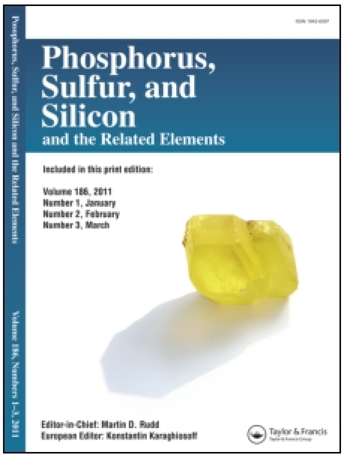

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ELECTRON-RICH THIAZENES: SOME PRINCIPLES OF SYNTHESIS AND STRUCTURE

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ELECTRON-RICH THIAZENES: SOME PRINCIPLES OF SYNTHESIS AND STRUCTURE†

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General methods of preparation and typical bond distances and bond angles (at sulfur and nitrogen) are reviewed for cyclic sulfur–nitrogen compounds. Correlations between sulfur–nitrogen bond distance and unstrained bond angles in SNS and NSN groups can be used to assess angular strain in 4 and 5 atom thiazene rings and the optimum ring geometries of larger thiazene cations such as $S_5N_5^+$ and $S_4N_4^{2+}$. The geometry of $S_3N_3^-$ is also discussed.

In this review we shall describe some recent work on the synthesis and structure of inorganic thiazenes (compounds containing S=N) with a view to showing how the results can be of value in other parts of nitrogen–heterocycle and sulfur–nitrogen chemistry.

During 1975 the most cited recent chemical papers[1] were concerned with the new metallic polymer polysulfur nitride[2] (see Figure 1)[3] and this exciting substance has stimulated a renaissance of interest in S–N compounds, especially those that are delocalized. In a recent review[4] we discussed some recent advances in the chemistry of each of the three main structural classes of cyclic sulfur–nitrogen compounds [summarized (1)–(3) below]. In this article we shall consider in more detail delocalized rings [type (3)], containing two-coordinate sulfur and nitrogen as in $(SN)_x$.

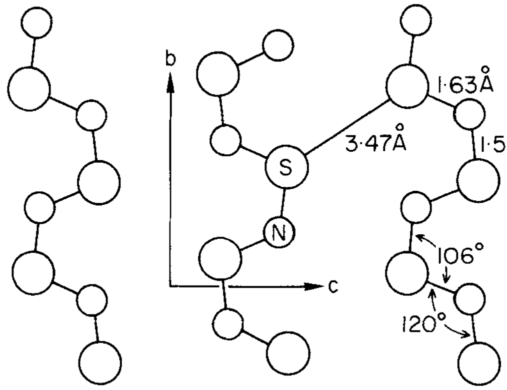


FIGURE 1 Chain structure of $(SN)_x$ projected onto (102) plane showing bond lengths and bond angles.

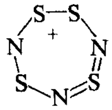
1) Sulfur imides [e.g. S_7NH and $S_6(NH)_2$] are structurally related to S_8 by replacing S by NH.

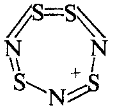
Much less is known about their oxidized analogues containing sulfur(IV) [e.g. $(SO{-}NH)_4$] or sulfur(VI) [e.g. $(SO_2{-}NR)_{3,4\,\mathrm{or}\,6}$]. The chemistry of the sulphur(IV) compound tetrathionylimide[5] is in particular need of further investigation; it could be a useful starting material for preparing derivatives $(SO.NR)_x$ (as yet unknown) and also perhaps sulfanuric halides $(NSOHal)_x$ by reaction with halogen.

2) The second class, with exocyclic bonds at sulfur, consists of chlorothiazines, $(NSCl)_3$ and $(NSOCl)_3$, and their derivatives.

