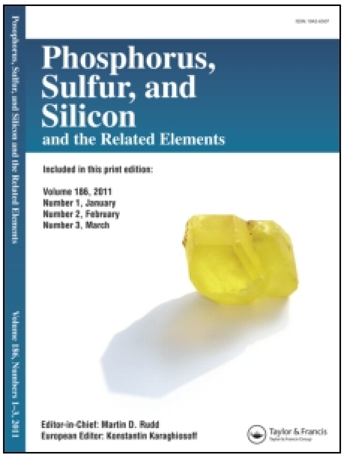

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CYCLIC SULFUR-NITROGEN COMPOUNDS

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CYCLIC SULFUR-NITROGEN COMPOUNDS†

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Recent studies of delocalized inorganic species containing a sulfur–nitrogen chain or ring are reviewed, and some general principles of structure and synthesis of cyclic thiazenes are discussed. Linear correlations between sulfur-nitrogen bond distance and (i) SNS bond angle and (ii) stretching wavelength are of value in deducing structural data for unstrained species.

The discovery of superconductivity in polymeric sulfur nitride, $(SN)_x$, has stimulated an enormous growth of interest in this first example of an inorganic covalent polymeric metal that contains no metal atoms. Polysulfur nitride shows many other properties of a metal such as high electrical conductivity (which increases with fall in temperature), high reflectivity of light and good thermal conductivity.[1] It is remarkable that the initial report[2] of the semiconductivity of this shiny gold-coloured material should have activated relatively little work before 1973 when Walatka, Labes and Perlstein[3] showed that single crystals have metallic conductivity down to 4.2 K. It is therefore a timely moment to survey recent advances in other parts of sulfur–nitrogen chemistry which also deal with electron delocalized systems (Table I). Perhaps other important and potentially useful thiazenes (i.e. species containing the unit S=N) also await some measure of "rediscovery".

In this review, we have two further aims. As recently as 1971, Professor W. L. Jolly rightly observed[4] that "during the last 15 years or so, this class of compounds has frustrated and mystified chemists, because structure determinations have often shown that structures which had been predicted, were wrong", so we also aim to show where some principles of synthesis and of structure are beginning to emerge.

TABLE I

Some examples of sulfur-nitrogen compounds containing π bonds

	A. Acyclic
Di-imides:	$S(=NR)_2$, $S(=N-SR)_2$, $R_2S(=NR)_2$
Polymeric:	$(SN)_x$
B. Cyclic, with organic and inorganic analogues	
S^{IV}:	$(NSX)_3$
S^{VI}:	$(NSOX)_3$ $(NSOF)_4$
	C. Cyclic, without analogues
Rings:	S_2N_2, $S_3N_2Cl^+$ $S_4N_3^+$, $S_5N_5^+$
Cages:	S_4N_4, $S_4N_5O^-$

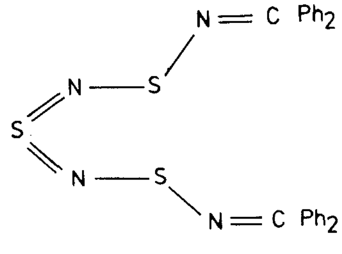
Sulfur–Nitrogen Chains

The relatively few chain compounds with two-coordinate sulfur (Table I) are conveniently prepared [Eqs. (**1**) and (**2**)] from tetrasulfur tetranitride[5] which is probably the most important starting material for synthetic S—N chemistry.

$$S_4N_4 + ArMgBr \rightarrow S(=N.SAr)_2 \qquad (1)$$

$$S_4N_4 + Ph_2CN_2 \rightarrow S(=N.S.N:CPh_2)_2 \qquad (2)$$

The central S_3N_2 portion of $S(NSPh)_2$ and of product (**2**), [structure (**3**)], is planar.[6]



(**3**)

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† Based on a plenary lecture given at the American Chemical Society's Centennial Symposium (Chemistry of Elemental Sulfur and its Binary Inorganic Compounds) in New York, April 1976.

TABLE II

Structural data for sulfur and sulfur imides[a]

d_{S-S} (Å) (atoms in 1:3 positions)	S_8 3.33	S_7NH 3.23	1,4-$S_6(NH)_2$ 3.01	$S_4(NH_4)$ 2.98	$S_4(NMe)_4$[b] 2.93
Ring N (°), mean	—	115.8	118.8	128.5	121.6
Ring S (°), mean	108.0	107.5	109.7	110.2	109.6

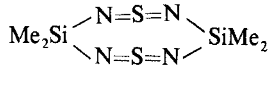
[a] Taken [except for $S_4(NMe)_4$[b]] from A. J. Banister, *Nature Phys. Sci.* **239**, 69 (1972).

[b] A. L. Macdonald and J. Trotter, *Canad. J. Chem.* **51**, 2504 (1973).

