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CYCLIC SULFUR–NITROGEN COMPOUNDS

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I. Introduction

In the following article an attempt has been made to bring together recent data on cyclic sulfur–nitrogen compounds. The major sections of the review are organized on the basis of ring size. Within each section the versatility of the sulfur–nitrogen compounds is simplified by using coordination numbers. In other words, the focal point is the sulfur atom which can be classified on the basis of the number of surrounding substituents. In addition, the coordination numbers two and three at the nitrogen atoms will also be taken in account for the ordering principle. Finally, sulfur–nitrogen compounds which contain one other element will be discussed in each section. The numerous reports, wherein three- or four-membered rings are formulated as intermediates, will not be considered.

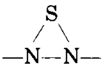
The literature has been surveyed up to the end of 1977. In many cases, the examples cited are meant to be representative and indicative rather than to be all-inclusive. In general, for the cohesion of this article the alphabetical order was used for writing the formulas.

II. Three-Membered Rings

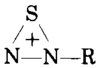
As stated in the introduction, the sulfur–nitrogen rings are classified according to the groups directly bonded to the sulfur atom. Thus, the coordination of the sulfur atom will be a reflection of the number of substituents rather than of the various oxidation states of sulfur.

There are 13 possible arrangements of sulfur with coordination numbers two, three, and four, which are shown in Table I. The sulfur ring compounds may contain these building blocks.

Three-membered rings with bivalent sulfur have so far not been reported. Several theoretical arrangements are possible [see structures



(I)



(II)

(III)

(I)–(III)]. Although the oxygen analog of (I) has been isolated (*96*, *110*, *239*), the repulsion between lone-pair electrons is probably the reason for the instability of these three-membered rings. On paper we would

TABLE I

ARRANGEMENTS OF SULFUR WITH COORDINATION NUMBERS TWO, THREE, AND FOUR

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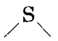
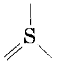
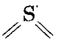
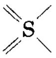
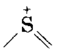
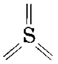
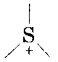
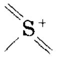
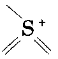
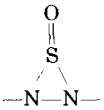
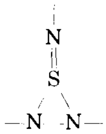
		
		
		
		
		
		

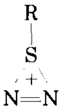
expect that compounds of types (IV) and (V) might be more stable, but they are not mentioned in the literature *(230)*.



(IV)



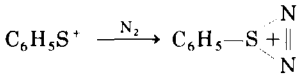
(V)



(VI)

Compound (V) presents a real challenge for the synthetic chemist. The groups attached to the nitrogens should have strong electron-withdrawing properties, so that the interaction of the lone pairs will be diminished.

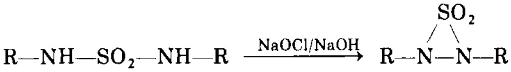
It was reported that the benzenesulfenium cation adds molecular nitrogen to form a cyclic adduct of type (VI) (*177*). Whether the



$$C_6H_5S^+ \xrightarrow{N_2} C_6H_5{-}S^{+}\langle N{\equiv}N \rangle \quad (1)$$

nitrogen forms a side-on or end-on adduct was not shown with certainty.

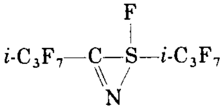
In the dioxide (VII) the sulfur extends its coordination number to four (*46a, 187b*).



(VII) (2)

Dioxide (VII) is prepared from the diamide with sodium hydroxide (*63, 245*) and hypochlorite. The structure was determined on the basis of an X-ray analysis (*248*). It is interesting to point out that the increasing size of substituents R is responsible for the stability of (VII). This observation is significant and could prove to be general and extremely useful for synthesis of other small ring systems. The R groups are in the trans configuration. This was found with ^1H NMR as well as by crystallography. The N—N bond (167 pm) is significantly longer than any analogous distance (for example, 147 pm in H_2NNH_2) and is, in fact, bracketed between the value for hydrazine and 175 pm found for the admittedly lengthened N—N bond in N_2O_4 (*2*).

