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Cyclic and Heterocyclic Thiazenes

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I. INTRODUCTION

The concepts of multiple bonding and π-electron delocalization have developed from the study of unsaturated organic compounds. Conjugated π systems involving purely inorganic linkages are less common, indeed examples of homonuclear π bonding involving the heavier elements, for example, $R_2Si{=}SiR_2$ (1) and $RP{=}PR$ (2), have only recently been characterized. When in conjunction with a lighter element (e.g., C, N, O), however, the heavier elements, in a variety of oxidation states, do form stable unsaturated linkages, either as single $-A{=}B-$ units or in repeated $(-A{=}B-)_n$ sequences. The extent and consequences of π conjugation in $(-A{=}B-)_n$ systems has been a subject of continued interest. In the cyclic phosphazenes $(R_2PN)_n$, for example, the small but discernible variations in the physical and chemical properties along homologous series of different ring sizes (n = 3, 4, 5, 6, . . . ,) afforded some of the best early evidence for a cyclic π-electron delocalization in inorganic frameworks (3). More recent work on inorganic and organic heterocycles built from catenated thiazyl linkages $-S{=}N-$ has provided another and perhaps closer analogy with benzenoid chemistry. Spurred in part by the discovery of the metallic (4) and superconducting (5) properties of the $(SN)_x$ polymer the study of such systems has developed rapidly since the early 1970s. The structural, physical, and chemical properties of these compounds form the subject of this chapter.

Although our knowledge of simple compounds of sulfur and nitrogen goes back to the last century, development of their chemistry was limited for many years by the absence of the necessary analytical and structural probes. In addition, the sensitivity of many derivatives to moisture, oxygen, heat, or shock provided little incentive for exploratory synthetic work. The last 10 to 15 years, however, have seen a complete reversal in this situation. Synthetic strategies have been developed to circumvent the manipulative problems, and a broad spectrum of physical methods has been applied to the study of electronic and molecular structure. Extensive input from the theoretical chemistry community has also provided a much clearer picture of the electronic factors that control thermodynamic and kinetic stability.

The burgeoning interest in sulfur–nitrogen chemistry is indicated by the proliferation of major review articles in the last 10 years (6–18). The recent papers of Chivers (7, 8) are particularly comprehensive, as is the book by Heal (16). Mention should also be made of the early seminal articles by Heal (19) and Becke-Goehring (20), which still provide excellent introductions to the initial phases of work in the area. In preparing the present discussion of the subject, a conscious effort has been made to illustrate its development in a logical rather than chronological way. The approach suffers from the omission of some details, which are well covered by one or more of the earlier reviews, but hopefully will provide the reader with an insight into the interpretative aspects of a branch of chemistry which has, for many years, been largely empirical. In short, the intention is to explore and develop relationships that exist between molecular structure, electronic structure, and chemical reactivity in compounds containing formally unsaturated –S=N– linkages. The extensive chemistry of the sulfur imides $S_x(NR)_y$ (7b, 16, 19) has been excluded. Likewise, simple sulfenamides (21) are not treated explicitly, nor are sulfur(VI) derivatives such as the cyclic sulfanuric halides $[X(O)SN]_x$ (16, 19, 22). Although formally unsaturated and conjugated, the chemical and structural consequences of π delocalization in the latter systems are, as in phosphazenes, more subtle.

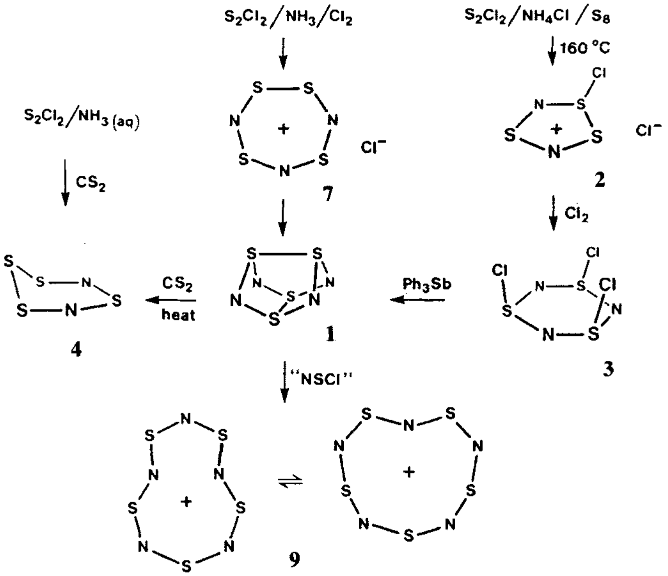
This chapter, which covers the literature through early 1987, is divided into three parts. It begins (Section II) with a summary of the synthesis, structural, and chemical properties of the binary compounds of sulfur and nitrogen. In Section III the discussion is expanded to include the chemistry of organic and inorganic heterocyclic compounds containing conjugated –S=N– units, the study of which has intensified dramatically in the last few years. Finally, in Section IV, the results of some recent studies of the reactivity patterns of molecules containing –S=N– units are summarized, with particular emphasis being placed on the interpretative parallels that exist between the properties of inorganic and organic π systems.

II. BINARY SULFUR–NITROGEN COMPOUNDS

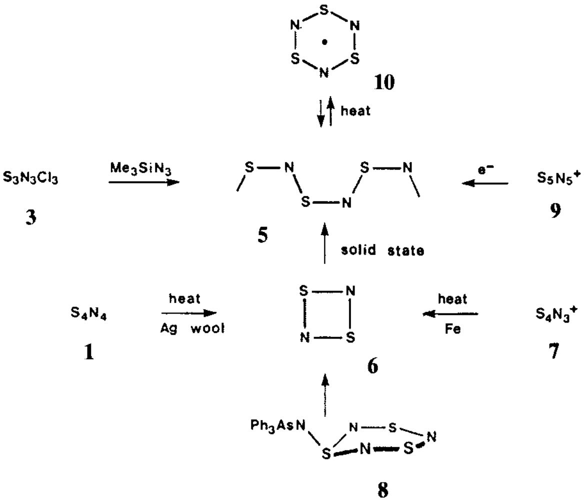
A. Preparative Methods and Structural Diversity

1. Neutral Compounds

Tetrasulfur tetranitride (S_4N_4, **1**), the best known binary compound of sulfur and nitrogen, was first isolated in 1835 from the reaction of sulfur monochloride and ammonia (23). The standard method for preparing S_4N_4 used today is still based on this reaction (24), but several alternative methods, used primarily for isotope incorporation, have recently been developed. ^{15}N-enriched material (for NMR studies) can be prepared in a stepwise manner starting from ammonium chloride, sulfur, and sulfur monochloride (25, 26). When heated at 160°C this mixture liberates $S_3N_2Cl_2$ (**2**) (Scheme I), which can then be oxidized, by chlorine or sulfuryl chloride, to $S_3N_3Cl_3$ (**3**) (27). Final reduction to S_4N_4 can be achieved in a variety of ways, most effectively with triphenylstibine (28), but also by mercury (29) or iron (30). The reaction of sulfur monochloride with ammonia has been used to generate ^{33}S-labeled S_4N_4 (31).



Scheme I



Scheme II

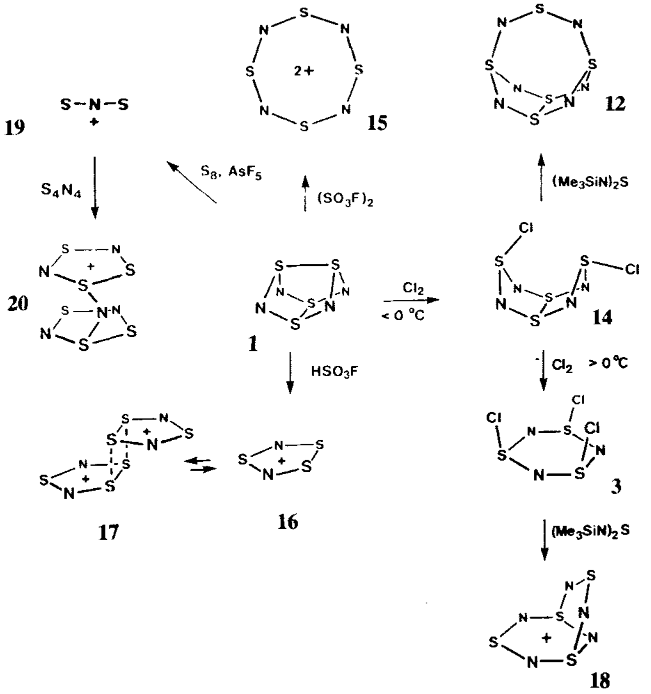
A second binary compound, tetrasulfur dinitride (S_4N_2, **4**), was also isolated before the end of the last century (32). Its correct elemental composition, however, was not established until 1925 (33), and its molecular formula not confirmed until 1951 (34). Early estimates suggested the formula N_2S_5 (32), an observation that attests to the tendency of the molecule to disproportionate above its melting point of 22.5°C (hence, the high sulfur content). The six-membered ring structure with a half-chair conformation was finally confirmed in 1981 (35, 36). Most early preparative methods involved a thermal decomposition, for example, of S_4N_4 in the presence of sulfur and/or carbon disulfide (37, 38). More recently the use of simple metathetical reactions, for example, between $Ni(S_2N_2H)_2$ and S_2Cl_2 has been explored (39). A simple procedure involving the reaction of aqueous ammonia with sulfur monochloride has also been developed (40); although the yield is low (<2%), the method provides a convenient preparation of small quantities (<0.5 g) starting from commercially available materials (35b). The solid state polymerization of S_4N_2 to $(SN)_x$ (**5**) has recently been reported (36); this process is presumably initiated by trace amounts of (radical) impurities since, when recrystallized from diethyl ether, solid S_4N_2 is indefinitely stable below its melting point (35b).

Disulfur dinitride (**6**) (Scheme II) was first generated (inadvertently) by Burt in 1910 (41) during an attempt to remove sulfur impurities from S_4N_4 by passing a vaporous mixture of the two over finely divided silver. At the time he noted the formation of a *blue film* [later characterized as $(SN)_x$ polymer]. This reaction has been studied extensively since then, and now constitutes the most widely used method of preparing high grade S_2N_2 [and hence $(SN)_x$ polymer] (42). Little is known of the role of the silver in this process, although the intermediacy of silver sulfide has been implicated (43). Glass wool has also been used to effect the cracking process (43). The experimental procedure in current use is based largely on that devised by Becke-Goehring (44), although minor modifications, largely involving variations in the cracking temperature and purification of the S_2N_2, have been suggested by many groups (42, 45–48). Other methods have been developed for the production of S_2N_2, involving the thermal decomposition of S_4N_3Cl (**7**) (49) and $Ph_3AsN{-}S_3N_3$ (**8**) (50), but neither of these offers a significant improvement over the traditional approach. An appealing and potentially important route involves the thermal decomposition of the adduct $S_2N_2{\cdot}2AlCl_3$ (51), which is itself easily prepared from S_4N_4 and $AlCl_3$ (52). In this connection the role of Lewis acids (perhaps zeolites) as catalysts for the cracking of S_4N_4 deserves further attention.

S_2N_2 is a colorless crystalline solid at room temperature which, like S_4N_4, is susceptible to detonation from thermal or mechanical shock. It is indefinitely stable in solution in organic media, but rapidly dimerizes to S_4N_4 in the presence of trace amounts of nucleophiles or reducing agents (see Section IV.D.2). In the solid state S_2N_2 mutates slowly (over several weeks at 0°C) into the $(SN)_x$ polymer **5** (Scheme II) (53). The conventional explanation of the reaction involves a topochemical change [crystals of S_2N_2 and $(SN)_x$ both belong to the space group $P2_1/c$] (47, 54, 55) in which the *a* axis of the dimer converts into the *b* axis of the polymer, chain extension occurring parallel to this axis. ESR studies implicate a radical process, but recent *ab initio* molecular orbital (MO) and configuration interaction (CI) studies suggest that the conversion involves a cascade effect initiated by only a few diradical centers (56). Consistently the rate of polymerization *decreases* with increasing purity of the starting material (57). It is interesting to consider whether initiation actually requires a radical source, as appears to be the case for S_4N_2 (35b, 36).

In addition to the routes involving the intermediacy of S_2N_2, $(SN)_x$ can be made directly by a variety of chemical methods. It is generated in high yield in the reactions of $S_3N_3Cl_3$ (**3**) with trimethylsilyl azide (58) and trimethylsilyl bromide (59), by the electrochemical reduction of $S_5N_5^+$ (**9**) salts (60, 61), and by radio frequency discharge through S_4N_4 vapors in a helium plasma (62). The physical properties of the polymer have been reviewed elsewhere (42).

The simplest binary compound, thiazyl NS· itself, can be generated by electrical discharge in gaseous mixtures (19), most notably of sulfur and nitrogen (63). It is also produced, to varying degrees, during the cracking of S_4N_4. As expected, it is extremely reactive, and rapidly converts into



Scheme III

the polymer upon condensation. The polymer itself has long been known to vaporize at reduced pressures to give a gas phase species, which upon condensation reforms the polymer as epitaxial films (64). The nature of the vapor phase intermediate has been the subject of much discussion (64–68). An open chain $(SN)_4$ structure has been suggested, but a recent photoelectron and mass spectrometric study coupled with extensive *ab initio* MO and CI calculations has provided compelling evidence supporting the formulation of this species as the cyclic $S_3N_3\cdot$ radical **10** (69). Consistently the IR spectrum of this material (in an argon matrix) (70) bears a striking resemblance to that of the cyclic $S_3N_3^-$ anion **11** (Scheme IV) (71).

The largest neutral binary compound, the basket-shaped molecule pentasulfur hexanitride (S_5N_6, **12**), was first isolated in 1978 from the reaction of $S_4N_5^-$ (**13**) with bromine (72). It is more conveniently reached by the coupling of $S_4N_4Cl_2$ (**14**) with *bis*(trimethylsilyl)sulfur diimide $Me_3SiNSNSiMe_3$ (Scheme III), or by the reaction of $S_3N_3Cl_3$ with $(Me_3Sn)_3N$ (73). The compound is extremely shock sensitive and, in solution, decomposes rapidly above room temperature to S_4N_4 (72).

2. *Binary Cations*

The longest-known binary sulfur–nitrogen cation is the $S_4N_3^+$ species **7** (Scheme I). It can be made by several routes; it is an intermediate in the ammonolysis of sulfur chlorides (74), the standard synthesis of S_4N_4, but is most conveniently prepared as its chloride salt by the action of anhydrous HCl or sulfur monochloride on S_4N_4 (75) or $S_3N_2Cl_2$ (26). A wide range of salts of the type S_4N_3X have now been prepared and structurally characterized (76). In all these the bond lengths and angles within the cyclic seven-membered $S_4N_3^+$ cation show little variation from one structure to another.

The 10-membered $S_5N_5^+$ cation **9** is best produced by the insertion of the SN^+ cation, generated *in situ* from $S_3N_3Cl_3$ with $FeCl_3$, $AlCl_3$, or $SbCl_5$ in SO_2Cl_2 (77, 78), or used directly as SN^+ AsF_6^- (79) into the S_4N_4 ring. Two structural variations have been reported, one with a heart-shaped appearance (80, 81) and the other a more azulenelike ring (60b, 81, 82). The validity of the former was once questioned; it was suggested to be an artifact arising from the superposition of two disordered azulene-shaped rings (10). Theoretical (EHMO and MNDO) calculations, however, have shown little energetic difference between the two forms (60b, 83b–d), indicating that both modifications are viable, the choice between them being determined by the lattice environment.

Treatment of S_4N_4 with strong oxidants [SbF_5, AsF_5, $SbCl_5$, $(FSO_3)_2$] provides salts of the eight-membered $S_4N_4^{2+}$ dication **15** (Scheme III) (84, 85). Several of these have been structurally characterized; all are essentially planar, although in some deviations from full D_{4h} have been noted (84). Another cation sometimes produced in strongly acidic media is the radical species $S_3N_2^{\cdot +}$ (**16**) (Scheme III). It has been observed by ESR spectroscopy ($g = 2.01$, $a_N = 0.315$ mT) in solutions of S_4N_4 with AsF_5, $(CF_3CO_2)_2O$, and $AlCl_3$ (86) and has been characterized structurally as its AsF_6 salt (87). Other salts of this cation have been shown to contain the dimeric $(S_3N_2)_2^{2+}$ cation **17** (88) (see Section III.C.2). A structurally analogous dimeric selenium–sulfur–nitrogen cation $(SN_2Se_2)_2^{2+}$, prepared by the oxidation of S_4N_4 with Se_4^{2+} salts (89) or from $Me_3SiNSNSiMe_3$ and $SeCl_4$ (90), is also known.

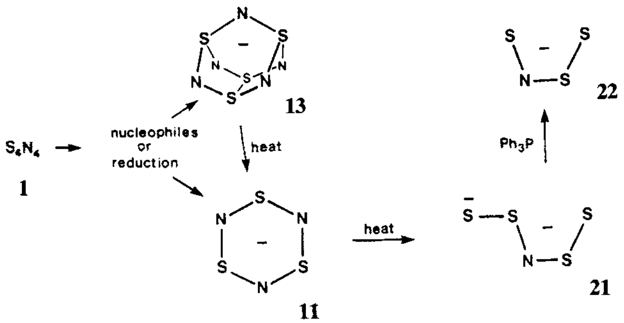
The bicyclic $S_4N_5^+$ cation **18** can be generated by the careful oxidation of the corresponding anion (72), but it is more easily prepared by the bridging of $S_3N_3Cl_3$ with $Me_3SiNSNSiMe_3$ (Scheme III) (91). The structure of S_4N_5Cl consists of a polymeric array of cations bridged by chloride ions (91), but in the AsF_6^- salt no ion pairing is observed (92). Replacement of chlorine by fluorine (93) or imine groups (73b, 94) produces discrete covalent structures.

Salts of the two acyclic cations NS^+ (95) and SNS^+ (**19**) (96, 97) have also been structurally characterized. The former can be prepared by the action of Lewis acids (e.g., AsF_5) on $S_3N_3F_3$ (79, 98, 82d), while the latter is obtained by mixing stoichiometric amounts of sulfur, S_4N_4, and AsF_5 in liquid sulfur dioxide with a trace of bromine (99). The linear SNS^+ cation has been used effectively in the synthesis of a variety of heterocyclic species (see Section III.A.3). Thus the reaction of S_4N_4 yields the unusual bridged cation $(S_3N_2)N(S_3N_2)^+$ (**20**) (Scheme III) (100a), while addition of S_2N^+ AsF_6^- to NSF affords $S_3N_2F^+$ AsF_6^- (cf. **2**) (100b).

3. Binary Anions

No binary sulfur–nitrogen anions were known prior to 1975. The bicyclic $S_4N_5^-$ anion **13** (101, 102) was first prepared from the methanolysis of $Me_3SiNSNSiMe_3$ (103), but was later found to be one of the two ubiquitous products obtained, in varying relative proportions, during the nucleophilic degradation of S_4N_4 with sulfide, cyanide, and azide ions (Scheme IV) (104, 105). It is also formed when S_4N_4 is dissolved in liquid ammonia (106). The other anion produced in these reactions is the $S_3N_3^-$ species **11** (71).

Both of these anions are thermally unstable and, as their alkali metal salts, are easily detonated. They can be conveniently handled in the solid state using large counterions, for example, Ph_4As^+ or $(Ph_3P)_2N^+$ (107). The thermal decomposition of $S_4N_5^-$ proceeds through $S_3N_3^-$ to the deep blue (λ_{max} = 582 nm) acyclic S_4N^- ion **21** (108, 109). This latter ion is also produced in the reaction of elemental sulfur with azide ion, and by the thermal decomposition of the heptasulfur imide anion S_7N^- (110). Reduction of S_4N^- with triphenylphosphine produces the S_3N^- ion (111, 112). On the basis of IR and Raman data obtained from $(Ph_3P)_2N^+$ S_3N^-, an open-chain (rather than cyclic) structure **22** has been proposed for this species, but no definitive X-ray evidence is available.



Scheme IV

B. Elementary Chemistry

The previous section provided a summary of the known binary compounds of sulfur and nitrogen, and illustrated some of the methods used to prepare and interconvert them. We turn our attention now to the fundamental chemical properties of these systems, and begin by recognizing the fact that both sulfur and nitrogen are electronegative elements; their Pauling electronegativities are 2.4 and 3.1, respectively (113). All binary, and most nonbinary, compounds containing these elements will perforce exhibit physical and chemical properties which reflect the high effective nuclear field generated by these atoms. Indeed the similarity of the ionization potential (IP = 9.36 eV) (114) and electron affinity (EA_{calc} = 2.907 eV) (115) of S_4N_4 to those of molecular iodine I_2 (IP = 9.34 eV, EA = 2.48 eV) (116, 117) suggest that sulfur nitrides should behave as pseudohalogens. Within this context the term *electron rich*, which is often used to describe sulfur nitride derivatives (8, 14, 15, 17), is potentially misleading. While the expression is certainly of relevance in describing their structural features (see Section II.C), in the same sense as boron hydride clusters are called *electron deficient*, it should not be equated with an enhanced susceptibility to oxidation.

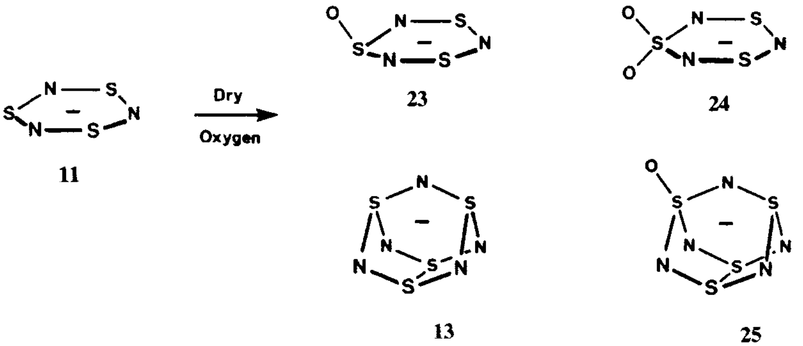
1. *Redox Reactions*

In accord with these remarks, neutral binary sulfur nitrides are not easily oxidized. The dication $S_4N_4^{2+}$ is only produced under extremely acidic, oxidizing conditions [AsF_5/SO_2, $(FSO_3)_2/HSO_3F$] (84, 85). Similarly, while chlorine (118), fluorine (119), silver difluoride (118c), and *bis*(trifluoromethyl)nitroxide (120) all oxidize S_4N_4 to the corresponding disubstituted products $S_4N_4X_2$ [X = Cl, F, $ON(CF_3)_2$] (see Section IV.A.2), milder reagents, for example, organic peroxides and iodine, do not affect it. Indeed iodide ion serves as a useful reducing agent for converting binary cations, for example, $S_4N_3^+$, to S_4N_4 (26). Exhaustive oxidation of S_4N_4 with $ON(CF_3)_2$ (121) and $(CF_3)_3C(O)Cl$ (122) affords the corresponding $S_4N_4X_4$ derivatives [X = $ON(CF_3)_2$, $O(CF_3)_3$], while with excess AgF_2 both $S_4N_4F_4$ (123, 124) and $S_3N_3F_3$ (123, 125) are produced. The tetrachloro derivative $S_4N_4Cl_4$ has never been observed; prolonged treatment of S_4N_4 with chlorine yields only $S_3N_3Cl_3$ (27) (Scheme III).