The first of these, thiazyl chloride trimer,[6] has received much less attention than sulfanuric chloride.[7]

3) The third class of cyclic S–N compounds consists of delocalized species that are without organic or inorganic analogues. They are usually without exocyclic bonds. Such compounds can be rings (S_2N_2, $S_3N_2Cl^+$, S_4N_2, $S_4N_3^+$, $S_4N_4^{2+}$ and $S_5N_5^+$) or cages (S_4N_4, $S_4N_5^-$ and $S_4N_5O^-$). The rings have 4, 5, 7, 8 or 10 atoms and are planar or close to planar. Theoretical studies have shown that for these electron-rich thiazenes the number of bonding electrons exceeds that indicated by canonical structures;[8,9] for instance such structures would suggest a 6π or 8π rather than 10π system for $S_4N_3^+$:

(I)


(II)


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† Plenary lecture given at the Second Reunion of the First International Symposium on The Chemistry of Inorganic Heteroatom Ring Systems, Madrid, June 1977.

We shall now consider, with special reference to thiazenes: (1) synthetic procedures for sulfur–nitrogen compounds and (2) molecular shapes, i.e. can we (1) suggest a likely synthetic route to a required compound and (2) rationalize its geometry? Initially we shall see that several S–N preparations nicely illustrate some basic general principles of heterocyclic synthesis. Rationalizations of bonding and geometry are, of course, more difficult, though some simple empirical bonding rules have been proposed by Jolly.[10] In a recent issue of Chemical Communications, Gillespie[11] discussed the structure of $[S_4N_4]^{2+}$ and summed up the situation in these words. "It seems that we do not yet have a satisfactory description of the bonding in S–N systems."

We now turn to the first subject for consideration.

1. PRINCIPLES OF S–N SYNTHESIS

The synthetic routes to Main Group-nitrogen heterocycles can be summarized under three main headings (cf. Table I):

1) *Condensation reactions*, especially with elimination of hydrogen halide, elementary hydrogen or Me_3SiCl.

TABLE I

Synthetic routes to inorganic heterocycles containing nitrogen especially borazines and phosphazenes[a]

1. *Condensation* especially $N\text{-}\boxed{H\quad Cl}\text{-}X$			
i)	$NH_4Cl + BCl_3$	$\xrightarrow[130^\circ]{}$	$(H\underset{\vert}{N}-\underset{\vert}{B}Cl)_3 + HCl$
	$RNH_2 + R'BH_2$	$\longrightarrow$	$(RNBR') + H_2$ ("hydride route")
ii)	$NH_4Cl + PCl_5$	$\xrightarrow[150^\circ]{}$	$(\underset{\vert}{N}=\underset{\vert}{P}Cl_2)_n + HCl$
2. *Azide route to derivatives*			
i)	$Ph_2BCl + LiN_3$	$\xrightarrow[\text{room T}]{}$	$Ph_2B.N_3 \xrightarrow[100^\circ]{} (Ph\underset{\vert}{N}-\underset{\vert}{B}Ph)_3$
ii)	$R_2PCl + LiN_3$	$\xrightarrow[>\text{room T}]{}$	$R_2P.N_3 \longrightarrow (\underset{\vert}{N}=\underset{\vert}{P}R_2)_n$
3. *Nitride or amide + halogen*			
i)	BN inert		
ii)	PN (*or* P_3N_5) $+ Cl_2$	$\xrightarrow[500^\circ]{}$	$(NPCl_2)_n$, no practical importance
	$R_2PNH_2 + Cl_2$	$\longrightarrow$	$R_2PCl_2NH_2 \xrightarrow{R_3N} (R_2PN)_n$

[a] Data taken from Ref. 14.

2) *The azide route*, which involves the thermal rearrangement of an intermediate azide. A related phosphazene synthesis employs S_4N_4 (Eq. 1) rather than an alkali metal azide (Eq. 2)[12] as the labile source of nitrogen.[13]

$$PCl_3^{C_6H_6} + S_4N_4^{SOCl_2} \xrightarrow[\text{room temp.}]{2\text{ hr.}} (NPCl_2)_3 \tag{1}$$

$$\begin{aligned} Ph_2PCl + NaN_3 &\xrightarrow[165^\circ]{} Ph_2PN_3 \\ &\xrightarrow[220^\circ]{6\text{ hr.}} \frac{1}{n}(NPPh_2)_n + N_2 \end{aligned} \tag{2}$$

This approach could perhaps be used more for producing nitrogen heterocycles.