When $CF_3N{=}SF_2$ and perfluoropropene were allowed to react at 83°C for 115 hours at autogenous pressure, a 4% yield of the three-membered compound,



which boiled at 75.5°C, was found (*117*). An analogous compound was isolated, when $CF_3CF{=}CF_2$ and $C_3F_7N{=}SF_2$ were allowed to react at 100°C in the presence of cesium fluoride (*58*). No structural proof is given for these two compounds.

III. Description of Sulfur–Nitrogen Compounds with Coordination Number Two at the Sulfur and Nitrogen Atoms

In the periodic table nitrogen and sulfur are located in a diagonal position. Therefore the ratio of radius to charge for both elements is nearly the same. As a result, the polar character of the S—N— bond is low and the electronegativity difference is small. These criteria are fulfilled for a S—N bond under the assumption that sulfur and nitrogen both have a coordination number of two. If we assume that only p electrons are involved, we can ignore the electronegativity difference between sulfur and nitrogen. The calculations for electronegativities by Hinze and Jaffé (*112*) gave for both elements the same value of 2.28 for the p electrons. In the application of simple Hückel molecular orbital (MO) theory, we treat SN rings as though they were homonuclear. The effect of this approximation is to assign nonbonding character to some orbitals, which otherwise would be weakly bonding (*80*). Johnson, Blyholder, and Cordes (*118*) concluded from Hückel MO calculations that the electronic spectrum of $N_3S_4^+$ is consistent with a 10-π-electron system. This suggests that in addition to the σ-framework electrons and the lone-pair electrons each sulfur atom provides two π electrons and each nitrogen provides one π electron. In cyclic S—N systems with coordination number two, the Hückel $4n + 2$ rule can be applied. A planar structure with delocalized bonding is favored when n, the number of π electrons, is 2, 6, 10, or 14. The method is justified by its simplicity, the agreement with valence bond formulation, and its success in structure correlation.

IV. Four-Membered Rings

A. DOUBLY COORDINATED SULFUR

The simplest known sulfur–nitrogen ring compound is N_2S_2 (*54*, *162*). It was shown by X-ray analysis that the molecule has a square-planar configuration with nearly equal S—N bond lengths. N_2S_2 is isoelectronic with S_4^{2+}. According to simple Hückel MO theory, the bonding properties can be described in the following way, that the molecule has one pair of bonding π electrons, 4 electrons are in nonbonding orbitals, and the π^* orbital is unoccupied.

The square-planar configuration with D_{4h} symmetry for the S_4^{2+} cation is lowered to D_{2h} symmetry for N_2S_2 (Fig. 1). According to MO theory, the molecule has only one pair of bonding π electrons. This is in agreement with a valence bond description (*78*, *119*, *237*).

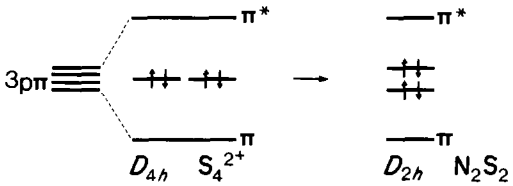


FIG. 1. Splitting of the four $3p\pi$ atomic orbitals.

On the other hand the structure of N_2S_2 can be compared with cyclobutadiene, but having two filled, instead of two half-filled, π nonbonding degenerate molecular orbitals (Fig. 2).

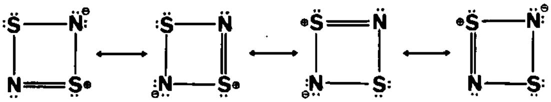
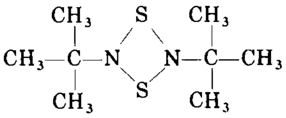


FIG. 2. Resonance structures for N_2S_2.

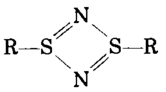
Further support for these bonding properties can be drawn from the structures of $N_2S_2(SbCl_5)_2$ and $N_2S_2BCl_3$. As a result, there is no appreciable lengthening of the S—N bonds (*180*). $N_2S_2(SbCl_5)_2$ and $N_2S_2SbCl_5$ are formed from N_2S_2 and $SbCl_5$ (*178*). The hitherto unknown $N_2S_2{}^{2+}$ is isoelectronic with P_4; whether, by analogy, it has a planar or tetrahedral structure, is an interesting question.