Other similar compounds $R_4S_3N_4$ have been found to be high sensitivity photoconductors for reusable electrophotographic plates,[7] and are also reported to be useful as pigments for electrophoretic imaging.[8] The diphenyl compound $S(=NSPh)_2$ decomposes in sunlight to give Ph_2S_2; this formation of disulfide is a potential source of instability in all such SN chain compounds. The short S/N chain sulfur di-imides $S(=NR)_2$ are rather more stable; particularly diaryl or *N*-sulfonyl-*N'*-aryl derivatives;[9] those with terminal Me_3Si or Me_3Sn groups (**4**) are useful reagents for heterocyclic synthesis, e.g.:[10]

$$4Me_3Sn.NMe_2 \xrightarrow[-2S(NMe_2)_2]{S_4N_4} 2S(N.SnMe_3)_2 \xrightarrow[-4Me_3SnCl]{2Me_2SiCl_2}$$

(**4**)



Cyclic Imides

Among the best-known cyclic sulfur–nitrogen compounds are the sulfur imides $S_{8-x}(NH)_x$; they are structurally related to S_8 by replacing sulfur atoms by NH groups and, as shown in Figure 1,

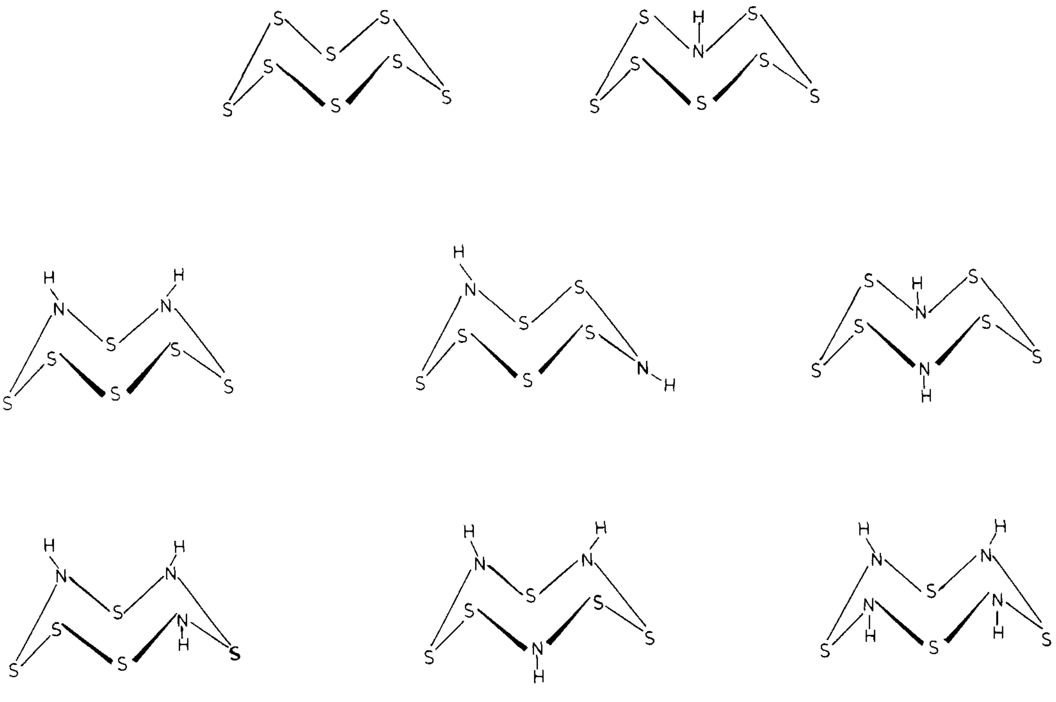


FIGURE 1 S_8 and the related sulfur imides.

TABLE III

Some examples of substitution reactions of sulfur imides

	Yield	Ref.
Condensation		
$S_7NH + RCOOH \xrightarrow[-H_2O]{} S_7N.COR$		(a)
$2S_7NH + SPCl_2 \xrightarrow[-2HCl]{} (S_7N)_2SO$	20%	(b)
Via metal salts		
$S_7NH \xrightarrow{KOH} S_7N^-K^+ \xrightarrow{CH_3I} S_7N.CH_3$	90%	(c)
$>NH \xrightarrow{NaH} >N^-Na^+ \xrightarrow{Ph_2P(S)Cl} > N.P(S)Ph_2$	80%	(d)
Via mercury derivatives[e]		
$>NH \xrightarrow{PhHgOAc} >N.HgPh. \xrightarrow[-PhHgCl]{X-Cl} >N.X$		
$X = Cl_2B, Me_3Sn, ClS$, etc.		(e)

[a] J. E. Colchester, P. Tavs and H. J. Schulze-Steinen, *J. Chem. Soc.* 4918 (1963).

[b] R. Steudel and F. Rose, *Z. Naturforsch., Teil B*, **30**, 810 (1975).

[c] M. H. Mendelsohn and W. L. Jolly, *J. Inorg. Nucl. Chem.* **35**, 95 (1973).

[d] J. M. Kanamueller, *J. Inorg. Nucl. Chem.* **36**, 3855 (1974).

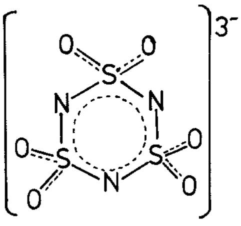
[e] H. G. Heal and R. J. Ramsay, *J. Inorg. Nucl. Chem.* **36**, 950 (1974).

they still retain the crown shape of S_8. Although these are formally "saturated" compounds with 3-coordinate nitrogen, the planarity or near planarity of the bonds at nitrogen is evidence of some electron delocalization, in which lone pair charge can be regarded as being donated into sulphur d orbitals or into some type of cage molecular orbitals. It is remarkable that, in $S_4(NH_4)$ and $S_4(NMe)_4$, an almost planar geometry survives even with four ring nitrogen atoms, all competing to reorganize their lone pairs. The contraction of the SN bonds and increasing nitrogen bond angle along the imide series (Table II) may well be caused, at least in part, by such nitrogen lone pair donation. Support for this conclusion is also provided by the poor Lewis basicity of the imides.

