one or more sulfur atoms have been replaced by a heteroatom, e.g., C, Si, Sn, Pb, P, As, Se, or a transition metal (plus associated ligands). There follows a detailed account of the molecular and electronic structures of important S–N heterocycles, a knowledge of which is necessary for understanding their spectroscopic properties and chemical reactions, which are described in subsequent sections.

II. General Synthetic Methods

To a casual observer the methods used for the preparation of S–N heterocycles are often obscure and even the expert can find the unpredictable nature of such reactions perplexing. The aim of this section is to provide a coherent account of synthetic strategies in terms of the typical reaction types exemplified in Table I. This overview begins with a description of the preparation of S_4N_4 and cyclothiazyl halides from ammonia or ammonium halides and sulfur halides and related condensation reactions. This is followed by

TABLE I. Some Examples of Synthetic Routes to S–N Heterocycles

1.	cyclocondensation	$NH_3 + SCl_2 \xrightarrow{Cl_2} S_4N_4$ $NH_4Cl + S_2Cl_2 + S_8 \rightarrow S_3N_2Cl^+Cl^-$ $Ni(S_2N_2H)_2 + S_2Cl_2 \xrightarrow{Et_3N} S_4N_2$ $RC(NH_2)NH + SCl_2 \rightarrow RC(NSN)_2CR$
2.	oxidation	$S_4N_4 + S_2O_6F_2 \rightarrow [S_4N_4^{2+}][FSO_3^-]_2$ $S_3N_3^- \xrightarrow{O_2} S_3N_3O^- \xrightarrow{O_2} S_3N_3O_2^-$
3.	reduction	$S_4N_3^+Cl^- \xrightarrow{KI} S_4N_4$ $(NSCl)_3 \xrightarrow{Fe} S_4N_4$
4.	cycloaddition	$NS_2^+ + RC{\equiv}CR' \rightarrow RR'C_2NS_2^+$ $^2/_3(NSCl)_3 + Me_2NCN \rightarrow (Me_2NCN)(NSCl)_2$ $NWCl_3 + S_4N_4 \rightarrow Cl_3WS_2N_3$
5.	metathesis	$(NSCl)_3 + Me_3SiNSNSiMe \rightarrow S_4N_5Cl$ $2S_3N^- + CuCl \rightarrow Cu(S_3N)_2^-$
6.	ring closure	
7.	ring expansion	
	a. insertion	$S_4N_4 + NS^+ \rightarrow S_5N_5^+$ $S_3N_2Cl^+Cl^- + R_2PN(SiMe_3)_2 \rightarrow (R_2PN)(SN)_2$
	b. via nucleophiles	$(Ph_2PN)_2(NSCl) + Ph_3Sb \rightarrow (Ph_2PN)_4(SN)_2$
8.	ring contraction	
	a. elimination of NSX	$Cl_2S_4N_4 + Cl_2 \xrightarrow{-NSCl} (NSCl)_3$
	b. promoted by nucleophiles	$S_4N_4 + N_3^- \rightarrow S_3N_3^-$ $S_4N_4 + Ph_3E \rightarrow Ph_3E{=}N{-}S_3N_3$ (E = P, As)

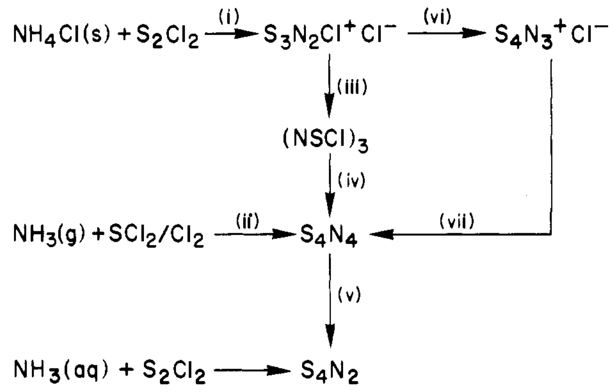


Figure 1. Preparation of S–N heterocycles from ammonia or ammonium salts and sulfur halides: (i) reflux, (ii) CCl_4 or CH_2Cl_2, (iii) Cl_2, (iv) Fe, Hg or Ph_3Sb, (v) S_8/CS_2, (vi) S_2Cl_2, (vii) KI.

details of the wide variety of S–N heterocycles that can be obtained by treating S_4N_4 with various reagents. Syntheses based on the use of the cyclothiazyl halides, $S_3N_2Cl_2$ and $(NSCl)_3$, are described next and this section concludes with an account of preparative routes which employ Si–N or Sn–N reagents, metallocyclothiazenes, S–N cations, S–N anions, and S–N oxides. For details of the various methods available for the preparation of *specific* ring systems the reader is referred to a recent book.[6]

In this section S–N rings will be represented by molecular formulas. Their molecular structures are discussed in section III and schematic drawings of the structures are depicted in Figures 8 and 16.

A. The Reaction of Ammonia or Ammonium Salts with Sulfur Halides and Related Cyclocondensation Reactions

The cyclocondensation reaction of ammonia (or ammonium salts) with sulfur halides is the most important route to S–N heterocycles since it provides an easy preparation of several key starting materials (Figure 1).[7] When conducted in carbon tetrachloride[8] or methylene dichloride[9] this reaction is the standard synthesis of S_4N_4, which, in turn, is used for the preparation of numerous sulfur–nitrogen ring systems (see section IIB). The reaction of ammonia with S_2Br_2 has been adapted for the synthesis of small quantities of ^{33}S-labeled S_4N_4.[10] The rapid addition of S_2Cl_2 to *aqueous* ammonia at 0–5 °C provides a quick and convenient source of S_4N_2.[11,12]

$S_3N_2Cl^+Cl^-$, another important reagent in S–N chemistry (see section IIC1), is formed as an intermediate in the synthesis of S_4N_4. It is best prepared, however, by the treatment of S_2Cl_2 with sulfur and ammonium chloride at 150–160 °C;[13] urea can be used instead of NH_4Cl.[14] Chlorination of $S_3N_2Cl^+Cl^-$ with Cl_2[13] or, more conveniently, SO_2Cl_2 produces $(NSCl)_3$[15] which is reduced to S_4N_4 by Fe,[16] Hg,[17] or Ph_3Sb.[18] This reaction sequence (Figure 1) has been used to produce ^{15}N-labeled S_4N_4.[18] Alternatively, treatment of $S_3N_2Cl^+Cl^-$ with S_2Cl_2 produces $S_4N_3^+Cl^-$, another intermediate in the S_4N_4 synthesis, which is reduced to S_4N_4 by potassium iodide.[18-20] By contrast the reduction of $(NSCl)_3$ with sodium azide or Me_3SiN_3 produces $(SN)_x$.[21]

The related cyclocondensation reactions between amidines and SCl_2, in the presence of an HCl acceptor, provides a source of eight-membered heterocyclothiazenes.[22]

$$RC(NH)NH_2 + SCl_2 \rightarrow RC(NSN)_2CR \qquad (1)$$

$$R = Me_2N,^{22a}\ Ar,^{22a}\ t\text{-}Bu^{22b}$$

The cage anion $S_4N_5O^-$ is obtained on hydrolysis of the mixture formed by the reaction of thionyl chloride with liquid ammonia.[23]

B. Preparation of S–N Heterocycles from S_4N_4

The molecule S_4N_4 exhibits very versatile chemical behavior and provides a source of many S–N heterocycles. For example, the thermolysis of S_4N_4 at ca. 300 °C using a Ag-wool catalyst generates S_2N_2,[24] the precursor of the polymer $(SN)_x$.[1] The syntheses of other S–N rings from S_4N_4 can be classified as follows: reactions of S_4N_4 with (a) halogens or other oxidizing agents, (b) nucleophiles or reducing agents, (c) metal halides or organometallic reagents, and (d) acetylenes.

1. Reactions with Halogens or Other Oxidizing Agents

The controlled halogenation of S_4N_4 with Cl_2 at −60 °C,[25] AgF_2,[25b] or F_2 diluted with an inert gas[26] produces 1,5-$S_4N_4X_2$ (X = Cl, F). The reaction of S_4N_4 with

$$S_4N_4 + X_2 \rightarrow 1{,}5\text{-}X_2S_4N_4 \qquad (2)$$

liquid bromine or ICl yields the salts $S_4N_3^+X_3^-$ (X_3 = Br_3, ICl_2).[27] In CS_2 solution, the solvent participates in the reaction to give $CS_3N_2Br^+Br_3^-$.[28] By contrast, Br_2 or ICl *vapor* react with solid S_4N_4 to give highly conducting polymers of the type $(SNBr_{0.4})_x$.[29,30]

The oxidation of S_4N_4 leads to several different cyclic sulfur–nitrogen cations depending on the reaction conditions. The use of excess Lewis acid favors oxidation over simple adduct formation. For example, $S_4N_4^{2+}$ is obtained by treatment of S_4N_4 with excess $SbCl_5$, AsF_5, SbF_5, or HSO_3F or by oxidizing $S_4N_4{\cdot}AlCl_3$ with chlorine in the presence of a stoichiometric amount of $AlCl_3$.[31] S_4N_4 is also oxidized quantitatively to $(S_4N_4^{2+})(SO_3F^-)_2$ by peroxydisulfuryl difluoride $S_2O_6F_2$.[32]

$$S_4N_4 + S_2O_6F_2 \rightarrow (S_4N_4^{2+})(SO_3F^-)_2 \qquad (3)$$

The dimeric cation $S_6N_4^{2+}$ is prepared by the oxidation of S_4N_4 with $(S_8^{2+})(AsF_6^-)_2$,[33] CF_3SO_3H,[34] or $FeCl_3$.[35] Although the cation radical $S_3N_2^{+}\cdot$ has frequently been detected by ESR spectroscopy (section IVD) in solutions of S_4N_4 with various oxidizing agents, e.g., AsF_5,[33] $(CF_3SO_2)_2O$,[34] or $AlCl_3$,[37] it has only been obtained in the solid state as the AsF_6^- salt prepared from S_4N_4 and $(Te_6^{4+})(AsF_6^-)_4$.[33]

Ring contraction also occurs when S_4N_4 is treated with electrophiles such as acyl halides or acid anhydrides.[38-40] The products are derivatives of the five-membered S_3N_2 ring. In the case of $(CF_3)_3COCl$, however, oxidative addition of $(CF_3)_3CO$ groups to give $N_4S_4[OC(CF_3)_3]_4$ takes place.[41a] The eight-membered ring is also retained when S_4N_4 reacts with the radical $(CF_3)_2NO\cdot$ to give di- and tetrasubstituted derivatives.[41b,c]

The treatment of S_4N_4 with AsF_5 in the presence of the stoichiometric amount of elemental sulfur and a *trace* of bromine is a convenient source of the linear NS_2^+ cation,[42] a useful reagent in cycloaddition reactions (section IIF).

$$^1/_2S_8 + S_4N_4 + 6AsF_5 \xrightarrow[Br_2]{SO_2} 4(NS_2^+)(AsF_6^-) + 2AsF_3 \qquad (4)$$

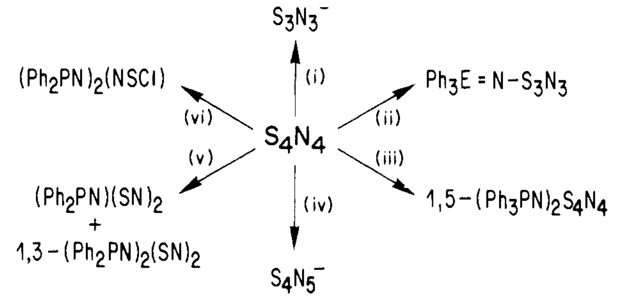


Figure 2. Preparation of S–N heterocycles from S_4N_4 and nucleophilic reagents: (i) $R_4N^+N_3^-$, (ii) Ph_3E (E = P, As) in C_6H_6, (iii) Ph_3P in CH_3CN, (iv) R_2NH, (v) Ph_2PH, (vi) Ph_2PCl.

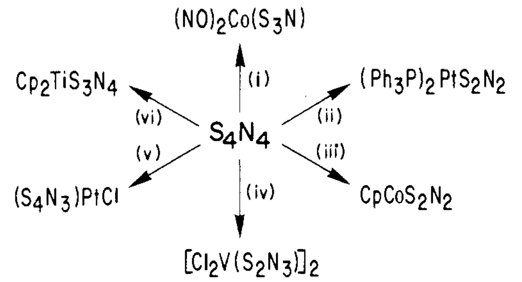


Figure 3. Preparation of metallocyclothiazenes from S_4N_4: (i) $Co_2(CO)_8$/NO, (ii) $(Ph_3P)_2PtC_2H_4$, (iii) $CpCo(CO)_2$ or CpCoCOD, (iv) VCl_4, (v) $(PhCN)_2PtCl_2$, (vi) $Cp_2Ti(CO)_2$.

2. Reactions with Nucleophiles or Reducing Agents

The reactions of S_4N_4 with nucleophiles produce a variety of S–N rings and cages (Figure 2). From the structures of the products it appears that the initial nucleophilic attack causes ring opening to give a linear intermediate which cyclizes and, in some cases, reacts further to give bicyclic or cage molecules.

For example, the degradation of S_4N_4 by anionic nucleophiles, e.g., N_3^-, S^{2-}, or CN^-, produces the six-membered ring, $S_3N_3^-$, and the cage anion, $S_4N_5^-$.[43] The latter ion is also formed on treatment of S_4N_4 with secondary amines.[44] Derivatives of a six-membered ring, $Ph_3E{=}N{-}S_3N_3$ (E = P or As), are obtained when S_4N_4 reacts with Ph_3P[45] (or, preferably, $Ph_3PNSiMe_3$)[46] in benzene or Ph_3As[47,48] (or Ph_3AsNH)[48] in CH_2Cl_2. In a polar solvent, e.g., acetonitrile, the reaction with Ph_3P also produces 1,5-$(Ph_3PN)_2S_4N_4$ and $[(Ph_3PN)_3S^+][S_4N_5^-]$.[49]

Cyclophosphathiazenes of the type $(R_2PN)_n(SN)_2$ can be prepared by the reaction of S_4N_4 with R_2PPR_2 (R = Me, Ph)[50,51] or Ph_2PH[51,52] in toluene at reflux. These heterocyclothiazenes include a six-membered ring (n = 1) and two structural isomers of an eight-membered ring (n = 2). A six-membered ring, $(Ph_2PN)_2(NSCl)$, is obtained in high yield when S_4N_4 and Ph_2PCl are heated at reflux in acetonitrile.[53]

3. Reactions with Metal Halides or Organometallic Reagents

Although S_4N_4 typically forms 1:1 adducts with Lewis acids (section VA1), the interaction with metal halides or organometallic reagents frequently gives rise to ring opening (Figure 3). For example, the reaction of S_4N_4 with $CuCl_2$[54] or aluminum trihalides[55,56] results in the formation of adducts of S_2N_2. In the latter case $NS_2^+AlCl_4^-$ is also produced.[57]

It is well-known from earlier work that S_4N_4 reacts with transition-metal halides in polar solvents to give complexes of the chelating ligands S_3N^- and $S_2N_2H^-$ and some improvements in the preparative and purification procedures have been described.[58] In the case of $PdCl_2$ this reaction also produces $Pd_2(S_3N)_2(S_3N_2)$ in which the S_3N_2 ligand bridges two Pd atoms in a symmetric, bidentate fashion.[59]

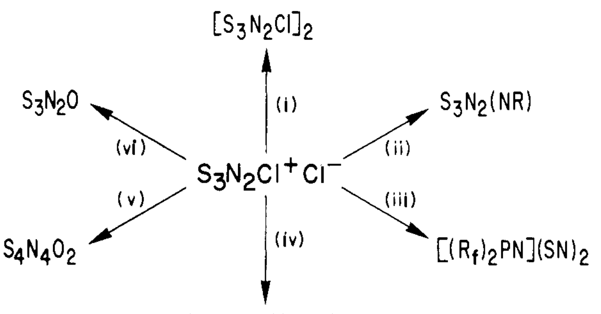


Figure 4. Preparation of S–N heterocycles from $S_3N_2Cl^+Cl^-$: (i) heat, (ii) $RN(SiMe_3)_2$, (iii) $(R_f)_2PN(SiMe_3)_2$, $R_f = CF_3$, C_2F_5, (iv) $Me_2NC(NH)NH_2{\cdot}HCl$, (v) $SO_2(NH_2)_2$, (vi) HCOOH.

$$S_4N_4 + MCl_2 \xrightarrow{\text{MeOH}} M(S_2N_2H)_2 + M(S_2N_2H)(S_3N) + M(S_3N)_2 \quad (5)$$

$$M = \text{Ni, Co, Pd, Pt}$$

Recently a variety of other metallocyclothiazenes have been obtained by treatment of S_4N_4 with organometallic reagents or metal halide complexes although the yields are low in many cases. As indicated in Figure 3, these include examples of the five-membered rings MS_2N_2 (M = Co,[60a] Pt,[60b] Pb,[60c]) and MS_3N (M = Co),[61] the six-membered ring MS_2N_3 (M = V,[62a,b] Mo,[62c–e] W[62c–e]), and the eight-membered rings MS_4N_3 (M = Pt)[63] and MS_3N_4 (M = Ti).[64]

4. Reactions with Acetylenes

Although the reactions of S_4N_4 with acetylenes yield 1,2,5-dithiazoles as the major products,[65a] several novel C–N–S heterocycles have been characterized as minor products.[65b,c] These include the seven-membered rings 1,3,5,2,4-trithiadiazepine and 1,3,5,2,4,6-trithiatriazepine (section IIIA4).[65b] The former can be viewed as the result of cycloaddition of the acetylene to the S_3N_2 moiety, while the formation of the latter requires cleavage of the acetylene C≡C bond.