Oxidation of S_4N_4 with liquid bromine and ICl yields S_4N_3X (X = Br_3^-, ICl_2^-) (76f), while bromination in carbon disulfide leads to incorporation of the solvent and formation of the dithiadiazolium salt $BrS–CN_2S_2^+Br_3^-$ (126) (see Section III.A.3). In the solid state S_4N_4 reacts with bromine and ICl vapors to produce highly conducting doped $(SN)_x$

polymers (127). Crystallographic evidence for a radical cation has been claimed (128a), but the results must be viewed with caution; the X-ray structure of the putative $S_4N_4^{\cdot+}$ cation bears a striking resemblance to that of $S_4N_4H^+$ $FeCl_4^-$ (128b). γ-Irradiation of S_4N_4 in the solid state produces a broad unresolved ESR signal that has been attributed to $S_4N_4^{\cdot+}$ (128c).

Predictably the binary anions are more easily oxidized. Attempts to generate the $S_3N_3\cdot$ radical in solution by chemical (129) or electrochemical (130) oxidation of $S_3N_3^-$ have been unsuccessful; the eventual product of such reactions is S_4N_4. Although radicals can be generated, their ESR spectra indicate the degradation of the six-membered ring to, *inter alia,* the $NSN^{\cdot-}$ radical anion (130b). The reaction of molecular oxygen with $S_3N_3^-$ has been monitored by ^{15}N NMR spectroscopy (131). The monocyclic oxyanion $S_3N_3O^-$ (**23**) is produced first (Eq. 1), but with increasing exposure periods the dioxyanion $S_3N_3O_2^-$ (**24**) and the two cage anions $S_4N_5^-$ (**13**) and $S_4N_5O^-$ (**25**) are also formed. [The latter is usually prepared from the reaction of thionyl chloride and liquid ammonia (132).] Attempts to perform a two-electron oxidation of $S_3N_3^-$ to the corresponding cation have also been unsuccessful. Although the early literature abounds with reports of saltlike materials of formula $S_3N_3^+X^-$ (133), and in spite of the fact that the $S_3N_3^+$ cation appears as a major fragment in the mass spectral fragmentation patterns of many sulfur nitride derivatives, no salt of the type $S_3N_3^+X^-$ has ever been definitively characterized. Electrochemical oxidation of $S_4N_5^-$ (**15**) produces S_5N_6 (**12**) (130a).



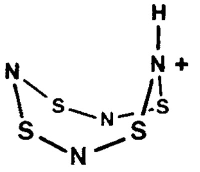
(1)

Consistently with its high electron affinity, S_4N_4 is very susceptible to both chemical (105) and electrochemical (0.93 V vs. Ag/0.1*M* $AgClO_4$) reduction (129a, 134). The first electrochemical reduction product, the $S_4N_4^{\cdot-}$ radical anion, is stable below −30°C; its nine-line ESR spectrum (a_N = 0.12 mT) is consistent with complete delocalization of spin density over four nitrogen atoms (135). At ambient temperatures the radical anion degrades rapidly to $S_3N_3^-$. Polarographic studies have identified two subsequent reduction steps (a) $S_4N_4^{\cdot -} + e^- \longrightarrow S_4N_4^{2-}$ and (b) $S_3N_3^- + 2e^- \longrightarrow S_3N_3^{3-}$ (130a). Exhaustive electrolysis at −2.8 V results in the transfer of eight electrons and the formation of SN_2^{2-}. If the reduction is performed in acetic acid, the tetraimide $S_4N_4H_4$ can be isolated. This conversion can also be effected by stannous chloride in methanol (136). Electrochemical data pertaining to the reduction of a variety of oxyanions [including $S_3N_3O^-$ (**23**) and $S_3N_3O_2^-$ (**24**)] has been reported; in all cases electron transfer is followed rapidly by structural degradation (137).

The anion $S_4N_5^-$ (**13**) can be reduced to a radical dianion $S_4N_5^{\cdot 2-}$ at −40°C (138). Its ESR spectrum, which exhibits a hyperfine pattern of 3 × 9 lines (a_N = 0.175 and 0.05 mT), indicates that the cagelike structure of the $S_4N_5^-$ unit is retained, with the unpaired spin density heavily localized on the four equivalent nitrogen atoms.

2. *Base Properties and Coordination Chemistry*

S_4N_4 is a weak base; its gas phase proton affinity (204 kcal mol^{-1}) (139a) is similar to that of ammonia (205 kcal mol^{-1}) (139b) but, unlike ammonia, it cannot be protonated in aqueous media. In nonaqueous media and in the presence of a nonnucleophilic anion, the monoprotonated cation $S_4N_4H^+$ is stable in solution and in the solid state; thus the reaction of $Et_2O{\cdot}HBF_4$ with S_4N_4 in methylene chloride affords $S_4N_4H^+ BF_4^-$ as bright red crystals (140). The boatlike structure **26**, which is also observed in its $[SnCl_5{\cdot}H_2O]^-$ (141) and $FeCl_4^-$ (128b) salts, is in marked contrast to the shape of the neutral compound (see Section II.C.1). Many Lewis acid adducts of the type $S_4N_4{\cdot}L$ are also known, and several of these (L = BF_3,



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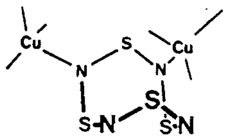

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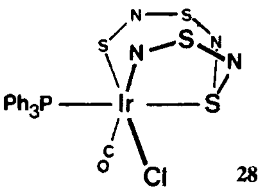
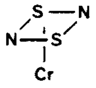


28

$SbCl_5$, SO_3, $FeCl_3$, FSO_2NCO, AsF_5, $TaCl_5$) (142) have been structurally characterized; all have essentially the same boatlike appearance of the $S_4N_4H^+$ cation. There are a few complexes in which S_4N_4 serves as a bidentate ligand, for example, in $S_4N_4 \cdot CuBr$ (**27**) (143); interestingly the cage structure of S_4N_4 remains intact in these cases. Sulfur coordination is rare, indeed the only known example is in the adduct **28** between S_4N_4 and Vaska's compound (144).

Disulfur dinitride forms adducts of the type $S_2N_2 \cdot 2L$ [L = $SbCl_5$, $AlCl_3$, $AlBr_3$, $CuCl_2$, $MoCl_4(NSCl)$] (51, 145, 146), and $S_2N_2 \cdot L$ {L = BF_3, $SbCl_5$, $SnCl_4$, $BeCl_2$, VCl_4, $[(Ph_3P)_2(CO)_2RuCl]^+$, $TiCl_4$} (145, 147) to both nonmetal and metal centered Lewis acids; coordination always occurs through nitrogen. Infusible and uncharacterized polymeric materials of composition $S_2N_2 \cdot SnX_2$ (X = Cl, Br, NMe_2, OMe) are obtained from S_4N_4 and tin (II) derivatives (148). The possibility that S_2N_2 could act as a six-electron η^4-ligand, for example, as in **29**, which is isolobal with **30**, has been considered theoretically (149), but there are no known examples of this mode of coordination. Although the isolobal analogy between **29** and **30** is appealing, the strong oxidizing power of S_2N_2 would more than likely lead to complete charge transfer from metal to ligand, with subsequent cleavage of the S_2N_2 ring (i.e., oxidative addition). Metallocycles of the type MS_2N_2 are numerous (see Section III.B.3).



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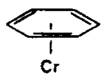

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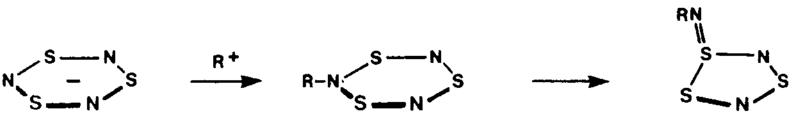
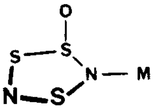
The anionic species $S_3N_3^-$ can be protonated at nitrogen by $Et_2O \cdot HBF_4$ (150, 141b), and acylated by $CF_3C(O)Cl$ (104), with concomitant collapse of the six-membered ring **31** to a five-membered heterocyclic structure of the type $S_3N_2(NR)$ (**32**) (Eq. 2). A wide range of other compounds based on **32** have been prepared by the action of acid anhydrides on S_4N_4 (151). The reasons for the general instability of **31** with respect to **32** are discussed in Section II.C.1.



(2)

11 **31** **32**

In the case of cyclic sulfur–nitrogen oxides, coördination can occur through either nitrogen or oxygen. The coordination properties of OS_3N_2 have been studied in depth. In most cases it binds through oxygen (to AsF_5, SbF_5, $SnCl_4$, $TiCl_4$) (152), for example, **33**, but there is one example of coordination through nitrogen, in $[Ag(S_3N_2O)_6]^+$ $[AsF_6]^-$ (**34**) (153). Coordination of the related heterocycle OCS_2N_2 is through oxygen in both $[Zn(OCS_2N_2)_6]^{2+}$ $2[AsF_6]^-$, and $S_2N_2CO{\cdot}AsF_5$ (154). The $S_3N_3O_2^-$ anion and the eight-membered heterocycle $S_4N_4O_2$ both coordinate through nitrogen, for example, in $Me_3SnS_3N_3O_2$ and $Me_3SiS_3N_3O_2$ (**35**) (155) and $[(S_4N_4O_2)_4Ag]^+$ $[AsF_6]^-$ (**36**) (156). In both cases coordination is to the nitrogen site adjacent to the sulfur(VI) center. Preferential binding at this site may be related to simple charge dispersive effects, that is, negative charge will always accumulate at the ends of the formally conjugated sequence, and these nitrogens will be expected to exhibit the strongest base properties.



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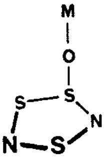

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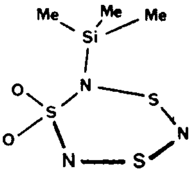

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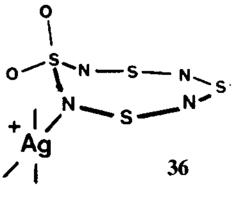

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C. Electronic Structures

Interest in the electronic structures of binary sulfur nitrides emerged in the 1960s following the structural characterization of the cagelike S_4N_4 molecule (157, 158) and the planar $S_4N_3^+$ cation (76a, 76b). An additional

TABLE I
Theoretical Studies of Binary Sulfur Nitrides

Compound	Method
$SN\cdot$	X_α (159), *ab initio* with STO-3G (160), extended bases (114, 161, 162), and UHF (163, 164)
NSN	HFS (165)
NNS	*Ab initio* with extended bases (166)
S_2N_2	CNDO-2 (167, 168) CNDO-S (169), INDO (triplet) (170), INDO/S-CI (171), X_α (159), Green's functions (172, 173), *ab initio* with STO-3G (160, 168, 174), extended bases (114, 162, 175, 176), triplet state (56), and CI (162, 177)
$S_3N_3^{\cdot}$	*Ab initio* with extended bases (179) and CI (69)
S_4N_2	EHMO (178), CNDO/2 (167), MNDO (35b), HFS (35b), *ab initio* with extended bases (179) and CI (180)
S_4N_4	EHMO (181, 182), CNDO/2 (183), CNDO-BW (184), CNDO-S (169), INDO-type ASMO (115), INDO-S/CI (171), X_α (159), HFS (91), *ab initio* STO-3G (185) and extended bases (114, 175, 176) and CI (186).
S_5N_6	HFS (187a) and *ab initio* with extended bases and CI (187b)
SN^+	*Ab initio* with extended bases (163)
SNS^+	CNDO/2 (188)
$S_3N_2^{\cdot +}$	MNDO (189) and *ab initio* with STO-3G basis (176)
$S_4N_3^+$	HFS (190)
$S_4N_4^{2+}$	EHMO (85), CNDO (85) and HFS (191)
$S_4N_5^+$	EHMO and CNDO/2 (192), HFS (91)
$S_5N_5^+$	EHMO (83a) and MNDO (60b, 83b, c)
NSN^{2-}	HFS (193)
SNS^-	HFS (194)
$SNSS^-$	HFS (111)
$SSNSS^-$	MNDO (195) and HFS (108)
$S_3N_3^-$	HFS (71, 196) (166), CNDO/2 (197), X_α (198), *ab initio* with extended bases (199)
$S_4N_5^-$	EHMO (191), CNDO/2 (191) and HFS (91)

and important stimulus was provided by the discovery of the solid state properties of the $(SN)_x$ polymer (5, 6, 42). Following on the heels of these latter reports came a series of theoretical papers addressing the electronic structures of the simple neutral binary compounds $SN\cdot$, S_2N_2, and S_4N_4 (see Table I) and the band structure of the polymer (see Refs. 42 and 200 and papers cited therein). The synthetic breakthroughs of the late 1970s, which afforded the binary anions $S_4N_5^-$, $S_3N_3^-$, S_4N^-, and S_3N^-, the cage molecule S_5N_6, and the cationic species $S_5N_5^+$, $S_4N_5^+$, $S_4N_4^{2+}$, $S_3N_2^{\cdot +}$ (and its dimer), and S_2N^+ added more fuel to the theoretical fires. Each of these species, along with a variety of unstable intermediates (e.g., NSN and $S_3N_3^{\cdot}$) and hypothetical exotica, has since been the subject of one or more self-consistent field (SCF) MO investications (see Table I).

With hindsight the discussions of the electronic structures of binary sulfur–nitrogen compounds can be classified into two groups. The first consists of analyses of single molecules with *ab initio* level methods, the focus being on the determination of total electronic energies, orbital energies and distributions, and excitation energies. In this connection the systematic work of Laidlaw and Trsic (17), of Palmer and co-workers (69, 114, 176, 179, 180) and of Gleiter (10) has been particularly revealing. In the second category we place the more empirical approach pioneered by Banister in the early 1970s (201) and extended more recently by Gimarc and Trinajstić (202, 203). Based largely on simple Hückel-type reasoning the intent has been to relate the stabilities of known and putative structures to their electron count. The viability of the planar $S_3N_3^-$ ion was correctly predicted using such an approach. Both philosophies, the quantitative and the qualitative, have been of value; one has provided the language of chemical bonding, while the other has afforded the necessary numerical details. In recent years the idealogical gap between the empiricists and the *ab initio* practitioners has closed considerably, in large part because of the ready availability of inexpensive, fast, and reasonably well-parameterized MO "packages" such as MNDO, CNDO, and EHMO. Although not without their limitations, especially in the study of molecules containing hypervalent sulfur (204), these *user friendly* codes have allowed experimentalists to explore in a more interactive way the details of electronic structure (ionization energies, electronic affinities, frontier orbital energies, and distributions, potential energy hypersurfaces) of direct chemical and structural significance.

We close this introduction with a caveat. In the preceding and following sections the use of valence bond representations has been avoided wherever possible (205). Connectivity lines in equations and schemes simply reflect the chemist's compulsion to tie nearest neighbor atoms together. They are not intended to imply any particular electron distribution.

1. The Hückel Approximation and Electron-Rich π Systems

While the many SCF level studies of sulfur–nitrogen ring systems have provided a quantitative basis for examining their structure–reactivity relationships, interpretation and even prediction of the results can be facilitated through the use of some of the analytical methods developed for the study of unsaturated hydrocarbons. Accordingly, we begin by comparing the electronic structures of the hypothetical HSNH radical and the ethylene molecule; each of these can be considered as the respective building block from which conjugated –S=N– of –HC=CH– systems can be built. If, for convenience, we describe the σ framework of both molecules in terms of

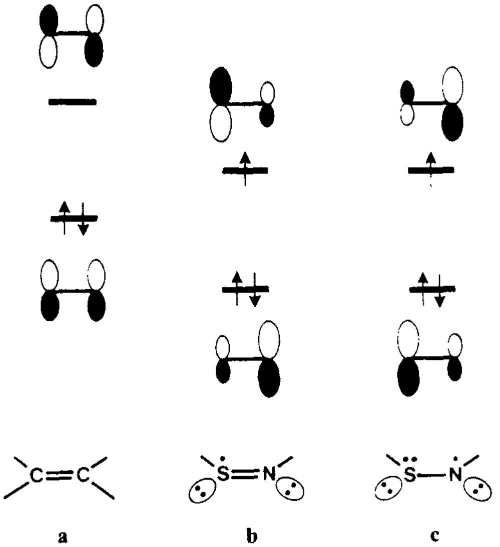


Figure 1. Qualitative diagram illustrating differences in the π-molecular orbital distributions and energies of (*a*) ethylene, (*b*) the hypothetical HSNH radical ($\alpha_S > \alpha_N$, and (*c*) $\alpha_S < \alpha_N$).

sp^2 hybrids at the nonhydrogen atoms, their electronic structures are seen to differ in the number of π electrons that each possesses; sulfur contributes an additional valence π electron (compared to carbon) which, when coupled with the single valence π electron of nitrogen, produces a three-electron π bond. In MO terms the π manifolds of both molecules can be visualized with the aid of the orbital diagram in Fig. 1. The *extra* π electron of HSNH occupies an antibonding level and provides an immediate indication of the relative strength of the π systems of the organic and inorganic units. It also illustrates the origin of the term *electron rich* that pervades the lore of SN chemistry.

An additional feature of the HSNH molecule is the nonequivalence of the orbital electronegativities of nitrogen and sulfur, here expressed in terms of their respective Coulomb parameters α_N and α_S. There has been some discussion (9, 17, 191, 201, 202) as to the relative magnitude of these parameters and, predictably, no real consensus has been reached. If the atomic electronegativities of sulfur and nitrogen are used (as in extended Hückel theory), then $\alpha_S > \alpha_N$. Following the approach of Streitweiser (206), however, the Coulomb parameter should reflect the ionization potential of the second π electron on sulfur, so that its orbital electronegativity should far exceed that of nitrogen (i.e., $\alpha_S < \alpha_N$). The consequences of the two options are compared in Fig. 1*b* and 1*c*. The bonding π orbital is always polarized towards the more electronegative center (be it S or N), while the antibonding π* distribution carries a greater proportion of the less electronegative atomic orbital. In both schemes there is a net transfer of π charge from S to N, but the degree of transfer is greater when $\alpha_S > \alpha_N$.

The question of parameterization can be further developed by comparing the Hückel orbital energy levels of the cyclic molecules, S_2N_2, $S_3N_3^-$, and $S_4N_4^{2+}$. Extending the argument just outlined, these ring systems should possess 6, 10, and 10 π-electron counts, respectively, numbers confirmed by SCF studies on each. The HMO π-orbital energies of the $(SN)_n$ perimeters (n = 2, 3, and 4) are easily obtained as the roots of the secular determinant

$$\begin{vmatrix} \alpha_S - \epsilon & 2\beta \cos(l\pi/n) \\ 2\beta \cos(l\pi/n) & \alpha_N - \epsilon \end{vmatrix} = 0 \qquad (3)$$

where $l = 0, \pm 1, \ldots, n/2$ (n even); $l = 0, \pm 1, \ldots, \pm(n-1)/2$ (n odd). As before, both the orbital energies and distributions are dependent on the magnitude of $(\alpha_S - \alpha_N)$; the polarization effects just noted now apply collectively to the π and π* manifolds (see Fig. 2). The separation and distributions of the two nonbonding orbitals in S_2N_2 and $S_4N_4^{2+}$ provide direct indications of the sense and magnitude of $(\alpha_S - \alpha_N)$.

Having reviewed the HMO patterns for $(SN)_n$ rings it is useful to compare the results with those of SCF MO calculations on the same compounds. In the case of S_2N_2 several *ab initio* theoretical studies (114, 172, 176) and UPS measurements (207) reveal that the orbitals b_{3g} and b_{2g} are nearly degenerate, the actual ordering depending on the level of the calculation. In the planar $S_4N_4^{2+}$ dication the energetic separation between the b_{2u} and b_{1u} levels is more clear cut (near 1 eV) (191), the latter lying higher (as depicted in Fig. 2). One might conclude from this that the simulation of frontier orbital distributions obtained from SCF calculations is best carried out at the Hückel level with the parameterization $\alpha_S > \alpha_N$. In contrast to this conclusion, however, the analysis of the *ab initio* HFS π-orbital distributions of several binary SN rings (17, 191) suggests that π-electron densities are better predicted by using $\alpha_S < \alpha_N$. The real lesson to be learned is that the effective electronegativity difference between sulfur and nitrogen is small, and that Hückel theory should not be used to probe electronic properties that are particularly parameter dependent.

Fortunately, the analysis of π-electron energies is less sensitive to the relative values of α_S and α_N. Moreover, if one assumes that the difference $|\alpha_S - \alpha_N|$ is small, it is possible to make a direct comparison between the

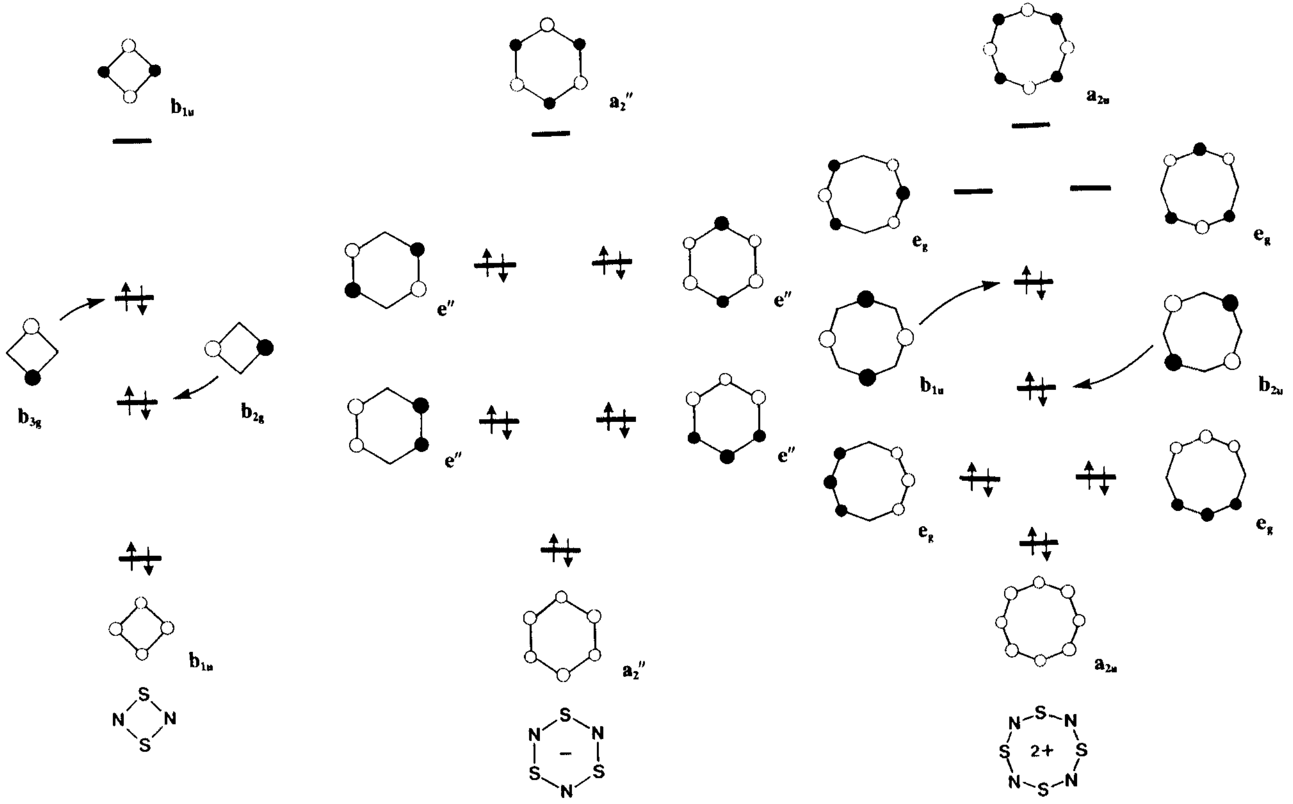


Figure 2. Qualitative π-molecular orbital diagrams (assuming $\alpha_S > \alpha_N$) for S_2N_2, $S_3N_3^-$, and $S_4N_4^{2+}$.

thermodynamic stabilities of electron-rich sulfur–nitrogen rings and those of benzenoid hydrocarbons. The magnitude of the resonance integral β_{SN}, on which such a comparison does depend, can easily be estimated spectroscopically. If, for simplicity, one assumes $\alpha_S \simeq \alpha_N$, then the 360 nm excitation energy found in $S_3N_3^-$ for the π^*(HOMO) – π^*(LUMO) transition (71) can be converted into a β_{SN} of 3.5 eV, a value that is remarkably similar to the spectroscopic β_{CC} values derived for linear polyenes (208).