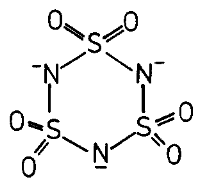
Derivatives of cyclic imides (Table III) are best prepared by condensation reactions (e.g. elimination of acid), or via alkali metal salts or heavy metal derivatives particularly PhHg compounds. Similar substitution procedures can be applied to the related metal "hydrothionitrosyls", e.g. $Ni(HN_2S_2)_2$.[11]

Very little is known about the sulfur (IV) analogues, thionyl imides $(SONR)_x$. There has been no confirmation of the report[12] that $(SNH)_4$ is oxidized in air at 110–120°C to give an air and water stable red crystalline tetramer $(SONH)_4$. Spectra (ir and uv) but no reactions were described (except slow polymerization at room temperature). The monomers RNSO are well known.[13] Like isoelectronic SO_2 they have not been found to polymerize. This contrasts with sulfuryl imides $RNSO_2$ which, like isoelectronic SO_3, polymerize readily.[14] Thus the thermal stability of cyclic thionyl imides may well prove inferior to that of the analogous cyclic sulfuryl imides.

Although the sulfur (VI) imides $(SO_2NR)_x$ contain formally saturated ring bonds, their anions $(SO_2N^-)_{3,4}$ are delocalized, structure I:

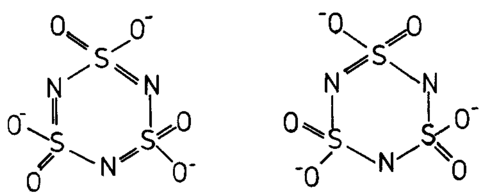


I



II

(5)



III

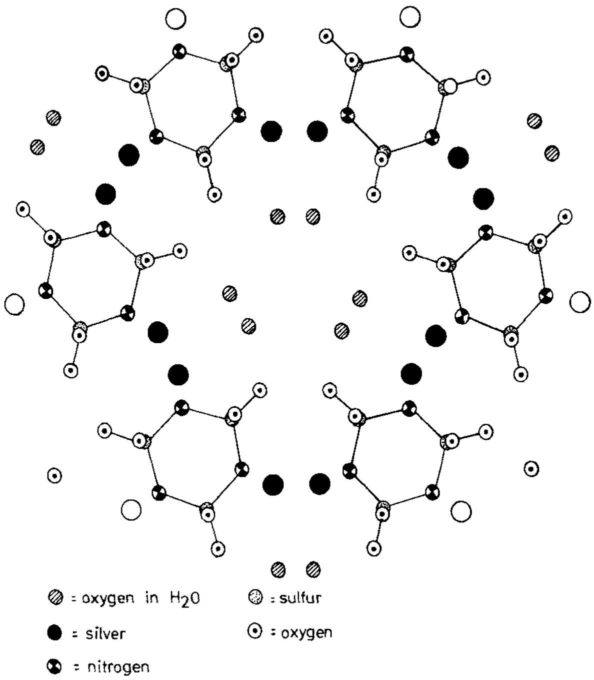


FIGURE 2 Structure of $(AgNSO_2.H_2O)_3$[15]

In $(SO_2NAg.H_2O)_3$ the geometry of the anion [which is formally both a trisulfimide (II) and a sulfanurate (III) anion] is about half way between the geometries expected for the two forms II and III.[15] The solid state structure is composed of zig-zag chains of interacting silver atoms (only 0.1 Å further apart than in silver metal) sandwiched between an array of trisulfimide rings which surround channels of water molecules—as in zeolites. Thus the silver salt is an unusual type of inclusion compound with hydrate water in the guest space (Figure 2).

The structural relationship between the trisulfimide and sulfanurate anions has an interesting consequence. Trisulfimide salts should, in principle, be convertible into sulfanuric fluoride or chloride as their respective acid halides.

The chemistry of cyclosulfimides has been relatively little studied even though some of the compounds have quite remarkable stability. For instance,[16] on heating the ammonium salt $(NH_4NSO_2)_3$ for 2 h with $LiOH.H_2O$ at 180°, it is merely converted to the lithium salt—and in over 80% yield!

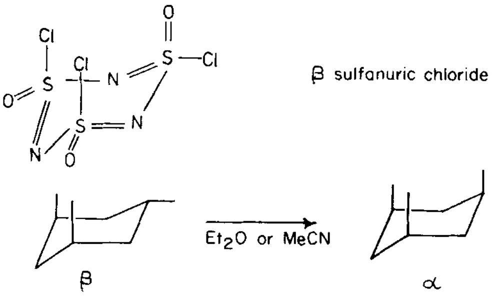
The Thiazenes (NSCl)$_3$ and (NSOCl)$_3$, and Their Derivatives

Unsaturated SN rings (i.e. thiazenes containing alternate sulfur and two coordinate nitrogen) are of two types (i) with exocyclic group(s) at S and (ii) without exocyclic groups. Compounds of the first type are sulfur analogues of cyanuric chloride $(NCCl)_3$; indeed $(NSOCl)_3$ was named sulfanuric chloride because of similarities in structure and physical properties to $(NCCl)_3$.[17]

Sulfanuric chemistry has been reviewed in detail elsewhere.[18] The stability of derivatives is comparable with that of cyclophosphazenes [$(NSOF)_3$ and $(NPF_2)_3$ are isoelectronic]. A major difference is that the chloride $(NSOCl)_3$ is much more sensitive to external donors than the chlorocyclophosphazenes. For instance, sulfanuric chloride forms a range of liquid adducts with donor molecules based on nitrogen or phosphorus, e.g. $(L.NSOCl)_3$ where L = C_5H_5N, Me_3N or Ph_3P.[19,20] The triphenylphosphine adduct (a viscous red oil) is liquid even though its molecular weight exceeds 500. Infrared spectra indicate that the intermolecular interactions, which are presumably responsible for the viscous oily nature of these adducts, may include unusually strong C–H hydrogen bonding.