C. Syntheses from Cyclothiazyl Halides

1. $S_3N_2Cl^+Cl^-$

The easily obtained cyclothiazyl halide $S_3N_2Cl^+Cl^-$ (section IIA) is useful for preparing other S–N ring systems via condensation reactions. For example, it can be converted to S_3N_2O by formic acid,[14] and the reaction with $SO_2(NH_2)_2$ produces $S_4N_4O_2$ (Figure 4).[14] Heating at ca. 90 °C or treatment with SO_2 transforms yellow $S_3N_2Cl_2$ into dark green $(S_3N_2Cl)_2$, which contains the $S_6N_4^{2+}$ cation.[66] Metathetical reactions with Si–N reagents result in the replacement of chlorine atoms by imino substituents to give covalent derivatives of the S_3N_2 ring,[14,67,68] but with $R_2PN(SiMe_3)_2$ (R = CF_3, C_2F_5) the six-membered ring $[R_2PN][SN]_2$ is formed.[69] The condensation reaction with dimethylguanidine hydrochloride, $Me_2NC(NH)NH_2{\cdot}HCl$, also produces a six-membered ring, $(Me_2NCN)(NSCl)_2$, in low yield.[70]

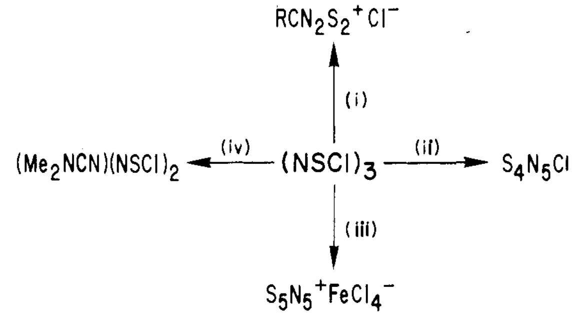


Figure 5. Preparation of S–N heterocycles from $(NSCl)_3$: (i) RCN or RCH=NN=CHR, (ii) $Me_3SiNSNSiMe_3$, (iii) $S_4N_4/FeCl_3$ in $SOCl_2$, (iv) Me_2NCN.

2. $(NSCl)_3$

The potential of $(NSCl)_3$ as a reagent for the synthesis of other sulfur–nitrogen heterocycles is limited by the ease with which the trimeric ring is cleaved to the monomer.[17,71] This dissociation is manifested by a reversible color change from pale yellow to mint green for solutions of $(NSCl)_3$ in CCl_4,[25a] CH_3CN,[72] or THF[72] above ca. 55 °C and has been exploited in the in situ generation of NS^+ salts, which undergo an insertion reaction with S_4N_4 to give the $S_5N_5^+$ cation (Figure 5).[73,74] In SO_2 solution $(NSCl)_3$ forms a 1:1 adduct with $SbCl_5$, formulated as $[(ClSN)_2(SN)^+][SbCl_6^-]$,[75] but the addition of more $SbCl_5$ produces $S_4N_4^{2+}$.[76] Heterocyclic rings containing carbon, $RCN_2S_2^+$, are obtained when $(NSCl)_3$ is heated at reflux with azines, RCH=NN=CHR,[77] or nitriles, RCN (R = *t*-Bu, Ph, CCl_3).[78] In the case of CF_3CN, the six-membered ring $(CF_3CN)(NSCl)_2$ is also isolated.[79] With Me_2NCN, however, both six-membered and eight-membered rings, $(Me_2NCN)(NSCl)_2$ and 1,3-$(Me_2NCN)_2(NSCl)_2$, can be prepared in good yields via a cycloaddition reaction of Me_2NCN with NSCl units generated from $(NSCl)_3$ in CCl_4 at 60 °C.[80]

Several reactions of $(NSCl)_3$ with nucleophilic or reducing reagents result in ring expansion to give S–N cages. For example, the chemical reduction of $(NSCl)_3$ to S_4N_4 is included in Figure 1.[16-18] The cathodic reduction of $(NSCl)_3$ in CH_2Cl_2 yields S_4N_4 at room temperature and S_5N_5Cl at −20 °C with current efficiencies of 90% and 49%, respectively.[81] The metathetical reaction of $(NSCl)_3$ with $Me_3SiNSNSiMe_3$ provides an excellent source of the bicyclic $S_4N_5^+$ cation,[82] while the related anion $S_4N_5^-$ is present in liquid ammonia solutions of $(NSCl)_3$.[83] Surprisingly, the treatment of $(NSCl)_3$ with $(Me_3Sn)_3N$ produces S_5N_6.[84]

D. Syntheses from Si–N or Sn–N Reagents

The use of $(Me_3Sn)_3N$ instead of ammonia allows kinetic control of the reaction with S_2Cl_2 and results in the formation of a five-membered metallothiazene ring.[85]

$$4S_2Cl_2 + 4(Me_3Sn)_3N \rightarrow (Me_2SnS_2N_2)_2 + 2Me_4Sn + 8Me_3SnCl + {}^1/{}_2S_8 \quad (6)$$

The reagent $Me_3SiN{=}S{=}NSiMe_3$ is extremely useful for the preparation of cyclic S–N compounds (Figure 6). A number of these reactions, e.g., with $RAsCl_2$ (R = Me,[86] Ph,[87a] *t*-Bu[87b]), $MeSiCl_3$,[88,89] $Cl_2S_4N_4$,[84] $(NSCl)_3$,[82] and $(Ph_2PN)(NSCl)_2$[90] involve metathesis and proceed in a predictable manner to give S–N rings or cages by the introduction of N=S=N bridges. By contrast, treatment of $Me_3SiN{=}S{=}NSiMe_3$ with PCl_5[91] or PF_5[92] unexpectedly gives a six-membered ring and a bicyclic compound, respectively, (Figure 6). Furthermore, the reaction with $MeAsCl_2$ produces a five-membered ring $MeAsS_2N_2$ when the arsenic reagent is in excess.[86]

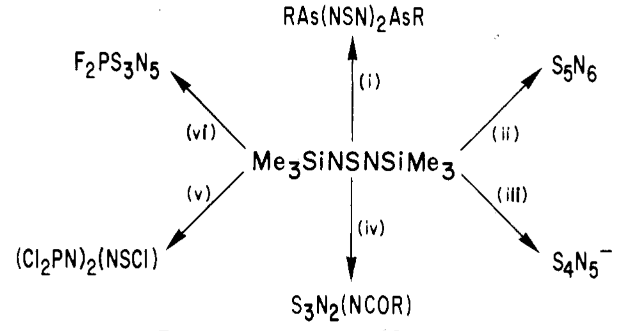
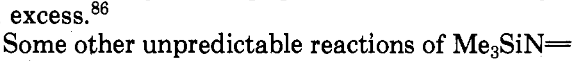


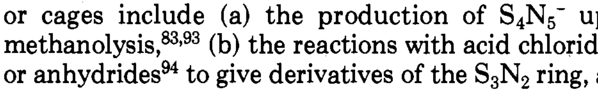
Figure 6. Preparation of S–N heterocycles from $Me_3SiNSNSiMe_3$: (i) $RAsCl_2$, (ii) 1,5-$Cl_2S_4N_4$, (iii) MeOH, (iv) RCOCl, (v) PCl_5, (vi) PF_5.

Some other unpredictable reactions of $Me_3SiN{=}S{=}NSiMe_3$ which are useful for the synthesis of S–N rings or cages include (a) the production of $S_4N_5^-$ upon methanolysis,[83,93] (b) the reactions with acid chlorides[39] or anhydrides[94] to give derivatives of the S_3N_2 ring, and (c) the formation of $S_4N_4O_2$ and $S_5N_5^+S_3N_3O_4^-$ on treatment with FSO_2NSO.[95]

An interesting development of the application of silylated sulfur diimides in the synthesis of S–N heterocycles involves the reaction of $ArNSNSiMe_3$ with SCl_2.[96] The metathetical elimination of Me_3SiCl is followed by an intramolecular condensation involving electrophilic attack of the sulfenyl chloride at the *o*-position of the aromatic ring to give inorganic analogues of naphthalene[96a] and phenazulene rings.[96b]

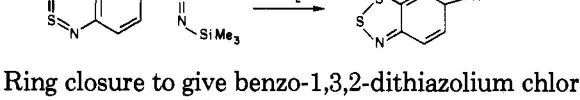


(7)



(8)

Ring closure to give benzo-1,3,2-dithiazolium chloride also occurs when benzene-1,2-disulfenyl chloride is treated with trimethylsilyl azide.[97]



(9)

E. Syntheses from Metallocyclothiazenes

There are several reports of the use of metallocyclothiazenes in the preparation of S–N heterocycles. For example, the five-membered rings S_3N_2O and S_2N_2CO are conveniently prepared by the metathetical reactions of $Me_2SnS_2N_2$ with SOF_2[98] or COF_2,[99] respectively.

$$Me_2SnS_2N_2 + SOF_2 \rightarrow S_3N_2O + Me_2SnF_2 \quad (10)$$

In a similar approach the readily prepared complex $Ni(S_2N_2H)_2$ (section IIB3) takes part in combined metathesis–condensation reactions to give five- and six-membered S–N rings.[100]

$$Ni(S_2N_2H)_2 \xrightarrow{S_2Cl_2,\ Et_3N} S_4N_2 \quad (11)$$

$$Ni(S_2N_2H)_2 \xrightarrow{COCl_2} S_2N_2CO \quad (12)$$

$$Ni(S_2N_2H)_2 \xrightarrow{SOCl_2,\ Et_3N} S_3N_2O \quad (13)$$

Further development of the synthetic applications of metallocyclothiazenes can be anticipated in view of the recent discovery of new ring systems (Figure 3).

F. Syntheses from S-N Cations

The cations SN^+ and S_2N^+ represent potential building blocks in the construction of S–N heterocycles. For example, the insertion reaction of NS^+ with S_4N_4 is described in section IIC2 and this type of reaction could probably be extended to other S–N heterocycles. The easily obtained NS_2^+ cation[42] undergoes cycloaddition reactions with acetonitrile or alkynes in SO_2 to give almost quantitative yields of the 1,3,2,4-dithiadiazolium and 1,3,2-dithiazolium cations, respectively (section IIIA2).[101] A more complex reaction occurs between NS_2^+ and S_4N_4 to give the nitrogen-bridged $(S_3N_2)_2N^+$ cation.[102]

The preparation of S_4N_4 by the reduction of $S_4N_3^+Cl^-$ with KI is mentioned in section IIA.[18–20] Highly explosive, covalent derivatives of the $S_4N_5^+$ cation are obtained by treating S_4N_5Cl with silylated sulfodiimides.[103]

G. Syntheses from S-N Anions

The acyclic anions S_3N^- [104] and S_4N^- [105] are potential sources of metallocyclothiazenes via metathetical reactions with metal halides. This procedure works well for S_3N^- with Cu(I) or Ag(I) halides,[106] but with other transition-metal halides, e.g., Ni(II) or Co(II), MS_2N_2H complexes are also formed and, in other cases, redox reactions occur.[104b]

The reactions of the cyclic $S_3N_3^-$ [107] or cage $S_4N_5^-$ [108] anions with electrophiles provide a rich source of other S–N heterocycles, but, in most instances, alternative synthetic routes are preferable. For example, the reactions of $S_4N_5^-$ with Br_2 or I_2 provided the first synthesis of S_5N_6,[108] which is best prepared, however, from $Cl_2S_4N_4$ and $Me_3SiNSNSiMe_3$ (Figure 6).[83]

Oxidation of $S_3N_3^-$ with electrophiles frequently produces S_4N_4 (and $(SN)_x$),[107] but controlled addition of molecular oxygen gives oxyanions in which the six-membered ring is preserved.[109]

$$S_3N_3^- \xrightarrow[\text{fast}]{O_2} S_3N_3O^- \xrightarrow[\text{slow}]{O_2} S_3N_3O_2^- \quad (14)$$

H. Syntheses from S-N Oxides

The reactions of $S_4N_4O_2$ with nucleophiles have been investigated in detail (Figure 7). The methoxide ion attacks the sulfur atom opposite to the SO_2 group to give the $MeOS_4N_4O_2^-$ anion, in which the eight-membered ring remains intact.[89,110] Other nucleophiles promote opening and, subsequently, contraction of the ring. For example, the six-membered rings $S_3N_3O_2^-$ and $O_2S_3N_3(MMe_3)$ are formed on treatment of $S_4N_4O_2$ with azide ion[109b,111a] or $(Me_3M)_3N$ (M = Si, Sn),[111b] respectively. With Ph_3As a derivative of the five-membered S_3N_2 ring is obtained.[112]

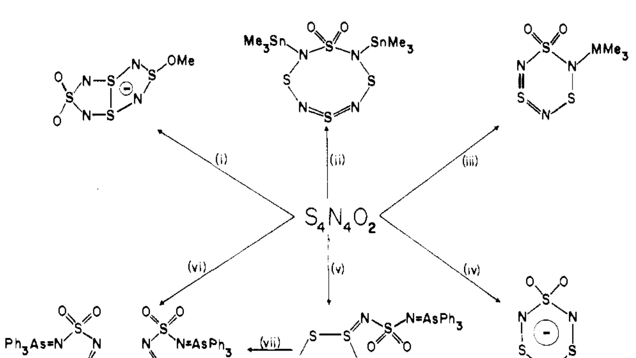


Figure 7. Reactions of $S_4N_4O_2$ with nucleophiles (i) NaOMe, (ii) $(Me_3Sn)_3N$ or Me_3SnN_3, (iii) $(Me_3M)_3N$ (M = Si, Sn), (iv) N_3^-, (v) Ph_3As, (vi) Ph_3As, (vii) in acetone for a few days.