A nitrogen-substituted four-membered ring was obtained as a product of the reaction between *tert*-$BuNH_2$ and SCl_2 in diethyl ether (*51*). It was claimed that compounds of this type are useful fungicides and inhibitors for corrosion.



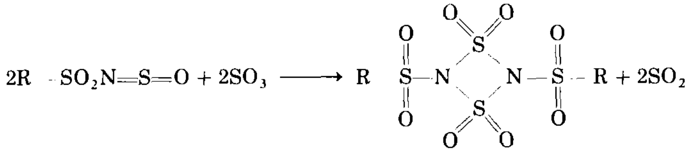
B. THREE- AND FOUR-COORDINATED SULFUR

A short report claimed that $(CF_3S)_3N$ reacts under UV irradiation to give traces of $(CF_3SN)_2$ (*38*). An analogous compound was found by the reaction of $S_3N_3F_3$ with $CF_3CF{=}CF_2$ (*84*). The cyclic structure for these compounds was assigned on the basis of physical measurements.



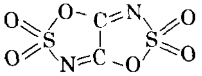
$R = CF_3, (CF_3)_2CF—$

It was found that $FSO_2N{=}S{=}O$ and $CF_3SO_2N{=}S{=}O$ react with SO_3 with formation of SO_2 to give a stable four-membered ring (*197*, *229*).



R = F, CF_3

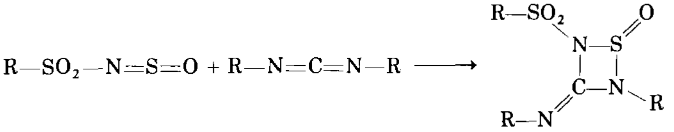
The monomer species R—SO_2NSO_2 could be stablized with pyridine or N_4S_4 with formation of the 1:1 adducts. When the ring is treated with C_6H_5CN, a new six-membered ring is formed, containing two nitrile and one NSO_2 group. Cyanogen and SO_3 give a bicyclic ring when allowed to react in a ratio of 1:2 (*196*).



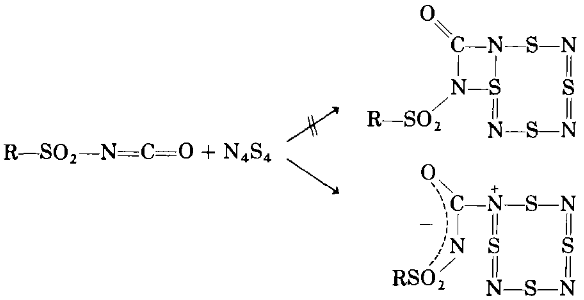
It is not a Lewis-acid Lewis-base adduct as stated earlier (*133b*), but it was found that $(CN)_2$ and SO_3 undergo a crisscross cycloaddition.

C. Four-Membered Rings Containing One Element Other Than Sulfur and Nitrogen

There are several papers that claim that four-membered rings are formed by the addition of iminosulfuroxides, isocyanates, ketene-imides, or phosphorus imides to S—N multiple bonds (*11*, *131*, *163*, *164*).



(3)



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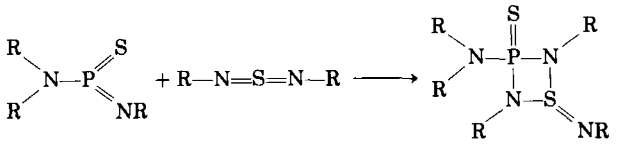
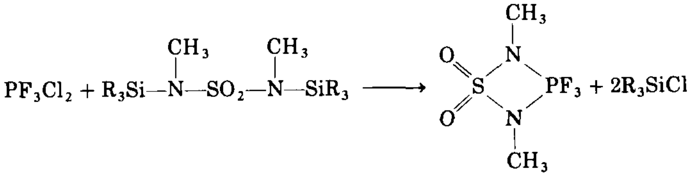


(5)

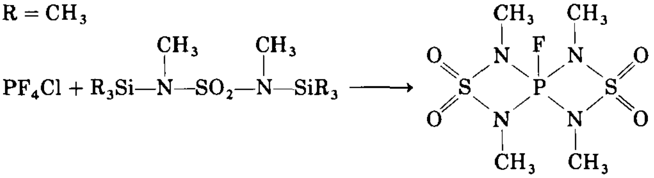
In all cases it was not shown whether cyclic compounds or zwitterionic species are formed. For the adduct of FSO_2NCO with N_4S_4 it was proved by an X-ray structure analysis that a dipolar cycloaddition did not occur, but a dipolar structure was observed, in which the carbon of the isocyanate group coordinates to a nitrogen atom of the N_4S_4 skeleton (*195*).