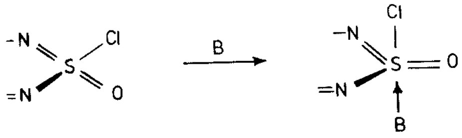
It is interesting that the sulfur (VI) site in sulfanuric compounds is such a good acceptor (cf. SO_3) that its Lewis acidity can be compared with that of boron. Irrespective of the ratio of reactants, the ring accepts three molecules of pyridine, like its boron analogue $(HNBCl)_3$, but with the difference that the BN adduct is an ionic solid whereas the SN adduct is liquid.

The formation of sulfanuric chloride adducts is important in the following two respects. First, it shows why amino derivatives are rarely obtained in good yields on reacting with primary or secondary amines [yields are much better using $(NSOF)_3$]. Transient adducts of $(NSOCl)_3$ are probably formed but, since amine adducts are very sensitive to hydrolysis and aminolysis, ring fusion quickly follows. Secondly, it sheds light on the isomerization of *β*-sulfanuric chloride to the *α* form which occurs in *polar* solvents. In this reaction (**6**), an equatorial chlorine becomes axial:

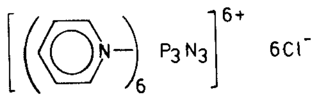


(**6**)

It has been suggested[21] that an intermediate 1:1 adduct is formed but if one looks at the stereochemistry at each sulfur atom in the adduct it can be seen that this does not facilitate exchange of the oxygen and chlorine atoms; ionization (or less likely a transient 2:1 adduct) is necessary. Similar ionization has been proposed for the pyridine adduct of $(NPCl_2)_3$, where each phosphorus atom carries two coordinated pyridine molecules (**8**).[22]



(7)

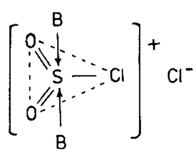


(**8**)

The strong Lewis acidity of sulfanuric chloride was an indication that isoelectronic sulfuryl chloride, which has no potentially donor atoms attached,

(**9**)

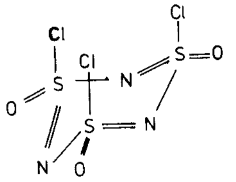
should be an even better acceptor than $(NSOCl)_3$. This proved to be the case; adducts $[(C_5H_5N)_2.SO_2Cl_2$; $(Et_3N)_2SO_2Cl_2$ and $Ph_3P.SO_2Cl_2]$ were readily obtained with nitrogen and phosphorus bases. Triphenylarsine and triphenylstibine were however converted to their dichlorides.[23] Nitrogen bases formed 2:1 adducts.[20] Since a covalent 2:1 adduct would require six coordinate sulfur and additional π bonding to two oxygen atoms, an ionic structure (**10**) is likely:



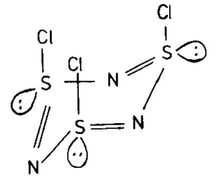
(**10**)

Thiazyl Chloride Trimer, $(NSCl)_3$

Despite the structural similarities between sulfanuric chloride (**11**) and its sulfur (IV) analogue, trichlorocyclotrithiatriazene, (**12**), their properties are markedly different; for instance the latter ring is even more sensitive to strong donors and to protic hydrogen, e.g.:



(**11**)



(**12**)

$$(NSCl)_3 + C_5H_5N \rightarrow (C_5H_5N)_2S_2Cl_2{}^{24} \quad (13)$$

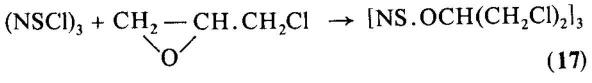
$$(NSCl)_3 + R_2NH \rightarrow RN{=}S{=}NR \quad (14)$$

$$R{=}SC_6F_5,{}^{25}\ SiMe_3{}^{26}$$

$$(NSCl)_3 + S_7NH \rightarrow S_4N_2{}^{26} \quad (15)$$

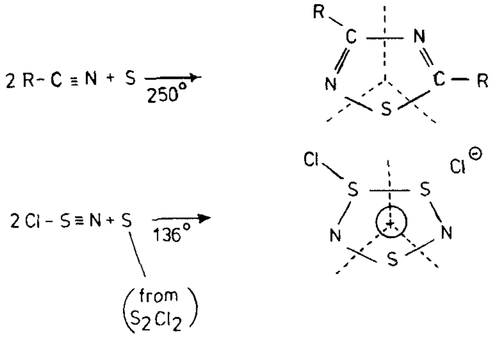
$$\begin{array}{l} (NSCl)_3 + LiN{=}CPh_2 \rightarrow (NS.N{=}CPh_2)_3 \\ \qquad\qquad\qquad\qquad \downarrow \text{decomp. } (-N_2) \\ \qquad\qquad\qquad\qquad (SN{=}CPh_2)_2{}^{24} \end{array} \quad (16)$$