The reactions of $S_4N_4O_2$ with electrophiles have been less well studied but the reagent SO_3 produces a variety of sulfur–nitrogen oxides including $(S_3N_3O_4)_2S$,[113a] $[S_6N_4^{2+}][S_3N_3O_4^-]_2$,[113b] and the six-membered ring $S_3N_2O_5$.[113b]

Titanium tetrachloride promotes the elimination of SO_2 from $S(NSO)_2$ to give an adduct of S_2N_2.[114]

$$S(NSO)_2 + TiCl_4 \rightarrow S_2N_2{\cdot}TiCl_4 + SO_2 \quad (15)$$

The cycloaddition reaction between the electrochemically generated NSO^- ion and S_2N_2 (from S_4N_4) has been reported recently.[115]

$$2NSO^- + S_4N_4 \rightarrow 2S_3N_3O^- \quad (16)$$

III. Molecular and Electronic Structures

A. Monocyclic Systems

In 1972 Banister proposed that *planar* S–N heterocycles belong to a class of "electron-rich aromatics", which conform to the well-known Hückel $(4n + 2)$-π-electron rule.[116] On the reasonable assumption that each sulfur contributes two and each nitrogen one electron to the π system, S_2N_2 (6π), $S_4N_3^+$ (10π), and $S_5N_5^+$ (14π) were cited as examples in support of this contention. However, this simple counting procedure belies the fact that the surplus of electrons is accommodated in π^* (or $n\pi$) orbitals in these electron-rich systems and does not predict, for example, that the π bond orders in S–N heterocycles are significantly lower than those in the corresponding aromatic hydrocarbons.[117–120]

The electronic structures of planar S–N rings have been discussed at the simple Hückel level (HMO) by Gimarc and Trinajstic,[117] at the extended Hückel level (EHMO) by Gleiter[118] and, more recently, at the ab initio level by Laidlaw and Trsic.[119] The S–N rings typically accommodate more π electrons than their neutral hydrocarbon analogues. Perhaps the most extreme example is $S_3N_3^-$ (10π e$^-$); cf. C_6H_6 (6π e$^-$). In considering the "π-electron richness" of the $S_3N_3^-$ ion it should be noted that all electron ab initio MO calculations show that the lowest empty orbitals in benzene are the degenerate π^* pair so that $C_6H_6^{4-}$ would also be a 10-π-electron system. The stability of $S_3N_3^-$ relative to $C_6H_6^{4-}$ can be attributed, in part, to its lower ionic charge and the greater ability of nitrogen to accommodate excess negative charge. However, because of its weaker *net* π bonding, planar $S_3N_3^-$ should be less stable than neutral C_6H_6. Moreover, the S–N ring has

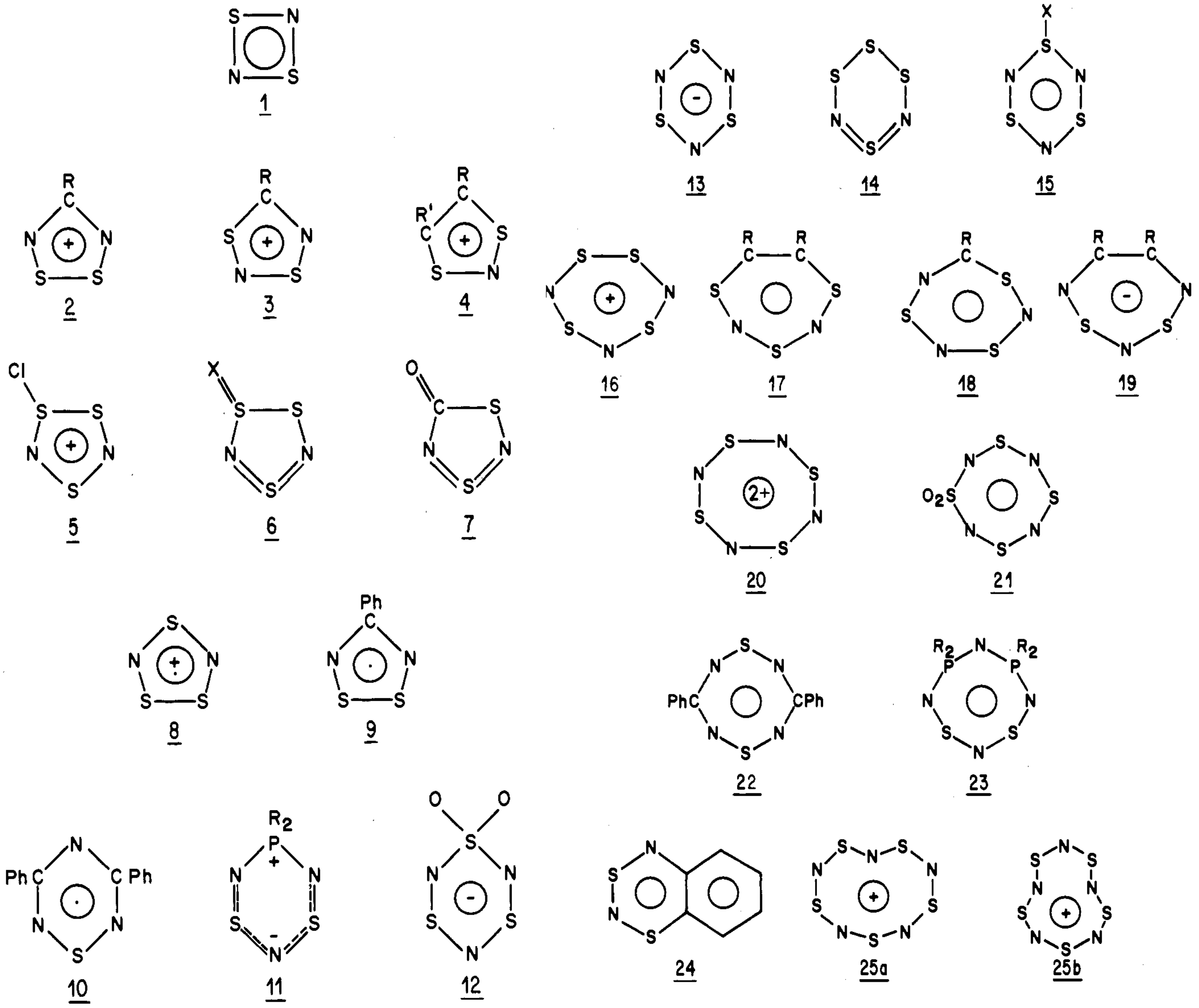


Figure 8. Schematic representation of the structures of monocyclic binary S–N rings and heterocyclothiazenes. Details of X-ray structures can be found in the following references: 1,[24] 2 (R = CCl$_3$,[121a] Cl[121b]), 3,[101] 4,[101] 5,[122] 6,[40,123] 7,[124] 8,[33] 9,[125] 10,[126] 11 (R = Ph,[50] Me$_3$SiNH[127]), 12,[109b] 13,[128] 14,[12,129] 15 (X = O$^-$,[109] NPPh$_3$,[45] NAsPh$_3$[47]), 16,[130] 17,[65b] 18,[65b] 19,[96b] 20,[31] 21,[131] 22,[22] 23 (R = Ph,[51] CF$_3$[69]), 24,[96a] 25.[132]

no exocyclic hydrogen substituents which would tend to stabilize lone-pair distributions. It would appear that the larger separation of nuclei, d(S–N) ~ 1.6 vs. d(C–C) ~ 1.4 Å, reduces the lone-pair repulsions so that the advantages of the π network of planar $S_3N_3^-$ are retained. The electronic structures of other S–N rings will involve additional factors and the balance between a π-electron-rich planar structure and other ring conformations is often delicate. Nevertheless the principles controlling the stability of $S_3N_3^-$ appear to be fundamental to all S–N rings.

Although ab initio MO calculations are to be preferred because of their less arbitrary input, HMO and EHMO calculations can give a useful indication of the π-electronic structures of π-electron-rich S–N rings. It is important, however, to recognize their limitations. For example, the choice of Coulomb parameters α_N and α_S is particularly difficult. The assumption that nitrogen is more electronegative than sulfur is appropriate for the frontier π orbitals but is not likely correct for the deeper π orbitals.[148] This is reflected, for example, in the polarization toward sulfur calculated for the π orbitals of $S_3N_3^-$.[128b] Even though the net charge on nitrogen is negative, and is largely due to the π electrons, it should be emphasized that the largest π population is on the sulfur centers. This is simply a reflection of the fact that each sulfur formally contributes two π electrons to the π system whereas nitrogen donates only one. Analysis of charge *redistribution* in S–N anions or cations is somewhat arbitrary. However, if one presumes that the ionic charge is initially distributed uniformly over all centers then, in accord with the usual concept of electronegativity, nitrogen normally accumulates charge at the expense of sulfur in these systems.

In the ensuing discussion the electronic structures of the S–N heterocycles illustrated in Figure 8 will be described according to ring size. The level of the theoretical approach for each ring system is indicated and, unless specified otherwise, the rings can be assumed to be planar.

1. Four-Membered Rings

The S_2N_2 molecule, 1, is π-isoelectronic with the pseudoaromatic cyclobuta-1,3-diene dianion, $C_4H_4^{2-}$, in the valence shell.[133] The upper occupied levels are not degenerate in 1, however, due to the lower symmetry (D_{2h}) of S_2N_2 compared to $C_4H_4^{2-}$ (D_{4h}). The electronic

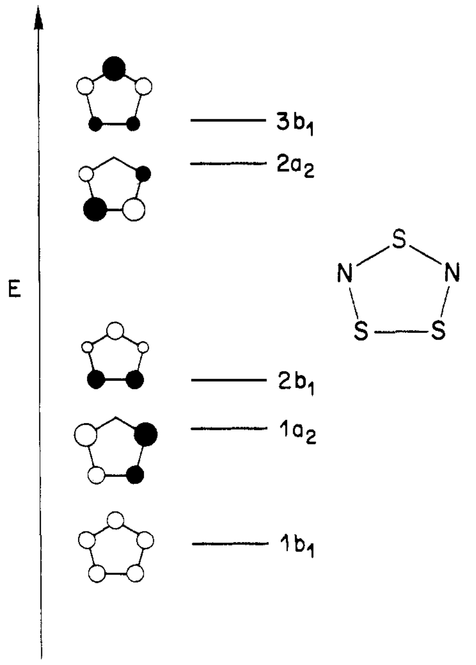


Figure 9. Qualitative π MO scheme for the S_3N_2 ring.[118,137]

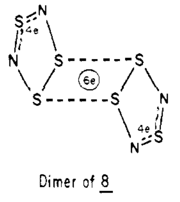
structure has been discussed at various theoretical levels.[134] Ab initio MO calculations[134a,136] indicate that the HOMO is a nonbonding π MO located on sulfur, which is of slightly higher energy than the nonbonding nitrogen-based MO, and this conclusion is supported by UV-photoelectron spectral data (section IVA).[134-136]

Ab initio valence-bond calculations, with sulfur 3d orbitals omitted, indicate that the primary Lewis valence-bond structure of S_2N_2 is a spin-paired diradical (or "long-bond") structure,[134b] in agreement with an INDO VB study.[134c]

2. Five-Membered Rings

Although the neutral S_3N_2 ring (8π) is unknown it provides a convenient reference point for the discussion of the electronic structure of five-membered rings. Unlike its hydrocarbon analogue $C_5H_5^-$ (D_{5h}), there are no degenerate levels in the π system of S_3N_2 (C_{2v}, Figure 9). However, MNDO calculations indicate only a small energy difference between $2a_2$ and $3b_1$ so that a triplet ground state seems probable.[118,137] The formation of a stable cyclic dianion $S_3N_2^{2-}$ (10π) is unlikely since both π^* levels would be fully occupied. On the other hand, the dication $S_3N_2^{2+}$ (6π) should be stable but has not been structurally characterized, although salts have been prepared.[138] The structures of several π-isoelectronic heterocyclothiazenes, **2**–**4**, have been determined by X-ray crystallography.[101,121]

The radical cation $S_3N_2^{+\cdot}$, **8**, is produced in solution by treatment of S_4N_4 with various oxidizing agents, but has been obtained in the solid state only as the AsF_6^- salt (section IIB1).[33] The dimer $S_6N_4^{2+}$, in which two S_3N_2 rings are connected by two long S–S bonds (ca. 3.0 Å), is present in other salts.[34,35] The related cation $Se_4S_2N_4^{2+}$ has a similar structure.[36] On the basis of semiempirical (EHMO) calculations, the bonding in the dimer has been described in terms of an electron-rich (6e$^-$) four-center bond using the dimerization of $H_2S_2^{+\cdot}$ as a model.[118,137] Recent ab initio SCF calculations of charge densities in $S_6N_4^{2+}$ show, however, that the long S–S bonds have the characteristics of closed shell rather than shared interactions.[139]



Dimer of 8

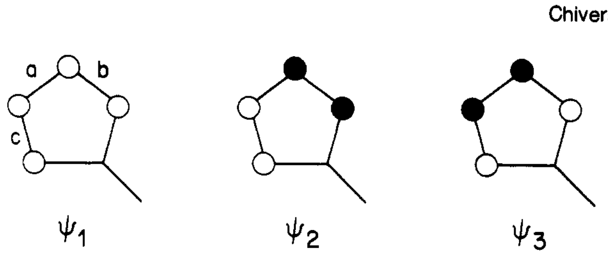


Figure 10. Schematic representation of the occupied MO's of **5** or **6**.[137]

A dimer with a similar structure to $S_6N_4^{2+}$, except that the two rings adopt a cis rather than a trans conformation, is formed by the 7-π-electron radical obtained by the one-electron reduction of **2**.[125]

The five-membered rings containing one three-coordinate sulfur atom $S_3N_2Cl^+$, **5**, and S_3N_2X, **6** (X = O, NR), are related to **8**. The structure of **5** can be viewed formally as an association of $S_3N_2^{+\cdot}$ with Cl·. The linear combination of the pπ orbitals of the four remaining centers provides a set of butadiene-like orbitals of which the lowest *three* are occupied (6π, Figure 10). The occupation of ψ_3 is expected to strengthen S–N bond a and weaken slightly bonds b and c in agreement with structural data.[122] Similar considerations apply to the neutral molecules **6** which are perceived as the union of $S_3N_2^{+\cdot}$ with O^- or RN^-.[118,137]

3. Six-Membered Rings

The $S_3N_3^-$ ion, **13**, is an interesting example of an electron-rich six-membered ring. It has been confirmed as a 10-π-electron system by a variety of ab initio MO calculations[128b,140] and by spectroscopic measurements (section IVB). The planar $S_3N_3^-$ ring, with approximately equal S–N bond distances,[128] has a π manifold reminiscent of benzene with the important difference that the degenerate π^* levels (2e″) are fully occupied in **13** (Figure 11). Consequently the π bond order in $S_3N_3^-$ is lower than that in benzene[117,128b] and the framework bonds are considerably weaker (section VE3).

The replacement of a sulfur atom in $S_3N_3^-$ by another heteroatom to give, for example, $R_2PS_2N_3$, **11**, or the introduction of one (**15**) or two (**12**) substituents on one sulfur lowers the symmetry of the ring to C_{2v} or C_s. As a result there are no degenerate π levels for **11**, which has eight endocyclic π electrons according to ab initio MO calculations (Figure 11).[50] The experimental geometry, in which the phosphorus atom is tilted out of the NSNSN plane by 0.28 Å, is slightly lower in energy (ca. 15 kcal mol^{-1}) than a planar PS_2N_3 ring. Calculations of the distribution of π charge density suggest that the internal salt model $R_2P^+S_2N_3^-$ is a useful approximate description of **11**. The electronic structure of the $S_3N_3O_2^-$ ion, **12**, can be described in a similar way, i.e., a combination of a sulfone (SO_2) group with an 8-π-electron pentadienyl-like $NSNSN^-$ fragment.[109b] Consequently the rings in **11** and **12** retain many of the

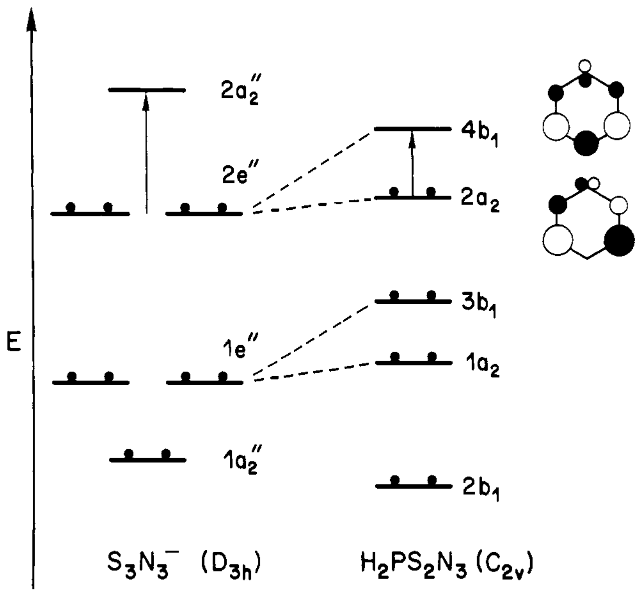


Figure 11. π MO scheme for $S_3N_3^-$ and PS_2N_3 showing the frontier orbitals of the PS_2N_3 ring.[50,141]

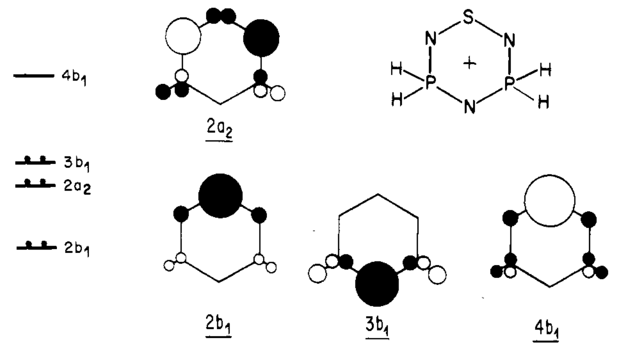


Figure 12. Composition of the occupied π MO's and the LUMO of the $P_2SN_3^+$ ring.[141]

structural and electronic features of the thiazene unit and the frontier orbitals are sulfur-based (Figure 11).[50]