3) *Nitride or amide + halogen*. Boron nitride, being so inert, cannot be used for preparing BN heterocycles. Curiously there does not seem to be a borazine method from a boron amide or imide plus halogen.[14]

Sulfur–nitrogen heterocycles are made by each of these three routes (see Table II).

Table II also shows the three most important starting materials (S_4N_4, $S_3N_2Cl_2$ and $(NSCl)_3$) for making inorganic S–N compounds. At the foot of the Table there are two syntheses from sulfur imides. These are of no importance in pure S–N chemistry but variations on a related approach, viz.[15]

$$3S_4(NH)_4 + 4(NSCl)_3 \longrightarrow 6S_4N_4 + 12HCl \text{ (almost quantitative in } C_5H_5N) \tag{3}$$

might offer access to three-element rings

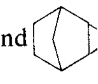
$$\left(\text{e.g. } {>}PCl + H{-}N{<}\substack{S-\\S-} \longrightarrow {>}P{-}N{<}\substack{S-\\S-}\right).$$

TABLE II

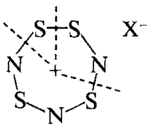
Synthetic routes to SN rings[a]

1. *Condensation*			
i)	$NH_3 + SCl_2$	$\longrightarrow$	S_4N_4
ii)	$NH_4Cl + S_2Cl_2$	$\longrightarrow$	$(NSCl)_3 \xrightarrow[(\text{from } S_2Cl_2)]{S} S_3N_2Cl_2$
2. *Azide route*			
i)	$S_2Cl_2 + LiN_3$	$\longrightarrow$	S_4N_4
ii)	$S_4N_4 + LiN_3$	$\longrightarrow$	$Li^+S_4N_5^-$
iii)	$PhSOCl + LiN_3$	$\xrightarrow[-40^\circ]{}$	$PhSON_3 \xrightarrow[0^\circ]{} (PhSON)_3$
3. *Nitride (or amide) + halogen*			
i)	$S_4N_4 + Cl_2$	$\longrightarrow$	$(NSCl)_3$
ii)	$(HNS)_4 + Cl_2$ *or* S_7NH	$\longrightarrow$	

[a] Data taken from Refs. 14 and 47.

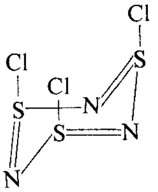
In addition to these three synthetic routes, there is a further useful principle in deducing S—N syntheses. This is that a possible synthesis can often be proposed from the structural components of the products.[4] Such "structural unit synthesis" is possible because of the variety of simple structural units that can be found in solution, for instance NS^+, NSCl, $NS^\bullet$ radicals and sulfur/nitrogen chains. Stability of sulfur/nitrogen cations, anions and even free radicals (e.g. $S_3N_2^+$,[16] and N—S•[17]) is a characteristic of sulfur/nitrogen chemistry.

Sometimes thermal decomposition indicates, in reverse, a feasible synthesis, for instance S_4N_3Cl:[18]

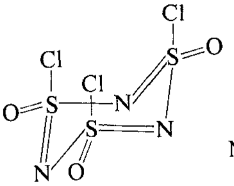


$$\longrightarrow \tfrac{1}{2}S_4N_4 + NSX + S \quad [X = Cl(120°C), Br(90°C)] \qquad (4)$$

Although such dissociation is a feature of sulfur(IV)-nitrogen rings, it is not the rule for sulfur(II) or sulfur(VI) rings, where destruction of S—N bonds frequently occurs, e.g. contrast the thermal decompositions (5)[19] and (6)[20]



$$\longrightarrow 3N{\equiv}S{-}Cl \quad (4\ \text{cm press., } 40°C) \qquad (5)$$



$$\xrightarrow{285°} N_2 + SO_2 + SOCl_2 + ---- \qquad (6)$$

We now turn to our second main topic—rationalizations of structure.