To preserve the ring in $(NSCl)_3$ reactions it is advisable to avoid temperatures in excess of 40–50°C when dissociation begins to occur. The yellow solution in carbon tetrachloride turns a vivid mint green above ~55°C due to the formation of thiazyl chloride monomer and other, as yet unidentified, dissociation products.[27] For these reasons (and by analogy with sulfenyl chlorides[28]) reactions with oxiranes (epoxides) were investigated and gave the first trithiatriazene derivatives (e.g. **17**).[5,29] Thiazyl chloride trimer was first prepared in 1896; it is one of the easiest sulfur–nitrogen syntheses[30] and yet after 80 years this is, as yet, the only method of obtaining stable derivatives.



$$(NSCl)_3 + \underbrace{CH_2 - CH}_{O}.CH_2Cl \rightarrow [NS.OCH(CH_2Cl)_2]_3 \quad (17)$$

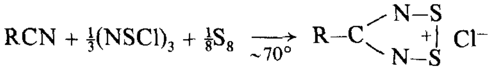
But perhaps the most important aspect of thiazyl chloride chemistry is its use for heterocyclic synthesis where it can behave as a sulfur analogue of a cyanide; for instance, one can compare the preparation of 1,2,4-thiadiazoles (**18**)[31] and $S_3N_2Cl_2$ (**19**):[30]



(**18**)

(**19**)

Instead of taking two moles of a CN compound and slotting in one S atom, or two moles of an SN compound and slotting in one S atom, one mole of each was taken, and one mole of S, to give high yields of a cationic CN_2S_2 aromatic system:



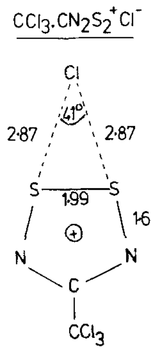
$$RCN + \tfrac{1}{3}(NSCl)_3 + \tfrac{1}{8}S_8 \xrightarrow[\sim 70^\circ]{} R-C\begin{matrix}N-S\\ +|\\ N-S\end{matrix}\ Cl^- \qquad (20)$$

1,2,3,5-dithiadiazolium salt

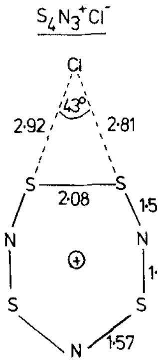
Another potentially aromatic CN_2S_2 ring (**21**) has been described by Roesky:[32]

(**21**)

The crystal structure (**22**)[33] of the trichloromethyl 1,2,3,5-dithiadiazolium derivative $[Cl_3C.CN_2S_2]Cl$ shows remarkably strong halogen-bridge bonding similar to that found in several organic 1,2-dithiolium halides.[34] The thermal parameters, which are about the same for the ring atoms and the chlorine, are consistent with such a strong interaction. Normally ionic chlorine vibrates much more than ring atoms. A similar chloride-bridge has been found[33] in $S_4N_3^+Cl^-$ shown in structure (**23**) above and so sulfur/sulfur/halogen three-centre interactions appear to be a common feature of both organic and inorganic 1,2-dithiolium halides.



(**22**)



(**23**)

Referring back to the synthesis of 1,2,3,5-dithiadiazolium chlorides [Eq. (**20**)] from a nitrile, NSCl and sulphur, this illustrates a useful principle in synthetic SN chemistry—that single-stage syntheses can often be deduced from the structural units of the product, even if these units cannot be isolated themselves (Table IV). A good example of this principle is provided by the preparation of $S_5N_5^+$ salts.

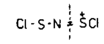
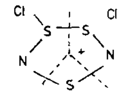
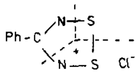
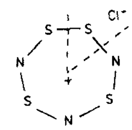
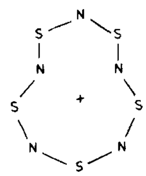
These were first prepared from S_4N_4 adducts.[35] It was hoped that the SN fragments formed during the decomposition of S_4N_4 in $SOCl_2$ [reaction (**24**)],

$$S_4N_4 + SOCl_2 \longrightarrow S_4N_3Cl + S(NSO)_2 + SCl_2 \qquad \textbf{(24)}$$

$$S_4N_4 + MCl_3 + SOCl_2 \longrightarrow \begin{cases}[S_3N_2Cl]MCl_4,\\ [S_4N_3]MCl_4, + S(NSO)_2\\ [S_5N_5]MCl_4,\end{cases} \textbf{(25)}$$

TABLE IV

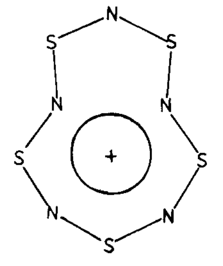
Structural Unit Syntheses

(1)[a]	$N(SCl)_2^+$		$\frac{1}{3}(NSCl)_3 + SCl_2 + BCl_3$
(2)[b]	$[S_3N_2Cl]Cl$		$\frac{2}{3}(NSCl)_3 + S$
(3)[c]	$[PhCN_2S_2]Cl$		$PhCN + \frac{1}{3}(NSCl)_3 + S$
(4)[d]	$[S_4N_3]Cl$		$\frac{3}{4}S_4N_4 + \frac{1}{2}S_2Cl_2$
(5)[e]	$S_5N_5^+$		$S_4N_4 + NS^+$

References (a) O. Glemser and J. Wegener, *Inorg. Nucl. Chem. Letters*, **7**, 623 (1971). (b) In the preparation of $S_2N_2Cl_2$ described in Ref. (d), S_2Cl_2 acts as the source of sulfur. (c) G. G. Alange, A. J. Banister, B. Bell and P. W. Millen, *Inorg. Nucl. Chem. Letters*, **13**, 143 (1977). (d) W. L. Jolly and K. D. Maguire, *Inorg. Syn.* **9**, 102 (1967). (e) A. J. Banister and H. G. Clarke, *Inorg. Syn.* **17**, 188 (1977).