The structural stability of cyclic π systems can be assessed in a number of ways. For a simple homocyclic π perimeter $(A)_n$ composed of n atoms of type A, the total Hückel π energy of the perimeter ϵ_π is defined by Eq. 4, where β_{st} is the resonance integral and ρ_{st} is the bond order for the interaction between the s^{th} and t^{th} sites.

$$\epsilon_\pi = n\,\alpha_A + 2\beta_{st}\left(\sum \rho_{st}\right) \qquad (4)$$

Hence, bond order can be viewed as a measure of the total π energy per linkage of the perimeter, and a plot of ρ versus n for a series of electron counts provides a simple measure of the skeletal stability of different ring sizes as a function of electron count. In Fig. 3 two such plots are shown, for 6- and 10-electron perimeters, which illustrate some of the important differences between electron-rich, electron-precise, and electron-deficient π systems. For both models maximum bond strength is achieved when the electron count is equal to n. Thus benzene, with n = 6, has a stronger π system than either $C_5H_5^-$ (n = 5) or $C_7H_7^+$ (n = 7). Similarly the stability

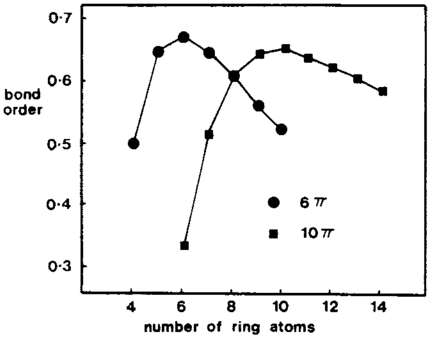


Figure 3. Relationship between π-bond order and number of atoms n in an A_n ring for 6 and 10 π-electron counts.

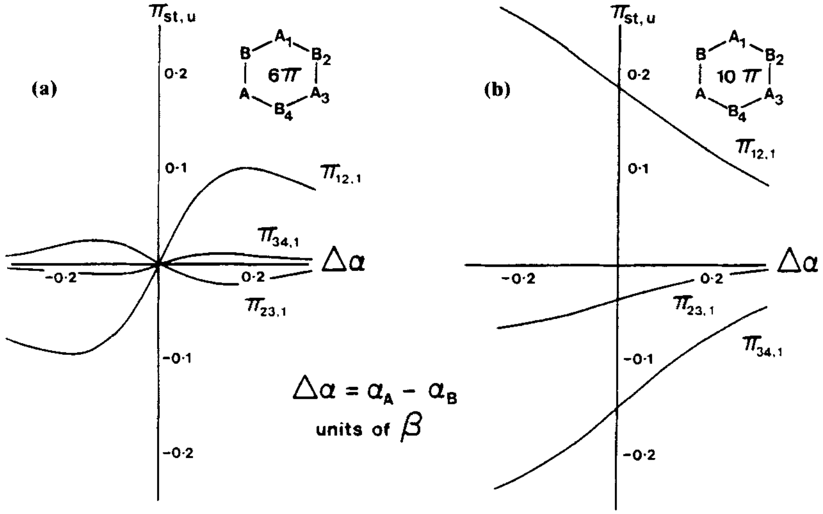


Figure 4. Bond-atom polarizabilities $\pi_{st,u}$ for (*a*) electron-precise (6π), and (*b*) electron-rich (10π) six-membered (AB)$_3$ rings. The horizontal axis defines the electronegativity difference between A and B (when $\Delta\alpha = 0$, A = B).

of the 10-electron perimeters falls off steadily along the series $n = 8$ (e.g., $S_4N_4^{2+}$), $n = 7(S_4N_3^+)$, and $n = 6(S_3N_3^-)$. The (mean) SN bond lengths and *ab initio* HFS overlap populations (71, 190, 191) for these three rings closely follow this trend.

2. *Perturbation and Polarization of Electron-Rich π Systems*

Further insight into the shape of the energy hypersurfaces of electron-rich π systems can be obtained using perturbation theory. To this end we consider the bond-atom polarizabilities $\pi_{st,u}$ (Eq. 5) (209) of a number of model electron-rich and electron-precise rings. The c_{xy} values in Eq. 5 refer to the coefficient of the xth atom in the yth MO. In essence the $\pi_{st,u}$ values define the sensitivity of the π-bond orders (and hence π energy) to small perturbations of the system, that is, they specify by how much the bond order ρ_{st} between atoms s and t will respond to an incremental change in the Coulomb parameter of the uth site?

$$\pi_{st,u} = \left(\frac{\partial \rho_{st}}{\partial \alpha_u}\right) = 2\sum_{j=1}^{m}\sum_{k=m+1}^{n}\frac{c_{uj}c_{uk}(c_{sj}c_{tk} + c_{tj}c_{sk})}{\epsilon_j - \epsilon_k} \qquad (5)$$

The important consequences of such an analysis are summarized in Fig. 4, which illustrates the variations in the three bond-atom polarizabilities of two $(AB)_3$ rings (one 6π, one 10π) as a function of $\Delta\alpha$, the electronegativity difference between the A and B sites. For a six-electron (electron-precise) π system $\pi_{st,u} = 0$ for all linkages when A = B (Figure 4*a*); that is, the bonds in such systems are invariant to small electronic perturbations. The minor structural changes occurring to the benzene nucleus following exocyclic substitution can be easily understood in this way. This insensitivity to substituent effects breaks down when A and B are different as, for example, in inorganic heterocycles like phosphazenes $(R_2PN)_3$, where the orbital electronegativity difference $\Delta\alpha$ between phosphorus and nitrogen is predictably large (i.e., $\alpha_P \gg \alpha_N$). Structural studies of many substituted and protonated phosphazenes thus all show the marked oscillatory behavior in bond lengths predicted in Fig. 4*a* (3, 210).

The electron-rich 10-electron $(AB)_3$ ring system (e.g., $S_3N_3^-$) differs in several ways from the electron-precise model. First, the coefficients for all the bonds are markedly nonzero even when A = B (i.e., $\Delta\alpha = 0$). Second, for small variations in $\Delta\alpha$ in either direction, the value of each coefficient changes in a relatively minor way. It is therefore the *electron richness* of the π system rather than the electronegativity difference between the ring atoms A and B that is the root cause for the observed polarizabilities of electron-rich rings. For chemically significant values of $\Delta\alpha$ bond-atom polarizabilities will remain relatively constant and large; all electron-rich (and electron-deficient) rings will be easily deformed.

These results are central to the understanding of the structural stabilities of binary sulfur–nitrogen rings, and their behavior towards perturbations induced by chemical substitution or lattice forces. The effects are well demonstrated by the dramatic structural changes that accompany the protonation of S_4N_4 (140) and $S_3N_3^-$ (150). In the former case it is not so much the symmetry lowering that causes the S_4N_4 cage to open [in $S_4N_4 \cdot CuCl$ (**27**) the cage remains intact] (143) as it is the localized electronegative perturbation that accompanies protonation that causes a severe polarization of the π system. Antibonding electron density in the π^* HOMO is localized into the bonds to the protonated nitrogen, and the planar SNSNSNS sequence is strengthened at the expense of the S–N(H)–S bonds. Overall the planar structure is stabilized relative to the cage. The weakness in the bonds to the protonated nitrogen can be offset by a slight puckering into a boatlike conformation. The calculated (MNDO) enthalpy and bond-order changes that accompany this structural modification are illustrated in Fig. 5.

Protonation of $S_3N_3^-$ to S_3N_3H effects a similar polarization of π^*-electron density into the S–N(H)–S bonds; the differences in the MNDO π-

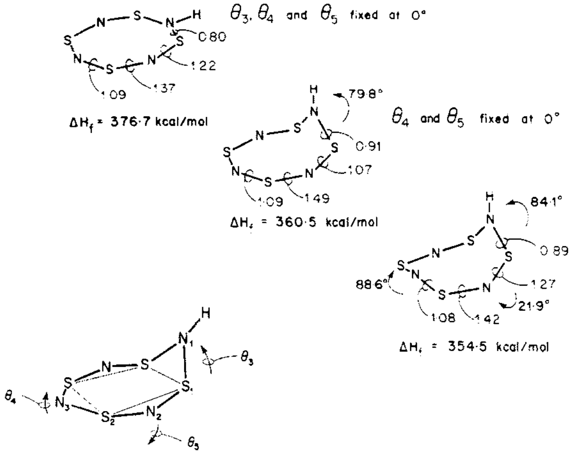


Figure 5. Total bond orders and heat of formation (MNDO) of $S_4N_4H^+$ as a function of the deformation coordinates θ_3, θ_4, and θ_5.

bond orders of $S_3N_3^-$ and S_3N_3H (Fig. 6) follow directly from the polarizability coefficients shown in Fig. 4*b*. In this case the ring π system is weakened to such an extent that the six-membered ring collapses into a five-membered structure with an exocyclic nitrogen (see Eq. 2).

3. *Aromaticity in Sulfur-Nitrogen Rings*

In the early 1970s Banister noted that all the planar sulfur–nitrogen rings known at that time were ($4n + 2$) π systems (201). He proposed that the Hückel ($4n + 2$) rule should therefore have some predictive value, and on that basis suggested, correctly, the viability of the planar 10π-electron $S_3N_3^-$ ion. In the absence of any more quantitative physical data (e.g., heats of formation, resistance to addition, paramagnetic shifts) commonly used in organic chemistry to assess aromatic character, however,

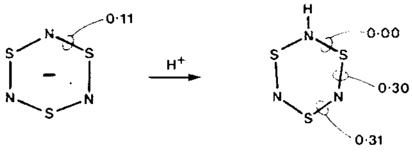


Figure 6. π-Bond order (MNDO) changes accompanying the protonation of the $S_3N_3^-$ anion.

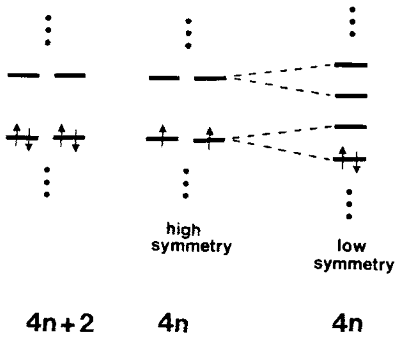


Figure 7. π-Orbital occupations of idealized (4n + 2) and 4n π perimeters.

the relevance of the term aromaticity in these inorganic systems remained largely untested for several years.

The concept of aromaticity stems from the long known dependence of the physical and chemical properties of cyclic polyenes on their electron count, that is, whether they are 4n or (4n + 2) π systems. The electronic origin of the effect lies in the degeneracy of the HMO levels of a cyclic π perimeter of N atoms (and N orbitals) (211). With full N-fold symmetry any 4n-electron count will give rise to an open-shell species (Fig. 7). Lowering of molecular symmetry will break the degeneracy pattern, but many of the properties of the real 4n systems can be viewed in terms of the ideal high symmetry case. Antiaromatic systems are therefore characterized by low reduction potentials, low energy electronic transitions (a small HOMO–LUMO gap) and paramagnetic ring current effects (which originate from the presence of low-lying excited states) (212–214).

To the synthetic chemist, however, the overriding criterion for aromatic or antiaromatic behavior is thermodynamic stability. There have been many attempts to quantify this idea in organic systems, most notably through the use of Hückel resonance energies (RE's) (213, 214). In the approach of Dewar, the RE of a (4n + 2) π-electron N-atom ($N = 4n + 2$) annulene can be defined by comparing its bond energy BE (π-electron energy/linkage) to that (BE$^{\infty}$) of the corresponding infinite polymer (Eq. 6) (214).

$$\mathrm{RE} = N(\mathrm{BE} - \mathrm{BE}^{\infty})\beta \tag{6}$$

Using the definition of BE derived from Eq. 4, this equation can be rewritten as

$$\mathrm{RE} = 2N(\rho_{st} - \rho_{st}^{\infty})\beta \tag{7}$$

For the N-atom N-electron ($N = 4n + 2$) perimeter this expression can be expanded analytically, but when molecules of differing electron–atom ratios are being compared, the problem is more complex. Recently, Gimarc, Jurić, and Trinajstić derived topological resonance energies (TREs) per linkage and per electron for a number of binary SN ring systems (known and hypothetical) by using Sach's theorem to generate the characteristic polynomial of the cyclic and acyclic (infinite) structures (203). The results depend on the reasonable assumption (see previous section) that the HMO resonance parameters for SN and SS linkages are similar to those between carbon atoms in benzenoid hydrocarbons. The additional assumption, that $\alpha_S < \alpha_N$, has little direct impact on the form of the results, which are truly functions of the topology of the system rather than its atomic constitution. They conclude that the TREs per electron of most planar (or nearly so) ($4n + 2$) π-electron binary SN rings are similar to those found in organic rings of the same size (i.e., the same number of constituent atoms). Interestingly a planar (12π electron) S_4N_4 is predicted to be strongly antiaromatic.

Despite this theoretical framework, the restricted number of binary sulfur nitrides available for study makes any comparison with theory difficult. There is, for example, no way of systematically assessing their relative resistance to addition reactions and, with only a limited body of ^{15}N NMR data available (7, 26), the interpretation of ring current effects is at best speculative. The recent preparation and characterization of a number of closely related heterocyclic systems with both $4n$ and ($4n + 2$) π-electron counts has, however, provided some useful opportunities for probing the thermodynamic and spectroscopic manifestations of aromatic–antiaromatic character. These issues are developed in Section IV.C.

4. *Self-Consistent Field (SCF) Calculations*

Thus far the description of the electronic structures of binary sulfur–nitrogen ring systems has been couched in the language of Hückel theory. Within this context the structural stability of these molecules, and their ease of deformation following coordination at nitrogen, can be simply rationalized in terms of their electron-rich configurations. While the interpretation is appealing in a heuristic way, the preoccupation with π-electron count is open to criticism. The approach neglects the effects of electron repulsion, particularly between in-plane nonbonding electrons, that is, the *lone pairs* on sulfur and nitrogen. In reality the molecular structures of sulfur nitrides, and their large endothermic heats of formation, depend as much on these latter, less easily anticipated, factors as they do on π-electron energies.

The other illusory aspect of the π-electron-rich terminology is that it ignores the high effective nuclear field experienced by the valence electrons in sulfur nitrides. In keeping with the earlier remarks on the redox and donor–acceptor properties of sulfur nitrides (Section II.B), the results of many theoretical and photoelectron studies indicate that all valence electrons are tightly bound.

The MO manifolds of S_4N_4, S_2N_2, and S_4N_2 have been studied in depth with different levels of theory. Although the *sp*-orbital basis set approach described above provides an adequate description of the principal features of their electronic structures, the inclusion of *d*-orbitals and/or polarization functions enhances overlap populations and more adequately allows for the prediction of bond lengths. Although the orbital sequencing near the top of the occupied stack differs from one calculation to another the chemically important features are the same. In the planar molecules the π manifold is buried in an array of in-plane lone-pair-type orbitals, that is, SN rings are lone-pair rich as well as π-electron rich. In the case of S_4N_4 the HOMO has been identified spectroscopically as being nitrogen based (215). It should be noted that this orbital ($2a_2$) is *not* the donor orbital of S_4N_4. The major orbital involved in the protonation process is a more energetically low lying, and therefore weakly basic, $4e$ function (Fig. 8). The nature of the transannular S--S interactions in S_4N_4 (2.59) (158) has been of considerable concern. Based on overlap population data the 1,5 interactions are bonding, albeit weakly, while the 1,3 interactions are not. On the other hand the results of a recent gradient analysis of S_4N_4 indicate that the form of the Laplacian of the charge density along the S--S vector more nearly resembles the closed-shell interactions found between nonbonded atoms (177). These issues are explored more thoroughly in Section III.D.1. *Ab initio* studies on the cage molecule S_5N_6 have revealed an extremely low overlap population for the bonds to the bridging NSN (187) unit, thus providing a rationale for the susceptibility of the molecule to

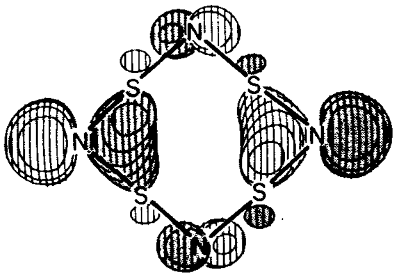


Figure 8. The $4e$ orbital (MNDO) of S_4N_4. It is to this orbital that an incoming proton binds.

thermally degrade to S_4N_4. The NSN fragment that would be released in this thermolysis, and that of $S_4N_5^-$ to $S_3N_3^-$ (Scheme IV), has also been examined theoretically; it is predicted to be less stable in the bent NSN (165) configuration than in the linear NNS (thionitrous oxide) form (166), and has an extremely low calculated (9–15 kcal mol^{-1}) barrier to disproportionation to dinitrogen and sulfur atoms (165).

The SN bonds in the neutral molecules are all polarized towards nitrogen, although the degree of charge transfer $S^{\delta+}—N^{\delta-}$ is strongly dependent on the basis set; inclusion of *d* functions on sulfur has the predictable result of decreasing bond polarity. *Ab initio* charge densities (114) for S_4N_4 (δ = 0.80) and S_2N_2 (δ = 0.69) are similar [the difference being in agreement with experimental core binding energies of sulfur and nitrogen (216)], and much larger than in SN itself (δ = 0.39). In this context a topological charge distribution argument has been developed to account for the observed structures of S_4N_4, β-P_4S_4, and As_4S_4 (realgar). Accordingly, the low coordinate site of a 44-electron A_4B_4 cage with D_{2d} symmetry will always carry the negative charge, and hence will be favored by the more electronegative element (217).

The calculated charge distributions in ionic compounds provide consistent results (17). *Ab initio* HFS studies on the binary cations $S_4N_4^{2+}$, $S_4N_3^+$, $S_4N_5^+$, and $S_5N_5^+$ reveal that the positive charge on the cation is distributed over the sulfur centers, while in the anions $S_4N_5^-$, $S_3N_3^-$, S_4N^-, S_2N^-, and SN_2^- the negative charge resides on nitrogen (17).

An early controversy over the symmetry of the charge distribution in $S_3N_3^-$ was caused by the incorrect use of an old version of CNDO (196). The present consensus is that the charge distribution in $S_3N_3^-$ is symmetric (71, 197–199), although recent studies on the stability of Hartree–Fock solutions for the $S_3N_3^-$ ring indicate the onset of symmetry breaking (into C_{2v}) of the wavefunction when the SN distance is increased (while maintaining D_{3h} symmetry for the nuclear coordinates) beyond 1.96 Å (218). The instability can be induced by both π^*–π^* and σ–σ^* excitations, indeed a combination of the two generates an instability far more readily than either of the two acting separately. Of the two possible π^*–π^* ($2e'' \longrightarrow 2a_2''$) excitations (see Fig. 2); that leading to overall ($\sigma + \pi$) charge localization on nitrogen is energetically preferred. The effect has been suggested as a potential diagnostic tool for anticipating pathways for thermal decompositions (218). Broken symmetry Hartree–Fock wave functions have also been found for $S_4N_4^{2+}$ and S_2N_2 when stretched SN bond lengths are used (219).

The conformational energy hypersurfaces of sulfur nitride rings has been studied by a variety of semiempirical methods. The preference for the planarity of $S_4N_4^{2+}$ has been studied by EHMO (85), CNDO (85), MNDO (220), as well as HFS *ab initio* (191) methods. All save CNDO (85) correctly predict the preference for the planar geometry relative to a C_{2v} or D_{2d} one. The CNDO method (167) also fails to predict the half-chair geometry of S_4N_2, while the MNDO (35b) and *ab initio* methods (with the HONDO gradient procedure) (179) accurately define both the observed conformation and other structural parameters (the latter method very impressively). MNDO has also provided a reasonably accurate prediction of the structure of $S_4N_4H^+$ (140). As mentioned earlier (Section II.A.2) the two conformational (heart and azulenelike) motifs possible for the $S_5N_5^+$ cation have been studied by both EHMO and MNDO; the calculated energy difference between them is small (60b, 83). The conformational characteristics of dithiatetrazocine derivatives, including $S_4N_4^{2+}$ and $S_4N_4Cl_2$, and the unusual structural dichotomy observed in these systems, are discussed in Section III.D.1.

The conformational characteristics of a number of acyclic species, including S_4N^- (195), S_3N^- (221), RNSNR (R = H, alkyl) (221), and OSNSNSO (195) have also been examined theoretically. The *cis* conformation of S_3N^- (Scheme IV) is predicted to be more stable than the *trans*, in agreement with the reported structures of several RS_3N derivatives (50, 112, 222, 223). The energetic preference for the *cis* isomer has been suggested to arise from weak Coulombic interactions between the 1,4 sulfurs. Extensive studies on the three conformational isomers (*cis–cis*, *cis–trans*, *trans–trans*) of simple sulfur diimides show little energetic difference between them (221). Consistently, recent gas phase studies on HNSNH have indicated the coexistence of two (*cis–cis* and *cis–trans*) isomers separated in energy by $\sim 50\ cm^{-1}$ (221d).

Few theoretical studies have been directed towards quantifying the electron acceptor studies of sulfur nitrides; there is only one report of a calculated electron affinity (2.907 eV for S_4N_4) (117). The more qualitative use of virtual orbital energies to assess ease of reduction and/or susceptibility to nucleophilic attack has been explored (see Section IV). In this connection caution should be exercised in comparing molecules with different overall charges. While the effect of ionic charges on LUMO (and HOMO) energies can be partly offset by normalizing on core levels, differences in solvation energies for species with different charges are not insignificant. The correspondence between trends in electrode potentials and trends in orbital energies is therefore only meaningful when comparing systems with the same overall charge (224).