In contrast, the substitution of S^+ for R_2P in $R_6P_3N_3$ to give the *π-electron-precise* $P_2SN_3^+$ ring results in more profound adjustments to the electronic structure of the ring since the energy of the π-type orbital on sulfur is *intermediate* between the energies of the two groups of π MO's of the phosphazene (NPNPN) unit. Ab initio MO calculations[141] suggest that the π system in $P_2SN_3^+$ can be analyzed in terms of the π systems of the fragments, PNP^+ and NSN. As shown in Figure 12, the lowest π MO, $2b_1$, is bonding throughout NSN while the next, $2a_2$, is primarily a nitrogen-centered lone-pair orbital. The HOMO, $3b_1$, is localized on the PNP unit [d(P–N) = 1.58 Å]. The π overlap populations indicate stronger P–N π bonding in this unit than in the P–N bonds connecting the PNP and NSN units consistent with the longer distances found for these P–N bonds [d(P–N) = 1.66 Å].[141]

The "fragment approach" has also been used to rationalize the molecular and electronic structures of S_4N_2, 14,[12] which have been investigated by CNDO/2,[142] EHMO,[143] MNDO,[12] and ab initio[12] (with configuration interaction)[144] methods. The CNDO/2 calculations predict a planar geometry,[142] but all other theoretical approaches favor the half-chair conformation over the planar ring by 6–14 kcal mol^{-1}. Indeed the molecular structure proposed by Palmer et al.,[144a] on the basis of ab initio MO calculations, bears a remarkable resemblance to the observed geometry in which the dihedral angle is 55°,[12,129] cf. calculated value of 57°.[144a] The S_4N_2 ring can be viewed as the result of the interaction of two pseudo-allyl fragments, SSS ($6\pi e^-$) and NSN ($4\pi e^-$).[12] As indicated in Figure 13 the bonding contribution of $2b_1$ to the S–S bonds is largely offset by the occupation of $3b_1$ which is antibonding in the SSS fragment. Similarly, the occupancy of both $1a_2$ and $2a_2$ effects a partial "cancellation" of bonding and antibonding contributions in the S–N connecting bonds. In contrast, for the NSN fragment only the bonding MO, $1b_1$, is occupied and one may therefore expect significant net π bonding in the NSN unit. This picture is consistent with the short S–N bonds observed for this unit (d(S–N) = 1.56 Å) relative to the S–N connecting bonds (d(S–N) = 1.68 Å).[12,129]

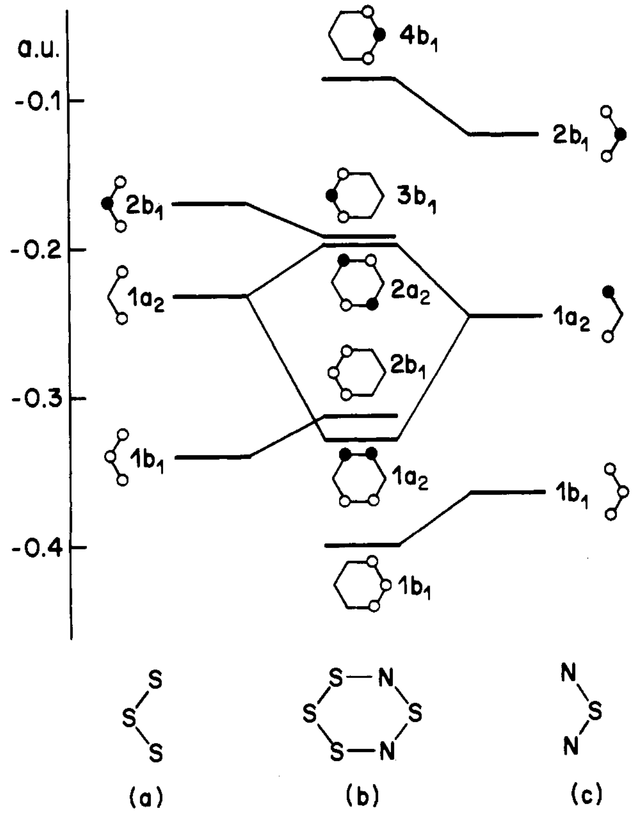


Figure 13. Correlation diagram for the π orbitals of SSS, NSN, and planar S_4N_2.[12]

4. Seven-Membered Rings

The well-known cation $S_4N_3^+$, **16**, a rare representative of a delocalized 10-π-electron seven-membered ring, is isoelectronic with the hypothetical [7]annulenide trianion $C_7H_7^{3-}$.[145,146] Ab initio MO calculations indicate that the two highest occupied π MO's, $2a_2$ and $3b_2$, are nearly degenerate and they are antibonding and bonding, respectively, with respect to the S–S unit (Figure 14).[146] Consequently, the π bonding across this unit is weaker than in the thiazene segment of the ring. In fact, the S–S bond lengths (2.07–2.09 Å) are typical for single bonds. The pseudodegeneracy of the higher π levels of $S_4N_3^+$ is reminiscent of the electronic structure of the hypothetical *planar* $S_3N_3^+$ ion ($8\pi e^-$, Figure 11),[128b] but it is a stable configuration since both levels are fully occupied in $S_4N_3^+$. In a *half-chair* conforma-

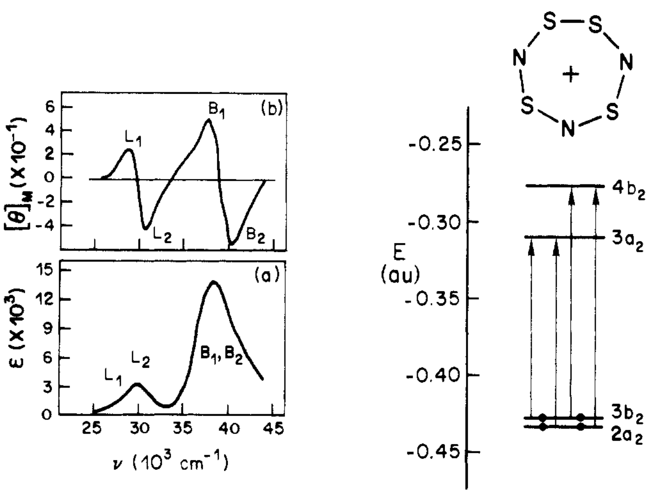


Figure 14. The two highest occupied ($2a_2$ and $3b_2$) and the two lowest unoccupied ($3a_2$ and $4b_2$) π MO's and (a) UV-visible and (b) MCD spectra of $S_4N_3^+$.[145,146]

tion, however, the e″ (HOMO) orbitals of $S_3N_3^+$ are split into nondegenerate levels and EHMO calculations indicate that this conformation is preferred over a planar ring by 0.43 eV.[143]

Two additional examples of 10-π-electron seven-membered cyclothiazenes, **17** and **18**, have been structurally characterized recently,[65b] but details of their electronic structures are not available. The related ring system, **19**, is unknown, but EHMO calculations of π charge densities suggest that it is a component of a CSN heterocycle based on a phenazulene ring system (eq 8).[96b]

5. Eight-Membered Rings

The $S_4N_4^{2+}$ cation is planar with equal S–N bond lengths (D_{4h}) (ca. 1.55 Å) except in the case of $[S_4N_4^{2+}][SbCl_6^-]_2$ in which the cation is slightly puckered towards a boat conformation.[31b] CNDO and EHMO calculations indicate that the planar conformation is stable but easily deformable.[32] This conclusion is supported by MNDO[147] and ab initio MO calculations,[148] which also demonstrate that $S_4N_4^{2+}$ is a fully delocalized 10-π-electron system. The latter calculations show that the strong π network in $S_4N_4^{2+}$ is more than sufficient to overcome the loss of S–S σ-bonding in the $S_4N_4^{2+}$ cage. The π manifold for $S_4N_4^{2+}$ is similar to that of the isoelectronic $C_8H_8^{2-}$ ion except that the degeneracy of the middle levels is split into two primarily nonbonding orbitals, $1b_{1u}$ and $1b_{2u}$, on sulfur and nitrogen, respectively (Figure 15). The former is higher in energy (cf. S_2N_2). The π* levels in $S_4N_4^{2+}$ are unoccupied.

The recent claim of the isolation of $[S_4N_4^{+}\cdot][FeCl_4^-]$,[149] in which the cation would be a 11-π-electron ring, should be viewed with circumspection since the structural parameters and other physical data reported for this salt do not eliminate the possibility that the cation is $S_4N_4H^+$ (section VA1).[150]

In $S_4N_4O_2$, **21**, the sulfone sulfur atom lies 1.52 Å and the two adjacent nitrogen atoms are 0.41 Å above the mean plane of the five-atom S_3N_2 unit which is coplanar to within 0.01 Å.[131] The metallocyclothiazene $Cp_2TiS_3N_4$ is structurally related to **21**, but less puckered and the variations in S–N bond lengths suggest a somewhat different electronic structure in these two rings.[64] In **21** the structural data indicate it consists of two N═S═N units linked by a sulfur atom and an SO_2 group, but this molecule has also been described as a delocalized 10-π-electron S_3N_4 system linked by an SO_2 group.

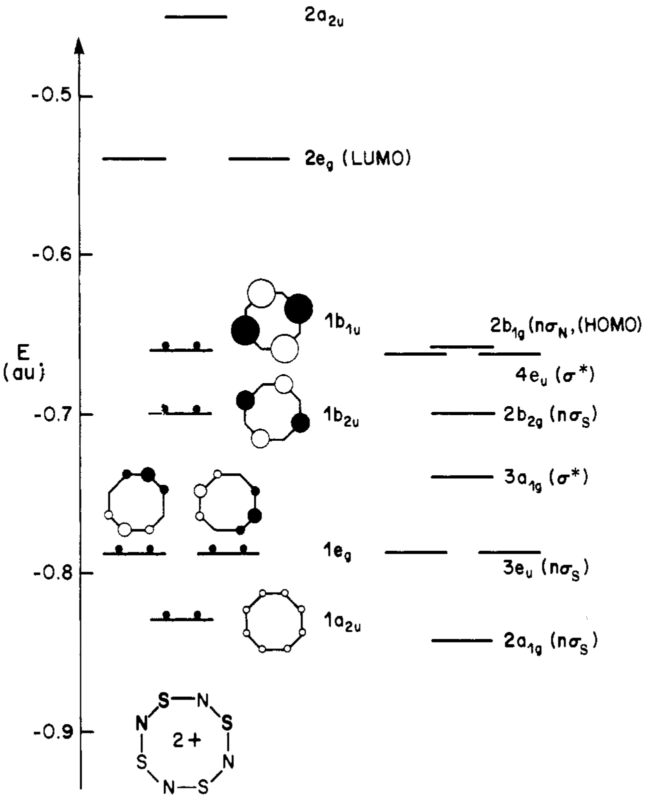


Figure 15. π MO's and upper occupied σ MO's of $S_4N_4^{2+}$.[148]

The geometry of eight-membered heterocyclothiazenes, 1,5-$E(NSN)_2E$, is markedly dependent on the effective electronegativity of the heteroatoms E. When E = CPh, **22**, the heterocyclic ring is planar and the C–N and S–N bond lengths are consistent with a delocalized 10-π-electron system.[22a] This view of the electronic structure of the tetrazocine ring, $S_2N_4C_2$, has been confirmed by ab initio[22b,152,153] and MNDO[22b,154] MO calculations. When E = $CNMe_2$ or PR_2 (R = Me, Ph), however, the molecule adopts a folded (butterfly) structure with a cross-ring S–S interaction of 2.4–2.5 Å (section IIIB2). By contrast the formation of transannular S–S bonding contacts is not geometrically favorable for the 1,3-isomers, **23**. These ring systems consist of a planar S_2N_3 unit with P atoms on the opposite (R = Ph)[51] or the same (R = CF_3)[69] side of the plane.

The 10-π-electron monocation, $RCS_3N_4^+$ (R = CF_3), a hybrid of **20** and **22**, has a planar structure.[155]

6. Ten-Membered Rings

$S_5N_5^+$ is an almost planar 14-π-electron ten-membered ring. Both heart-shaped, **25a**,[132d] and azulene-like, **25b**,[132a,b,c] conformations of the ring have been reported for different salts. It is possible that the heart-shaped structure is a consequence of the superposition of two azulene-like rings, i.e., structural disorder.[156] However, MNDO calculations,[157a] in contrast to earlier EHMO results,[157b] have shown that **25a** and **25b** have *almost equal* energies. Consequently, **25a** could be the most stable isomer in certain salts.

Although it is not a monocyclic system, benzo-1,3-dithia-2,4-diazene, **24**, has an essentially planar structure and can be considered as an S–N analogue of naphthalene with two additional electrons, i.e., 12-π-electrons.[96a]

7. Summary and Conclusions

MO calculations have shown that the energies of the π manifolds of S–N rings are lower and the size of the HOMO–LUMO gaps is smaller for S–N rings compared to their hydrocarbon or cyclophosphazene counterparts. The excess of electrons is accommodated in nπ or π^* (antibonding) orbitals, which are primarily sulfur based. Various consequences of the occupation of these π^* levels and the small HOMO–LUMO gap, e.g., intense colors, redox activity, cycloaddition reactions, and susceptibility to nucleophilic degradation, are discussed in sections IV and V.

B. Bicyclic and Tricyclic S–N Rings and Cages

1. The Nature of S–S Interactions

There is a strong tendency, especially among larger S–N rings (eight atoms or more), to reduce the number of antibonding electrons in the π manifold by the formation of long transannular S–S bonds (2.4–2.7 Å). This gives rise to bicyclic (folded), tricyclic, or cage structures (Figure 16). The nature of the S–S interactions in these unusual compounds has been a central issue in attempts to understand their structures and bonding. Theoretical approaches have included the empirical procedure of Banister,[167] semiempirical (primarily EHMO and MNDO) and ab initio MO calculations, and the use of "increased-valence" structures.[168]

Banister has rationalized the cage framework of S_4N_4 on the assumption that all six edges of the almost regular S_4 tetrahedron represent S–S bonds,[167] and this conceptually simple view can be extended to explain the structures of $S_4N_5^+$ and $S_4N_5^-$. In contrast, an EHMO analysis of various conformations of S_4N_4 by Gleiter requires the formation of only two S–S σ-bonds in the cage structure[118] and ab initio MO calculations confirm that only the unbridged pairs of sulfur atoms of the S_4 tetrahedron in an S–N cage take part in a bonding interaction.[82b] The overlap populations indicate that these S–S bonds are weak[82b] and the calculated charge densities are characteristic of closed shell rather than shared interactions.[139]

Although there are as yet no simple, universal bonding rules for rationalizing the structures of S–N cages, MO calculations on individual molecules do provide some helpful insight as shown by the following examples.

2. Tetrasulfur Tetranitride, S_4N_4

Tetrasulfur tetranitride, **26**, has been the subject of many theoretical discussions at both the semiempirical and ab initio levels in recent years.[82b,120b,134a,139] The unusual structure of S_4N_4, in which the sulfur atoms are three coordinate and the nitrogen atoms are two coordinate, is the inverse of that found for the isoelectronic cages, α-P_4S_4 and As_4S_4. The preference for the more electronegative atoms to occupy the lowest coordination sites in these molecules has been explained in terms of the rule of topological charge stabilization.[169] EHMO calculations for a 44-electron X_8 unit with D_{4d} geometry indicate that these sites are expected to carry the negative charge and, hence, will be favored by the more electronegative atoms.