Becke-Goehring and co-workers have synthesized a number of four-membered rings with four-coordinated sulfur, which are summarized in Eqs. (6)–(10) (*35*, *36*).



(6)

$R = CH_3$



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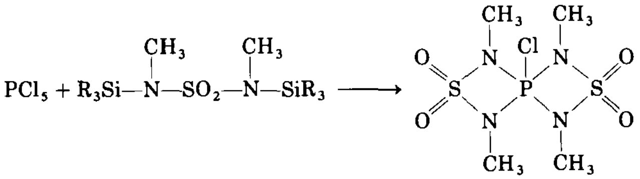

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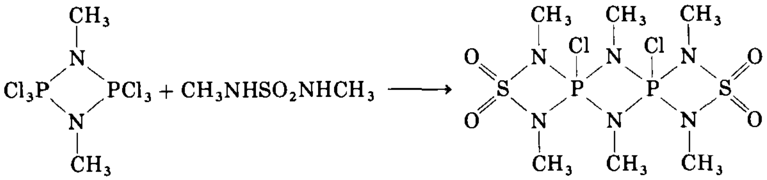

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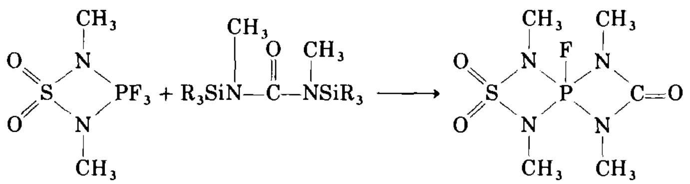
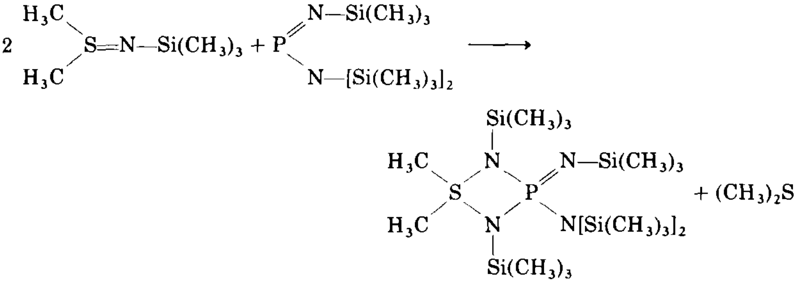
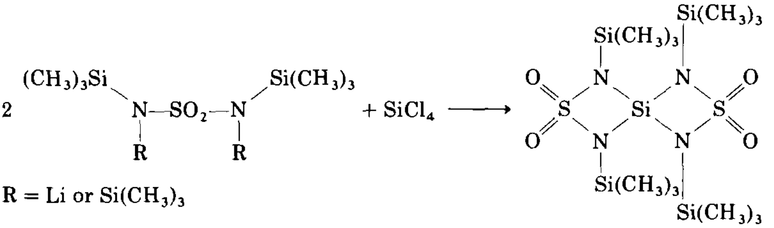

(10)

A condensation of iminosulfone and amino-iminophosphane results


(11)

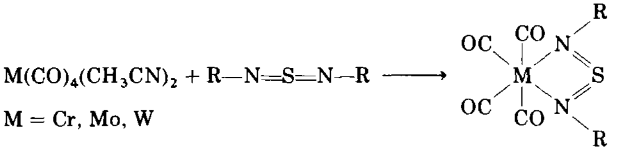
in the formation of a dimethyl sulfur-substituted four-membered ring, which is also obtained by the reaction of $[(CH_3)_3Si]_2N—P[NSi(CH_3)_3]_2$ with $(CH_3)_2S{=}NSi(CH_3)_3$ (*9*).