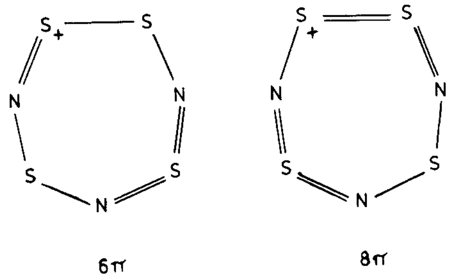
might be trapped by Lewis acids to give, ultimately, new SN species. Reaction (**25**) was carried out for several metal halides but difficulties in separation were least when M = Fe, Al, Ga and In. In each case the products were isolated at the end of up to six recrystallizations from thionyl chloride. At each recrystallization the air-sensitive crystals were hand-sorted in a dry box with the aid of a hand lens. Optimizing the conditions of synthesis and purification so as to isolate the three types of products took several months. One of these product types contained a new cation $S_5N_5^+$. The most likely reaction mechanism seemed to be that free S_4N_4 coordinated to the NS^+ produced as a reaction intermediate, and the $S_5N_5^+$ formed after rearrangement was stabilized in the crystal by an anion (MCl_4^-) of compatible size. A *direct* synthesis, also in thionyl chloride solution [Eq. (**26**)], was attempted and gave the same $S_5N_5^+$ salts in about 80% yields. Pure materials could be obtained in one afternoon[36] instead of the week or so required by the optimized S_4N_4-adduct method. Crystal structure determinations were carried out on $[S_5N_5]AlCl_4$ (with a heart-shaped cation) and on a chlorostannate $[S_5N_5][Cl_3PO.SnCl_5]$.[37] In the latter case the cation had a shape similar to that of azulene (**27**). This geometry has also been reported for the compound $[S_5N_5][S_3N_3O_4]$.[38]

$$S_4N_4 + \tfrac{1}{3}(NSCl)_3 + MCl_3 = [S_5N_5]MCl_4; \quad M = Fe, Al. \qquad (\mathbf{26})$$



(**27**)

The $S_4N_4/SOCl_2/MCl_3$ method for obtaining $S_5N_5^+$ salts posed a problem: why, for each metal M, should three apparently unrelated SN cations ($S_3N_2Cl^+$, $S_4N_3^+$ and $S_5N_5^+$) be formed simultaneously in a single reaction? Was there a mechanistic reason for this or perhaps a common *structural* factor? Table I shows some of the main types of cyclic sulfur-nitrogen rings. The three SN cations above belong to that small class of species which are without organic or inorganic analogues and cannot be represented adequately by the usual V.B. structures (Table I*C*). In 1972, neither their structures nor even their stoichiometries had been rationalized. No one knew, for instance, if (say) S_3N_2 or $S_3N_2^{2+}$ should be preparable. There was even disagreement over the bonding in $S_4N_3^+$, the best known of these species. Friedman[39] had concluded that the UV spectrum of $S_4N_3^+$ is consistent with a "10π system conjugated throughout the entire ring, though limited in extent across the SS bond; each sulfur atom donates 2π electrons and the 3d orbitals of sulfur undoubtedly participate in bonding". Later,[40] an all valence electron SCF MO treatment in conjunction with ESCA measurements confirmed that $S_4N_3^+$ is a 10π system. This π count emphasizes how misleading are the simple V.B. canonical structures; they inevitably represent some sulfur atoms as divalent and the π total is then 6 or 8:



(**28**)

The π count found (10 electrons) does not include the extensive in-plane contributions from what classically would be regarded as lone pair electrons on nitrogen and sulfur.

The SCF calculation[40] showed that the other two cations formed in the $S_4N_4/SOCl_2/MCl_3$ reactions (viz. $S_3N_2Cl^+$, 6π and $S_5N_5^+$, 14π) can also be regarded as being aromatic. Support for the aromaticity of $S_5N_5^+$ was also provided by an interpretation of uv/visible spectra.[41]

So in summary, theoretical calculations by three sets of workers, supported by ESCA and electronic spectra indicated that the connection between $S_3N_2Cl^+$, $S_4N_3^+$ and $S_5N_5^+$ (but assuming that this has a heart-shape rather than the azulene shape) is their aromaticity.