5. *Electronic, MCD, and UV-Photoelectron Spectroscopy*

The ground and excited state electronic structures of sulfur nitrides and their derivatives have been studied by a variety of spectroscopic methods. Herein, we summarize the results of the three techniques, electronic, MCD, and photoelectron spectroscopy, which have made the greatest impact on the interpretation and understanding of electronic structure.

The chemistry of sulfur–nitrogen compounds is nothing if not colorful. Virtually all compounds, be they acyclic, cyclic, or cage structures, exhibit intense visible absorption bands. One of the major thrusts of recent theoretical investigations has been the assignment of these bands to the appropriate electronic excitations which, in planar systems, are nearly always electric dipole allowed π^*–π^* transitions. Extensive work by Laidlaw and Trsic, using the Hartree–Fock–Slater (HFS) technique, has been particularly helpful. The transition state method and also corrected one-electron energy differences have been used to predict excitation energies (17, 225). The calculation of transition moments has also aided in the confirmation of assignments.

An important experimental technique used in the interpretation of electronic spectra has been magnetic circular dichroism (MCD) spectroscopy. The method relies heavily on the perimeter model of Platt, as developed by Michl, for its interpretive basis (226, 227). Accordingly, the basic features of the MCD spectrum can be determined solely from a knowledge of the number of electrons and the number of atoms in the cyclic π system. The first demonstration of the technique involved the confirmation of the assignment of the 360-nm band in the electronic spectrum of $S_3N_3^-$ as a degenerate $2e'' \longrightarrow 2a_2''$ excitation (see Fig. 2). The appearance of the negative A term confirmed the degeneracy of the excited state, a situation that can only occur for $(4n + 2)$ perimeters with either two electrons or two electron holes, as in $S_3N_3^-$ (228). Later work on the $S_3N_3^-$ derivatives, for example, XS_3N_3 ($X = Ph_3PN$, Ph_3AsN, and O^-) (229, 230) illustrated the expected pattern in the signs of the two B states arising from the splitting of the degenerate excited state of the parent compound. The MCD spectrum of the 10π-electron 7-atom $S_4N_3^+$ perimeter revealed the power of the technique in observing bands not resolvable by normal electronic spectroscopy (231). Thus while only two bands are seen in the UV–visible spectrum, four transitions (two formally allowed B_1 and B_2 and two formally forbidden L_1 and L_2) are seen in the MCD spectrum (see Fig. 9). The calculated (HFS) intensities and one-electron transition energies (190) are in close agreement with experiment. In addition to those already cited, MCD spectra for S_2N_2, S_4N_2, and a wide range of $(4n + 2)$ π-electron heterocycles have been reported (230). The correspondence between the observed patterns and those predicted by the simple perimeter approach is impressive.

The other major experimental probe used in the study of the electronic structures of sulfur derivatives is ultraviolet photoelectron spectroscopy (UPS). In general the correlation, via Koopmans' theorem, between experimental ionization potentials and calculated orbital energies in S_2N_2

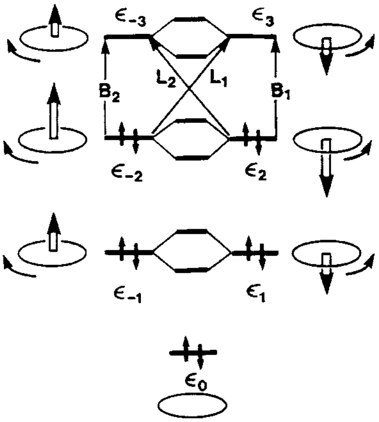


Figure 9. Qualitative MO diagram for a 10π-electron 7-atom perimeter, indicating the four π–π excitations (L_1, L_2, B_1, B_2). Orbital magnetic moments are shown (left and right) by heavy arrows. The splitting of the degeneracy of HOMO and LUMO caused by the nonequivalence of the ring atoms of $S_4N_3^+$ is illustrated in the center.

(207, 114, 172, 176), S_4N_2 (180), and S_4N_4 (114) is good for low-energy cationic states, while for IP's > 12 eV series breakdowns in the one-particle picture are observed. In the case of S_2N_2 and S_4N_2 a large number of shake-up states, involving simultaneous photoexcitation to their low-lying π-type LUMOs, are prominent features.

In addition to its use as an electronic probe, UPS has proven to be particularly valuable in the characterization of transient species, most notably the elusive $S_3N_3^{\cdot}$ radical (see Scheme II) (69). In this case good correlation between calculated and observed IP values could only be obtained by using *ab initio* calculations with a better than double-ζ basis set and including CI. The ground state of the radical is predicted to be $^2A_2$ (9π), while that of the corresponding cation $S_3N_3^+$ is calculated to be $^3A_2$ (8π).

III. HETEROCYCLIC THIAZENES

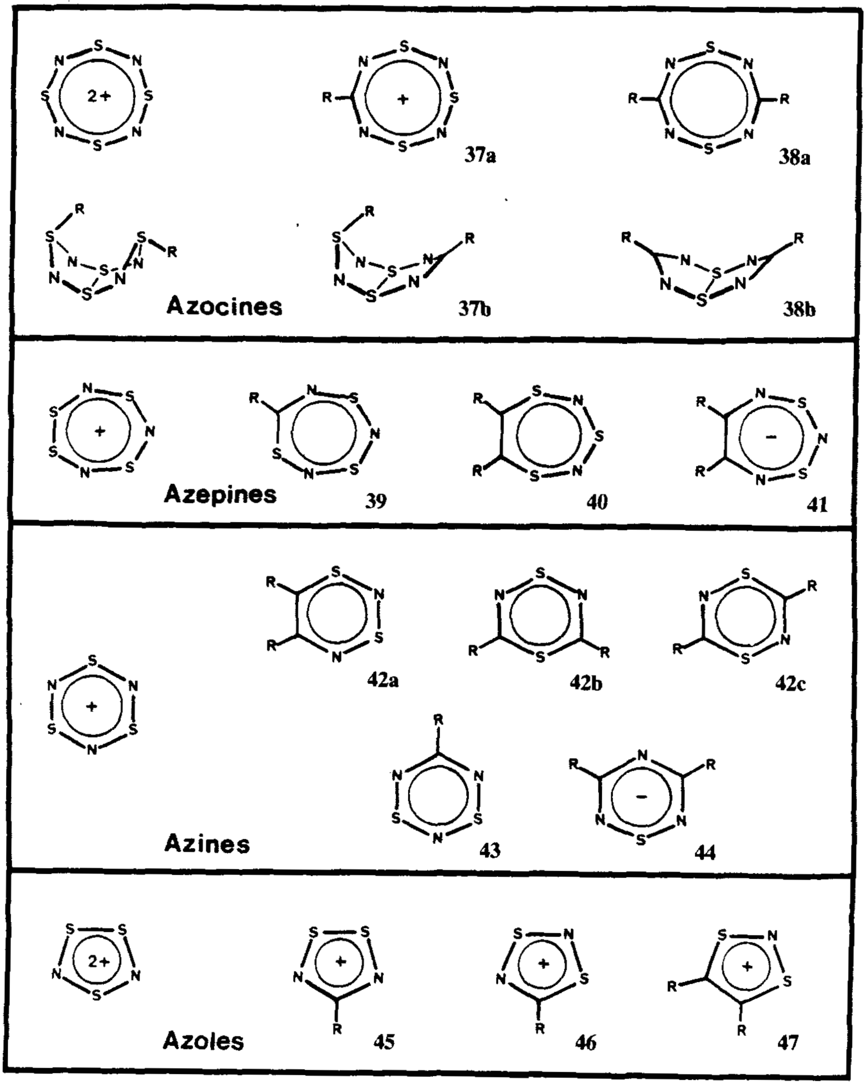
The binary sulfur–nitrogen compounds discussed in the previous section now form a subgroup of a rapidly expanding class of heterocyclic compounds that contain unsaturated –S=N– linkages. Although the classification is artificial it is convenient to divide these heterocyclic rings into two groups, (a) *organic* heterocycles (incorporating carbon), and (b) *in-*

organic heterocycles (incorporating other inorganic elements, e.g., phosphorus). By virtue of their lower sulfur and nitrogen contents, these hybrid systems are generally easier to handle (less prone to detonation and hydrolysis) than the binary systems. Moreover, the introduction of the heterogroup also allows the use of a broader range of spectroscopic methods (e.g., ^{1}H, ^{13}C, and ^{31}P NMR) for structural and chemical analysis. Most importantly the chemistry of these hybrid systems is far more extensive than that of the purely binary derivatives; their study facilitates our understanding of the binary systems and allows the building of conceptual bridges to classical organic heterocyclic chemistry. The potential applications of some of these heterocycles in the design of molecular metals is also providing a major stimulus for exploratory work.

A. Synthetic Routes to Organic Thiazenes

It is useful to begin the discussion of cyclic organothiazenes with an overview of the structural types that have been established. To facilitate this process we show, in Scheme V, a compilation of known heterocycles along with the isoelectronic binary compounds to which they are related. Broadly speaking there are four main classes: (a) 8-atom 10π-electron azocines, (b) 7-atom 10π-electron azepines, (c) 6-atom 8π-electron azines, and (d) 5-atom 6π-electron azolium derivatives. As illustrated in this scheme, the trithiatetrazocines and the 1,5-dithiatetrazocines can exist as either planar eight-membered rings, that is, **37a**, **38a**, or in puckered conformations, that is, **37b**, **38b**. This structural dichotomy is similar to that observed between $S_4N_4^{2+}$ and $S_4N_4Cl_2$, and can be interpreted using the same electronic arguments (see Section III.D.1). The 10π-electron azepine rings **39**, **40**, and **41** can be viewed as offshoots of the $S_4N_3^+$ framework, while the array of antiaromatic 8π-electron diazines and triazines **42**, **43**, and **44** are all formed by isoelectronic modification of the hypothetical $S_3N_3^+$ cation. Finally, 7π-electron azolium salts **45**, **46**, **47** can all be considered as derivatives of the $S_3N_2^{2+}$ cation.

The design and characterization of these mixed inorganic–organic systems has undergone a period of rapid growth since the beginning of this decade. The synthetic methods used to generate them vary considerably; in many cases rational mechanistic arguments can be invoked, but often a seemingly minor modification of an exocyclic substituent can drastically alter the course of a reaction. Rather than discuss the preparation of each compound individually, we shall focus attention on some of the most common synthetic approaches, indicating, where appropriate, any limitations or exceptions.



Scheme V

1. Ring Closure Reactions with Silylated Sulfur Diimides

One of the most important breakthroughs in sulfur–nitrogen chemistry was the synthesis of *bis*(trimethylsilyl)sulfur diimide ($Me_3SiNSNSiMe_3$) [from $SOCl_2$ and $NaN(SiMe_3)_2$] by Scherer and Weis (232), which early on was recognized as a convenient reagent for the incorporation of the NSN unit into cyclic or open-chain systems (233–235). The trimethylstannyl analogue $Me_3SnNSNSnMe_3$ (236) and the recently prepared dipotassium salt $2K^+(NSN)^{2-}$ (237) have also been used to this end, as have monosilylated sulfur diimides $RNSNSiMe_3$ (238) and trimethylsilylsulfinylamine Me_3SiNSO (239). Polymeric materials have been prepared from bifunctional reagents such as $Me_3SiNSNC_6H_4NSNSiMe_3$ (240). A thermally unstable selenodiimine $Me_3SiNSeNSiMe_3$ has recently been generated, and undergoes similar metathetical reactions to $Me_3SiNSNSiMe_3$ (241).

$$RS\text{–}Cl + Me_3SiNSNSiMe_3 \longrightarrow RS\text{–}NSN\text{–}SR + 2Me_3SiCl \quad (8)$$

$$Ph_2CNS\text{–}Cl + Me_3SiNSNSiMe_3 \longrightarrow Ph_2CNS\text{–}NSN\text{–}SNCPh_2 + 2Me_3SiCl \quad (9)$$

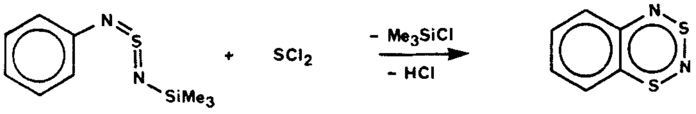
$$(CO)_5MoPPh_2Cl + K_2N_2S \longrightarrow (CO)_5MoPPh_2\text{–}NSN\text{–}PPh_2Mo(CO)_5 + 2KCl \quad (10)$$

$$Me_3SiNSNC_6H_4NSNSiMe_3 + SCl_2 \longrightarrow (C_6H_4NSN\text{–}S\text{–}NSN)_x + 2Me_3SiCl \quad (11)$$

$$Me_3SiNSO + SCl_2 \longrightarrow OSN\text{–}S\text{–}NSO + 2Me_3SiCl \quad (12)$$

$$RNSNSiMe_3 + SCl_2 \longrightarrow RNSN\text{–}S\text{–}NSNR + 2Me_3SiCl \quad (13)$$

Equations 8–13 illustrate the use of these metathetical coupling reagents in the design of open chain and polymeric materials. The formation of α,ω chains of the type RNSNSNSNR via the route shown in Eq. 13 is limited, however, to R = alkyl (238); when R = phenyl, electrophilic attack of the intermediate sulfenyl chloride at the ortho position of the aryl group competes with chain extension, and the benzo-1,3,2,4-dithiadiazine system **48** is produced (Eq. 14) (242).



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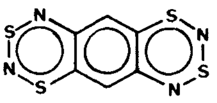

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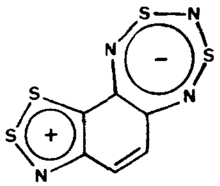

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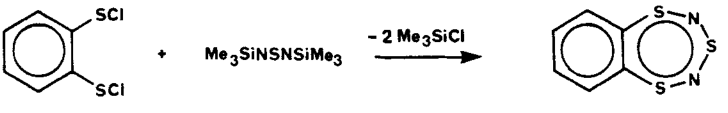
Attempts to generate the tricyclic species **49** via a modification of the reaction shown in Eq. 11 have not afforded the expected product; instead the phenazulenelike structure **50** is obtained (243). Similarly, attempts to effect a ring closure of PhSNSNSiMe$_3$ with SCl$_2$ to produce benzo-1,3,5,2,4-trithiadiazepine (**51**) have been unsuccessful. The compound can, however, be made by a simple coupling reaction between Me$_3$SiNSNSiMe$_3$ and *bis*(chloromercapto)benzene (Eq. 15) (242, 244). The monocyclic trithiadiazepine **40** (R = H) has been formed in an elegant cyclization sequence involving (Me$_3$SiN)$_2$S and chloro-*bis*(chloromercapto)ethane, the product of which spontaneously eliminates HCl to afford the aromatic 10π-electron H$_2$C$_2$N$_2$S$_3$ system (Eq. 16) (244). Cyclization of ClC(O)SCl with Me$_3$SiNSNSiMe$_3$ produces the five-membered ring OCS$_2$N$_2$ **52** (Eq. 17) (245).



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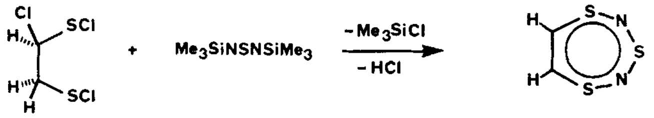

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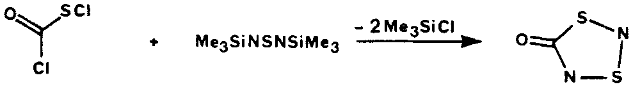


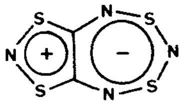
(17)

52

2. *Thiazenes from Alkynes and Tetrasulfur Tetranitride*

Early work on the reaction of diphenylacetylene with S$_4$N$_4$ indicated the formation of a variety of novel heterocycles in addition to the long known 4,5-diphenyl-1,3,2-thiadiazole (246). A claim that the 5,6-diphenyl derivative of 1,2,3,4-dithiadiazine **42a** had been produced was later shown to be in error (247a,b). The compound in question is actually the 1,4,2,6-dithiadiazine **42b**. The corresponding 1,4,2,5-derivative **42c** (R = Ph) has recently been obtained by the action of Et$_3$O$^+$BF$_4^-$ on thiobenzamide *S*-

oxide, followed by treatment with base (248). Also produced in the PhCCPh/S_4N_4 reaction is the unusual bicyclic derivative **53** (247a,b). The reaction of dimethylacetylene dicarboxylate with S_4N_4 leads to a range of products, all in rather low yield, including the carboxylate derivatives of the 1,3,5,2,4,6-trithiatriazepine (**39**) (R = CO_2Me) (247a,b). Other activated acetylenes with S_4N_4 lead to similar results (247c). Thermal decarboxylation of **39** (R = CO_2Me) yields the unsubstituted compound HCS_3N_3 (**39**) (R = H) (249). The use of vinyl phenyl sulfoxide (250a), a known acetylene equivalent, and of *bis*(trimethylsilyl)acetylene (250b) with S_4N_4 leads to incorporation of a –C≡C– unit into the S_4N_4 ring, and formation of the azulenelike **54**. This compound, like the tricyclic material **50** (243), packs in a head to tail fashion in the solid state, suggestive of the dipolar charge distributions depicted.



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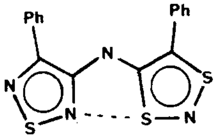
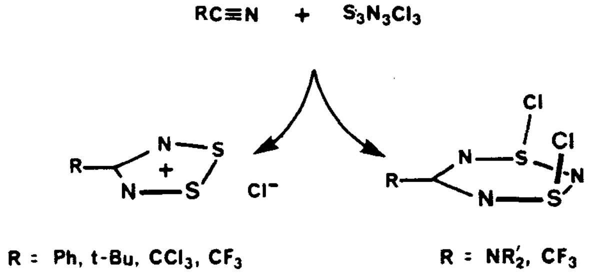


53

3. *Thiazenes from Nitriles and Thiazyl Chlorides*

The reactions of nitriles with thiazyl halides have provided a rich but somewhat unpredictable source of several heterocyclic systems (Eq. 18). Treatment of $S_3N_3Cl_3$ in refluxing RCN (R = Ph, *t*-Bu, CCl_3) leads to the chloride salts of the 1,2,3,5-dithiadiazolium cation **45** (R = Ph, *t*-Bu, CCl_3) in moderate to high yield (251). By contrast the analogous reaction with dialkylcyanamides R'_2NCN (R′ = Me, Et, *i*-Pr) provides a simple and direct method for generating the 5-amino- (R = R'_2N) derivatives of the 1,3-dichloro-1,3,2,4,6-dithiatriazine **55** (252). The 1,3-dichloro-5,7-*bis*(dimethylamino)- derivative of 1,3,2,4,6,8-dithiatetrazocine has also been reported to be formed (under different conditions) when R = NMe_2, but no structural confirmation has been provided (252). Trifluoromethyl cyanide reacts far less specifically; depending on the reaction temperature, the solvent, and the composition of the reaction vessel variable amounts of the 1,2,3,5-dithiadiazolium chloride **45** (R = CF_3), the 1,3-dichlorodithiatriazine **55** (R = CF_3), and the 1,3,5,2,4,6,8-trithiatetrazocinium cation **37a** (R = CF_3) (as its $S_3N_3O_4^-$ salt) are produced (253).



45 55

(18)

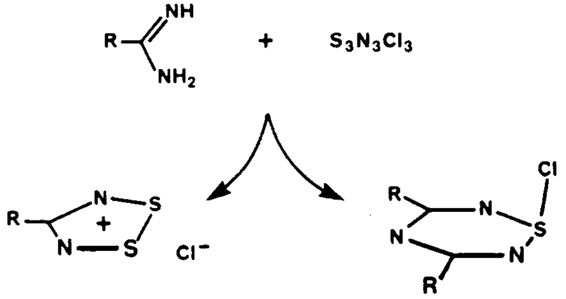
The mechanisms of these reactions have been the subject of some discussion. In a formal sense at least they can be viewed in terms of the addition of S–Cl bonds across the C≡N triple bond; indeed a careful study of the reaction of Me_2NCN with sulfur dichloride and ammonium chloride has led to the isolation of the open-chain salt $[(Me_2NC(Cl)N)_2SCl]^+ [Cl_3]^-$ (254), the structure of which has been interpreted in terms of the double addition of SCl_2 across the unsaturated CN linkage. The potential intermediacy of a dimeric species $S_2N_2Cl_2$ in the reactions involving $S_3N_3Cl_3$ has also been suggested (253a, 254), but no substantive evidence has been presented. In this regard it should be noted that recent theoretical studies on the $S_2N_2Cl_2$ species have shown it to be thermodynamically unstable (in the gas phase) with respect to the trimer (255). The reactions of nitriles RCN (R = Ph, p-ClC_6H_4, Me) other than Me_2NCN with sulfur dichloride and ammonium chloride lead to 1,2,3,5-dithiadiazolium salts **45**. The isomeric 1,3,2,5-dithiadiazolium cation **46** has been prepared (for R = Me) in high yield by the cycloaddition of acetonitrile to the binary salt $S_2N^+ AsF_6^-$ (see Section II.A.2) in liquid sulfur dioxide (Eq. 19) (256). The 5-bromomercapto cation **46** (R = BrS) is obtained, as its tribromide salt, in the reaction of S_4N_4 with bromine in carbon disulfide (126).

46

(19)

4. *Thiazenes from Amidines and Related Compounds*

The reactions of amidines (and their hydrochlorides) with sulfur chlorides and thiazyl chlorides have been used to produce a variety of heterocyclic compounds. Thus the reaction of benzamidine with sulfur dichloride provides a simple source of the chloride salt of the 1,2,3,5-dithiadiazolium cation **45** (R = Ph). This latter salt is also formed in the reaction of benzamidine hydrochloride with $S_3N_3Cl_3$ (Eq. 20) (257). When the free amidine is used instead of its hydrochloride, however, the yield of $PhCN_2S_2^+Cl^-$ is suppressed, and the major tractable product is the 1-chloro-3,5-diphenyl-1,2,4,6-thiatriazine **56** (R = Ph) (258). Compounding the problem the reaction of pivalamidine with $S_3N_3Cl_3$ yields 3-chloro-5-*t*-Bu-1,3,5,2,4,6,8-trithiatetrazocine (**37b**) rather than either of the first two ring systems (259), while dimethylguanidinium hydrochloride and $S_3N_2Cl_2$ (260) provided the first characterized example of a 1,3-dichloro-1,3,2,4,6-dithiatriazine (**55**) (R = NMe_2).

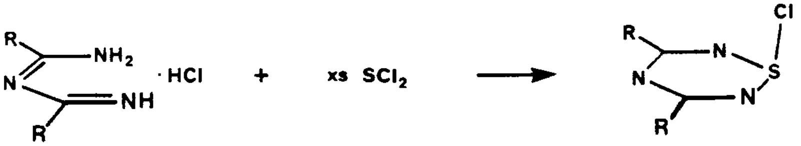


45 **56**

R = Aryl

(20)

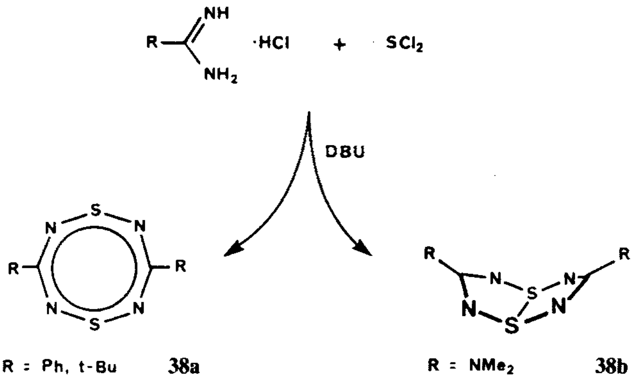
1-chloro-1,2,6,6-thiatriazines (**56**) are more conveniently reached through the reactions of *N*-imidoylamidines with sulfur dichloride (Eq. 21) (261, 262). A similar condensation approach has also been used to generate the selenotriazine derivative $Ph_2C_2N_3SeCl$ (262). The perchlorinated thiatriazine $Cl_3C_2N_3S$ (**56**) (R = Cl) is obtained by the reaction of sodium dicyanoamide with thionyl chloride (263).