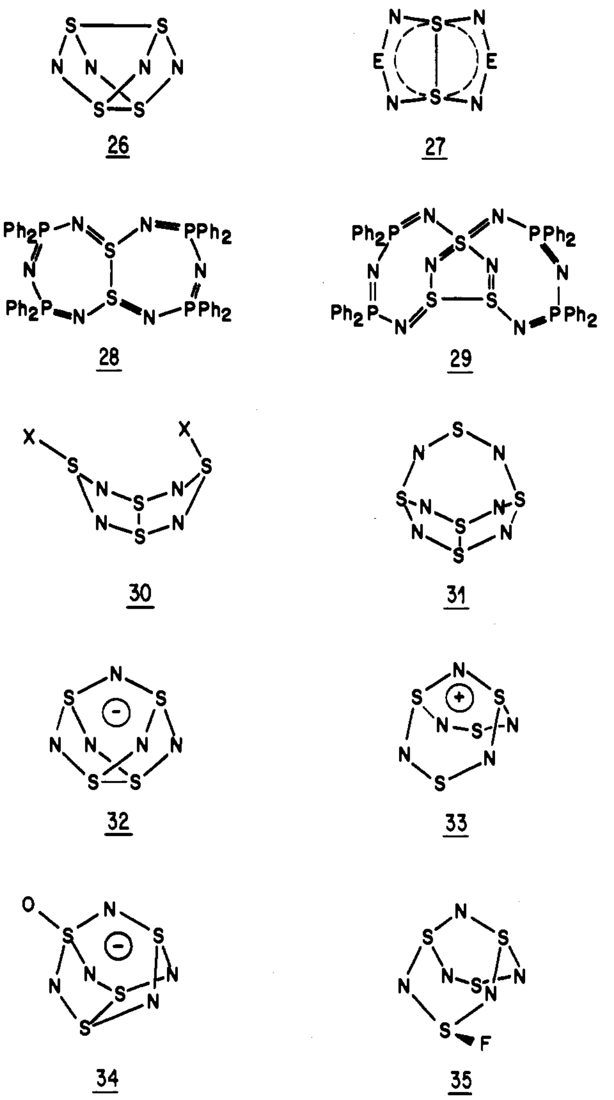


Figure 16. Schematic representation of bicyclic, tricyclic, and cage S–N and P–S–N molecules and ions. Details of the X-ray structural investigations can be found in the following references: **26**,[158] **27** (E = $CNMe_2$,[22a] PMe_2,[159] PPh_2[51]), **28**,[160] **29**,[53a] **30** (X = Ph_3PN,[49] Cl,[161] NMe_2[162]), **31**,[108,163] **32**,[128c,164] **33**,[82,165] **34**,[23] **35**.[166]

Gleiter has presented an intuitively appealing explanation of the cage structure based on an EHMO analysis.[118,170] A planar (D_{4h}) S_4N_4 molecule would be a 12-π-electron system with an open-shell configuration (Figure 15), unstable with respect to Jahn–Teller distortion. Correlation of the MO's of the hypothetical planar molecule with those of the experimental (D_{2d}) conformation shows that the orbital degeneracy of the ground state is lost in the latter and four of the previously π^* electrons are accommodated in S–S σ bonds. The possibility of four-center bonding between all four sulfur atoms has been suggested on the basis of electron-density measurements,[158] but calculated charge densities indicate that these S–S bonds involve closed-shell interactions.[139]

Ab initio calculations identify the HOMO of **26** as a nitrogen-based lone-pair orbital and not the cross-ring S–S bond, while the LUMO is the S–S (σ^*) orbital

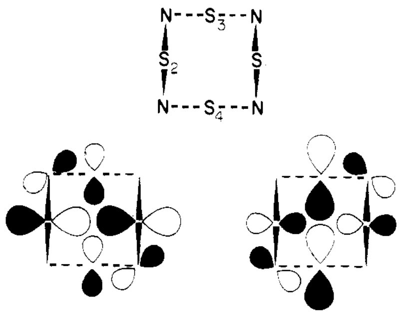


Figure 17. The LUMO's of S_4N_4.

(Figure 17).[82b,134a,171] This conclusion is supported by recent measurements of the X-ray fluorescence spectra of S_4N_4.[172]

3. Bicyclic Compounds, 1,5-E(NSN)$_2$E

The structural alternatives for molecules of the type 1,5-E(NSN)$_2$E, planar, **22**, or folded, **27**, can be understood by comparing their electronic structures with that of the unperturbed 10-π-electron system in $S_4N_4^{2+}$, **20**. Heteroatom incorporation transforms the nonbonding π HOMO of **20** into an antibonding orbital localized over the NSN linkages.[22b,152-154] Strong electron-donor substituents on the heteroatom increase the electron density on the ring in **27** and, hence, weaken the S–N bonds. Puckering of the molecule alleviates this weakness by redistributing the orbital into a transannular S–S bonding interaction. Other related examples of cross-ring S–S bonds include the cyclophosphathiazenes **28**[160] and **29**.[53a]

4. Disubstituted Derivatives, 1,5-$X_2S_4N_4$

The effect of adding π-donor substituents to the 1,5-sulfur atoms of S_4N_4 is similar to that of heteroatom substitution, i.e., a folded structure, **30**, is formed. MNDO calculations of the heats of formation of planar and puckered [d(S–S) = 2.6 Å] forms of **30** (X = Cl, F, NH_2) predict a higher stability for the latter conformation.[154] In the solid state these derivatives (X = Ph_3PN,[49] Cl,[161] NMe_2[162]) all exhibit an exo, endo configuration of the substituents as depicted by structure **30**. By contrast, the ^{19}F NMR spectra of solutions of **30** (X = F[173] or $ON(CF_3)_2$[174]) indicate equivalent substituents (section IVC).

5. Tetrasulfur Pentanitride Anion and Cation, $S_4N_5^{\pm}$, and Pentasulfur Hexanitride, S_5N_6

The tetrasulfur pentanitride ions **32** and **33** can be considered as disubstituted derivatives of S_4N_4 in which the substituents (a bridging N atom) are in endo, endo positions. In the anion **32** there is one cross-ring S–S bond [d(S–S) = 2.66[128c] or 2.71 Å[164]], whereas in the corresponding cation **33** these sulfur atoms are separated by a distance (ca. 4.0 Å[82,165]) which exceeds the sum of the van der Waals radii for sulfur (3.7 Å). These ions, and related S–N cages, e.g., S_5N_6, **31**, have been examined by the EHMO method by using a model in which the NSN units containing the unbridged sulfur atoms were treated as two pseudo-allylic 5-π-electron fragments.[175] If the bridging atom or group is able to withdraw π^*-electron density from the S_4N_4 cage, e.g., N^+, the S–S bonding interaction will be weakened and a large S–S separation is expected. By contrast, if the bridge provides a high-lying filled orbital, e.g., N^- or NSN, a stable structure with a short S–S distance is predicted.

Ab initio MO calculations provide further insight into the bonding in S–N cages. For example, the calculated overlap populations indicate that the introduction of an N^- bridge weakens the S–N bonds in the S_4N_4 cage,[82b] consistent with the observed thermal instability of the $S_4N_5^-$ anion (section VC3).[105,176] The X-ray structural parameters have prompted the suggestion that S_5N_6, **31**, can be viewed as NSN and S_4N_4 units linked through weak S–N bonds. The S–N connecting bonds are long, ca. 1.70 Å, compared to those in the NSN bridge, ca. 1.54 Å.[108,163] The latter unit appears to have some "in molecule diradical" character,[177] which may account for the facile (and, in the solid state, explosive) thermal decomposition of S_5N_6 to S_4N_4 and sulfur.[108]

6. Derivatives of Tetrasulfur Pentanitride, S_4N_5X

Two structural isomers are possible for S–N cages of the type S_4N_5X. In the first, exemplified by $S_4N_5O^-$, **34**, the exocyclic substituent is attached to a sulfur atom which is bonded to three nitrogens, whereas in the other isomer the sulfur atom bearing the substituent is connected to only two nitrogens, e.g., S_4N_5F, **35**. In the latter case, there is no cross-ring S–S bond and the exocyclic substituent may adopt a syn or anti conformation with respect to the S_4N_5 cage. The anti conformation has been established by X-ray crystallography for S_4N_5F, although MNDO calculations suggest there is very little energy difference between the two conformers.[166] However, the calculated barrier to inversion at the three-coordinate sulfur atom, which is necessary for the anti → syn isomerization, is substantial (46.7 kcal mol^{-1}).[166]

IV. Spectroscopic Studies

In this section special emphasis will be placed on spectroscopic studies, e.g., photoelectron, UV–visible, MCD, and ESR spectra, which provide experimental data to corroborate calculations of the electronic structure of electron-rich S–N rings and cages described in section III.

A. Photoelectron Spectra

Photoelectron spectra (PES) supply information about the binding energies of either inner-core (X-ray PES) or valence-level (UV-PES) electrons. The data obtained provide experimental support for MO calculations of electronic energy levels and atomic charges in various molecules. UV–PES are most readily obtained for reasonably volatile compounds and studies of S–N heterocycles have included S_2N_2,[134-136,178] derivatives of the S_3N_2 ring,[179,180] S_4N_2,[144] S_4N_4,[134,178,179,181] $S_4N_4O_2$,[179] and the eight-membered rings $RC(NSN)_2CR$ (R = Ph, Me_2N;[22b,152] R = t-Bu[22b]).

The UV–PES for S_2N_2 show that the two upper π levels are nearly degenerate with the π_S orbital (primarily nonbonding electrons located on the two sulfur atoms) being of slightly higher energy ($\Delta E \sim 0.5$ eV) than π_N.[134] The binding energies for S ($2p_{3/2}$) and N (1s) obtained from the X-ray PES data are consistent with charge transfer of ca. 0.19 e^- from sulfur to nitrogen, somewhat smaller than the value obtained (0.40 e^-) from MNDO calculations.[178]

Several groups have reported the UV[134,181] and X-ray[134,180,181] PES of S_4N_4 and good agreement between experimental ionization potentials and Hartree–Fock–Slater eigenvalues has been obtained.[182] The X-ray PES data indicate a slightly greater S → N charge transfer in S_4N_4 compared to S_2N_2 consistent with MO calculations by the MNDO[178] or SCF-Xα[183] methods. The UV and X-ray PES data are also compatible with a modest S–S bonding interaction in S_4N_4.[178,181]

The UV–PES of *t*-BuC(NSN)$_2$CBu-*t*, **27** (E = *t*-BuC), shows four well-resolved peaks with ionization potentials less than 11 eV and good agreement with calculated orbital energies for the highest five MO's of the model compound, **27** (E = CH),[22b] was obtained. The experimental (UV–PES) and calculated values (ab initio MO calculations with configuration interaction) for the first nine ionization potentials of S_4N_2, **14** were also found to be in reasonable agreement.[144b]

The X-ray PES of $S_4N_4O_2$ exhibits distinct binding energy values for three types of sulfur atoms and two pairs of unequivalent nitrogen atoms consistent with the known structure **21**.[180] Similarly, the X-ray PES of S_3N_2 derivatives show three sulfur (2p) and two nitrogen (1s) binding energies as expected for **6**.[179]

B. UV–Visible and MCD Spectra

In contrast to unsaturated organic ring systems or cyclophosphazenes, electron-rich S–N heterocycles usually exhibit intense colors ranging from yellow, **13**, through orange, **16**, **20**, and **25**, and red, **14**, to blue, **11** and **24**. The colors are due to low energy ($\pi^* \rightarrow \pi^*$ or $n \rightarrow \pi^*$) transitions. Laidlaw and Trsic have had considerable success in correlating the experimental values (from electronic spectra) with excitation energies calculated by the transition-state method (Table II).[182,184] Unambiguous assignments of UV–visible absorption bands to the appropriate electronic transitions can usually be made by comparing the calculated transition moments for the various alternatives.

In several instances the technique of magnetic circular dichroism (MCD) spectroscopy has been used to corroborate assignments based on UV–visible spectroscopic data. For example the assignment of the intense 360-nm band for $S_3N_3^-$ to a π^* (2e'') → π^* (2a$_2$'') (HOMO → LUMO) excitation[128b] has been confirmed by the measurement of the MCD spectrum of $S_3N_3^-$.[186] The interpretation relies on the application of the Platt perimeter model,[187] as developed by Michl.[188] The $S_3N_3^-$ ion is an unusual example of a $(4N + 2)$-electron n-center ($N = 2$, $n = 2N + 2$) π-electron perimeter, which will have two π-holes. As such, the $2e'' \rightarrow 2a_2''$ transition, which is doubly degenerate (Figure 11), is predicted to generate a negative A term in the MCD spectrum, as a result of the splitting of the excited state by the magnetic field. The MCD spectrum of $S_3N_3^-$ does indeed display the characteristic shape of a negative A term.[186]

TABLE II. Experimental and Calculated Electronic Transition Energies for S–N Rings and Cages

S–N heterocycle	λ_{max}, eV expt	λ_{max}, eV calcd	assignment	ref
S_4N_2	2.72	2.48	$7a'' \rightarrow 11a'$	12, 144c
	3.29	3.16	$10a' \rightarrow 11a'$	
$S_3N_3^-$	3.44	3.60[a]	$2e'' \rightarrow 2a_2''$	128b, 182
$Ph_3P{=}N{-}S_3N_3$	2.59		*e*	109b, 189
	3.76			
$Ph_3As{=}N{-}S_3N_3$	2.54		*e*	109b, 189
	3.69			
$OS_3N_3^-$	2.44		*e*	109b
	3.65			
$(R_2PN)(SN)_2$	2.13–2.28[b]	2.21[c]	$2a_2 \rightarrow 4b_1$	50
	4.59[d]	4.43[c]	$3b_1 \rightarrow 4b_1$	
$O_2S_3N_3^-$	2.21		*e*	109b
	3.42			
$S_4N_3^+$	3.53	3.64	$2a_2 \rightarrow 3a_2$	145, 146
	3.78	3.73	$3b_2 \rightarrow 3a_2$	
	4.64	4.40	$2a_2 \rightarrow 4b_2$	
	4.96	4.48	$3b_2 \rightarrow 4b_2$	
$S_4N_4^{2+}$	3.58	3.71	$1b_{1u} \rightarrow 2e_g$	148
	4.13	3.75	$4e_u \rightarrow 2e_g$	
	4.73	4.73	$1b_{2u} \rightarrow 2e_g$	
t-BuC(NSN)$_2$Bu-*t*	3.40	3.36	$2b_{1u} \rightarrow 2b_{2g}$	22b
	4.43	4.08	$1a_u \rightarrow 2b_{2g}$	
	4.54			
	5.30	5.15	$2b_{1u} \rightarrow 2b_{3g}$	
$S_4N_4H^+$	2.62		*e*	229
	3.82			
$S_5N_5^+$	2.91		*e*	185
	4.06		*e*	
$S_4N_5^-$	3.49	3.55[a]		105b, 182
S_5N_6	3.31	3.02	$5a_2 \rightarrow 7b_2$	108b, 177
	4.96		$11a_1 \rightarrow 7b_2$	

[a] Obtained by adding 0.50 eV to the one-electron energy differences.[182] [b] Exact value depends on the nature of R. [c] R = H. [d] R = Me. [e] See text.

The MCD spectrum of $S_4N_3^+$, **16**, indicates that each of the two electronic absorption bands at 340 and 263 nm consists of two pairs of nearly degenerate transitions.[145] This conclusion has recently been confirmed by Hartree–Fock–Slater calculations of the electronic transitions (Figure 14 and Table II).[146] The UV–visible spectrum of $S_4N_4^{2+}$, a classic example of an eight-atom 10-π-electron perimeter, shows peaks at 346 and 262 nm attributed to $n\pi_S \rightarrow \pi^*$ and $n\pi_N \rightarrow \pi^*$ transitions, respectively, which should give rise to a pair of positive A terms in the MCD spectrum.[148,188] The electronic spectrum of $S_5N_5^+$ has not been assigned unambiguously, but it has been suggested that one of the bands (327 or 426 nm) is due to an $n \rightarrow \pi^*$ transition.[157]

Monosubstituted derivatives of the type S_3N_3X, **15** (where X = O^-, Ph_3PN, Ph_3AsN) exhibit remarkably similar electronic spectra (Table II) and molecular structures.[120b] The result of the addition of a single exocyclic substituent on the π-electronic structure of the S_3N_3 ring is the loss of degeneracy for the HOMO's (2e''). Consequently, the strong absorptions at 480–510 and 330–340 nm have been assigned to the HOMO (π^*) → LUMO (π^*) and HOMO-1 (π^*) → LUMO (π^*) transitions, respectively.[109b] This assignment is supported by the MCD spectra of $Ph_3E{=}N{-}S_3N_3$ (E = P, As).[189]

The similarity between the electronic structures of $(R_2PN)(SN)_2$, **11**, and $S_3N_3O_2^-$, **12**, referred to in section IIIA3, is also reflected in their UV–visible spectra. Both these heterocycles have an intense purple color due to a visible absorption band at ca. 560 nm attributed to the HOMO (π^*) → LUMO (π^*) transition.[50,109b]

The pale yellow color of 1,5-$(R_2PN)_2(SN)_2$, **27** (E = Ph_2P, Me_2P) is in contrast to the dark orange color (λ_{max} ~ 460 nm) of the structural isomers 1,3-$(R_2PN)_2(SN)_2$, **23**. In the absence of a cross-ring S–S bond, the latter isomers are π-electron-rich (10-π electrons) and the strong visible absorption band has been tentatively

TABLE III. ^{15}N NMR Parameters of Unsaturated S-N Heterocycles and Related Acyclic Systems

compound	chemical shift[a]	$^2J_{NN}$,[b] Hz	ref
S_4N_4	123.2		18
1,5-$Cl_2S_4N_4$[c]	~172 (2 N), 182 (2 N)		120b
1,5-$(Ph_3P{=}N)_2S_4N_4$	153.6 (2 N), 159.8 (2 N)		18
S_4N_5Cl	39.3 (1 N), 225.1 (4 N)		18
$S_4N_5^-$	53.3 (1 N), 138.7 (4 N)		18
$S_4N_5O^-$	104.0 (1 N), 129.0 (2 N), 147.9 (2 N)		109b
$S_3N_3^-$	148.4		18
$S_3N_3O^-$	225.4 (2 N), 288.3 (1 N)		109b
$S_3N_3{-}N{=}PPh_3$	203.5 (2 N), 282.5 (1 N)		18
$S_3N_3{-}N{=}AsPh_3$	209.6 (2 N, d), 282.6 (1 N, tr)	2.2	18
$S_3N_3O_2^-$	215.2 (2 N), 353.3 (1 N)		109b
$(Ph_2PN)(SN)_2$	116.2 (2 N, d), 336.2 (1 N, tr)	2.8	50b
$(Me_2PN)(SN)_2$	123.2 (2 N, d), 338.9 (1 N, tr)	3.0	50b
$[(PhO)_2PN](SN)_2$	135.8 (2 N, d), 407.4 (1 N, tr)	2.7	50b
S_4N_2	266.3		18
S_3N_2O[d]	255.8 (1 N), 326.0 (1 N)		195
$S_4N_3^+$	366.4 (1 N, tr), 376.1 (2 N, d)		18, 194
$[SSNSS]^-$	244.2		196
$Ph_3P{=}N_aSN_bSS$	86.9 (N_a), 472.0 (N_b)		18
$[SSNS]^-$	616.7		196

[a] δ (in ppm) downfield of NH_3(l) at 25 °C (d = doublet; tr = triplet). [b] Coupling constants are only available for highly enriched (99%) samples; coupling to exocyclic substituents, e.g., ^{31}P, is not included in this data. [c] Measured at −80 °C in CH_2Cl_2. [d] Chemical shifts were quoted relative to aqueous NH_4NO_3, for which the shift is 376.25 ppm downfield of NH_3(l) at 25 °C.