A spiro silazane has been obtained by the following reaction (*10*).


R = Li or $Si(CH_3)_3$

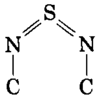
(12)

The reaction of carbonyls with sulfur diimides leads to metal containing four-membered rings (*140*, *155*).

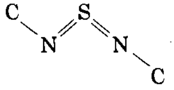

M = Cr, Mo, W

(13)

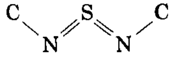
The sulfur diimides function as bidentate ligands. The structure of sulfur diimides has been a matter of dispute, because three possible planar conformations of the CNSNC skeleton may occur.



cis–cis



trans–cis



trans–trans

X-Ray data for bis(*p*-tolyl)sulfur diimide have shown this compound to have the trans–cis form in the solid state, and complete neglect of differential overlap (CNDO) calculations on similar compounds also lead to the conclusion that this conformation is the most stable one (*98*, *133*). From the NMR and other results the most plausible structure for the above metal complexes involves a *trans–trans*-sulfur diimide bonded to the $M(CO)_4$ fragment.

V. Five-Membered Rings

A. Radical Cations

At this point, it is necessary to survey the reactions of radical cations that have been studied. Working with sulfur–nitrogen compounds it was found that the reactions take place with formation of radicals.

The intensive change in color during the reactions may be caused by radical formation or solvatochromie (*37*). In 1962 Chapman and Massey observed a radical cation (*47*) when they treated N_4S_4 with concentrated sulfuric acid, which they supposed to be N_2S^+. Later Jolly and co-workers and other workers (*11*, *147*, *154*) found on the basis of electron spin resonance (ESR) measurements that the species was more probably $N_2S_2{}^+$ with a square-planar structure. According to the acid concentration proton-containing radicals were also detected. It is well known that strong acids such as FSO_3H or CF_3SO_3H easily form carbenium ions. This method cannot be applied in the sulfur–nitrogen field because the nitrogen will be protonated under these conditions. Therefore, we used the corresponding anhydrides, and, in fact, the reactions occur according to the following equation (*205*).

$$CF_3SO_2OSO_2CF_3 + N_4S_4 \rightarrow N_2S_3{}^+CF_3SO_3{}^- + CF_3SO_2N_3S_3 \qquad (14)$$

$N_2S_3{}^+CF_3SO_3{}^-$ can be isolated in high yield. It is a black-brown crystalline solid that is very sensitive to oxygen. ESR measurements gave a spectrum of five lines with an intensity ratio of 1:2:3:2:1 and a separation of 3.15 G. This spectrum is consistent with a radical containing two equivalent nitrogen atoms and is clearly the same spectrum as that obtained from the solution of N_4S_4 in sulfuric acid and from a solution of N_4S_4 in SbF_5. However, the X-ray structural investigations (*77*, *126*) clearly demonstrated that the hitherto recognized $N_2S_2{}^+$ radical is in reality the $N_2S_3{}^+$ radical.

Gillespie and co-workers (*77*) have shown that N_4S_4 is oxidized by AsF_5 and leads to the formation of $N_2S_3{}^+AsF_6{}^-$ in small quantities. The $N_2S_3{}^+$ radical is unusual in that it is a stable radical ion and is the only known sulfur–nitrogen radical that has been obtained as a stable crystalline salt.

The $N_2S_3{}^+$ cation is a planar five-membered ring (Fig. 3). The average bond length in the $N_2S_3{}^+$ ion is 158.7 pm. This is comparable to the average S—N distance in the S—N ring compounds. As an isolated $N_2S_3{}^+$ ion would be expected to have C_{2v} symmetry, the different lengths of the S_1—N_1 and S_1—N_2 bonds may be due to distortion of the ion in the crystal. Indeed, the difference in $N_2S_3{}^+CF_3SO_3{}^-$ is 2 pm, and in $N_2S_3{}^+AsF_6{}^-$ 3 pm.

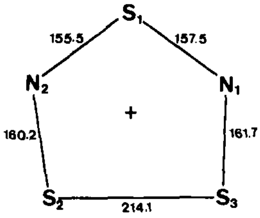


FIG. 3. Structure of the $N_2S_3{}^+$ radical.