2 THE STOICHIOMETRY OF SULFUR-NITROGEN RING SYSTEMS CONTAINING 2-COORDINATE SULFUR AND NITROGEN

The stoichiometry of such species can be rationalized on the basis that nitrogen and sulfur atoms provide one and two π electrons respectively; the known planar or close to planar SN rings (except $S_3N_2^+$) are found to follow the Hückel rule thus:[4,9] S_2N_2 and $S_3N_2Cl^+$ (6π); $S_3N_3^-$ and $S_4N_3^+$ (10π); $S_4N_4^{2+}$ and $S_5N_5^+$ (14π). The least stable species are S_4N_2 (a red oil which decomposes rapidly at room temperature[21]) and $S_3N_3^-$ (several salts are known which explode on percussion or heating[22]). The most stable rings are those with five or more ring atoms and a high positive charge at sulfur; if *d* orbitals make a significant contribution to bond energies (still a matter of controversy, e.g. for S_2N_2[23]), then this is to be expected, for the sulfur atoms will contribute contracted lower energy 3*d* orbitals to the bonding M.O.'s.

This rationalization of stoichiometry and planarity, presented in 1972,[9] predicted several new species which were subsequently prepared (such as $S_3N_2^{2+}$ and $S_4N_4^{2+}$), but it gave no idea of the *degree* of stabilization associated with $4n + 2\pi$ electrons or the relative importance of other stabilizing factors (such as the absence of strain). The work discussed below provides some hint that lack of strain may be more important than "$4n + 2$ stabilization" in promoting ring stability.

3 RATIONALIZATIONS OF GEOMETRY FROM BOND DISTANCE/BOND ANGLE CORRELATIONS[24,25]

As described earlier,[4,9] the basic suppositions in our model of bonding in SN systems containing two-coordinate sulfur, are that it is legitimate to include sulfur 3*d* orbitals and that if these 3*d* orbitals are sufficiently stabilized so as to make a significant contribution to π bonding then they should be similarly available to receive in-plane donation from nitrogen lone pair electrons. This (3-centre) model suggests that the N angles and the mean NS distances should be interdependent in a series of similar S—N—S compounds. (A similar island model has been described earlier for cyclophosphazenes.[26])

Bond angles and distances for open chain SN compounds, and for other species that are largely free from angular strain, have been collected[4,24,25] and despite the variation in compound type, a plot of bond distance (d_{NS}) and bond angle (S—N—S) gives a smooth curve which (from a least squares treatment) approximates to a straight line (1).

$$d_{NS} = 180.0\,(\pm 1.5) - 0.160\,(\pm 0.012)\hat{N} \qquad (1)$$

The structural data[24,27] for line (1) have also been treated by a statistical method[30] which weights the points taking into account the errors in both d_{NS} and nitrogen bond angle. The method provides both the best straight line and the standard errors (in brackets) of the intercept and slope:

$$d_{\mathrm{NS}} = 177.46\ (\pm 0.87) - 0.1421\ (\pm 0.0068)\hat{\mathrm{N}} \qquad (2)$$

Most points (85%) lie within 2.0 esd's in bond distance of this best straight line; all points lie within 2.5 esd's. Standard errors are computed assuming that all deviations from linearity are due to errors in the structure determinations. This is not true in a few cases, for instance $(\mathrm{NSF})_4$ shows $\hat{\mathrm{N}}$ errors of only 0.14 esd's but the less flexible $(\mathrm{NSF})_3$ has $\hat{\mathrm{N}}$ errors of −2.35 esd's, giving some indication that in the trimer, ring nitrogen angles are compressed to lower values by angular strain. Thus although Eq. (2) gives a superior estimate of the best straight line, Eq. (1) gives a more valid assessment of the errors.