56

(21)

Derivatives of the eight-membered 1,5,2,4,6,8-dithiatetrazocine ring system $R_2C_2N_4S_2$ (R = NMe_2, *t*-Bu, Ar) **38** have been obtained through the condensation of amidines with sulfur dichloride in the presence of DBU (Eq. 22) (264, 265). The yield is extremely dependent on the nature of the substituent R at carbon, and is best (~50%) when R = NMe_2. Molecules of this type are known to exist in one of two structural forms, (a) a planar ring **38a** for R = Ph and (b) a butterflylike structure **38b** with a short transannular S--S contact for R = NMe_2 (265). The electronic issues underlying this structural dichotomy are addressed in Section III.C.1.



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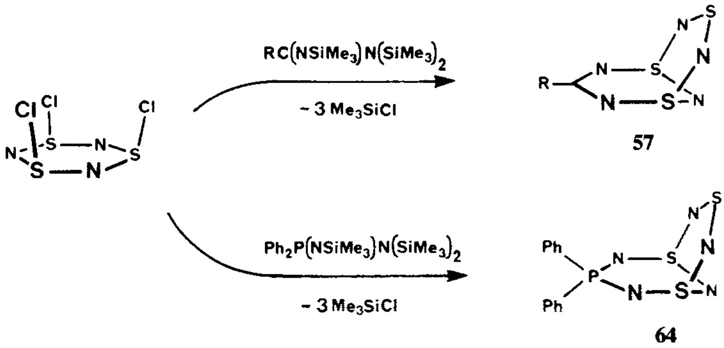
The use of persilylated amidines instead of amidines has proven a major advance in the design of specific, high yield syntheses. For example, the reactions of $RC(NSiMe_3)N(SiMe_3)_2$ (R = Ph, *p*-MeC_6H_4, CF_3) with $S_3N_3Cl_3$ afford the –NSN– bridged 1,3,2,4,6-dithiatriazines RCN_5S_3, (**57**) (Eq. 23a) (266, 267); when R = aryl the NSN bridge can be cleaved oxidatively with chlorine to afford the 1,3-dichloro- derivative **55** (266, 268); however, when R = CF_3 the bicyclic structure is impervious to attack by chlorine. The bicyclic structure of **57** can be reconstructed by treatment of **55** (R = Ph, NMe_2, CF_3) with $Me_3SiNSNSiMe_3$ (266, 269, 270).



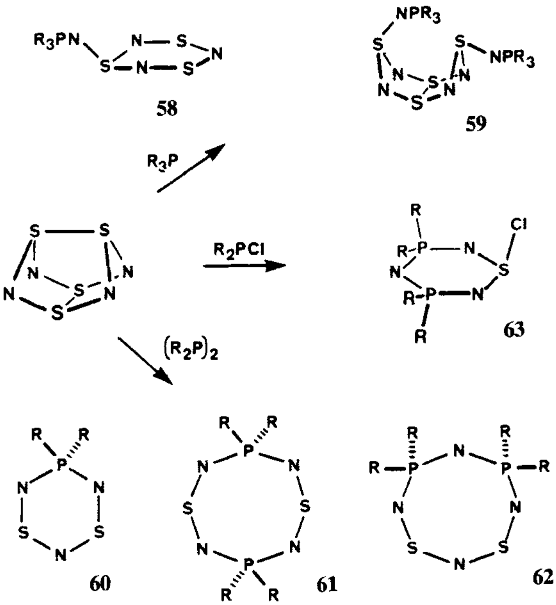
(23a)

(23b)

B. Synthetic Routes to Inorganic Thiazenes

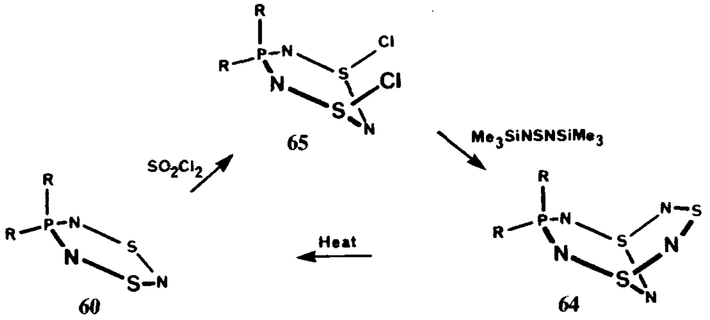
1. *Phosphorus-Containing Rings*

Early studies on the reactions of S_4N_4 with tertiary phosphines and *N*-trimethylsilyl phosphinimines demonstrated that stable thiazene heterocycles possessing exocyclic phosphinimine ligands could be obtained, for example, **58** and **59** (Scheme VI) (271–273). More recent work using diarylphosphines, diphosphines, phosphites, and aminophosphinimines has furnished a wide range of phosphorus(V)-containing heterocycles (274–277). The dominant products are usually phosphadithiatriazines (**60**) (R = Ph, Me, OPh, CF_3) with smaller amounts of the 1,5- and 1,3-diphosphadithiatetrazocines **61** and **62**. The former (R = Ph, Me) can be generated directly by slow thermal decomposition of the corresponding phosphadithiatriazine **60** (without solvent) (278, 279), while the latter is obtained in good yield from the reaction of $Ph_2PN(H)PPh_2$ with S_4N_4 (279). When mixed chlorophenylphosphines $Cl_3Ph_{x-3}P$ are used, the corresponding, six-membered *S*-chlorodiphosphathiatriazines (**63**) are produced in high yield (280).



Scheme VI

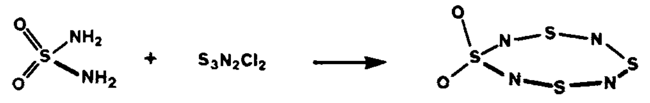
Bicyclic derivatives ($R_2PN_5S_3$, **64**) were first prepared (for R = F) from the reaction of PF_5 with $Me_3SiNSNSiMe_3$ (281). They are more conveniently generated through a modification of the method first used to prepare the corresponding organic structure **57**. Thus the reaction of $Ph_2P(NSiMe_3)N(SiMe_3)_2$ with $S_3N_3Cl_3$ (Eq. 23b) affords **64** (R = Ph) in good yield (282, 283). Thermolysis of these derivatives provides a direct route to the six-membered $R_2PN_3S_2$ compounds (**60**) (Eq. 24) (282–284). Regeneration of the bicyclic structures can be effected by treatment of **60** with SO_2Cl_2 or $PhICl_2$ to yield $R_2PN_3S_2Cl_2$ (**65**), followed by coupling of the latter with $Me_3SiNSNSiMe_3$ (Eq. 24) (284).



(24)

2. *Cyclic Sulfur–Nitrogen Oxides*

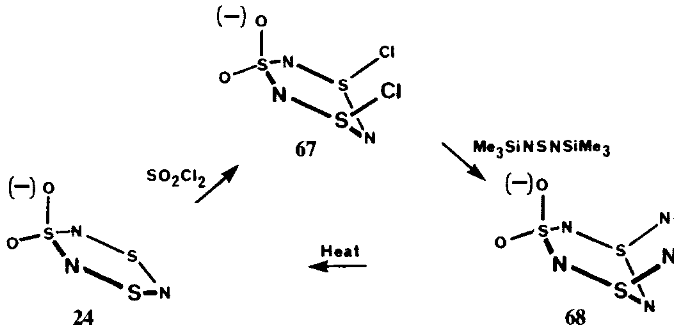
In an earlier section we noted the formation of a variety of cyclic and cage oxyanions, for example, $S_4N_5O^-$, $S_3N_3O^-$, $S_3N_3O_2^-$ during the oxidation of $S_3N_3^-$ with molecular oxygen (Eq. 1) (131). In addition to these anionic species several neutral heterocycles are also known, the most important of which is the eight-membered derivative $S_4N_4O_2$ (**66**), easily prepared from sulfamide $O_2S(NH_2)_2$ and $S_3N_2Cl_2$ (**2**) (Eq. 25) (285).



(25)

66

The chemistry of $S_4N_4O_2$ has been studied extensively. As with S_4N_4, its treatment with nucleophiles leads to both ring contracted and open-chain derivatives (286, 287). When azide is used, the $S_3N_3O_2^-$ species **24** is produced (see Section IV.B.1 for a discussion of the mechanism of this reaction) (131, 286b). Oxidation of $S_3N_3O_2^-$ with SO_2Cl_2 then affords the dichloride $O_2S_3N_3Cl_2^-$, (**67**), which reacts with $Me_3SiNSNSiMe_3$ to give the bicyclic derivative **68** (isoelectronic with **57** and **64**) (Eq. 26) (282). Like the bicyclic $R_2PS_3N_5$ molecules, this species readily thermolyzes, with loss of the bridging NSN group, to $S_3N_3O_2^-$ (**24**) (282). A neutral monochloride $O_2S_3N_3Cl$ (**69**) has also been structurally characterized; it is obtained in low yield by the oxidation of the neutral compound $(O_2SN_2S_2)_2$ with chlorine (288). The five-membered ring S_3N_2O (**70**) is readily prepared from $S_3N_2Cl_2$ (**2**) and formic acid (285).



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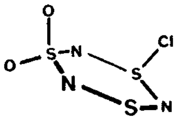

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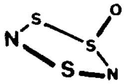

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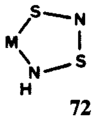
3. *Metallocyclothiazenes*

In addition to the numerous adducts formed between sulfur nitrides and transition metals (Section II.B.2), there are a large number of metallocycles containing chelating S_xN_y ligands. In view of the recent and comprehensive reviews by Kelly and Woollins (289a), Roesky (289b), and Chivers and Edelmann (289c) on this subject we confine the present discussion to a summary of the known ligand types. Regrettably there is no discernible methodology in the synthetic routes used to these compounds; most involve treatment of a metal center (usually in a high valent state) with S_4N_4. Yields are, not surprisingly, variable. Five-membered metallocycles, for example, **71**, **72**, and **73**, incorporating $[SNSN]^{2-}$, $[SNSN(H)]^-$, and $[SNSS]^-$ ligands are common products. For example, $NiCl_2$ and S_4N_4 in methanol produce largely $Ni(S_2N_2H)_2$, with smaller amounts of $Ni(S_2N_2H)(S_3N)$ and $Ni(S_3N)_2$ (290). Similar complexes of cobalt, palladium, and platinum are known

(291). More recently it has been shown that complexes of the S_3N^- ligand can be reached in a more systematic way from metathetical reactions of $[(Ph_3P)_2N]^+$ $[S_3N]^-$ with metal halides (292). Curiously, when $PtCl_2(NCPh_2)_2$ instead of $PtCl_2$ is reacted with S_4N_4, the unusual complex **74**, which contains (formally) a tridentate $S_4N_3^-$ ligand, is produced (293).

Metallocycles involving the earlier transition metals are also known. S_4N_4 reacts with the halides of tungsten, vanadium, and molybdenum to give a variety of neutral and anionic complexes, all of which contain an 8π-electron metallodithiatriazine MN_3S_2 unit, for example, $Cl_2VN_3S_2$ (**75**) (294). Reduction of S_4N_4 with titanocene dicarbonyl affords the six-membered TiS_3N_2 and eight-membered TiS_3N_4 rings **76** and **77** (295).

71



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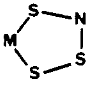

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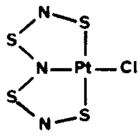

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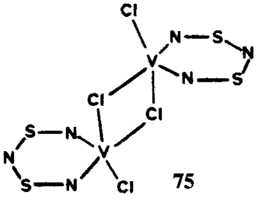

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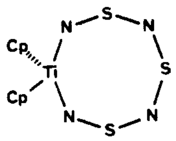

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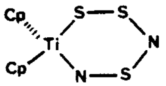

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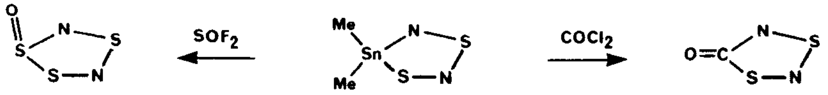
The potential of cyclometallothiazenes as synthetic reagents has attracted some attention. Both the $Ni(S_2N_2H)_2$ complex (39) and the dimethylstannyl reagent $Me_2SnS_2N_2$ (**78**) (236) act as convenient sources of S_2N_2. The former, mentioned earlier (Section II.A.1), reacts with sulfur monochloride to produce S_4N_2, while the latter has been used to prepare the heterocycles OS_3N_2 (**70**) and OCS_2N_2 (**52**) (Eq. 27) (296).



70 **78** **52**

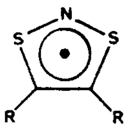
(27)

C. Redox Chemistry of Heterocyclic Thiazenes

Some of the most important advances in sulfur–nitrogen chemistry have emerged from recent studies of the redox chemistry of the heterocyclic systems just described. In constrast to the binary sulfur nitrides, which are generally unstable to electron transfer (see Section II.B.1), many of the hybrid derivatives obtained by blending –S=N– units with unsaturated organic or organic fragments undergo redox reactions to afford remarkably stable radical and/or antiaromatic systems. The following section provides a summary of how these systems can be generated, emphasizing the novel modes of molecular association and rearrangement that have been observed.

1. Dithiazolyl Radicals

The existence of stable 1,2,3- and 1,3,2-dithiazolyl radicals **79** and **80** has been known for several years, and a wide range of derivatives of this type have been characterized by ESR spectroscopy (297, 298). The radicals are extremely stable in solution, and interest has been shown in the use of some 1,3,2-derivatives as spin probes. They can be made by the elec-



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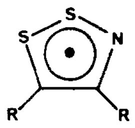

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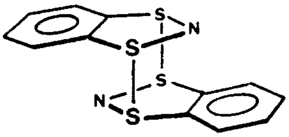
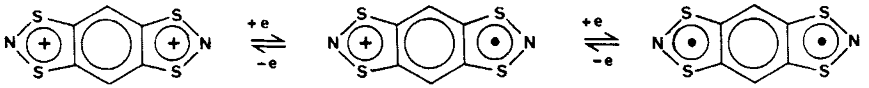


81

trochemical or chemical (by Zn powder) reduction of the corresponding dithiazolium salts, and are also produced in the reaction of alkynes and tetrasulfur dinitride (297b). The 1,2,3- and 1,3,2-benzodithiazolyl radicals are also observed in the potassium metal reduction of 1,3,2,4-benzodithiadiazine and 1,3,5,2,4-benzotrithiadiazepine, respectively (299). The 1,3,2-benzodithiazolyl radical forms a charge transfer salt with tetracyanoquinodimethane, but the compressed pellet conductivities are not high (300). In the solid state it forms a dimer (**81**) in which two benzodithiazolyl rings are bridged by two long (3.174 Å) bonds (301).

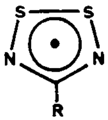
As an extension of this work, the stepwise reduction of the tricyclic benzobis(dithiazolium) dichloride **82**, prepared from 1,2,4,5-benzenetetrasulfenyl chloride and trimethylsilylazide, affords the radical cation **83**, which forms a 2:1 semiconducting salt with TCNQ, and then the neutral benzobis(dithiazole) **84** (Eq. 28) (302, 303). The electronic, and even the molecular structure of this latter compound are still not established. A diradical structure has been suggested; ESR evidence indicates the existence of dimers (perhaps as in **81**) that render exchange interactions between the two radical electrons $S = \frac{1}{2}$ negligible.



82 **83** **84** (28)

2. *Dithiadiazolyl Radicals*

The chemical or electrochemical reduction of dithiadiazolium salts yields the corresponding dithiadiazolyl radicals **85** and **86** (253c, 256, 301, 304). The 4-phenyl-1,2,3,5- derivative forms a dimer (**87**) in the solid state in which the two heterocyclic rings eclipse one another; the shortest interannular contact is between the sulfur atoms [mean $d(S$---S) = 3.109 Å] (305). The structure of the 4-CF_3-1,2,3,5- derivative has been studied in the gas phase, by electron diffraction, and in the solid state, as the simple dimer $(CF_3CN_2S_2)_2$ and as the mixed dimer–cation salt $(CF_3CN_2S_2)_3Cl$ (253c). In both structures the CN_2S_2 rings lie cofacially; in the mixed salt the atoms in each ring of the dimeric unit are eclipsed (**88**) [d(S---S) = 2.988 Å], as in the 4-phenyl derivative, but in the simple dimer **89** the rings are rotated one with respect to the other by ~95° so that there is only one short interannular S---S contact (2.997 Å).



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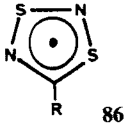

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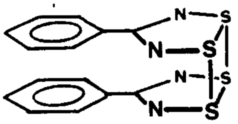

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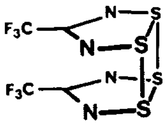

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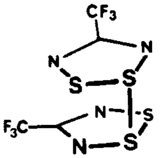

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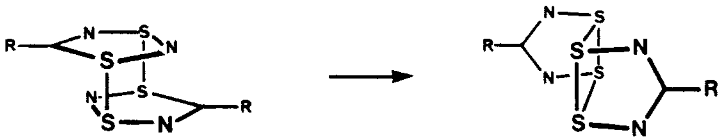
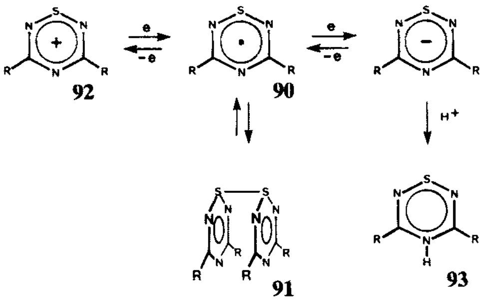
There are fewer examples of the 1,3,2,5-dithiadiazolyl system **86**, and a recent study of the 5-methyl derivative suggests a possible reason (306). It can be prepared by the treatment of the corresponding dithiadiazolium chloride with triphenylantimony and isolated as a deep purple solid at −25°C. When solutions of this material in SO_2–$CFCl_3$ are allowed to stand at room temperature, however, the characteristic ESR pattern of the 1,3,2,5-radical **86** slowly decays, and another signal corresponding to the 1,2,3,5-radical **85** grows in. Studies of the rate of isomerization indicate a second-order process that is photochemically activated; the putative transition state involves a cofacial association of two radicals (Eq. 29). The electronic aspects of this reaction are described in Section III.D.2.



(29)

3. *Thiatriazinyl Radicals*

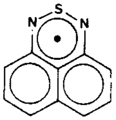
Stable 1,2,4,6-thiatriazinyl (and selenotriazinyl) radicals **90** are generated by the reduction of the corresponding S–Cl (or Se–Cl) compounds **56** with Zn (307) or, more easily, with triphenylantimony (258, 262). In the solid state these radicals exist as diamagnetic dimers. The structure of *bis*-(3,5-diphenyl-1,2,4,6-thiatriazine) (**91**) consists of a cofacial eclipsed arrangement of two C_2N_3S rings, the closest interannular contact being the



Scheme VII

S---S separation [2.666 Å; cf. 2.39 Å in $S_2O_4^{2-}$ (308)]. The selenotriazinyl $Ph_2C_2N_3Se\cdot$ radical dimerizes in a similar fashion with d(Se---Se) = 2.792 Å (262). The thiatriazine ring is the first heterocyclic thiazine system, the stability of which has been demonstrated over a triad of oxidation states (cation, neutral radical, and anion) (Scheme VII). Oxidation of **90** (R = Ph) with $NOPF_6$ affords the thiatriazinium cation **92**, while reduction by sodium in liquid ammonia yields the anionic species $(Ph_2C_2N_3S)^-$, **44** (R = Ph), isolated as the neutral imide $Ph_2C_2N_3SH$ (**93**) (309).

ESR data on the related polycyclic radical phenaleno[1,9*cd*]-[1,2,6]thiadiazinyl (**94**) have been reported (310a). Interest has been displayed in the use of such radicals (pseudoodd-alternate hydrocarbons) in the design of one-dimensional metals (310b), but examples of systems exhibiting the desired solid-state packing pattern, for example, **95**, have yet to be characterized.



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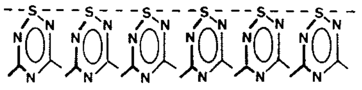

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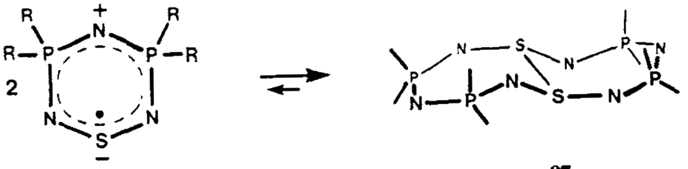
The *inorganic* S-chloro diphosphathiatriazine $Ph_4P_2N_3SCl$ **63** can also be reduced to a neutral radical $Ph_4P_2N_3S\cdot$ **96** (311). The spin distribution in this latter radical, however, is much more localized over the NSN moiety than in the corresponding *organic* heterocycle $Ph_2C_2N_3S\cdot$ (Fig. 10); its electronic structure is best represented by an internal salt formulation (i.e., a disguised sulfur diimide radical anion). In contrast to the $Ph_2C_2N_3S\cdot$ species, which associates without skeletal cleavage, the $Ph_4P_2N_3S\cdot$ radical dimerizes (reversibly) into the 12-membered $Ph_8P_4N_6S_2$ macrocycle **97** (Eq. 30) (311). The mechanism for this transformation is discussed in Section III.D.2.