Experimental error and the influence of temperature appear to be not significant, because the determination of the structure by X-ray crystallography at −120°C showed no significant differences. $N_2S_3{}^+$ would be a 7-π-electron ring. However, the difference in bond lengths of the average S_1—N_1 and S_1—N_2 as well as N_1—S_3 and N_2—S_2 is 156.5 and 160.9 pm, respectively. It appears that these differences can be explained on the basis of simple valence bond structures. If it is assumed that structures in which there is more than one charged atom and an S—S double bond are relatively unimportant and may be ignored, there are nine possible structures. In Fig. 4 the first four figures

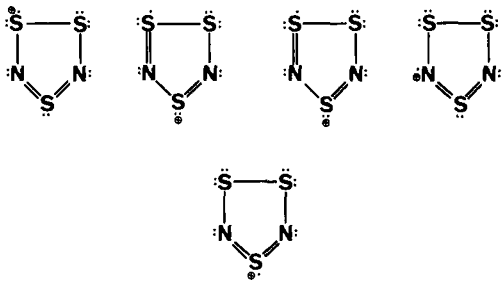


FIG. 4. Resonance structures of $N_2S_3^+$.

represent two structures as a consequence of the presence of the C_2 axis. Assuming that each of these structures has equal weight leads to the differences in bond lengths as they were found. The $N_2S_3^+$ structures can also be described as $N_4S_6^{2+}$ cations with two extremely long S—S bonds.

B. COMPOUNDS RELATED TO $N_2S_3^+$

The $N_4S_6^{2+}$ cation consists of two symmetry-related planar $N_2S_3^+$ rings held together by two very long S—S bonds of 302.7 pm. Therefore the bonding in $N_4S_6^{2+}$ can be regarded as consisting of two $N_2S_3^+$ rings linked together in a 4-center 6-electron bond (Fig. 5).

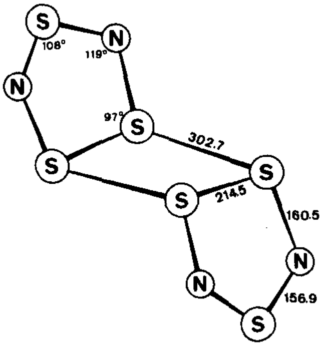


FIG. 5. Structure of $N_4S_6^{2+}$.

The compound was prepared in low yield from N_2S_3Cl and chlorosulfonic acid and isolated as $N_4S_6^{2+}$ $(ClSO_3OSO_3)_2^{2-}$ (*21*). N_2S_3Cl has been known since 1880 (*57*), but very little is known about its chemistry and its structure. It can be prepared from N_4S_4, S_2Cl_2 or NOCl, $N_3S_3Cl_3$, and NO or, more conveniently, from $N_2S_3Cl_2$ either by heating in vacuum or by reduction with anhydrous formic acid (*21, 30, 120*).

$N_3S_3Cl^+Cl^-$ is another example of a five-membered ring (*277*) that is closely related to the $N_2S_3^+$ radical. It is interesting to compare the geometry of $N_2S_3^+$ with that of $N_2S_3Cl^+$. The latter is slightly puckered, but nevertheless the bond angles are very similar, as are the bond distances. Using the same criteria as mentioned above, only three reasonable valence bond structures can be written (Fig. 6).

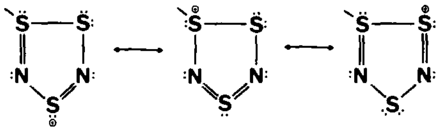


FIG. 6. Resonance structures of $N_2S_3Cl^+$.