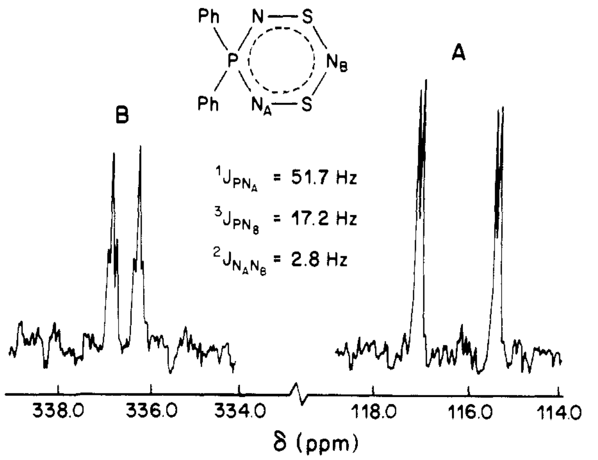


Figure 18. ^{15}N NMR spectrum of $Ph_2PS_2{*}N_3$ (*N = 99% ^{15}N).[50]

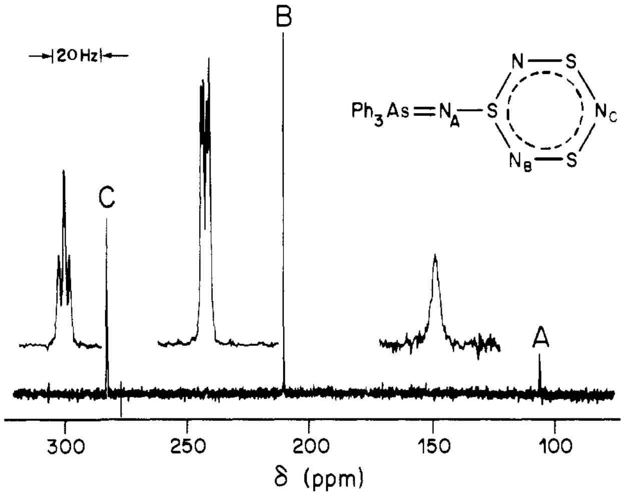


Figure 19. ^{15}N NMR spectrum of $Ph_3As{=}N{-}S_3N_3$ (99% enriched in ^{15}N).[18]

ascribed to a HOMO (π*) → LUMO (π*) transition.[51]

The UV-visible spectrum of S_4N_4 has been measured in different solvents over a range of temperatures[190] and the earlier assignments have been revised.[181]

C. ^{15}N NMR Spectra

The ^{14}N NMR chemical shifts of several S–N heterocycles have been reported, but the lines are usually very broad due to the quadrupole moment of ^{14}N (I = 1; 99.6%) and low symmetry around the nitrogen nuclei, e.g., S_4N_2 ($\Delta h_{1/2}$ = 110 Hz),[191] S_4N_4 ($\Delta h_{1/2} \sim$ 600 Hz),[192] and $S_4N_5^-$ ($\Delta h_{1/2}$ = 1600 Hz).[93] By contrast, the ^{15}N nucleus ($I = {}^1/_2$) gives rise to narrow signals and is, in principle, a more useful probe for studying the structures of S–N rings and cages. It is usually necessary, however, to prepare ^{15}N-enriched samples due to the low natural abundance of ^{15}N (0.37%) and poor solubility of many S–N heterocycles. In view of the expense involved, this procedure is only warranted in carefully selected cases, e.g., when ^{15}N–^{15}N coupling patterns can provide crucial structural information.

The first application of ^{15}N NMR spectroscopy in inorganic chemistry[193] involved the S–N heterocycle, $S_4N_3^+$. In this classic example, reported by Logan and Jolly in 1965,[194] the ^{15}N NMR spectrum exhibits the doublet–triplet pattern expected for structure **16**. More recently the ^{15}N NMR spectra of a variety of S–N rings and cages have been reported (Table III). The ^{15}N chemical shifts span a wide range of values, 40–400 ppm, which is even more pronounced for related acyclic systems. For example, the chemical shift difference for the two inequivalent nitrogen atoms in $Ph_3PNSNSS$ is ca. 385 ppm[18] and for the catena anions $SSNSS^-$ and $SSNS^-$ the δ values are 244 and 617 ppm, respectively.[196] In certain unsaturated nitrogen derivatives, e.g., nitrosyl (XN=O) or azo (XN=NX) compounds, there is a correlation between the nitrogen NMR chemical shifts, δ, and the wavelengths, λ, of the lowest electronic transition (n → π*).[193] This correlation does not apply to electron-rich S–N systems because the intense visible absorption bands are either magnetic dipole forbidden (e.g., π* → π*) or the charge circulation is closer to sulfur than to nitrogen, i.e., the LUMO's are based mainly on sulfur.[193] Consequently, the λ values are not relevant to nitrogen shielding.

A few applications of ^{15}N NMR spectroscopy to structural problems in S–N heterocycles have been reported. The ^{15}N NMR spectra of the compounds $R_2PS_2N_3$ all show a characteristic pattern of a downfield doublet of triplets and an upfield doublet of doublets (Figure 18) consistent with the six-membered ring structure, **11**, established by X-ray crystallography for R = Ph. Thus the NMR data confirm that the other derivatives (R = Me, OPh), which are thermally unstable oils, also have cyclic structures. The coupling constant, $^2J_{^{15}N-^{15}N'}$, in these neutral compounds is significantly smaller (2–3 Hz) than the corresponding value (8.5 Hz) for the cation, $S_4N_3^+$.

Derivatives of the type XS_3N_3, **15**, exhibit similar coupling constants (ca. 2 Hz) and characteristic chemical shifts of ca. 200–220 and 280–290 ppm for the nonequivalent endocyclic nitrogen atoms (Figure 19). This information afforded the first indication that the anion $S_3N_3O^-$ was among the products of the oxidation of $S_3N_3^-$ by molecular oxygen (section IIG).[109,120b]

^{15}N NMR spectroscopy would be the technique of choice for the study of fluxional behavior in S–N cages. For example, a series of degenerate intramolecular rearrangements can be constructed leading to equivalence of all five nitrogen atoms in $S_4N_5^-$, **32**.[175] No experimental evidence in support of stereochemical nonrigidity in S–N cages has been presented, however, probably because the activation energy necessary for such a process is sufficient to disrupt the cage, e.g., by loss of N_2S (section VC3).[105]

Three structural isomers, with different orientations of the exocyclic substituents, are possible for 1,5-$X_2S_4N_2$ derivatives, **30**. In the solid state an exo, endo configuration of substituents is usually found (section IIIB4).[49,161,162] This isomer should exhibit two distinct ^{15}N NMR signals, corresponding to two inequivalent pairs of nitrogen atoms, and this pattern is found for X = $NPPh_3$[18] and X = Cl at low temperatures.[120b] However, the ^{19}F NMR spectra of **30** (X = F[173] or $ON(CF_3)_2$[174]) show a single fluorine resonance indicative of either an endo,endo or, more likely, and exo,exo conformation. It is unlikely that exo,endo → exo,exo isomerization occurs rapidly at ambient temperatures since the necessary inversion at sulfur would require 47 kcal mol^{-1} for X = F, according to MNDO calculations.[154]

No examples of the application of ^{33}S NMR spectroscopy in S–N chemistry are known due to the inherent difficulties associated with the relatively large quadrupole moment of ^{33}S ($I = {}^3/_2$; 0.76%) and the low symmetry around the sulfur nuclei in most S–N heterocycles. It is likely, however, that reasonably narrow signals and characteristic chemical shifts could be obtained for sulfur in an approximately tetrahedral environment, e.g., SN_2O_2 in **12** or spirocyclic SN_4 in **29** (cf. SO_4^{2-}).[197]

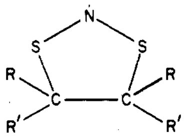
D. ESR Spectra

The frequent and rapid color changes observed in certain reactions of S–N heterocycles suggest the involvement of free radicals. The best characterized is the radical cation $S_3N_2^{+}\cdot$, **8**, which usually dimerizes in the solid state (section IIIA2).[33] This radical is easily produced in solution when S_4N_4 is oxidized, e.g., by $(CF_3SO_2)_2O$[34] or AsF_5,[36] or on treatment of other S–N compounds, e.g., $R_{4-n}Si(NSN)_nSiR_{4-n}$ (n = 1–3) or $R_3SiNSNSNSNSiR_3$ with $AlCl_3$ in CH_2Cl_2.[37] The ESR spectrum of $S_3N_2^{+}\cdot$ shows a characteristic 1:2:3:2:1 quintet consistent with coupling of the unpaired electron with two equivalent ^{14}N nuclei (I = 1).[33,34,36,37] The spectrum of this radical enriched in ^{15}N (99%) and ^{33}S (59.2%) also confirms the presence of two equivalent sulfurs and a third, unique sulfur nucleus.[198] Further analysis of the ESR data indicates that the unpaired electron is accommodated in a π orbital which is antibonding with respect to the S–S bond ($2a_2$ in Figure 9).[137,198]

The related 7-π-electron radical 5-methyl-1,3,2,4-dithiazol-2-yl, prepared in solution by reduction of the cation **3** with silver powder or electrochemically, is also long lived and does not dimerize even at –100 °C.[101] The ESR spectrum consists of three equally intense lines (attributed to coupling with one of the inequivalent nitrogen nuclei) each of which consists of a 1:4:7:7:4:1 sextet apparently due to exactly equal coupling to the other nitrogen nucleus and the three equivalent protons of the methyl group. The isomeric radical $PhCN_2S_2\cdot$, 4-phenyl-1,2,3,5-dithiazolyl, prepared by the reduction of the cation **2** with metals, is probably present in solid samples of the dimer since the ESR spectrum exhibits a broad signal ($g \sim 2.00$) characteristic of a single unpaired electron.[125] The ESR spectrum of the six-membered, seven π-electron radical $Ph_2C_2N_3S\cdot$, **10**, ($g = 2.0059$) consists of seven lines with equal hyperfine coupling constants to all three nitrogen nuclei.[126] This radical dimerizes via a long S–S bond in the solid state.

The thermally unstable radical anion $S_4N_4^{-}\cdot$ is formed when S_4N_4 is reduced by potassium metal or electrochemically in ether solvents.[199,200] This radical gives rise to a nine-line ESR spectrum, consistent with the presence of four equivalent nitrogen nuclei (a_N = 1.185 G,[200] 1.17 ± 0.2 G[201]), and has a half-life of ca. 8 s at –30 °C. The decay of $S_4N_4^{-}\cdot$ obeys a first-order rate law (E_A = 11.1 ± 0.5 kcal mol^{-1}) and probably occurs via intramolecular bond rupture[201] to give the $S_3N_3^-$ ion.[44]

Extensive ESR investigations by Sutcliffe and coworkers,[202-207] using isotopic enrichment, have established that the long-lived radicals 1,3,2-dithiazol-2-yl, **36** and 1,3,2-dithiazolidin-2-yl, **37**, are formed in the reactions of S_4N_2, **14**, with strained olefins or alkynes, respectively. The large g factors found for **37** suggest partial delocalization over the SNS unit but the substituents, R and R′, have little effect on the hyperfine coupling constants.[207] The benzo derivative of **37** exhibits similar ESR parameters.[97] The ESR spectrum of the isomeric radical, **38** (^{33}S-enriched), prepared from o-substituted anilines with sulfur and Br_2 or Cl_2, indicates that two nonequivalent sulfur atoms are present.[208]



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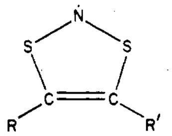

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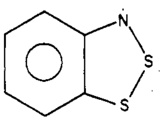

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E. IR and Raman Spectra

There are only a few examples of a complete vibrational analysis of an electron-rich S–N heterocycle. The IR and Raman spectra of S_2N_2, **1**, have been interpreted on the basis of D_{2h} geometry.[209-211] The earlier assignments[212] of IR-active vibrations have been confirmed,[211] but there is disagreement over the numerical values of the harmonic force constants.[209-211]

The technique of ^{15}N-enrichment has been used in several cases to distinguish S–N from S–S[12,213] or anion vibrations.[214] The IR and Raman spectra of $S_4{}^{14}N_4$ and $S_4{}^{15}N_4$ have been assigned in accordance with the D_{2d} structure, **26**.[213] Force constants were calculated and good agreement between observed and calculated wave numbers was obtained.[213,215] A strong Raman band at 218 cm^{-1} for solid S_4N_4 was assigned to the symmetric stretching vibration of the weak cross-ring S–S bonds. Indeed Raman spectroscopy is a useful probe for detecting transannular S–S interactions in bicyclic or cage S–N molecules or ions.[159] The strongly Raman active

TABLE IV. S-S Bond Lengths and Raman Stretching Frequencies in S-N Bicyclic and Cage Compounds

S-N heterocycle	d (S-S), Å	ν (S-S), cm^{-1}	ref
$(Ph_2PN)_4(SN)_2$	2.38	245	160a
S_5N_6	2.43	269	108
$1,5-(Ph_3P{=}N)_2S_4N_4$	2.45	259	49, 216
$1,5-Cl_2S_4N_4$	2.48	260	161, 216
$Ph_2P(NSN)_2PPh_2$	2.53	268	51
$Me_2P(NSN)_2PMe_2$	2.55	250	159
S_4N_4	2.60	218	158, 213
$S_4N_5O^-$	2.63	222	23, 213
$S_4N_5^-$	2.66, 2.71	186	128c, 164, 216

vibrations occur at frequencies in the range 180–300 cm^{-1} for S–S bond lengths of 2.4–2.7 Å (Table IV). These bonds are substantially longer than a S–S single bond (ca. 2.06 Å) for which vibrational frequencies of 400–420 cm^{-1} are observed.[217]

The vibrational spectra of $S_4N_4^{2+}$ cation as its FSO_3^- or $AlCl_4^-$ salts are consistent with a flexible planar structure with D_{4h} symmetry (see section IIIA5).[32,214] A normal coordinate analysis has been carried out for $S_4N_4^{2+}$ and gave a value of 6.56 mdyn Å^{-1} for the S–N valence force constant.[214] The vibrational spectra of $S_4{}^{14}N_2$ and $S_4{}^{15}N_2$ suggest a structural change (increase in symmetry) in going from the solid state to solutions.[12]

The IR and Raman spectra of Na^+, K^+, and R_4N^+ salts of the $S_3N_3^-$ ion, **13**, have been assigned according to the D_{3h} symmetry found by X-ray crystallography for the n-Bu_4N^+ salt.[128b] For the Cs^+ salt, however, additional weak bands, indicative of a lowering of the symmetry of the anion, were observed. A comparison of the IR spectra of various S_3N_2 derivatives, **6**, has led to the identification of four characteristic vibrations of the S_3N_2 ring at ca. 990, 920, 740, and 660 (±20) cm^{-1}.[40]

V. Reactions

The knowledge of electronic structures and, in particular, the composition and energies of frontier orbitals, developed in section III, is helpful in understanding many aspects of the reactivity of electron-rich S–N rings and cages. In this section we shall examine the rich diversity of their chemical behavior in the context of that information. The discussion is organized according to the following unifying themes, which portray the fate of S–N heterocycles in various reactions: (a) adduct formation, (b) redox reactions, (c) ring contraction, (d) ring expansion, and (e) chain formation.