96 **97** (30)

4. *Monomeric and Dimeric Dithiatriazines*

Reduction of the 1,3-dichloro-dithiatriazine derivatives $R_2PN_3S_2Cl_2$ (**65**) and $O_2S_3N_3Cl_2^-$ (**67**) proceeds directly to the corresponding unsubstituted dithiatriazines $R_2PN_3S_2$ (**60**) and $O_2S_3N_3$ (**24**). Although several oxidized derivatives based on the 1,3,2,4,6-dithiatriazine ring system **43** (Scheme V) have been generated, for example, **55**, **57**, attempts to produce the reduced heterocycle itself have had mixed success. For example, the re-

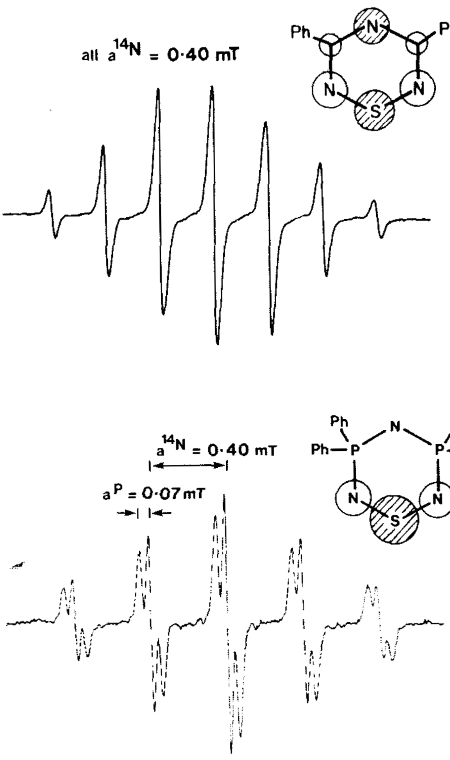
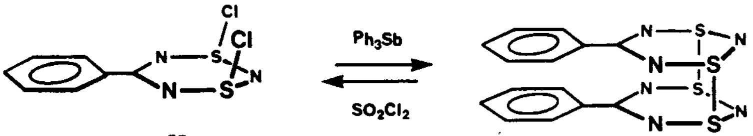


Figure 10. ESR spectra of $Ph_2C_2N_3S\cdot$ (above) and $Ph_4P_2N_3S\cdot$ (below). Approximate SOMO distributions for each radical are inset.

duction of $CF_3CN_3S_2Cl_2$ with Zn is reported to give a red thermally unstable compound, for which the formula $CF_3CN_3S_2$ was claimed (253, 270). Likewise the reduction of $Me_2NCN_3S_2Cl_2$ with $(Me_3Si)_2Hg$ affords a red solid having elemental analysis and mass spectrum consistent with $Me_2NCN_3S_2$; the compound also reacts with norbornadiene to produce a 1,3-norbornenyl cycloadduct (269). In neither case has the molecular structure or even the molecular weight been determined.



55 **98** (31)

The reduction of $PhCN_3S_2Cl_2$ with triphenylantimony also leads to a compound with the elemental composition $(PhCN_3S_2)_n$. In this case, however, the structure of the product has been established crystallographically as the cofacial dimer $(PhCN_3S_2)_2$ (**98**) (Eq. 31), in which the two CN_3S_2 rings are linked by two long S---S (mean length 2.527 Å) bonds (266b). The electronic reasons for the formation of the dimeric structure are explored in Section III.D.3. Oxidation of **98** with sulfuryl chloride reforms the 3,5-dichlorodithiatriazine **55**, while treatment with norbornadiene yields the 1,3 adduct of **43** (R = Ph).

In an interesting development of this work, Banister and co-workers recently showed that the dithiadiazolyl dimer **87** can be converted directly into the dithiatriazine dimer **98** in a solid-state reaction involving formally the insertion of excited nitrogen atoms generated in a low pressure dc discharge (312).

D. Electronic Aspects of Intra- and Intermolecular Interactions

The synthetic advances outlined in the previous sections have generated a variety of novel closed- and open-shell heterocyclic systems, many of which exhibit unusual solid-state structures. In this section we address the electronic interpretation of these geometrical features. For convenience, the discussion is divided into three parts; the first offers a rationale for the intramolecular S---S interactions found in dithiatetrazocine derivatives, while the second and third treat the electronic nature and chemical consequences of intermolecular binding in various dimeric systems.

1. *Jahn–Teller Effects in Dithiatetrazocines*

In 1970 Gleiter outlined, in a now classic paper, a simple and useful way of rationalizing the molecular structure of S_4N_4. Using symmetry arguments he predicted that a planar S_4N_4 molecule with D_{4h} symmetry would possess a triplet ground state and hence be susceptible to a pseudo-first-order Jahn–Teller distortion (182). He also pointed out that a distortion of the planar molecule into a D_{2d} structure would invert the ordering of the a_{2u} LUMO and e_g HOMOs, thereby affording a singlet ground state (Fig. 11) and, at the same time, allowing the development of some transannular binding between 1,5-sulfur atoms. As mentioned in Section II.C.3 the extent of these interactions has been a subject of continued debate. From a thermodynamic viewpoint, however, these discussions have provided little substantive information. There is, for example, no way that we can measure or calculate the strength of the transannular interactions in S_4N_4, for example, by opening the D_{2d} cage into a planar D_{4h} modification and assessing the concomitant enthalpy change, since it would be impossible to extract the S---S bond energy component from the reorganizational energy term associated with the torsional motion of the skeletal SN bonds.

A natural corollary to the arguments presented by Gleiter was the prediction of planarity for the 10π-electron $S_4N_4^{2+}$ cation. The Jahn–Teller stable singlet ground state and the robustness of the cyclic π system (Fig. 3) precluded any tendency of the molecule to pucker. More recently the issue of transannular interactions has been raised again as a result of the characterization of a number of tetrazocine structures, some of which ex-

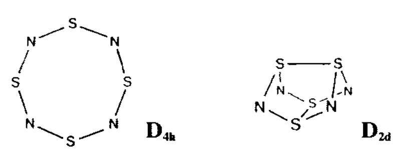


Figure 11. Inversion of the a_{2u} (LUMO) and e_g (HOMO) of a planar 12π-electron S_4N_4 ring accompanying a structural distortion from D_{4h} to D_{2d}.

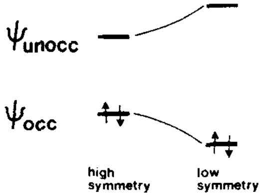
hibit planar geometries, for example, **37a** and **38a** (253, 264, 313), while others possess puckered geometries with short (2.40–2.60 Å) transannular S---S contacts, for example, **37b**, **38b**, **59**, and **61** (118d, 259, 264, 269b, 272, 314–316). There is only limited information on the relative energetics of the two geometries available for molecules of this type. MNDO and *ab initio* MO studies on the planar and puckered conformations of the model 1,5-dithiatetrazocines $H_2C_2N_4S_2$ and $(NH_2)_2C_2N_4S_2$ (220, 265, 317, 318) show that the planar geometry is destabilized in the presence of π-donor ligands, although the MNDO method underestimates the magnitude of the effect. Similar trends have been noted in $S_4N_4X_2$ derivatives, but further high level studies are certainly in order to quantify the energetic differences.

While the quantitative aspects of the structural dichotomy still require exploration, the phenomenon itself can be easily understood, and even anticipated, in terms a second-order Jahn–Teller effect (319). Accordingly, the susceptibility of a molecule with a high symmetry nuclear framework to a symmetry lowering distortion along the qth vibrational coordinate can be related, using perturbation theory, to the magnitude of the expression

$$\sum_k \frac{\langle \Psi_0 | (\partial V/\partial q | \Psi_k \rangle^2}{(\epsilon_0 - \epsilon_k)}$$

where the summation is taken over all the excited electronic states Ψ_k. Essentially, this term assesses the extent of electronic relaxation that accompanies a nuclear displacement. In attempting to estimate its magnitude the denominator is normally approximated by the energy gap between the orbitals that describe the distribution of the *excited* electron in the ground (Ψ_0) and excited (Ψ_k) states. The value of the numerator is determined in part by symmetry; a second-order Jahn–Teller distortion requires the availability of a deformation mode that transforms as the direct product of the representations of a high-lying occupied orbital ψ_{occ} with a low-lying vacant orbital ψ_{unocc}. As the deformation progresses the two orbitals will mix and *repel* one another, the occupied one being stabilized at the expense of the unoccupied (see Scheme VIII). The magnitude of the effect, that is, the stabilization of the total electronic energy, is then inversely proportional to the original energy separation $|\epsilon_{\mathrm{occ}} - \epsilon_{\mathrm{unocc}}|$ of the two orbitals in the high symmetry form. In most (but not all) cases second-order effects arise from HOMO–LUMO interactions, for which the energy separation is smallest.

Application of these ideas to the analysis of dithiatetrazocine structures requires a knowledge of the symmetries and energies of their frontier orbitals. These can be easily deduced with reference to the π manifold of



Scheme VIII

the parent $S_4N_4^{2+}$ dication (see Fig. 2). The orbital of concern in the present context is the HOMO, which in $S_4N_4^{2+}$ is the nonbonding distribution b_{1u}; in $H_2C_2N_4S_2$ this orbital correlates with one that is slightly antibonding with respect to the N–S linkages (Fig. 12). The orbital energy is also raised (at the Hückel level) by the electropositive perturbation occasioned by the replacement of two S^+ units by carbon atoms. Incorporation of a yet more electropositive group, for example, R_2P (as in $R_4P_2N_4S_2$, **61**), accentuates the energetic destabilization of the HOMO, and further weakens the π system as this orbital evolves into a more antibonding distribution. The same effect can also be achieved by the introduction of π-donor ligands at the 1,5 positions (e.g., NH_2) (see Fig. 12).

The "prescription" for a second-order Jahn–Teller distortion is now apparent. Relatively electropositive perturbation of the 1,5 positions of the $S_4N_4^{2+}$ structure, and/or the presence of π-donor ligands, creates an unstable high-lying occupied orbital. The remaining requirement for a C_{2v}

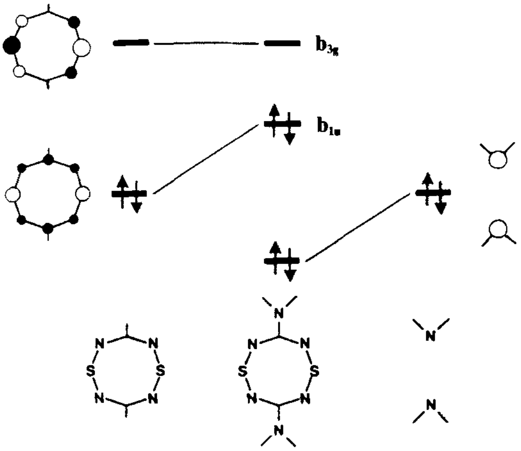


Figure 12. Effect of π-donor ligands (e.g., NH_2) on the energy of the b_{1u} HOMO of a dithiatetrazocine ring.

distortion to be Jahn–Teller allowed is the presence of a low-lying virtual orbital, which is symmetrically disposed to interact with the HOMO. Contrary to a recent report (265), there is no low-lying π level that can mix with the b_{1u} HOMO as the distortion into C_{2v} proceeds. There is, however, a suitable in-plane distribution of a_{1g} symmetry (at the MNDO level it is the 3LUMO, i.e., the third lowest unoccupied MO) (320). The changes that occur in this orbital and the b_{1u} HOMO as the ring puckers are illustrated in Fig. 13. The σ/π mixing, which accompanies the deformation, partitions some of the antibonding character of the occupied orbital into the unoccupied, strengthening the N–S linkages in the process. To the extent that the energy of the a_{1g} orbital is relatively independent of the nature of the ligand on carbon, the energy gap between the Jahn–Teller active orbitals will decrease as the π HOMO is raised. The a_{1g}–b_{1u} mixing leads to a new HOMO, which has a small but distinctly nonzero overlap population between the two sulfur atoms. There are other, more deeply lying orbitals with nonzero overlap populations across the 1,5 contact, but their bonding and antibonding effects are (approximately) mutually canceling. This new a_1 HOMO is the primary contributor to whatever S---S bond there might be.

The arguments just outlined apply equally to any molecule based on the tetrazocine skeleton. In the case of S_4N_4 itself it is these second-order effects rather than the first-order mixing just noted that lead to the observed

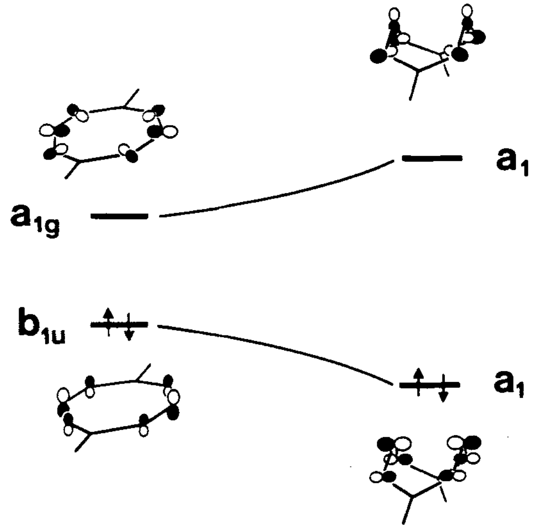


Figure 13. The a_{1g}–b_{1u} orbital mixing that drives the second-order Jahn–Teller distortion of dithiatetrazocines from D_{2h} to C_{2v} symmetry.

Figure 14. The LUMO of the $S_4N_5^+$ cation.

structure. The redistribution of antibonding character between filled and unfilled orbitals, and the concomitant development of some transannular S---S binding, lead to a net stabilization of the D_{2d} structure relative to the D_{4h} geometry. These concepts can be further extended to account for the structural differences between the $S_4N_5^+$ and $S_4N_5^-$ ions (91, 192). In the cation the LUMO (Fig. 14) is a π*-type distribution spread over the two equivalent NSN fragments (93). In the corresponding anion this orbital is occupied, and since it is antibonding, it severely weakens the *local* π bonds. Compression of the butterfly shape does not alter the molecular symmetry, but does provide a mechanism for orbitals of *local* π and σ symmetry to mix. As before, some transannular S---S binding may develop, but the structural change is probably driven as much by the need to strengthen the skeletal SN bonds.

2. *Radical Associations and Rearrangements*

The structural dichotomy observed for dithiatetrazocines arises from the instability in the π system, which can be alleviated through a σ/π mixing process; the degree of transannular S---S binding is not easily defined, let alone measured. A related problem, where the question of bond strength can more readily be assessed, involves the association of two π radicals, the dithionite system being a pertinent example (308a). In contrast to a simple disulfide linkage, in which the S–S bond can be described, in VB or MO terms, as a two-center two-electron interaction, the S---S bond in dithionite involves the overlap of the two π* SOMOs of the 5π-electron $SO_2^{\cdot -}$ radical anion (Fig. 15). The in-phase combination of these two orbitals, what one might call the S---S σ orbital, still retains its role as a π* distribution with respect to the S–O linkages.

Like the $SO_2^{\cdot -}$ radical (308), the thiatriazinyl radical $Ph_2C_2N_3S\cdot$, (**90**, R = Ph) exists in the solid state as a diamagnetic dimer. The cofacial arrangement of the two radical partners is the same, but in **91** the S---S "bond" is slightly longer (258). From an electronic standpoint the interaction is also very similar to the dithionite case. MNDO calculations on a model 7π-electron $H_2C_2N_3S\cdot$ system show that the $3b_1$ SOMO is strongly antibonding over the NSN unit. Interannular bond formation in $(H_2C_2N_3S)_2$

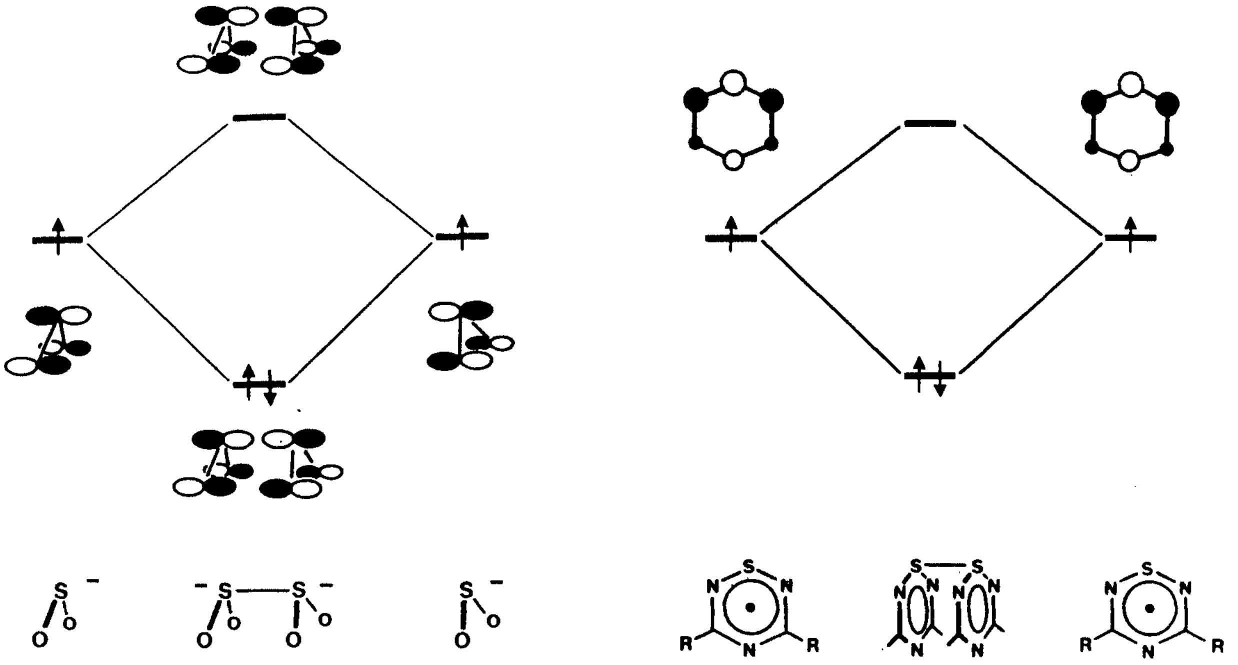


Figure 15. Cofacial overlap of the π^* SOMOs of two thionite radicals (left) and two thiatriazinyl radicals (right) to form S---S bridged dimers.

essentially arises from the in-phase overlap of two such orbitals, as in Fig. 15. The diffuse nature of the $3b_1$ orbital and its dual role as a π^* orbital with respect to the S–N linkages is well illustrated by the observed structural differences between the $Ph_2C_2N_3S^+$ cation **92** (as its PF_6^- salt), the radical dimer $(Ph_2C_2N_3S)_2$ (**91**) and the imide $Ph_2C_2N_3SH$ (**93**). These structures, which represent the three oxidation states (6π, 7π, and 8π) of the thiatriazine ring, show changes in the endocyclic bond lengths, which reflect the progressive occupation of the $3b_1$ orbital (308); calculated MNDO bond orders for model $H_2C_2N_3S^+$, $H_2C_2N_3S\cdot$, and $H_2C_2N_3SH$ derivatives follow the same trend (Fig. 16).

There is only limited information on the thermodynamic strength of the interannular bond in thiatriazine dimers. The dissocation constant of $(Ph_2C_2N_3S)_2$ is considerably greater ($3 \times 10^{-2} M$ in CH_2Cl_2) (262) than that of dithionite ($10^{-9} M$ in H_2O) (321), in accord with the observed trend in S---S distances, but may well be dependent on the nature of the 3,5 substituents and solvation effects. In the selenotriazine dimer $(Ph_2C_2N_3Se)_2$ the dissociation constant ($5 \times 10^{-4} M$) is smaller, and hence the interannular bond stronger, that is, $4p/4p$ overlap is more effective than $3p/3p$ (182, 262).

The dimerization of the diphosphathiatriazinyl radical $Ph_4P_2N_3S\cdot$ (**96**) into the 12-membered heterocycle **97** (Eq. 30) is in sharp contrast to the cofacial arrangement found in $(Ph_2C_2N_3S)_2$ **91**. Although steric demands would certainly militate against the cofacial approach of two $Ph_2P_2N_3S\cdot$ radicals, they do not, by themselves, explain the observed rearrangement.

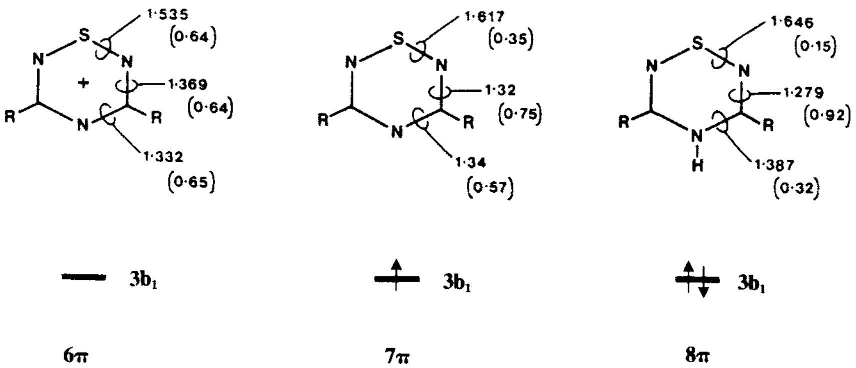


Figure 16. Structural changes accompanying the sequential reduction of a thiatriazine ring. Bond lengths (in Å) are mean values taken from R = Ph derivatives, those for the 7π system referring to the radical dimer structure. π-Bond orders (MNDO) for R = H are quoted in parenthesis. Occupancy of the $3b_1$ orbital (see Figure 15) is shown at bottom.

The thermodynamic issues are clearly quite subtle, perhaps involving ring strain; a single large ring is slightly more stable than two smaller rings. The other question, how this structural metamorphosis might occur, is best approached by recalling the internal salt formulation for **96** (see Section III.C.3); accordingly, the heterocycle is electronically equivalent to a sulfur diimide radical anion $[RNSNR]^{\cdot -}$. The relevance of this analogy arises from the fact that these latter anions (with simple organic ligands R and R′) undergo rapid scrambling reactions (e.g., Eq. 32) whose mechanism must be very similar to that involved in the conversion of **96** to **97** (311b).

$$[RNSNR]^{\cdot -} + [R'NSNR']^{\cdot -} \rightleftharpoons [RNSNR']^{\cdot -} + [R'NSNR]^{\cdot -} \qquad (32)$$

The mechanism for both reactions (Eq. 30 and 32) is proposed to involve a S to N association of two radical units (Fig. 17). Such a dimer, bound by the overlap of the two SOMOs, is centrosymmetric [as is dithionite in aqueous solution (322)], and can easily isomerize via a four-center tran-

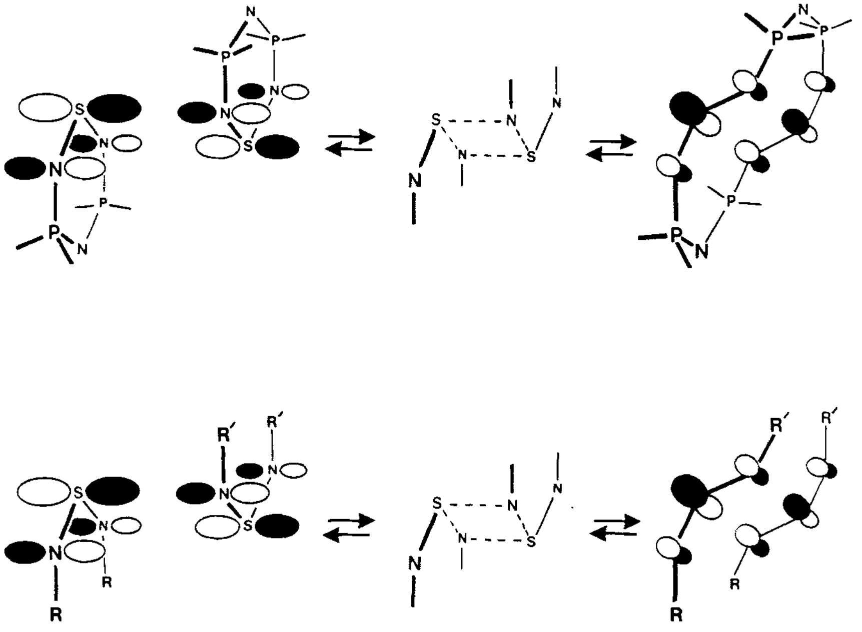


Figure 17. Structural and orbital changes accompanying (above) the conversion of two $R_4P_2N_3S\cdot$ radicals to a 12-membered $R_8P_4N_6S_2$ ring and (below) the skeletal bond exchange of sulfur diimide radical anions. Note the inversion symmetry of the SOMO pairings on the left (u) and right (u).