Extrapolation of (2) to linear $\mathrm{S{=}\overset{+}{N}{=}S}$ gives an anticipated $d_{\mathrm{N=S}}$ of 151.6 (±0.3) pm which compares well with the sulfur di-imide double bond distances (150.65 and 150.2 pm) found[31,32] in $\mathrm{Me_2Si(NSN)_2SiMe_2}$ and $\mathrm{MeSi(NSN)_3SiMe}$, and the SN double bond distance of 152.1 pm predicted by Nyburg[33] from a bond order/bond distance relationship. A distance of ~151 pm can only be regarded as "typical" for S=N, since even in linear SNS configurations some variations can be expected with changes in atomic charge distribution and in sulfur hybridization.

This agreement in values for $d_{\mathrm{N=S}}$ emphasizes the attraction and the danger in using such a relationship between d_{NS} and bond order. Since both σ and π M.O. energies can vary considerably, a bond distance close to 151 pm can still arise when the bond energy of a *lower* formal covalent bond order is augmented by σ and π polarity.

Returning to a consideration of line (1), the position of compounds at long d_{NS} is consistent with little or no donation into *d* orbitals. Points at short d_{NS}, e.g. from SN cations, correspond to significant donation into *d* orbitals. This is, of course, only a convenient simplified model which fits the known structural data; it does not constitute *proof* of lone pair donation into *d* orbitals. But it does indicate that bond strengthening is associated with electron drift from nitrogen and also, as a consequence, that perturbation at sulfur is likely. It is therefore not surprising that there is also a correlation, for acyclic compounds, between S—N distance and *sulfur* bond angle—with a main difference being that the sulfur angle changes by only 2.1° for each 1 pm change in S—N distance compared with 9.9° for the nitrogen angle.

Despite the variation in chemical type all points lie within 2.5 esd's of the best straight line computed by the method of Seheult and Roberts.[30]

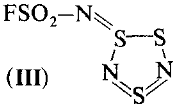
$$d_{\mathrm{SN}} = 212.7\ (\pm 2.1) - 0.478\ (\pm 0.019)\hat{\mathrm{S}} \qquad (3)$$

where d_{SN} is in pm. A simple least squares treatment of the same data gives Eq. (4). As for Eq. (1), errors in slope and intercept give a more accurate idea of the reliability of Eq. (4) [and indeed of Eq. (3)] for predictive purposes.

$$d_{\mathrm{SN}} = 211.3\ (\pm 4.5) - 0.466\ (\pm 0.039)\hat{\mathrm{S}} \qquad (4)$$

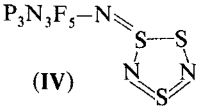
Line (3) highlights one glaring inconsistency. An electron diffraction study of $\mathrm{Me_2S(NH)_2}$ indicated[34] parameters (d_{SN} = 153 pm, $\mathrm{N\hat{S}N}$ = 135°) very different from the solid state.[35] They also give a point 4.8 pm above the line and so either the correlation breaks down for this compound or the electron diffraction results are in error (or both).

It has been found[24,25] for both nitrogen and sulfur angles that cyclic systems tend to give points (with respect to the line for acyclic species) at lower bond angles for a given distance. This is clearly due to ring strain, and is most marked for $\mathrm{S_2N_2}$ where the SN distance (165.4 pm)[36] corresponds (using Eqs. 2 and 3) to $\hat{\mathrm{S}}$ = 99.0 and $\hat{\mathrm{N}}$ = 84.9. The experimental values (X-ray: $\hat{\mathrm{S}}$ = 89.6°, $\hat{\mathrm{N}}$ = 90.4°) correspond to ~9° and ~5° strain at S and N respectively. The strain is also significant in five-membered rings [e.g. calculated as ~7° ($\mathrm{N\hat{S}N}$) and ~15° ($\mathrm{S\hat{N}S}$) strain in $\mathrm{S_3N_2^+}$; the structure is reported in Ref. 16]. Strain is probably important in determining the geometry (and reactivity†) of other $\mathrm{S_3N_2}$ rings, for instance in compounds (**III**) and (**IV**)[38] it may be the cause of long d_{SS} (for a delocalized ring) and smaller bond angles at the lowest sulfur atom than expected from the values of the adjacent SN distances.