Because of the inability of the three-coordinated sulfur atom to engage in π bonding, π bonding is restricted to the NSNS skeleton attached to the SCl group. The structure of $N_2S_3Cl^+Cl^-$ is rather unusual; one of the chlorine atoms is ionized, and the second is covalently bound to a sulfur atom of the ring. The different nature of the two chlorine atoms in $N_2S_3Cl^+Cl^-$ is also apparent in its reactions, the ionically bound chlorine being exchanged under milder conditions than the covalently bound chlorine (*22, 159, 202*).

$$N_2S_3Cl^+Cl^- \begin{cases} +MCl_3 & \rightarrow N_2S_3Cl^+MCl_4^- \\ +RSO_3H & \rightarrow N_2S_3Cl^+RSO_3^- + HCl \\ +2RSO_3H & \rightarrow N_2S_3^{2+}(RSO_3^-)_2 + 2HCl \\ +SbCl_5 & \rightarrow N_2S_3Cl^+\ SbCl_6^- \\ +2SbCl_5 & \rightarrow N_2S_3^{2+}\ (SbCl_6^-)_2 \end{cases} \qquad (15)$$

$$R = Cl, F, CF_3 \qquad M = Al, Sb, Fe$$

$N_2S_3Cl^+Cl^-$ itself can be prepared from ammonium chloride or urea and S_2Cl_2 at reflux temperature (*120, 214*).

In the reaction of $N_2S_3Cl^+Cl^-$ with amino compounds it was observed that it is possible to replace the two chlorine atoms by one imino group, =N—R, when R is an electron-withdrawing substituent (*167, 207, 214*) or by an oxygen atom.

$$N_2S_3Cl^+Cl^- \left\{ \begin{array}{lll} + P_3N_3F_5N[Sn(CH_3)_3]_2 & \rightarrow N_2S_3NP_3N_3F_5 + 2(CH_3)_3SnCl & (16) \\ + P_4N_4F_7N[Sn(CH_3)_3]_2 & \rightarrow N_2S_3NP_4N_4F_7 + 2(CH_3)_3SnCl & (17) \\ + C_3N_3F_2N[Sn(CH_3)_3]_2 & \rightarrow N_2S_3NC_3N_3F_2 + 2(CH_3)_3SnCl & (18) \\ + RN[Si(CH_3)_3]_2 & \rightarrow N_2S_3NR + 2(CH_3)_3SiCl & (19) \\ + [(CH_3)_3Si]_4N_2SO_2 & \rightarrow (N_2S_3N)_2SO_2 + 4(CH_3)_3SiCl & (20) \\ + CF_3SO_2NH_2 & \rightarrow N_2S_3NSO_2CF_3 + 2HCl & (21) \\ + HCOOH & \rightarrow N_2S_3O + 2HCl + CO & (22) \end{array} \right.$$

The question whether the five- membered 6-π-electron ring is preserved in the products or a six-membered 8-π-electron ring is formed could be established by X-ray investigations (*206*, *208*, *238*).

The data for the structures demonstrate that neither the bond angles nor the bond lengths within the five-membered rings are markedly influenced by the different substituents (Fig. 7). By comparing the average bond lengths of $N_2S_3Cl^+$ 169.8 with $P_3N_3F_5NS_3N_2$ 172.1, and $FSO_2NS_3N_2$ 172.4 pm, respectively, it is clearly shown that a decrease in electron density results in a shorter average bond length within the five-membered ring.

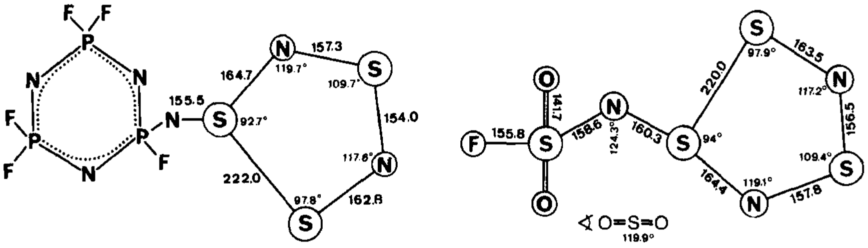


FIG. 7. Structure of $P_3N_3F_5NS_3N_2$ (left) and $FSO_2NS_3N_2$ (right).

In addition to the above-mentioned method, five other routes are so far known for the preparation of substituted N_2S_3 rings (*44*, *134*, *203*, *205*, *214*, *217*, *238*).