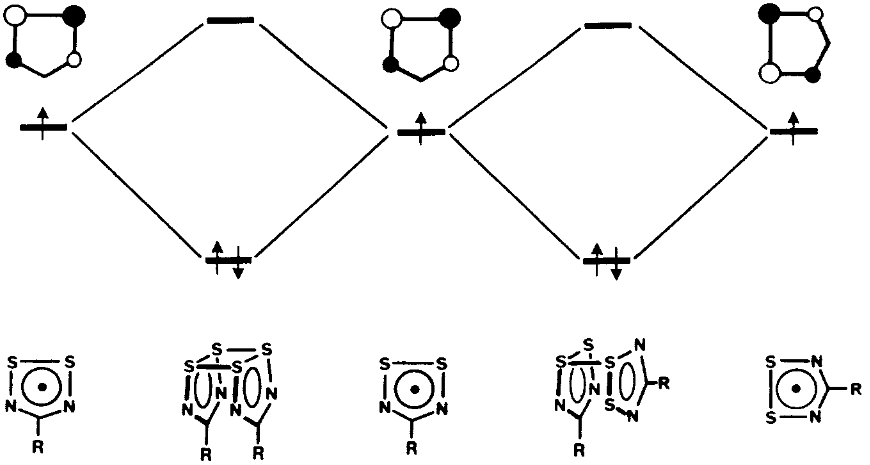


Figure 18. Possible overlap modes for the SOMOs of two cofacially aligned 1,2,3,5-dithiadiazolyl radicals.

sition state that conserves the inversion symmetry of all orbital pairings on the two interacting halves (311b).

The association and rearrangements of the dithiadiazoyl radicals and the $(S_3N_2)_2^{2+}$ dication **17** provide another interesting development. In all these structures intermolecular binding arises through the overlap of the a_2 SOMOs on each radical (Fig. 18). It is readily apparent that a variety of dimerization geometries is possible; the cofacial arrangements of **87** and **88** rely primarily on two S—S interactions, while in **89** one S—S contact is complemented by long-range overlap between two S—N pairs.

Energetically the difference between the two modes of binding is likely to be very small (MNDO estimates are in the order of 5 kJ mol^{-1}) (253c), the final choice being dependent more on lattice forces than on interannular binding preferences. The *trans* geometry adopted by the $(S_3N_2)_2^{2+}$ dication (Scheme III) (88, 176, 189) is probably a manifestation of ion pairing effects. The S—S separation in all the dithiadiazolyl-type dimers is notably longer than in the thiatriazinyl radical dimer **91**, indicative perhaps of the more diffuse nature of the interacting SOMOs. Studies of the thermodynamics of association of $(S_3N_2)_2Cl_2$ and $(PhCN_2S_2)_2$ also suggest a weak linkage (ΔH_{dim} = -47 and -35 kJ mol^{-1}), indeed both of these dimers are slightly paramagnetic in the solid state (299).

The isomerization of 1,3,2,5-dithiadiazolyl radicals **86** (R = Me, *t*-Bu) (306, 323) to their 1,2,3,5-dithiadiazolyl counterparts **85** (Eq. 29) complements the rearrangement of **96** to **97** (Eq. 30). The reaction, which is second

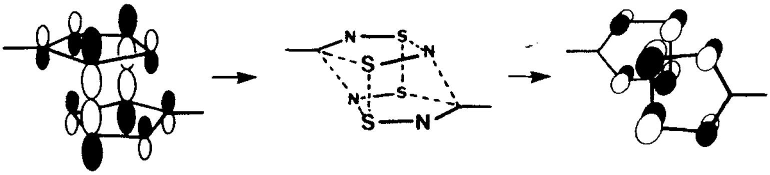


Figure 19. Conversion of 1,3,2,5-dithiadiazolyl radicals to 1,2,3,5-dithiadiazolyl radicals through a photochemically allowed centrosymmetric transition state formed by the association of two radicals. Note the inversion symmetries of the SOMO pairings on the left (g) and right (u).

order in radical, is proposed to proceed via a weakly associated intermediate bound by the interaction between the SOMOs of the two radical halves (Fig. 19). Inspection of the inversion symmetries of the SOMO pairings in the reactant (g) and product (u) dimers, however, reveals that a concerted rearrangement would be thermally forbidden (323). The isomerization is predicted to be photochemically allowed, in agreement with experiment.

In light of this discussion on the isomerizations of heterocyclic thiazyl radicals we close this section with a comment on the dimerization of S_2N_2 to S_4N_4 (see Section II.A.1). There has been only one theoretical study of this process, in which it was suggested that it should be thermally allowed (324). However, the arguments presented, involving the overlap properties of the HOMO and LUMO of two cofacially aligned dimers, are not compelling, nor do they address the fact that in solution and in the absence of nucleophiles and reducing agents S_2N_2 is stable indefinitely (44). An alternative mechanism for the reaction can be built from the concepts just outlined; accordingly we consider the consequences of the centrosymmetric approach of two S_2N_2 units (Fig. 20). Such an orientation does not lead to any net interaction by itself, but if one of the rings is reduced (to $S_2N_2^{\cdot-}$)

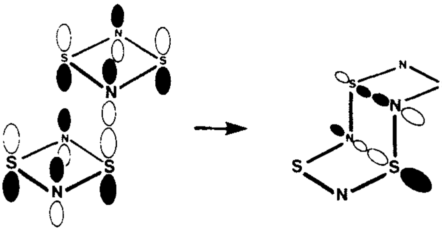


Figure 20. SOMO–LUMO overlap in a $(S_2N_2)_2^{\cdot-}$ adduct, and its thermally allowed isomerization to $(S_4N_4)^{\cdot-}$

substantial binding will arise through the interaction of the SOMO of the radical with the LUMO of the neutral molecule; an analogous mode of association between $SO_2^{\bullet -}$ and SO_2 is known to give a strong bond (ΔH_f $(SO_2)_2^{\bullet -} = -24\ \text{kcal mol}^{-1}$) (325). Once formed, the $(S_2N_2)_2^{\bullet -}$ radical cluster can readily isomerize to $S_4N_4^{\bullet -}$ (Fig. 20) via a transition state similar to that proposed for the conversion of **96** to **97**. In practice, only catalytic amounts of reducing agent would be necessary; a chain reaction involving reduction of S_2N_2, association with a neutral S_2N_2, rearrangement and subsequent electron transfer from $S_4N_4^{\bullet -}$ to S_2N_2 would lead to complete conversion of $\dot{S}_2N_2$ to S_4N_4, as shown:

$$e^- + S_2N_2 \longrightarrow S_2N_2^{\bullet -}$$

$$S_2N_2^{\bullet -} + S_2N_2 \longrightarrow S_4N_4^{\bullet -}$$

$$S_4N_4^{\bullet -} + S_2N_2 \longrightarrow S_4N_4 + S_2N_2^{\bullet -}$$

3. *The Dithiatriazine Dichotomy*

In the previous section we examined the electronic features of dimers produced by the interaction of thiazyl radicals. Association of monomer units is also observed in the structure **98**, but the electronic criteria involved are somewhat different from those seen above. A qualitative explanation of this dimeric structure, which is in sharp contrast to the monomeric forms of the isoelectronic rings $R_2PN_3S_2$ (**65**) and $SO_2N_3S_2^-$ (**24**), can be developed by considering the electronic structures of all EN_3S_2 molecules (E = R_2P, SO_2^-, RC) in terms of that of their parent, the $S_3N_3^+$ cation. *Ab initio* MO calculations have confirmed a triplet ground state for this latter species (69), by virtue of the half-occupancy of the degenerate e'' orbitals shown in Fig. 21. This degeneracy can be lifted by replacement of one (charged)

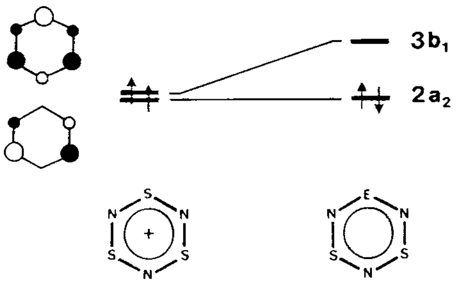
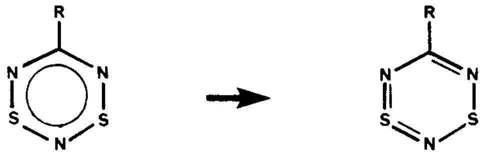


Figure 21. Splitting of the degeneracy of the e'' orbitals of $S_3N_3^+$ by the incorporation of a less electronegative atom at one sulfur site, and its effect on ground-state multiplicity.

sulfur atom with an isolobal heterogroup E, thereby producing, in C_{2v} symmetry, a b_1 and a_2 pair. With an electropositive perturbation the b_1 level is raised in energy with respect to the a_2, which has a node at the heteroatom site.

With large perturbations, as expected for E = R_2P and SO_2^-, the b_1–a_2 splitting is sufficient to overcome spin pairing energies, and singlet ground states are found for such derivatives. Their intense low energy absorption bands (~550 nm) have been assigned to the b_1–a_2 excitation (131, 274, 326). In the case of an $S^+ \longleftrightarrow CR$ replacement, the orbital electronegativity difference is less acute, and the energetic separation between the high- and low-spin states cannot be anticipated from purely one-electron arguments. MNDO calculations on a variety of RCN_3S_2 derivatives (R = H, NH_2, F, Ph) predict the triplet to be more stable than the singlet by 12 to 15 kcal mol^{-1} (266). Interestingly, analogous calculations on the isoelectronic thiatriazine anion $H_2C_2N_3S^-$ (44, R = H) predict the singlet to be more stable by 28 kcal mol^{-1} (309). HFS results on RCN_3S_2 (R = H, NH_2) have been less definitive. Convergence to a singlet state could only be achieved for R = NH_2, but no data on the energy of the corresponding triplet was provided (269b, 327). More recent *ab initio* level calculations including corrections for differences in correlation effects (328) have shown that the energy difference between the two spin states of RCN_3S_2 (R = H, NH_2) favors the triplet slightly when C_{2v} symmetry is imposed. When this requirement is relaxed, the nuclear framework of the singlet state undergoes a second-order Jahn–Teller distortion, driven by a mixing of the b_1 LUMO with the a_2 HOMO (see Fig. 21), which stabilizes the singlet state relative to the triplet. On the basis of this evidence, monomeric dithiatriazines (**43**) are predicted to possess singlet ground states with distorted structures, for example, **99**. Similar distortions, which can be viewed as involving charge localization into single a valence bond structure, are certainly observed in the solid-state structures of the related derivatives **23** and **58** (131).



43 **99**

Regardless of the multiplicity of the ground state of dithiatriazines (**43**), the dimeric structure found for **98** illustrates the propensity of many strongly antiaromatic compounds to self-associate (see Section IV.C); the formation

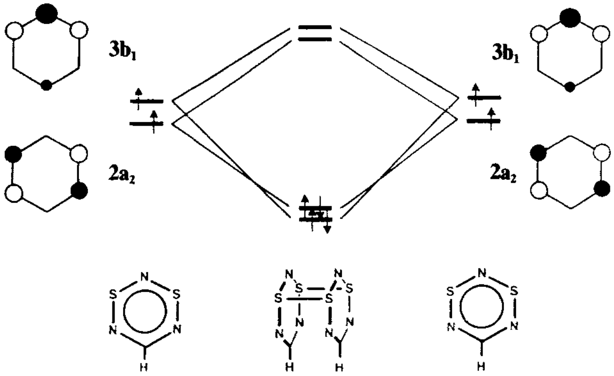


Figure 22. Formation of two interannular S---S bonds in dithiatriazine dimers by the overlap of *singly occupied* b_1 and a_2 orbitals of two triplet units.

of interannular S---S bonds (albeit weak ones) is energetically favorable to an unstable π system. Figure 22 indicates how the interannular interaction in $(HCN_3S_2)_2$ can be built from the overlap of the π^* orbitals of two triplet HCN_3S_2 units. The net S---S *bonds* arise from the in-phase combinations of the b_1 and a_2 orbitals on each ring. It remains to be seen if variations in the exocyclic R group will have a major structural effect. In this regard the compound $[Me_2NCN_3S_2]_x$ (269) deserves further study.

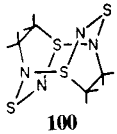
IV. REACTIVITY PATTERNS

In previous sections we focused attention on relationships between electronic and molecular structures of sulfur–nitrogen ring systems. Comparisons with organic chemistry are particularly instructive, affording insight into both common and unique features of organic and inorganic ring systems. In the last few years considerable progress has been made in extending these analogies with organic chemistry to the interpretation of chemical reactivity patterns. The present section summarizes the results of this work.

A. Addition Reactions and Frontier Orbital Effects

1. Olefin Cycloadditions

The potential chemical analogies between unsaturated –S=N– and –(H)C=C(H)– linkages were recognized over 20 years ago, when Becke-



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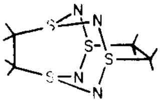

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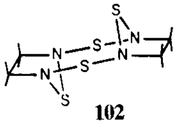

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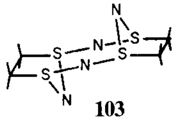


103

Goehring and co-worker explored the reactions of olefins with S_4N_4 and obtained adducts of the type $S_4N_4 \cdot (\text{olefin})_2$ (329); at the time they suggested that the compounds were products of a Diels–Alder-like cycloaddition, for example, **100**. Later, two alternative formulations **101** (182) and **102** (330) were put forward. Finally, two independent crystallographic studies of the *bis*(norbornadiene) adduct (331) and also an elegant chemical analysis of the *bis*(*trans*-cyclooctene) derivative (332) established that addition occurred in a 1,3 fashion, for example, **103**. Following these structural characterizations Fukui and co-workers rationalized the regiochemistry of addition in frontier orbital terms, stressing the kinetic control exerted by the interaction of the olefin HOMO with the low-lying LUMO of S_4N_4 (333). Consistently, only electron-rich olefins, for example, norbornadiene, norbornene, and *bis*(cyclopentadiene), add to S_4N_4 (333).

Similar arguments have since been used to rationalize the considerably different rates of the two electrocyclic additions shown in Eqs. 33 and 34, the latter being much slower (334). In essence the dichotomy is related to the subtle but predictable differences in the LUMO energies of the two heterocycles **58** and **60** (R = Ph). Using a perturbational MO approach, the relative energies can be established by considering the consequences of perturbing the LUMO of their common precursor, the 8π-electron five-atom $N_3S_2^-$ anion, by incorporation of a phosphonium $(R_2P\langle)^+$ or sulfonium $(RS\langle)^+$ cation. Thus, while the effects of 3*d*, or hyperconjugative, orbital mixing from phosphorus are likely to be small, the lone-pair orbital of the sulfonium group will raise the b_1 LUMO (Fig. 23) substantially. The HOMO–LUMO transition energies and reduction potentials (−1.25 V for **55** and −1.10 V for **57**, both vs. SCE) of the two heterocycles support this interpretation that the LUMO of $Ph_3PNS_3N_3$ is higher lying, and therefore kinetically less accessible to attack by the HOMO of an incoming nucleophile. As in the case of S_4N_4, neither of these two molecules undergoes cycloaddition with olefins less nucleophilic than norbornadiene. In the case

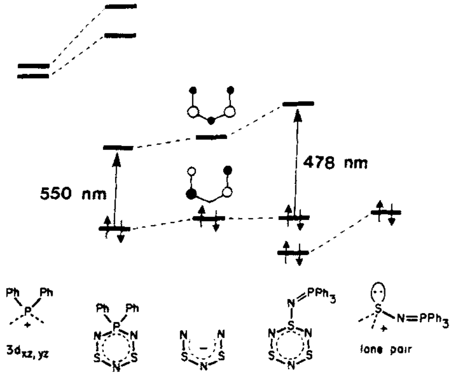
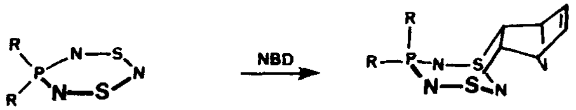


Figure 23. Evolution of the frontier orbitals of $R_2PN_3S_2$ (left) and $R_3PN-S_3N_3$ (right) derivatives from a common pseudopentadienyl $N_3S_2^-$ precursor.

of the SNS^+ cation, however, (4 + 2) cycloadditions with a variety of nitriles, alkenes, and alkynes have been reported (256, 335). It has been suggested that the positive charge on the cation renders it more kinetically susceptible to reaction with less nucleophilic centers. To date there have been no reports of additions controlled by a reverse ($HOMO_{heterocycle}$–$LUMO_{olefin}$) electron demand.



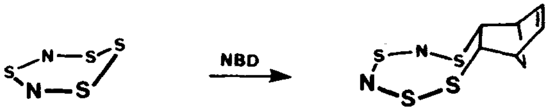
(33)

60

(34)

58

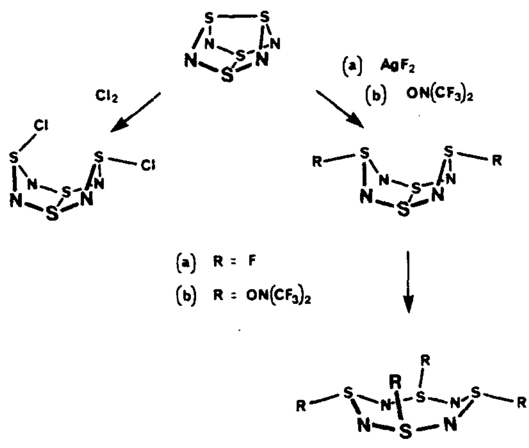
Many cycloadducts of binary and heterocyclic systems with electron-rich olefins have now been structurally characterized (274, 277, 331, 334–336); indeed the ease of preparing such compounds in high yield has provided a means of derivatizing many otherwise unstable or intractable materials (284). The regiochemistries of the additions are almost always the same, that is, 1,3-S,S, but there are claims, based largely on NMR evidence, that *N,N*-addition is also possible (299, 337). In all the reported structures of norbornadiene adducts the SN-substrate adds to the *exo* side of the olefin double bond, in keeping with the slight preference predicted for *exo* addition to strained olefins (338). Reactions involving radical rather than concerted mechanisms have also been observed. The reaction of S_4N_2 with norbornadiene, for example, is known to afford radical intermediates (297); under carefully controlled conditions the heterocycle **104** (Eq. 35), the structure of which indicates a (symmetry forbidden) addition across an S–S σ bond, can be isolated in 15% yield (339).



4 **104** (35)

2. *Polar and Radical Oxidations of Dithiatetrazocines*

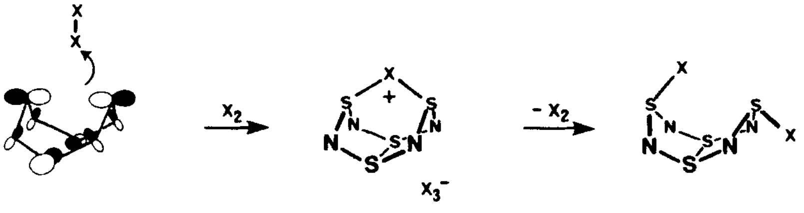
In earlier sections we outlined the structural properties of the frontier orbital distributions associated with the S---S interactions in dithiatetrazocines and related derivatives. Regrettably, the preoccupation with the ground-state strength of these "bonds" has clouded some important questions regarding their chemical reactivity; only recently has attention been drawn to the electronic factors that might affect the thermodynamics and kinetics of oxidative addition to these linkages. Historically most synthetic efforts have been focused on the oxidation of S_4N_4, and a variety of di- and tetra-substituted products have been isolated by direct addition reactions (Scheme IX). While structural characterization of $S_4N_4R_2$ deriva-



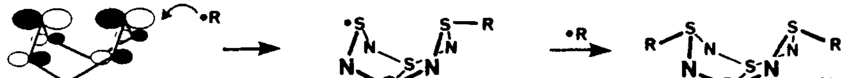
Scheme IX

tives relies on ^{19}F NMR evidence for R = F (118c, 119) and $ON(CF_3)_2$ (120), the structures of $S_4N_4Cl_2$ (118d) and the tetra-substituted compounds $S_4N_4R_4$ [R = F, $ON(CF_3)_2$] have been confirmed crystallographically (121, 124). The observed stereochemistries can be divided into two groups, one in which oxidation across the S---S contact produces an *exo–endo* geometry (as in $S_4N_4Cl_2$), while in the other addition affords the *exo–exo* pattern [as in $S_4N_4R_2$ and $S_4N_4R_4$, R = F, $ON(CF_3)_2$].

Each of these substitution patterns can be understood in terms of the mechanism, polar or radical, by which oxidation proceeds (220, 340). The electronic basis for the interpretation stems from the isolobal correspondence between the S---S σ and σ^* orbitals of S_4N_4 and the π and π^* orbitals of an olefin, and accordingly utilizes frontier orbital reasoning similar to that used to account for the rates and stereochemistries of addition to olefins (341). The polar oxidation route can thus be viewed as involving the attack of a halogen X_2 on the S---S σ-bonding orbital of S_4N_4 (Eq. 36). Subsequent uptake of X^- should then occur in a position *trans* to that of the X^+ unit. The symmetrical addition of nucleophilic radicals (e.g., nitroxides) implies a different frontier orbital pairing, this time involving the SOMO of the radical with the S---S σ^* LUMO (Eq. 37).



(36)



(37)

The polar route should be kinetically preferred for more electron-rich molecules, such as the heterocyclic derivative $Ph_4P_2S_2N_4$ (**61**) (R = phenyl); consistently this latter molecule reacts rapidly with bromine to give the *trans* product **105** (Eq. 38) (342). Chlorination of the dithiatetrazocine **38b** (R = NMe_2) is also fast, producing this time not a covalent structure but the trichloride salt of the asymmetrically bridged *chloronium* cation $[(Me_2N)_2C_2N_4S_2Cl]^+$ (see Fig. 24) (340). The approach of the trichloride ion, that is, sideways on to the cation and *trans* to the bridging chlorine, and also the bond length changes within the anion and cation collectively

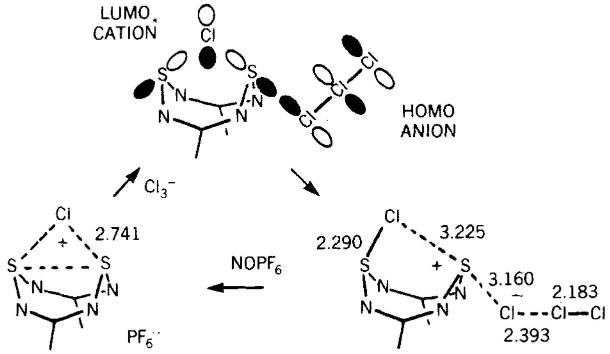
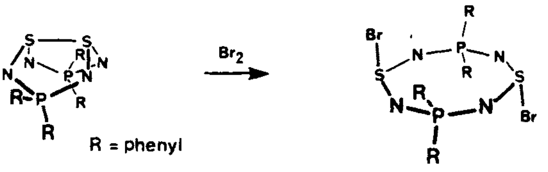


Figure 24. Structural features (bond lengths in Å) of S---Cl---S bridging unit in PF_6^- and Cl_3^- salts of $[(Me_2N)_2C_2N_4S_2Cl]^+$.