(**III**)

$d_{\mathrm{SS}} = 220$ pm



(**IV**)

$d_{\mathrm{SS}} = 222$ pm

Unfortunately, highly delocalized six-to-ten-membered rings with two-coordinate sulfur ($\mathrm{S_4N_5^-}$,[39] $\mathrm{Ph_3PNS_3N_3}$,[40] $\mathrm{Ph_2AsNS_3N_3}$,[41] $\mathrm{S_4N_3^+}$,[42] $\mathrm{S_4N_4BF_3}$,[43] and $\mathrm{S_5N_5^+}$,[44,45]) give points which are too scattered to show a significant correlation and so are of no predictive value.

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† Thermochemical measurements have shown that the chief driving force for the rapid ring opening of five-membered sulfur heterocycles is ring strain.[37]

The above bond distance/bond angle correlations, which have been described in more detail elsewhere,[24,25] enable us to formulate new "rules" (Section 4) for rationalizing cyclic SN structures which up-date those due to Jolly.[10] Theoretical calculations[8] have shown that his Rule 2 (that 3-coordinate sulfur atoms cannot engage in $p\pi$–$p\pi$ bonding) is incorrect.

4 STRUCTURAL GUIDELINES FOR SULFUR–NITROGEN COMPOUNDS

1) Bond angles (NSN) at sulfur atoms usually lie between 95° and 125° depending upon (a) oxidation state ($S^{II} \approx 95°$–$100°$; 2-coordinate $S^{IV} \approx 120°$; $S^{VI} \approx 112$–$117°$) (b) coordination number (e.g. $N\hat{S}N$ for 3-coordinate sulfur has been found to be 101–108° in SN_3 systems and ≈112–114° in other XSN_2 systems) and (c) cyclic strain (which is affected by ring size and the nature of any third element in the SN ring). In sulfur–nitrogen anions of various types, $N\hat{S}N$ has been found at values between 106° and 114°.

2) Bond angles ($S\hat{N}S$) at nitrogen atoms usually lie between 115° and 129° for 3-coordinate N. Nitrogen angles vary widely (90°–150°) in systems with 2-coordinate N; in unstrained systems, $S\hat{N}S \approx 110°$–$130°$). Within the broad category of SNS^{IV} (one atom S^{IV} and $S\hat{N}S \approx 90°$–$155°$) strained Hückel species usually have $S\hat{N}S \approx 90°$–$122°$, but with re-entrant N angles at 136°–147°. In S^{VI} compounds $S\hat{N}S \approx 118°$–$121°$.

3) For unstrained NSN and largely unstrained SNS^{IV} systems there are, respectively the empirical relationships

$$d_{SN} = 212.7\ (\pm 2.1) - 0.478\ (\pm 0.019)\hat{S}$$

$$d_{SN} = 177.46\ (\pm 0.87) - 0.1421\ (\pm 0.0068)\hat{N}$$

The error limits given are lower bounds because the scatter of points is not due solely to experimental error; more realistic errors (given by least squares treatments) are about double these figures.

4) Sulfur–nitrogen species which obey the Hückel $4n + 2$ rule (where each N atom is taken to provide one π electron and each S atom two π electrons) are planar or close to planar except when distorted by steric strain. Rings can be regarded as Hückel analogues when a group which formally provides no π electrons but does not seriously interrupt the π system (e.g. $>SCl^+$, possibly $>S{=}O$ but not $>NR$) is inserted into a Hückel ring (e.g. $>SCl^+$ in S_2N_2 gives $S_3N_2Cl^+$). Non-Hückel rings (e.g. $S_3N_2^{+}$[16]) are not necessarily unstable. Extensive delocalization of π charge is also found in some acyclic systems (e.g. polythiazyl).

5) Lone pair *bonding* interactions (which can be regarded as donation into empty orbitals) are generally of greater structural importance than lone pair-lone pair *repulsions* between directly attached atoms [though lone pair repulsions can affect the preferred conformation, for instance of $(NSCl)_3$ and $S_3N_2O_2$]. Lone pair secondary interactions (bonding) between both adjacent and non-adjacent neighbours often affect bond distances, bond angles and the preferred conformation (e.g. of $S_5N_5^+$).