In each case, 6, 10, or 14π electrons can be calculated just from the formulae—one π electron per N atom, two π electrons per S atom and using the 4n + 2 rule suggestions can be made as to possible new species (e.g. $S_3N_3^-$ and species with RC replacing N). Species containing NN bonds (in parenthesis in Table V) may not be isolable because such bonds would interrupt "hands over the

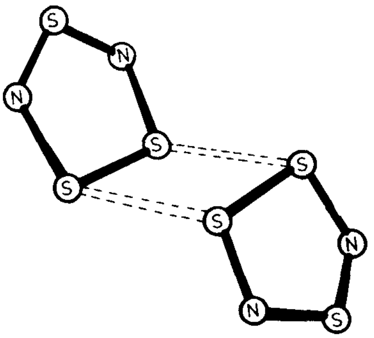
TABLE V

π Electron counts for SN species

No. of N atoms	No. of S atoms 2.	3.	4.	5.
2.	$\underline{S_2N_2}$ (6π)	$\underline{S_3N_2}^{2+}$ (6π)	$\underline{S_4N_2}$ (10π)	Weakly contracted d orbitals
3.	($S_2N_3^+$)	$\underline{S_3N_3}^-$ (10π)	$\underline{S_4N_3}^+$ (10π)	
4.		(S_3N_4)	$\underline{S_4N_4}^{2+}$ (10π)	S_5N_4
5.	Explosive?			$\underline{S_5N_5}^+$ (14π)

nitrogen" d_π–d_π overlap between sulfur atoms and would probably introduce greater kinetic instability. The SCF calculations indicated that a significant positive charge at sulfur (due to cation charge and/or S/N ratio approaching one) may well be an important source of stabilization in these compounds; note in this connection that S_4N_2 is an *unstable* red oil.[42] Consequently, low-nitrogen species, except cations, are also omitted. By the same token high charge anions, even when unstrained, are not expected to have high stability; however this destabilization can be offset by choosing counter ions of suitable shape and size (as found for $S_5N_5^+$) and by introducing exocyclic oxygen to carry much of the charge [cf. $(NSO_2)_3^{3-}$].

When the electron counting approach is used for "predicting" the stoichiometry of new species it does, of course, have definite limitations. The method says nothing about the *degree* of stabilization associated with (4n + 2) π electrons, it ignores destabilization due to ring strain and it also ignores the effects of competing stabilization energies. For instance, it gives no hint of the remarkable stability of the stable free radical cation $S_3N_2^+$ (in the hexafluoroarsenate[43] or of its association in pairs (**29**) in the chlorodisulfate.[44] These are the first new S_3N_2X compounds since the discovery[45] of S_3N_2Cl in 1880.



(**29**)

We now turn to another aspect of the problem of rationalizing SN structures.

Bond Angle–Bond Distance Correlations in SN Compounds

Wide variations in bond angle at two-coordinate nitrogen is a well-known feature in cyclophosphazenes (particularly in the flexible tetramers and larger rings) and in the classical approach this is generally rationalized[46] by taking into account two systems of delocalization (π_s, *in* the ring plane, and π_a perpendicular to the ring). A similar approach can be adopted for sulfur–nitrogen compounds. As illustrated in Figure 3, the nitrogen lone pair can donate into the $d_{x^2-y^2}$ and d_{xy} orbitals on the neighbouring sulfur atoms giving (because of the nodes at sulfur) three centre islands of π_s charge. It is therefore likely that the effect of lone pair donation would be mostly felt by the two *adjacent* NS bonds. As nitrogen lone pair donation increases, its stereochemical activity diminishes (so that $S\hat{N}S$ opens out) and strengthening of the adjacent NS bonds arises from two factors. First, the sulfur d orbital lobes overlap more effectively with the N lone pair hybrid and, secondly, the change in hybridization at nitrogen (increasing s character $sp^2 \rightarrow sp$) strengthens both the σ and π_s components.

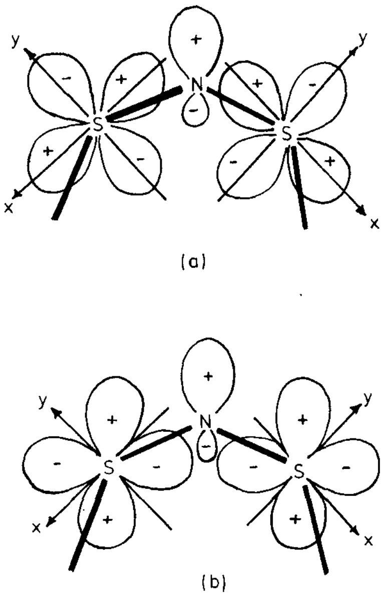


FIGURE 3 (a) Overlap of sulfur $d_{x^2-y^2}$ orbital with nitrogen lone pair. (b) Overlap of sulfur d_{xy} orbital with nitrogen lone pair.

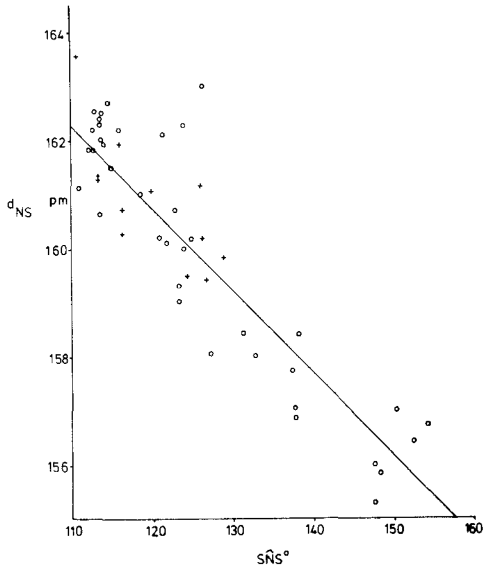


FIGURE 4 Nitrogen–sulfur distance/nitrogen bond angle for S—N—S^{IV} species ($d_{NS} = 179.99 - 0.1599\hat{N}$).