A. Adduct Formation

1. With Lewis Acids

Electron-rich S–N heterocycles behave as weak Lewis bases with nitrogen as the coordination site in the formation of adducts with Lewis acids. For example, disulfur dinitride forms numerous complexes of the type $S_2N_2{\cdot}L$ (L = BCl_3,[218] $SbCl_5$,[219,220] $SnCl_4$,[114] $BeCl_2$,[114] VCl_4,[62a] $[(Ph_3P)_2(CO)_2RuCl]^+$,[114] and $TiCl_4$[114]) and $S_2N_2{\cdot}2L$ (L = $SbCl_5$,[219,220] $AlCl_3$,[55] $AlBr_3$,[56,114] $CuCl_2$[54]). The latter adducts all have similar structures, **39**, in which a planar S_2N_2 ligand is coordinated through nitrogen atoms to the Lewis acid. The S–N bond distances are not significantly different from those in free S_2N_2 and the bond angles at N and S are ca. 95 and 85°, respectively.[55,220] The displacement of S_2N_2 from its complex with $AlCl_3$ by S_4N_4 at 80 °C in high vacuum has been proposed as the method of choice for the preparation of S_2N_2.[221]

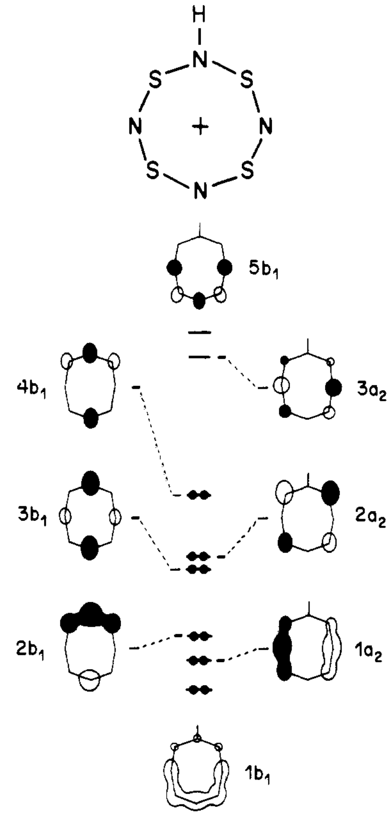
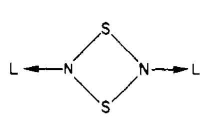


Figure 20. Composition and relative energies of the π MO's of $S_4N_4H^+$.[229]

$$S_2N_2{\cdot}\ 2AlCl_3 + S_4N_4 \rightarrow S_4N_4{\cdot}2AlCl_3 + S_2N_2 \qquad (17)$$

S_4N_4 reacts with a wide variety of Lewis acids to give adducts claimed to include 2:1, 1:1, 1:2, and 1:4 stoichiometries.[222] Adducts of the type $S_4N_4{\cdot}L$ are the most common and have been structurally characterized by X-ray crystallography for L = BF_3,[223] AsF_5,[224] $SbCl_5$,[225] SO_3,[226a] FSO_2NCO,[226b] $TaCl_5$,[227] and $FeCl_3$.[228] All these adducts have a similar structure, **40**, in which one nitrogen atom is coordinated to the Lewis acid and the S_4N_4 ring is flattened into a puckered boat with no cross-ring interactions. A similar structure is adopted by the S_4N_4 rings in *trans*-$SnCl_4{\cdot}2S_4N_4$[60c] and the protonated cation $S_4N_4H^+$.[229]



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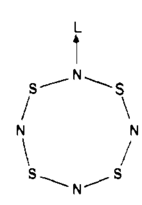

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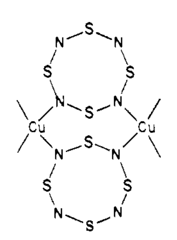

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The formation of the N–H σ bond primarily involves the nitrogen-based σ lone-pair orbital (4e) of S_4N_4. The protonation of S_4N_4 lowers the symmetry and lifts the orbital degeneracy of the 12-π-electron ground state (Figure 20). MNDO MO calculations also reveal that there is a polarization of π charge towards the protonated nitrogen atom. The six occupied π MO's of $S_4N_4H^+$ consist of three bonding $(1b_1,2b_1,1a_2)$, two nonbonding $(3b_1,2a_2)$, and one antibonding $(4b_1)$, which largely offsets the bonding contribution of $2b_1$ (Figure

20).[229] The net result of the localization of π^* electrons in the skeletal bonds to the protonated nitrogen is a strengthening of the SNSNSNS fragment at the expense of the S–N(H) bonds. Indeed a product of ring contraction, $S_3N_2NH_2^+$, is also formed in the protonation of S_4N_4 (section VC2). In contrast to the other 1:1 adducts, the complexes $CuX{\cdot}S_4N_4$ (X = Cl, Br) have polymeric structures, **41**, in which two S_4N_4 ligands bridge two copper atoms via 1,3-N,N coordination sites.[230]

In addition to simple adduct formation, the interaction of S_4N_4 with excess Lewis acid can lead to oxidation to give S–N cations (section IIB1) or cleavage of the eight-membered S_4N_4 ring to give S_2N_2 adducts. The latter process occurs spontaneously with $CuCl_2$,[54] Al_2X_6 (X = Cl,[55] Br[56]), VCl_4,[62] and, on heating, with $S_4N_4{\cdot}TiCl_4$ and $S_4N_4{\cdot}2BeCl_2$.[114] Infusible solids of composition $S_2N_2{\cdot}SnX_2$ (X = Cl, Br, OMe, NMe_2), which may have polymeric structures, are obtained from S_4N_4 and tin(II) salts.[231]

The sulfur-nitrogen oxides S_3N_2O, **6** (X = O), and $S_4N_4O_2$, **21**, form adducts in which coordination to either exocyclic oxygen atoms or ring nitrogen atoms is observed. For example, coordination occurs through oxygen in $S_3N_2O{\cdot}L$ (L = AsF_5, SbF_5)[195] and $2S_3N_2O{\cdot}L$ (L = $SnCl_4$, $TiCl_4$),[195] whereas in complexes with silver(I), $[Ag(S_3N_2O)_2]^+$ AsF_6^- [232] and $[Ag(S_4N_4O_2)_4]^+$ AsF_6^-,[233] the nitrogen atoms are bound to the metal. In the latter case all the coordinated nitrogen atoms are adjacent to the sulfur(VI) center.

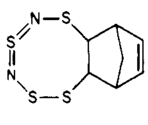
Coordination occurs via oxygen in adducts of S_2N_2CO, **7**, with Lewis acids, e.g., $[Zn(S_2N_2CO)_6][AsF_6]_2$.[234]

2. *With Olefins*

A number of electron-rich S–N heterocycles undergo reversible cycloaddition reactions with olefins, e.g., $S_4N_4{\cdot}2L$ (L = norbornene,[235] norbornadiene (NBD),[235] or *trans*-cyclooctene[236]). At first there was disagreement over the regiochemistry of the addition, but it has now been established by X-ray crystallography that one C=C bond in each diene molecule adds across an SNS unit in $S_4N_4{\cdot}2NBD$.[237,238] The preference for the 1,3-S,S mode of addition can be rationalized from a consideration of the LUMO of S_4N_4 (Figure 17), which is antibonding with respect to opposite pairs of sulfur atoms. Consequently, the HOMO of the olefin will add concertedly across nearest neighbor pairs of sulfur atoms.[239]

An S,S mode of addition is also observed for the 1:1 adducts of NBD with $(R_2PN)(SN)_2$, **11**,[50b,69,90] 1,3-$(R_2PN)_2(SN)_2$, **23** (R = Ph),[51] and $Ph_3P{=}NS_3N_3$, **15** (X = Ph_3PN).[240] This regiochemistry is readily rationalized from a consideration of the composition of the frontier orbitals of **11** (Figure 11).[50b] Both the HOMO and LUMO are primarily sulfur based and of the correct symmetry to overlap with the LUMO and HOMO, respectively, of an olefin. The formation of the NBD adduct of **11** occurs very rapidly and is of practical value in characterizing and storing unstable derivatives, e.g., R = Me,[50b] F,[90] CF_3,[69] since the free heterocycle can be regenerated by mild heating of the adduct. The rates of addition of NBD to other S–N heterocycles differ significantly, that for **15** (X = Ph_3PN) being several orders of magnitude slower than that for **11** (R = Ph). Comparisons of the energies of the interacting frontier orbitals in these cycloadditions have led Oakley et al. to suggest that the HOMO (olefin)–LUMO (SN heterocycle) interaction controls the kinetics of these reactions.[240]

The interaction of NBD with S_4N_2, **14**, results in rupture of the cyclic skeleton of **14** and produces **42**,[241] presumably via insertion of the olefin into an S–S bond, **43**[242] and the radical **36** (section IVD).



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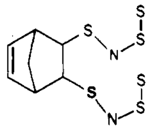

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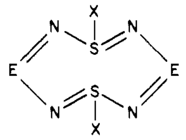
B. Redox Reactions

Electron-rich S–N heterocycles are easily oxidized. This process usually occurs without change in the size of ring and, since it involves the removal of π^* electrons, results in a strengthening of the π framework. The same S–N heterocycles are also good *electron acceptors* since the acceptor orbitals (LUMO's) are low lying relative to those in aromatic hydrocarbons or cyclophosphazenes (section III). The LUMO's are π^* orbitals, antibonding with respect to S–N linkages. Consequently, the addition of electrons will promote ring opening to give chains which often recyclize to smaller rings. In this section redox reactions which occur with retention of ring size will be discussed and those which take place with contraction or expansion of the ring are considered in sections VC and VD.

1. *Oxidation*

The weak intra- or intermolecular S–S bonds found in S–N bicyclic, cage, or dimeric molecules are easily cleaved by halogens. The oxidative addition of Cl_2 to S_4N_4 must be conducted at low temperatures to avoid the decomposition of 1,5-$S_4N_4Cl_2$ (**30** (X = Cl), section IIB1). By contrast, the bifunctional derivatives, **44**,



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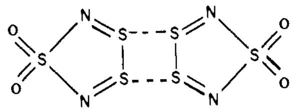
obtained from the addition of halogens across the S–S bond of heterocyclothiazenes, **27** (E = Ph_2P,[243] $CNMe_2$[80,244]) have much higher thermal stability.

Dimers such as $(PhCN_2S_2)_2$ (section IIIA2) or $S_6N_4O_4$, **45**,[245] also react readily with halogens. In the former case the products are salts of the cation **2**,[246] while **45** reacts with Cl_2 to give $S_3N_2O_2Cl_2$, **46**, which decomposes at −30 °C to $S_3N_3O_2Cl$, **47**.[247]



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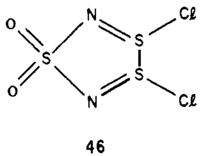

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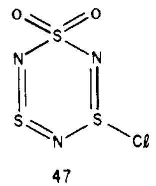

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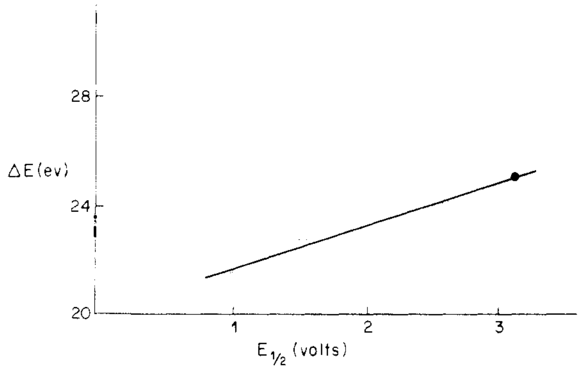


Figure 21. $\Delta E = \Delta[\epsilon(\pi\ \text{LUMO}) - \epsilon(\pi\ \text{LOMO})]$ vs. $E_{1/2}$ for $(Ph_2PN)_2(SN)^+$ (□), $(Ph_2PN)(SN)_2$ (△), $S_3N_3^-$ (○), and $(Ph_2PN)_3$ (●).[141]

The six-membered rings, **11** and **12**, are readily oxidized by a source of Cl_2, e.g., SO_2Cl_2 or $PhICl_2$, to give $(Ph_2PN)(NSCl)_2$[90] and $(NSO_2)(NSCl)_2^-$,[248] respectively.

Surprisingly, only a few examples of the oxidation of neutral S–N heterocycles to the corresponding cations have been reported, e.g., $S_4N_4 \rightarrow S_4N_4^{2+}$ (eq 3).

2. Reduction

Fukui et al. have pointed out that the energetically low-lying LUMO of S_4N_4 implies *electron-deficient* properties.[249] This assertion is substantiated by the facile electrochemical reduction of S_4N_4 at −0.93 V (vs. Ag/0.1 M $AgClO_4$) to the anion radical $S_4N_4^{-}\cdot$, which takes on an additional electron at low temperatures to give the unstable dianion $S_4N_4^{2-}$.[250] In the presence of a proton source the product is $S_4N_4H_4$.[251]

The reduction of the cations **2**–**4** to the corresponding radicals, e.g., **9**, can be achieved with silver powder, sodium dithionite or via a reversible electrochemical reduction (cyclic voltammetry).[101] The radical **10** is produced by the reduction of the corresponding cation, as a chloride salt, with triphenylantimony.[126]

The electrochemical reduction potentials of the series of related six-membered rings, P_3N_3, $P_2SN_3^+$, PS_2N_3, and $S_3N_3^-$, correlate well with the energies of the LUMO's adjusted for the effect of charge (Figure 21).[141] Both of the electron-rich rings, **11** (R = Ph) and **13**, are better electron acceptors than the electron-precise P_3N_3 ring as a consequence of the lowering of the LUMO energy by the substitution of the more electronegative sulfur atoms for phosphorus in the PSN rings (section IIIA3).

C. Ring Contraction

Ring contraction is a common feature of the reactions of electron-rich S–N heterocycles. It can occur under the influence of nucleophilic or reducing agents, electrophiles, or on thermolysis.

1. Reactions with Reducing Agents or Nucleophiles

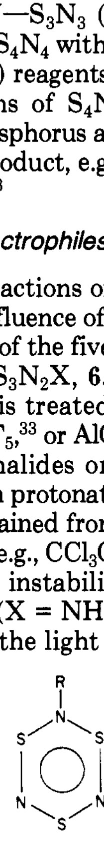
The outcome of nucleophilic degradation is frequently similar to that observed for the reduction of S–N rings. This parallel behavior can be rationalized since both processes will populate the π^* (S–N antibonding) LUMO's and, hence, foster ring-opening reactions. The anion radical $S_4N_4^{-}\cdot$, formed by the electrochemical reduction of S_4N_4, undergoes an intramolecular bond rupture with an activation energy of 11.1 ± 0.5 kcal mol^{-1} [201] to give $S_3N_3^-$, **13**.[44,251] The nucleophilic degradation of S_4N_4 by anionic nucleophiles also produces salts of **13** (section IIB2). Similarly, both the electrochemical reduction[115] and the nucleophilic cleavage of $S_4N_4O_2$, **21**, yield the ring-contracted anion $S_3N_3O_2^-$, **12**.[109b,111a]

The polarity of the S–N bond, $S^{\delta+}$–$N^{\delta-}$, is expected to attract the initial nucleophilic attack to the sulfur atom, e.g., the formation of $MeOS_4N_4O_2^-$ from **21** and methoxide ion (Figure 7). However, subsequent rearrangement often gives products in which the nucleophile is bonded to nitrogen. For example, derivatives of the type $Ph_3E{=}N{-}S_3N_3$ (E = P, As) are formed from the reactions of S_4N_4 with Ph_3E (E = P, As).[45,47,48] Other phosphorus(III) reagents, e.g., Ph_2PX, stimulate ring-opening reactions of S_4N_4 and, if X is a good leaving group, the phosphorus atom is incorporated into the ring-contracted product, e.g., **11** and **23** (X = H)[51,52] or $(Ph_2PN)_2(NSCl)$.[53]

2. Reactions with Electrophiles

Ring-contraction reactions of electron-rich S–N heterocycles under the influence of electrophiles commonly involve the formation of the five-membered ring $S_3N_2^{+}\cdot$, **8**, or its derivatives S_3N_2X, **6**. The radical cation is obtained when S_4N_4 is treated with oxidizing agents, e.g., $(CF_3SO_2)_2O$,[34] AsF_5,[33] or $AlCl_3$,[37] while **6** is produced from S_4N_4 and acyl halides or acid anhydrides (X = RC(O)N=)[38-40] and on protonation (X = NH_2^+).[252] The same products are obtained from the reactions of $S_3N_3^-$, **13**, with electrophiles, e.g., CCl_3COCl[43c] or $HBF_4{\cdot}Et_2O$.[252]

The reasons for the instability of the six-membered ring, **48**, relative to **6** (X = NH_2^+) have been discussed by Oakley et al.[252] in the light of MNDO MO calculations on the model compound S_3N_3H (**48**, R = H). The formation of the N–H σ bond probably involves the nitrogen-based σ lone-pair orbital (4e) of $S_3N_3^-$ [128b] and results in extensive polarization of the π^* electron density into the skeletal bonds to the protonated nitrogen (cf. $S_4N_4H^+$, section VA1). Consequently the π bond order in those S–N bonds is reduced to zero, while that in the remaining S–N linkages is increased to ca. 0.3 (cf. 0.11 in $S_3N_3^-$).[252] The localized weakening of the cyclic structure results in the observed ring contraction.