5 THE SHAPES OF $S_4N_3^+$, $S_5N_5^+$ and $S_4N_4^{2+}$

The correlations for unstrained species (Eqs. 2 and 3) are now used in predictions of ring geometry. As shown earlier these can be regarded as Hückel species (10, 14 and 10π electrons respectively) and so will tend to be planar with

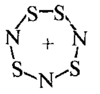
$$a\hat{S} + b\hat{N} = 180°\ (a + b - 2) \text{ where } a = \text{number of ring S atoms and } b = \text{number of ring N atoms} \quad (5)$$

If each ring is unstrained then Eqs. (2) and (3) also apply, and Eqs. (2), (3) and (5) can be combined (since $d_{NS} = d_{SN}$) to give a unique solution for $\hat{S}$, $\hat{N}$ and d_{SN}.

Table III shows values deduced in this way for $S_4N_3^+$. (In the absence of X-ray data on other de-

TABLE III

Calculated and experimental structural parameters for $S_4N_3^+$ and $S_4N_4^{2+}$

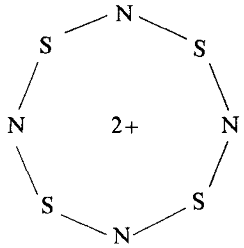
	Calc[a]	Found[b]
	$\hat{S} = 116.7(4)°$	$116.6(5)°$
	$\hat{N} = 144.4(6)°$	$144.4(7)°$
	$d_{SN} = 156.9(1)$ pm	$155.8(10)$ pm
	$d_{SS} = 206.5(2)$ pm	$206.6(4)$ pm
	$\hat{S} = 118.7(5)°$	$119.5°$
	$\hat{N} = 151.3(5)°$	$150.5°$
	$d_{SN} = 156.0(1.5)$ pm	154.5 pm

[a] Mean angles and distances were deduced using Eqs. (2), (3) and (5). Errors are lower limits; more realistic values are about double (see text).

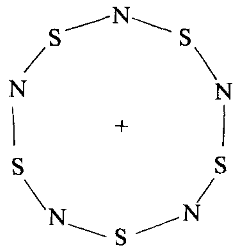
[b] Ring parameters for $S_4N_3^+$ are known with highest accuracy for $(S_4N_3)_2SbCl_5$: B. Kruss and M. L. Ziegler, *Z. anorg. Chem.* **388**, 158 (1972). The $\hat{S}$ given above is the mean of the experimental $N\hat{S}N$ and $S\hat{S}N$ for two crystallographically distinct cations. Errors are average values of the quoted esd's and so are upper estimates. Data for $S_4N_4^{2+}$ are for structure A, i.e. $[S_4N_4][SbF_5][Sb_3F_{14}]$, described in Ref. 10.

localized —N—S—S— compounds we have assumed that $N\hat{S}S = N\hat{S}N$)

For larger rings like $S_4N_4^{2+}$ and $S_5N_5^+$, bond angles are being forced out to high values:

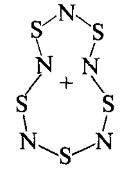


$S_4N_4^{2+}$

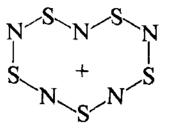


$S_5N_5^+$

but the strain can be alleviated by buckling (i.e. no longer planar) or by re-entrant atoms; in $S_5N_5^+$ it is the latter situation. As described earlier[4] we suggest that the apparent heart shape may arise from disorder and that this is most likely to occur with a highly symmetrical anion (**VI**).



(**V**) $S_3N_3O_4^-$ (Ref. 44)
$Cl_3POSnCl_5^-$ (Ref. 45)



(**VI**) $AlCl_4^-$ (Ref 46)

If the electric field at the cation sites is of high symmetry (due to high symmetry anions packed in a high symmetry anion sub-lattice) then one expects several close-energy orientations of the cation—particularly if there are no groups attached to the SN ring. The statistical average is then a spurious structure.