Figure 4 shows the correlation between $S\hat{N}S$ and the mean (d_{NS}) of the two NS distances for quite a wide variety of S—N—S^{IV} compounds where there appears to be little or no angular strain.[47] Deviation from this relationship can be expected for small rings (e.g. S_2N_2) where ring strain results in smaller angles. Also bonds are shortened and angles are less if all the sulfur atoms are in the +6 oxidation state. Angles are again less if the nitrogen lone pair points into the ring. Thirdly in negatively charged cyclic species such as $S_4N_5^-$ and $(NSO_2)_3^{3-}$, negative nitrogen results in reduced π bonding and hence long d_{SN}. The six membered rings in these anions are unable to accommodate the associated small $S\hat{N}S$ and so there is some angular strain.

Without these special cases, unstrained and largely unstrained species give points which (as determined by a least squares treatment) fall on a curve which deviates very little from the best straight line:[47]

$$d_{NS} = 179.99 - 0.1599\hat{N} \qquad \text{(I)}$$

Distances are in pm and angles are in degrees. The correlation coefficient (—0.87) is rather low but all 65 points lie within 3.5 esd's of the line. There are four compounds which give points which deviate markedly from this line. These are $\beta(SN)_x$, $S(NSO)_2$, $[N(SCl)_2]^+$ and heart shaped $[S_5N_5]^+$. It is hardly surprising that $\beta(SN)_x$ with large standard deviations (estimated at about 8 pm in distance and 5° in angles)[48] should give a point well off the line. The more recent x-ray study[49] of $\alpha(SN)_x$ gives a point only 0.2 pm from line I. Both $S(NSO)_2$ and $[N(SCl)_2]^+$ are chain species and should therefore be largely unstrained. No esd's were quoted and so perhaps the structural data are in error.

It has been found for the cation in $[S_5N_5]AlCl_4$ that the reported atomic positions and (to a large extent) the temperature factors can be simulated from a disordered arrangement[50] and so this structure determination may also be in error.

Line I, relating bond distance and nitrogen bond angle is not only a useful check on known structural data, it can also be used in conjunction with other correlations for predicting molecular shapes. For many types of sulfur nitrogen species it has been found that[51]

$$d_{SN} = 4.672\,\lambda_{SN} + 110.12 \quad \text{Corr. coeff.} = +0.989 \qquad \text{(II)}$$

where d_{SN} is the SN distance (in pm) and λ_{SN} is the SN stretching wavelength (in μm). A similar relationship has been found by Steudel *et al.*[52] Correlation II (with 22 points) shows that the S—N bond vibration is remarkably insensitive to the nature of the groups attached at sulfur and nitrogen, since the deviation from the straight line (except for compounds with methyl groups at sulfur) is generally less than 2 pm.

For NSN compounds, a correlation (42 points) has been found[51] between the ν_{asym} and ν_{sym} NSN stretching frequencies (in cm^{-1}):

$$\nu_{asym} = 1.51\,\nu_{sym} - 73.1 \quad \text{Corr. coeff.} = -0.975 \qquad \text{(III)}$$

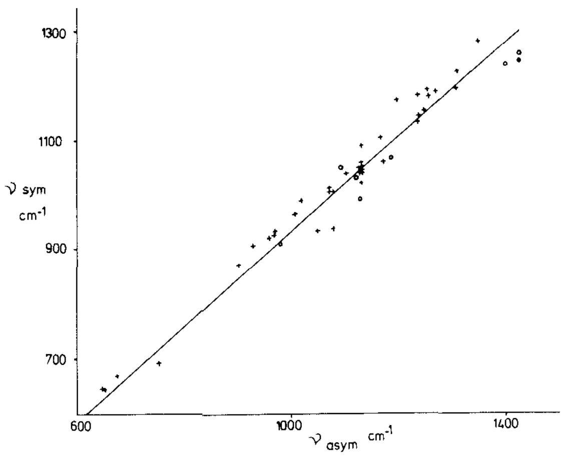
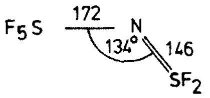


FIGURE 5 Linear relationship between ν_{asym} and γ_{sym} stretching frequencies for NSN compounds.

and this assists in locating the SN stretching vibrations and hence deducing the mean stretching frequency needed (as wavelength) in Eq. (II). Figure 5 includes points based on published assignments (crosses) and also a few points (circles) based on assignments deduced using the $\nu_{\text{asym}}/\nu_{\text{sym}}$ relationship.

Thus, with the aid of Eqs. (II) and (III), ir data for SN compounds can be used to estimate d_{SN}; and in the case of S—N—S compounds, this value can be inserted into Eq. (I) to estimate the nitrogen bond angle. The following data [structure (**30**)] illustrate the method (the distance in pm and the angle are deduced from $\nu_{SN} = 1320$ and $760\ \text{cm}^{-1}$ (Ref. 52) using Eqs. (I) and (II):



(**30**)

Earlier in this article, Professor Jolly's comment was quoted in which he observed that the rationalization of the structures of sulfur–nitrogen compounds had frustrated and mystified chemists for many years. Now, we are in the more fortunate position that important principles of structure and synthesis are being recognized and these should facilitate new syntheses and the emergence of new technological applications for sulfur–nitrogen compounds.

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