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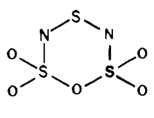
The reaction of S_4N_4 with an excess of SO_3 produces the six-membered ring $S_3N_2O_5$, **49**,[253] and $(S_6N_4^{2+})(S_3N_3O_4^-)_2$,[113b] in which the anion **50** is isoelectronic with **49**, and has a remarkably similar structure.[254]



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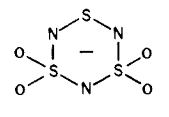

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The ring contraction of S_4N_4 to $S_4N_3^+$, **16**, occurs with certain electrophiles, e.g., liquid Br_2 or ICl,[27] or S_2Cl_2.[2]

3. *Thermolysis*

Electron-rich S–N heterocycles are thermodynamically unstable with respect to the loss of N_2 and their structural frameworks are weaker than those of cyclophosphazenes due, in part, to the partial occupation of π^* MO's. In addition there is often a low kinetic barrier to decomposition and caution must be exercised to avoid explosions. Under suitably controlled conditions, however, thermal decomposition can be used to prepare other S–N compounds. The classic example is the generation of S_2N_2 by thermolysis of S_4N_4 at ca. 300 °C using a silver-wool catalyst.[24] More recently, other cyclothiazenes, e.g., $Ph_3As{=}N{-}S_3N_3$[48] and $S_4N_3{}^+Cl^-$,[255] have been used to produce S_2N_2 under milder conditions.

The thermally initiated reductive elimination of an unstable NSN fragment[256] converts bicyclic to monocyclic S–N rings, e.g., $S_4N_5{}^- \rightarrow S_3N_3{}^-$.[105] Kinetic measurements of this process for **45** (E = Me_2P) gave an activation energy of 24.5 ± 1.4 kcal mol^{-1} for the release of NSN.[90] The thermolysis of **45** (E = F_2P) has been used to prepare the unstable six-membered ring **11** (E = F_2P) as an NBD adduct.[90] The reverse of this process, the cycloaddition of an NSN moiety is comparable to the cycloaddition of olefins to an S–N ring in terms of frontier-orbital considerations since the NSN unit and an olefin are isolobal.[90]

4. *Elimination of NSX*

The best known example of ring contraction via loss of NSCl occurs in the synthesis of $(NSCl)_3$ by chlorination of S_4N_4. The intermediate product 1,5-$Cl_2S_4N_4$ (**30**, X = Cl) undergoes an eight- → six-membered ring contraction, with elimination of NSCl either prior to or immediately after the addition of the second mole of Cl_2.[257] Although $S_4N_4F_4$ is thermally more stable than $S_4N_4Cl_4$,[258a] it undergoes ring contraction with elimination of NSF on treatment with AsF_5 (eq 18).[258b] The six-membered ring $(NSF)_3$ is the major product of the fluorination of S_4N_4 under certain conditions (section IIB1).[259]

$$S_4N_4F_4 + AsF_5 \rightarrow [S_4N_4F_3{}^+][AsF_6{}^-] \xrightarrow{-NSF} [S_3N_3F_2{}^+][AsF_6{}^-] \quad (18)$$

The chlorination of 1,3-$(Ph_2PN)_2(SN)_2$, **23** (R = Ph), produces the six-membered ring $(Ph_2PN)_2(NSCl)$, presumably via loss of NSCl from 1,3-$(Ph_2PN)_2$-$(NSCl)_2$.[243]

D. Ring Expansion

Ring expansion reactions of electron-rich S–N rings, although less common than ring contraction, have been observed in several instances. Insertion reactions or the dimerization of reactive monomer units are the most prevalent examples of this type of behavior.

1. *Dimerization*

Considerable interest has focussed on the mechanism of the polymerization of S_2N_2 to $(SN)_x$ (section VE1), but S_2N_2 is also known to dimerize to S_4N_4 in organic solvents in the presence of nucleophiles.[260,261] Fukui et al.[262] have explained the structural reorganization involved in this process in terms of the HOMO–LUMO interactions of two S_2N_2 molecules oriented so that the sulfur atoms of one molecule interact with the nitrogen atoms of the other (Figure 22). In this way two new S–N σ bonds, S_1–N_3 and N_2–S_4 are formed and the S–N π bonds, S_1–N_2 and N_3–S_4, are weakened. In addition, an S_2–S_3 interaction develops. Deformation of this "stacking model" to give the S_4N_4 cage can be achieved by twisting about the S_2–S_3 fulcrum with formation of an S_1–S_4 bond.[262]

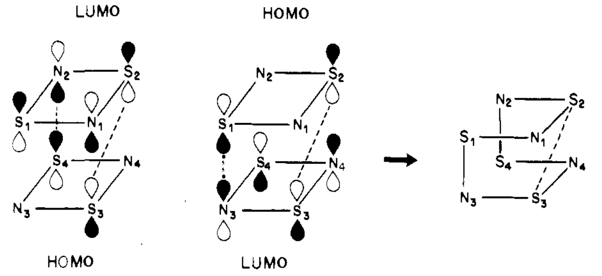


Figure 22. Orbital interactions in the dimerization of S_2N_2 to S_4N_4.[262]

Reduction of $(Ph_2PN)_2(NSCl)$ with triphenylantimony yields the twelve-membered ring, **28**.[160] The ease with which this ring-opening dimerization occurs has been attributed to the strongly S–N antibonding character of the LUMO (π^*) of the $P_2SN_3{}^+$ ring (Figure 12).[141] In contrast, reduction of $(PhCN)_2(NSCl)$ produces the radical **10**, which dimerizes without cleavage of the ring.[126]

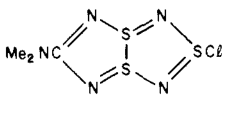
Certain derivatives of **11** undergo a spontaneous six- to eight-membered ring expansion under ambient conditions. In the two known examples, however, different isomers of the eight-membered ring were isolated. The decomposition of **11** (R = Me) produced the 1,5-isomer **27** (E = Me_2P)[159] whereas the 1,3-isomer **23** was obtained from **11** (R = CF_3).[69] It is possible that these products are formed by the dimerization of an $(R_2PN)(SN)$ moiety generated by spontaneous cleavage of the ring in **11**.

2. *Insertion Reactions*

The preparation of $S_5N_5{}^+$ salts, **25**, from NS^+ and S_4N_4 (sections IIC2 and IIF) is the best known example of a ring expansion reaction in S–N chemistry. In a recent variation of this approach, $S_5N_5{}^+Cl^-$ was prepared by the direct reaction of S_4N_4 with $(NSCl)_3$ in formic acid.[263] Ring-expansion reactions also occur in the preparation of S_4N_4 from $S_3N_2Cl^+$, **5**, via $S_4N_3{}^+$ (Figure 1), but the mechanism of these transformations is uncertain.[2]

The reactions of Si–N reagents with cyclothiazyl halides can bring about ring expansion. For example, the six-membered rings **11** (R = CF_3, C_2F_5) may be prepared from $S_3N_2Cl^+Cl^-$ and $R_2PN(SiMe_3)_2$.[69] Six- → eight-membered ring expansion occurs when $(Ph_2PN)_2(NSCl)$ is treated with Me_3SiNSO[265] or $Me_3SiNSNSiMe_3$,[53a,264] to give **23** (R = Ph) or **29**, respectively. The latter transformation can be viewed as a double insertion of SN groups from the sulfur diimide (NSN) reagent into separate P_2SN_3 rings with the common sulfur atom becoming the spirocyclic center.

A six- → eight-membered ring expansion also takes place in the reaction of $(Me_2NCN)(NSCl)_2$ with Me_3SiNSO to give 1,5-$Me_2NC(NSN)_2SCl$, **51**, a hybrid of **27** (E = Me_2NC) and **30** (X = Cl) with a similar folded structure and an endo chlorine atom.[80]



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3. Oxidation

The oxidation of anions, $S_3N_3^-$ or $S_4N_5^-$ (**32**) with halogens results in substantial structural reorganizations to give S_4N_4[107] and S_5N_6 (**31**),[108] respectively. The same products are obtained from the electrochemical oxidation of $S_3N_3^-$ and $S_4N_5^-$.[250a] Interestingly, the reduction of $(NSCl)_3$ with metals[16,17] or azides[21] also produces S_4N_4, in addition to $(SN)_x$.[21] It is possible that a common intermediate, the $S_3N_3\cdot$ radical, is involved in these redox reactions of the trithiazyl ring.

In contrast to the ring contraction reaction observed when **23** (R = Ph) is oxidized by Cl_2 (section VC4), an eight- → twelve-membered ring expansion to give $(Ph_2PN)_4(SN)_2^{2+}$, the dication of **28**, occurs on treatment of **23** with Br_2 or Cl_2.

E. Chain Formation

The formation of open-chain intermediates is implicated in a number of ring-contraction reactions described in section VC. In this section the production of stable catena molecules and ions from S–N rings will be discussed. Ring → chain transformations can occur spontaneously or under the influence of nucleophiles or electrophiles, heat, or light.

1. Polymerization

The spontaneous topochemical polymerization of S_2N_2 to $(SN)_x$ at 0 °C,[24] the most prominent example of a polymerization reaction in S–N chemistry, has been described in detail by Labes et al.[1] On the basis of EHMO calculations, this process is both thermally and photochemically allowed,[266] and the photo-induced polymerization occurs at −65 °C in tetrahydrofuran.[267] INDO-type calculations[268] for S_2N_2 and several deformed structures of $(SN)_2$, as well as the partially polymerized units, $(SN)_4$ and $(SN)_6$, show that the triplet biradical nature (section III1) emerges in deformed structures of $(SN)_2$ in accord with the ESR signal (g = 2.005) observed at the initial stage of polymerization.[24] No triplet character is predicted for $(SN)_4$ or $(SN)_6$ consistent with the fact that the system gradually becomes diamagnetic as polymerization proceeds.

The direct polymerization of S_4N_4 can be induced by a radiofrequency discharge.[269] The reactions of powdered S_4N_4 with bromine or the interhalogens, ICl or IBr, yield highly conducting polymers or approximate composition $(SNBr_{0.4})_x$ and $[(SN)(IX)_{0.4}]_x$, respectively.[29,30] The polymerization of S–N rings to $(SN)_x$ can also be promoted electrochemically. The electrochemical reduction of salts of the $S_5N_5^+$ cation, **25**, in SO_2 or CH_2Cl_2 at low temperatures produces microcrystalline $(SN)_x$.[270,271]

2. With Nucleophiles

Nucleophilic attack ruptures the cage of S_4N_4 to give open-chain intermediates which, in many cases, cyclize to give ring-contracted products (Figure 2 and section VC1). Some nucleophiles, however, produce stable S–N chains. The cleavage of S_4N_4 by Si–N or Sn–N reagents is the most widely studied example of this behavior (eq 19 and 20).[272-278] At elevated temperatures the latter reaction proceeds further to give the five-membered ring $(Me_2SnN_2S_2)_2$ (cf. eq 6). The reaction of S_4N_4 with the primary amine, $PhCH_2NH_2$, produces an open-chain tetrasulfide, PhCHNSSSSNCHPh.[279]

$$2Me_3SiNR_2 + S_4N_4 \rightarrow 2Me_3SiNSNSNR_2 \quad (19)$$

$$2(Me_3Sn)_3N + S_4N_4 \rightarrow 3Me_3SnNSNSnMe_3 + {}^1/_8S_8 \quad (20)$$

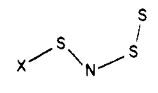
Treatment of S_4N_4 with aryl Grignard reagents yields small amounts of ArSNSNSAr, in addition to the major product, ArSSAr.[280,281] The reaction of S_4N_4 with diazo compounds, e.g., Ph_2CN_2, gives the catenated derivative, $Ph_2CNSNSNSNCPh_2$,[282] a member of a class of compounds used as electrophotographic pigments.[283]

The primary product of the reaction of $S_4N_4O_2$ with Ph_3As is a derivative of the S_3N_2 ring, which decomposes in acetone with the elimination of S_4N_4 and sulfur to give the 11-atom chain, $Ph_3AsNSO_2NSNSNSNSO_2NAsPh_3$ (Figure 7).[284]

The reaction of $S_3N_2Cl^+Cl^-$, **5**, with amines can also lead to chains. For example, when **5** is treated with Me_3SiNMe_2 in the molar ratio 1:3 the product is $Me_3SiNSNSNMe_2$. The reaction of **5** with $C_6F_5N(SnMe_3)_2$ gives $C_6F_5NSNSNSNC_6F_5$.[285]

3. Thermolysis

Thermally induced ring contraction reactions were described in section VC3. In a few cases, the thermal breakdown of electron-rich S–N rings produces stable catenated species. For example, the six-membered rings $S_3N_3^-$, **13**, and $Ph_3P{=}N{-}S_3N_3$, **15** (X = $Ph_3P{=}N$), undergo ring opening in boiling acetonitrile to give $SSNSS^-$[105,176] and $Ph_3P{=}NSNSS$,[48] respectively. Both the anion and the neutral molecule have a catenated cis–trans structure, **52**, with short (ca. 1.9 Å) polar, terminal S–S bonds. It is pertinent to note that ab initio MO calculations on the uniform deformation of the $S_3N_3^-$ ion suggest the decomposition channel which gives NSN + SNS^-.[286]



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The S_7N^- ion, obtained by the deprotonation[287] or electrochemical reduction[288] of S_7NH, decomposes above ca. −50 °C to give **52** (X = S^-).

VI. Summary and Conclusions

Many aspects of the molecular structures, chemical behavior, and spectroscopic properties of electron-rich S–N heterocycles derive from the fact that the HOMO and LUMO are both normally π^* or $n\pi$ orbitals. The result of the partial occupation of π^* orbitals is a weakened π framework which is readily deformed or even disrupted under the influence of heat or upon adduct formation. The intense colors of many S–N rings are also a manifestation of their electron richness and can be attributed to $\pi^* \rightarrow \pi^*$ (or $n\pi \rightarrow \pi^*$) electronic transitions.

Electron-rich S–N heterocycles are easily oxidized. They are also good electron acceptors and this property can be attributed to the low energy of their acceptor orbitals (LUMOs) relative to those of the corresponding aromatic hydrocarbons or cyclophosphazenes. The LUMO's are usually strongly antibonding with respect to the S–N bonds and, consequently the usual result of addition of an electron or nucleophilic attack is ring opening to give catenated species or ring-contracted products.

Although the possibilities for the preparation of novel binary sulfur–nitrogen heterocycles appear to be limited, there are already indications that the scope for the incorporation of heteroatoms such as carbon, phosphorus, or transition metals into these ring systems is considerable. These heterocyclothiazenes may prove to be suitable precursors for linear polymers, related to $(SN)_x$, but containing carbon or other heteroatoms as well as thiazyl units. In addition to an alternative synthetic approach, electrochemical techniques should provide valuable information on the redox properties of new compounds.

The characteristically small HOMO–LUMO energy gaps found for electron-rich sulfur–nitrogen rings suggest photochemical activity. To date, however, there has been no major effort to study the photochemistry of these compounds. Mechanistic studies of the ubiquitous ring-contraction and ring-expansion reactions also represent a virgin field. Finally, an evaluation of the effect of the amalgamation of unsaturated sulfur–nitrogen rings with transition metals on their electronic structures and chemical reactivity represents an interesting challenge.

VII. Acknowledgments

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