A probable shape for unstrained $S_4N_4^{2+}$ (Table III) can be calculated similarly. The predictions for $S_4N_4^{2+}$ compare well with the figures subsequently published by Gillespie, Slim and Tyrer[11] for one isomer. Again (as for $S_5N_5^+$) the high symmetry of the cation means that various types of disorder are

TABLE IV

Deduction of structures of some SN species

Compound	IR [and Ref.]			d_{SN} (pm) [1]		
		ν_{SN} (cm^{-1})	λ_{SN} (μm)		Expt.	Calc.
$CF_3N{=}SF_2$	[2]	1388	7.20	[3]	144.7(0.6)	143.8
$BrN{=}SF_2$	[4]	1215	8.23		—	148.6
$(H_2N{-}SO_3)K$	[5]	805	12.42	[6]	166.6(0.6)	168.2

Compound	IR [and Ref.]			d_{SN} (pm) [1]			$N\hat{S}N$ (°)	
		ν_{SN} (cm^{-1})	λ_{SN} (μm)		Expt.	Calc.	Expt.	Calc. [7]
$S(NSPh)_2$	[8]	1138 1087	8.99	[9]	152.9(0.5)	152.1	126.7(0.4)	127
$S(NI)_2$	[10]	1094 1047	9.34		—	153.7	—	123
$SF_2(NSF_5)_2$	[11]	1350 1280	7.60		—	145.6	—	140

[1] Experimental values (and esd's) are from x-ray structure determinations; calculated figures were obtained using the relationship:[14,47] $d_{SN} = 4.672\lambda_{SN} + 110.12$ pm where λ_{SN} (in microns) is the wavelength of the SN vibrational absorption or the mean of ν_s SN and ν_{as} SN for NSN compounds converted to wavelength.

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possible at the cation sites, and this has been observed.[11]

Very few other simple Hückel molecules and cations, containing similar numbers of sulfur and nitrogen atoms, remain to be prepared (perhaps $S_3N_3^{3+}$?); the simplest low-strain *anion* is $S_3N_3^-$. Unfortunately, there are no analogues of $S_3N_3^-$ to provide data for any firm deduction of the structure of this species.[22] However, sulfur bond angles for delocalized six-membered rings have been observed[25] at ~111.5–116.5° (with $d_{SN} \approx 155.5$–162.5 pm) and nitrogen angles for negatively charged species[24] are also below 120° (due to enhanced stereochemical activity of the nitrogen lone pair). Thus both angles will be strained out above the preferred angles (since planar $S_3N_3^-$ requires $\hat{S} + \hat{N} = 240°$) and there will be a tendency to buckling to reduce the strain. The published data ($d_{SN} = 160.0$ pm, $\hat{S} = 117.7°$, $\hat{N} = 123.2°$)[47] are consistent with this interpretation. It is interesting that, in its sensitivity to angular distortion, nitrogen appears to be "softer" than sulfur (we also noted earlier that for 1 pm change in distance, $\hat{N}$ changes 4–5 times more rapidly than $\hat{S}$).

Perhaps the use of distance/angle correlations can be used to predict and rationalize the geometries not only of sulfur–nitrogen species but also, for instance, of isoelectronic carbon–sulfur–nitrogen rings, e.g. analogues of the electron-rich Hückel cations $S_4N_3^+$ and $S_5N_5^+$; so far no such compounds are known.

Deduction of structural data from bond distance/bond angle correlations, as described above, is not confined just to cyclic species. There is for acyclic sulfur–nitrogen compounds a linear relationship,[4,48] based on data for 33 sulfur–nitrogen species, between SN distance and the wavelength of the SN vibrational absorption. Structures can then be deduced as shown in Table IV. In summary, one can see that correrelations between SN bond distance and $\hat{N}$, $\hat{S}$ and vibrational data allow useful deductions of structure. They can also be used to check if a hypothetical sulfur–nitrogen species is likely to be seriously destabilized by ring strain.

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