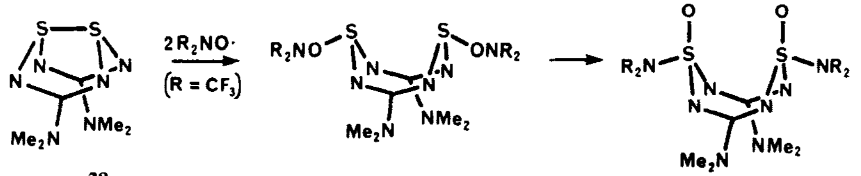
reflect the incipient nucleophilic attack of the anion on the cation. When the trichloride anion is replaced by a nonnucleophilic counterion, for example, PF_6^-, the structure of the cation relaxes to a completely symmetrical S---Cl---S geometry (340), a perfect analogue for the bridged halonium cations of interest to organic chemists (343).



61 **105**

(38)

The importance of the accessibility of the S---S σ^* orbital to the radical pathway is illustrated by the lack of reactivity of S_4N_4, $Ph_4P_2N_4S_2$ (**61**), and $(Me_2N)_2C_2N_4S_2$ (**38b**) (R = NMe_2) towards nonnucleophilic radicals. Neat peroxydisulfuryl difluoride $(FSO_3)_2$, for example, takes over 2 days to oxidize S_4N_4, while $ON(CF_3)_2$ reacts almost instantly. Correspondingly, $(Me_2N)_2C_2N_4S_2$, with its higher-lying LUMO, is attacked only slowly with $ON(CF_3)_2$ and $Ph_4P_2N_4S_2$ not at all (340). Consistent with the stereochemical features noted in the oxidation of S_4N_4, addition of $ON(CF_3)_2$ to $(NMe_2)_2C_2N_4S_2$ proceeds in a symmetrical fashion. The initial product, however, immediately rearranges by an *intramolecular* Arbusovlike reaction to yield the sulfur (VI) derivative **106** (Eq. 39) (340).



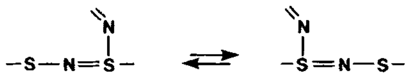
38a **106** (39)

B. 1,3-Nitrogen Shifts

1. Ring Expansion and Contraction Reactions

The addition reactions described in the previous section proceed with retention of the basic skeletal framework of the heterocyclic ring. The majority of reactions involving sulfur–nitrogen systems are not this straightforward. Indeed, the disconcerting tendency of sulfur nitrides to undergo major structural changes following seemingly simple reactions has always posed a daunting problem to synthetic chemists. Notable are the many reactions of S_4N_4 with nucleophiles [e.g., cyanide, azide and sulfide ions, amines, phosphines, diazomethanes (104, 105, 271–277)], which all result in cleavage of the S_4N_4 unit. Depending on the reagent involved, open chain, cyclic, and cage species can be formed; usually a mixture of products is generated and, in the absence of any fast spectroscopic probe, the observation and characterization of the reaction intermediates represents a difficult if not impossible task.

While there is certainly no single explanation for all of these complex multipath reactions, a recent ^{15}N and ^{31}P NMR study of the reactions of the heterocyclic derivative $PhCN_5S_3$ (**57**) with tertiary phosphines has provided strong evidence for a 1,3-nitrogen shift (Eq. 40) as a kinetically important pathway for structural reorganization (344).



$$-S-N=\overset{\overset{\diagdown\!\!\diagdown N}{|}}{S}- \rightleftharpoons -\overset{\overset{\diagdown\!\!\diagdown N}{|}}{S}=N-S- \qquad (40)$$

The sequence of events in the reaction of triphenylphosphine with **57** is summarized in Fig. 25, which shows the growth and decay of the ^{31}P NMR signals of the two intermediates generated prior to formation of the final product, the *endo*-substituted trithiatetrazocine **107**. As indicated in this figure, the dithiatriazine **108** is formed rapidly and specifically (even at 40°C). The subsequent step involves a 1,3-shift of an endocyclic nitrogen to produce the ring-expanded *exo*-trithiatetrazocine **109**. When triphenyl-

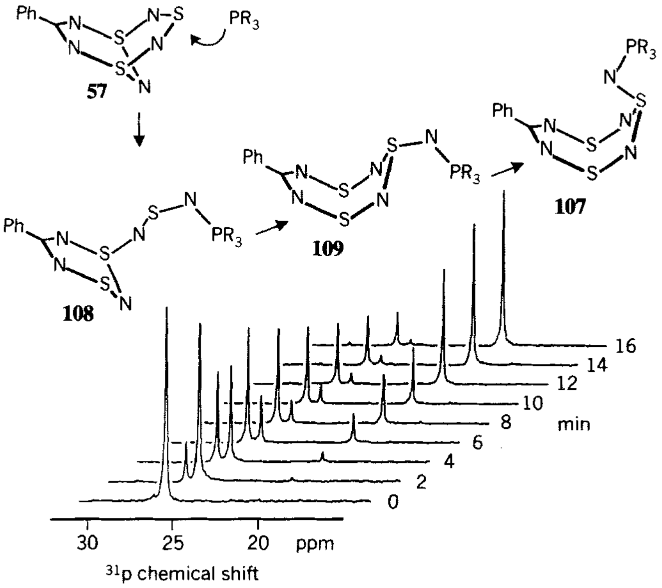
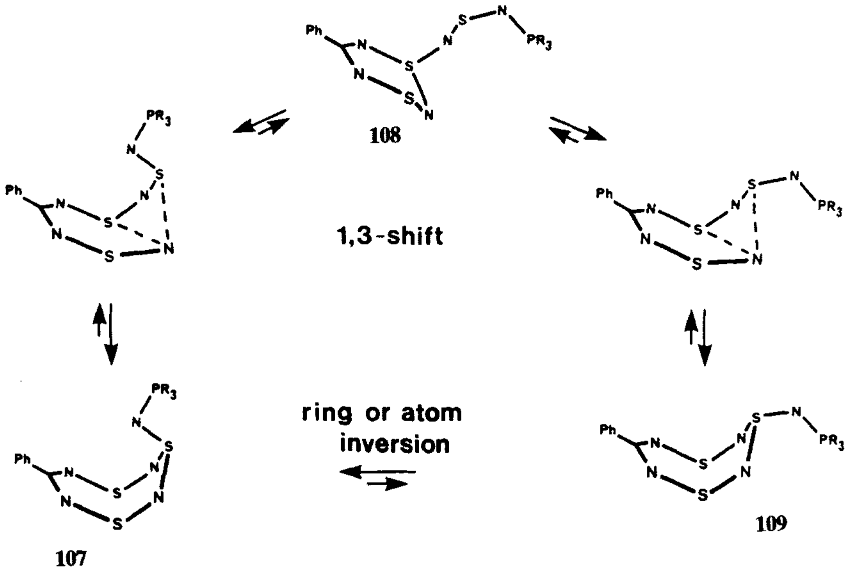


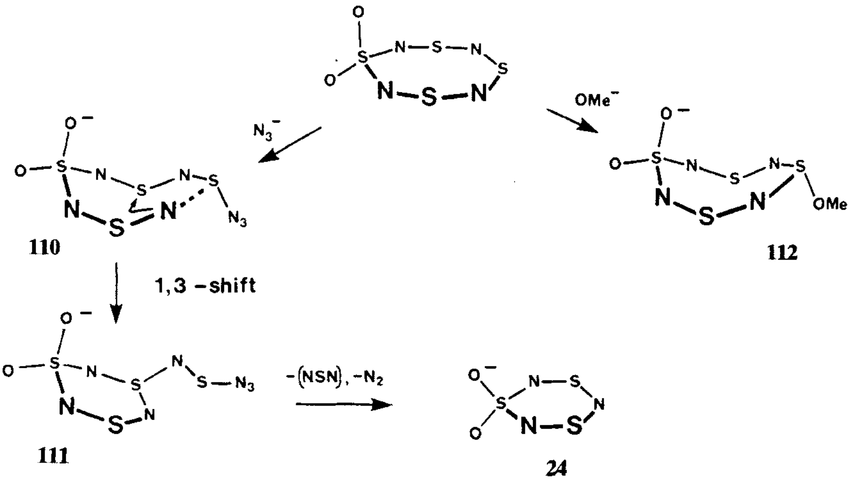
Figure 25. ^{31}P NMR spectrum of the reaction of triphenylphosphine with $PhCN_5S_3$ as a function of time in $CDCl_3$, at room temperature.



Scheme X

arsine is used in place of triphenylphosphine, this latter step is sufficiently slow to allow the isolation and structural characterization of the isomer of the arsenic equivalent to **109**. The conversion of the kinetically favored *exo* isomer **109** to the thermodynamically favored *endo* isomer **107** can, in principle, occur by two pathways (Scheme X), (a) an atom or ring inversion, and (b) a series of steps involving ring contraction of **109** to **108**, torsional reorientation of the exocyclic ligand, and reexpansion to **107**. In view of the high barriers expected for the inversion route, the 1,3-shift route is the favored mechanism for the isomerization (344).

Many other reactions involving ring size changes can be interpreted in these terms. The formation of $S_3N_3O_2^-$ (**24**) from the reaction of azide ion with $S_4N_4O_2$ (**66**) (131, 286b) provides a good example (Scheme XI). Accordingly the reaction begins with the attack of azide at sulfur to produce the tetrazocine derivative **110** (isoelectronic with **107** and **109**). A 1,3-nitrogen shift step then leads to the ring contracted species **111** (cf. **107**), which eliminates dinitrogen and NSN to afford $S_3N_3O_2^-$ (**24**). While there is no direct evidence for either **110** or **111**, the isolation of **112** from the reaction of $S_4N_4O_2$ with methoxide ion (285, 286) provides strong support for the intermediacy of **110**. A similar mechanism can be invoked for the conversion of S_4N_4 to $S_3N_3^-$ in the presence of azide ion (104, 105).

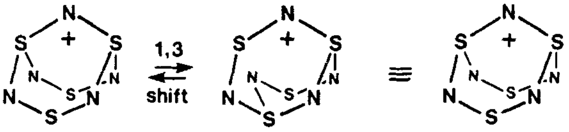


Scheme XI

2. *Degenerate and Pseudodegenerate Rearrangements*

The ring contraction and expansion reactions just described find an interesting parallel in the fluxional properties of some bicyclic systems.

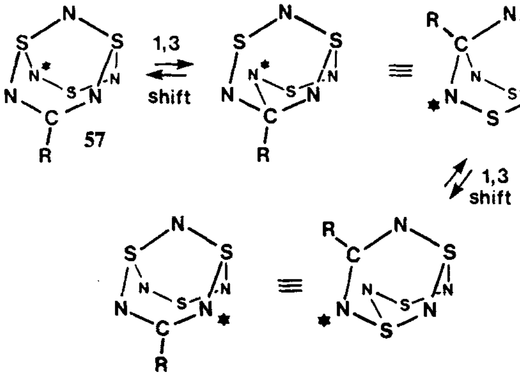
The idea for such skeletal rearrangements was first proposed in a theoretical paper by Bartetzko and Gleiter in 1980 (192). They suggested a series of degenerate 1,3 shifts as a mechanism by which all the nitrogen atoms of the $S_4N_5^+$ (**18**) cation could interconvert (Eq. 41).



18

(41)

Such behavior has recently been observed (282) in the bicyclic system **57**, which can be viewed as an isoelectronic derivative of the $S_4N_5^+$ cation in which an S^+ unit is replaced by a CPh group. Accordingly, when $PhCN_2^*N_3S_3$ ($^*N$ = 99% ^{15}N), prepared by the reaction of $PhC(NSiMe_3)N(SiMe_3)_2$ with $S_3^*N_3Cl_3$, is dissolved in chloroform at ambient temperatures a slow scrambling process (Scheme XII), involving a series of 1,3-nitrogen shifts, exchanges the different nitrogen sites, and results in the slow incorporation of ^{15}N nuclei into the carbon bound nitrogen positions. The progress of the reaction can be monitored by ^{15}N NMR spectroscopy (Fig. 26).



Scheme XII

The inorganic heterocycle $Ph_2PN_5S_3$ (**64**), in which the S^+ unit of $S_4N_5^+$ has been replaced by Ph_2P, does not undergo this 1,3 shift (282). Presumably such a pathway would be inhibited by the need to form a five coordinate phosphorus atom. Instead it thermally decomposes rapidly ($\Delta E^\ddagger$ = 25 kcal mol^{-1}) at or above room temperature with loss of the bridging NSN group, to form the phosphadithiatriazine $Ph_2PN_3S_2$ (**60**) (Eq. 24) (284).

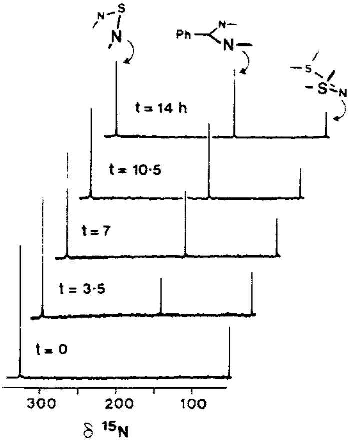


Figure 26. ^{15}N NMR spectrum of $Ph_2CN_2^*N_3S_3$ ($^*N$ = 99% ^{15}N) as a function of time in $CDCl_3$, at room temperature. The *t* = 0 spectrum was obtained at −40°C, where fluxional behavior is frozen out.

C. Aromatic and Antiaromatic Behavior

We noted in Section II.C.3 that the restricted number of binary sulfur–nitrogen ring systems precluded any experimental assessment of their relative aromatic or antiaromatic behavior. However, the wide range of heterocyclic organic and inorganic ring systems now available allows such comparisons to be contemplated.

The dithiatriazine derivatives EN_3S_2 (**43**, **60**, **24**) (E = RC, R_2P, SO_2^-), for example, are all prime examples of 8π-electron antiaromatic systems. The intense low energy π*–π* transitions (~550 nm) observed for $R_2PN_3S_2$ (**60**) and SO_2^- (**24**) are visual reminders of that fact. Satisfyingly, in the 10π-electron heterocycle $Ph_4P_2N_4S_2$ (**62**) the λ_{max} value shifts to a region (460 nm) more in keeping with an aromatic system; apparently conjugation is still present through *two* phosphorus (V) centers. Complementing this spectroscopic evidence is the observation that the addition of norbornadiene to **60** is faster ($\Delta E^{\ddagger}$ = 6 kcal mol^{-1}) than to **62** ($\Delta E^{\ddagger}$ = 11 kcal mol^{-1}) (279), as would be expected if the latter were more aromatic. Antiaromatic character is most fully developed in RCN_3S_2 (**43**) derivatives (see Section III.D.3); while the multiplicity of the ground state of such compounds is still open to question, their tendency to dimerize, for example, **98**, is a direct manifestation of their electron count. Similarly the kinetic resistance of RCN_5S_3 derivatives **57** to thermal degradation via loss of the bridging NSN unit reflects the inherent instability of the product that would be generated.

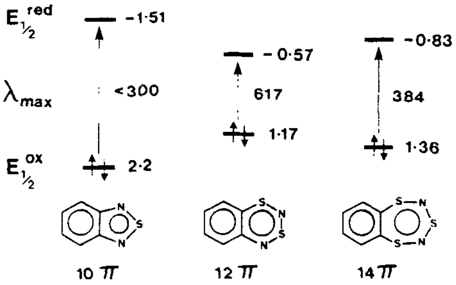


Figure 27. Trends in half-wave potentials (in V vs. SCE) and λ_{max} values (in nm) for benzo-2,1,3-thiadiazole, benzo-1,3,2,4-dithiadiazine, and benzo-1,3,5,2,4-trithiadiazepine.

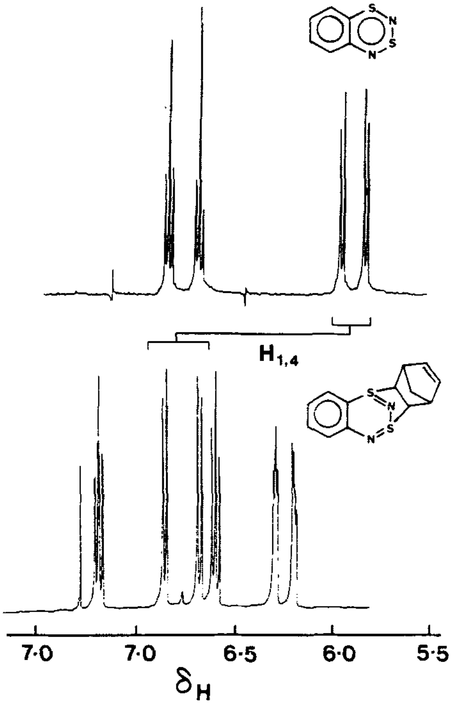
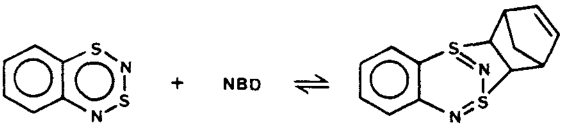


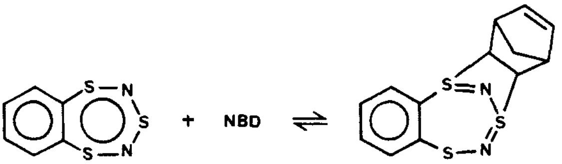
Figure 28. Aromatic region of the ^1H NMR spectra of benzo-1,3,2,4-dithiadiazine and its norbornadiene adduct (both in $CDCl_3$).

Similar physical and chemical trends are observed in the organic heterocycles shown in Fig. 27. Thus the antiaromatic 12π-electron benzodithiadiazine exhibits the lowest energy electronic absorption. Likewise the oxidation and reduction potentials of the three compounds follow the expected damped oscillatory trend. The antiaromatic electron count of **48** is also manifested in the strong paramagnetic shift experienced by the 1,4-ring protons (Fig. 28). Addition of norbornadiene to **48** (Eq. 42) destroys its antiaromatic electron count, and the chemical shifts of the 1,4 protons in **113** return to a region typical of a benzenoid aromatic (242).



48 **113**

(42)



51 **114**

(43)

The aromatic heterocycle benzotrithiadiazepine (**51**) also adds norbornadiene (Eq. 43), but the complex **114** dissociates more readily in solution than does **113**. Qualitatively the 14π-electron system **51** is more resistant to addition than the 12π-electron ring **48**. This concept can be quantified if we neglect the entropy changes in the two reactions (Eq. 42 and 43). Following the approach of Dewar (214) the equilibrium constants for Eqs. 42 and 43 can be converted, via Eq. **44**, into a *difference* in the delocalization energies of **48** and **51** of ~5 kcal mol^{-1}, a value that is quite in keeping with the differences in delocalization energies observed between classical aromatic and antiaromatic annulenes (of similar size to **48** and **51**).

$$-2.303RT \log \frac{K_{\mathrm{diss}}\,(\mathbf{113},\,\mathbf{48})}{K_{\mathrm{diss}}\,(\mathbf{114},\,\mathbf{51})} = \Delta E_{\mathrm{deloc}}\,(\mathbf{113},\,\mathbf{48}) - \Delta E_{\mathrm{deloc}}\,(\mathbf{114},\,\mathbf{51}) \qquad (44)$$

These arguments can be expanded to illustrate other analogies with organic chemistry. For example, just as benzene is more resistant to addition than naphthalene (214), so too is the monocyclic trithiadiazepine **40**

(R = H) itself relative to benzotrithiadiazepine **51**. The former fails to react at all with olefins, and undergoes a variety of simple aromatic electrophilic substitution reactions (244c, 249). Likewise the thermodynamic resistance of $Ph_2C_2N_4S_2$ (**38a**) to oxidation compared to the ease of oxidation of $(Me_2N)_2C_2N_4S_2$ (**38b**) parallels the classical differences between benzene and *p*-phenylenediamine.

V. CONCLUDING REMARKS

Much of what we know of the chemistry of binary sulfur–nitrogen compounds has been learned the hard way. The methods used for their preparation and interconversion were developed with patience and serendipity, but with little knowledge of the electronic factors that might influence thermodynamic or kinetic stability. Even now many fundamental issues remain unresolved. The observation that iodine oxidizes $S_3N_3^-$ to S_4N_4 (129, 130), for example, still represents a veritable Pandora's box for those who would venture a mechanistic interpretation. For that matter, the solid-state polymerization of S_2N_2 to $(SN)_x$ (42), the reaction that catalyzed much recent work, is far from completely understood. Nevertheless, while these and other questions still remain, the relationships between structure and reactivity are much clearer than they were a decade ago. The electron-rich skeletons of binary sulfur–nitrogen rings are structurally fragile. Their highly polarizable π systems are easily distorted by seemingly minor perturbations; small chemical modifications induce large structural changes. The chemistry of these compounds is dominated by the high electronegativities of sulfur and nitrogen. In many ways they resemble the heavier halogen atoms; they react with many nucleophiles and reducing agents, often with structural degradation, but interact more selectively with oxidants, acids, and electrophiles to afford stable cationic derivatives.

The development of heterocyclic thiazene chemistry has opened many new avenues of research. Recent studies on the redox properties of these heterocyclic systems has led to the characterization of a variety of stable π radicals. The different modes of self-association of these radicals, and the bimolecular rearrangements that they can undergo, are crucially important findings. Similarly, the recognition of an intramolecular mechanism for structural change, facilitating both ring expansions and contractions, represents a major advance in the understanding of kinetic and thermodynamic stability. Future experimental and theoretical studies, directed primarily towards the clarification of mechanisms and the characterization of transition states, will undoubtedly refine and quantify these ideas, and allow both the reinterpretation of old results and the prediction of new chemistry. The design of molecular and polymeric materials with specific uses, for example, as low-dimensional conductors, will hopefully follow.

From a pedagogical viewpoint the results obtained from the study of these inorganic rings provide an appealing demonstration of the generality of structure–reactivity principles in chemistry. Frontier orbitals, aromaticity, and delocalization energy were constructs developed to interpret organic phenomena. They appear to be equally useful in understanding inorganic chemistry, as they should be.

ABBREVIATIONS

CNDO	Complete Neglect of Differential Overlap
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
EHMO	Extended Hückel Molecular Orbital
ESR	Electron Spin Resonance
HFS	Hartree-Fock-Slater
HMO	Hückel Molecular Orbital
HOMO	Highest Occupied Molecular Orbital
INDO	Intermediate Neglect of Differential Overlap
LUMO	Lowest Unoccupied Molecular Orbital
MCD	Magnetic Circular Dichroism
MNDO	Modified Neglect of Diatomic Overlap
NMR	Nuclear Magnetic Resonance
SCF	Self-Consistent Field
SOMO	Singly Occupied Molecular Orbital
TCNQ	Tetracyanoquinodimethane
UV	Ultraviolet

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