1. The reaction of isocyanates or iminosulfuroxides with N_2S_3O

$$N_2S_3O + CF_3SO_2N{=}C{=}O \rightarrow CF_3SO_2NS_3N_2 + CO_2 \qquad (23)$$

$$N_2S_3O + FSO_2N{=}S{=}O \rightarrow FSO_2NS_3N_2 + SO_2 \qquad (24)$$

2. The reaction of N_4S_4 with anhydrides

$$N_4S_4 + ROR \rightarrow RNS_3N_2 \tag{25}$$

$$R = SO_2F, SO_2CF_3, C(O)CF_3, C(O)CCl_3, P(O)F_2$$

3. The reaction of $(CH_3)_2SnN_2S_2$ with SOF_2

$$(CH_3)_2SnN_2S_2 + SOF_2 \rightarrow N_2S_3O + (CH_3)_2SnF_2 \tag{26}$$

4. The reaction of $(CH_3)_3SiNSNSi(CH_3)_3$ with $CF_3C(O)Cl$ yields $CF_3C(O)NS_3N_2$.

5. The reaction of $(CH_3)_3SiNSO$ with FSO_2NSCl_2 gives $FSO_2NS_3N_2$. $CF_3C(O)NS_3N_2$ was originally formulated as a six-membered ring (*134*).

N_2S_3O is the only oxide of a five-membered sulfur nitrogen ring so far known. It is a red oily liquid that can be distilled under vacuum without decomposition. The versatility of N_2S_3O for the preparation of N_2S_3-containing ring systems was shown. A fluorine compound with a composition of $N_2S_3F_2$ has been reported in the literature. It has, however, been assigned the acyclic structure FSN=S=NSF; a closer study has yet to be made (*88*, *89*).

$N_2S_3Br_2$ was reported to be one of the products by the reaction of N_4S_4 with bromine in carbon disulfide. It decomposes already at room temperature. Whether this compound has a linear or cyclic structure is not known (*278*).

C. FIVE-MEMBERED RINGS CONTAINING ONE ELEMENT OTHER THAN SULFUR AND NITROGEN

Tetrasulfur tetranitride was prepared in 1835 by the reaction of disulfur dichloride with ammonia, although its composition was not established until 1850 (*60*, *81*, *82*, *90*). For kinetically controlled reactions we used, instead of ammonia, a tin-substituted derivative of ammonia, and we allowed this to react with S_2Cl_2. Instead of N_4S_4 we obtained a cyclic five-membered ring.

$$4S_2Cl_2 + 4N[Sn(CH_3)_3]_3 \rightarrow (CH_3)_2SnN_2S_2 + 2(CH_3)_4Sn + \tfrac{1}{2}S_8 + 8(CH_3)_3SnCl \tag{27}$$

The same compound is formed when N_4S_4 and $N[Sn(CH_3)_3]_3$ are allowed to react at elevated temperatures; at lower temperatures a sulfur diimide could be isolated as an intermediate (*190*, *193*, *218*, *219*).

$$N_4S_4 + 2N[Sn(CH_3)_3]_3 \rightarrow 3(CH_3)_3Sn{-}N{=}S{=}N{-}Sn(CH_3)_3 + \tfrac{1}{8}S_8 \tag{28}$$

$$2(CH_3)_3Sn{-}N{=}S{=}N{-}Sn(CH_3)_3 + \tfrac{1}{4}S_8 \rightarrow [(CH_3)_2SnN_2S_2]_2 + 2(CH_3)_4Sn \tag{29}$$

Structural investigations show clearly that the molecule in the solid state consists of two five-membered and one four-membered ring (Fig. 8). The tin atoms have coordination number five. The molecule has C_i symmetry. By the way, this is the first example of a four-membered tin nitrogen ring whose structure was determined by X-ray analysis. This molecule is also a dimer in solution but monomeric in the gas phase. Another interesting feature of the structure is that the molecule has nearly a planar form in the solid state. All the S—N bonds are of different length; they will be discussed in detail later.

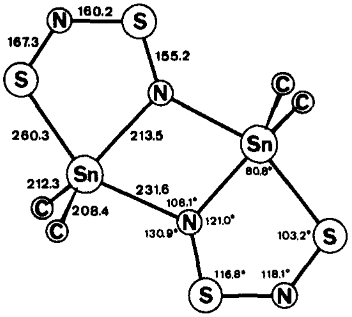


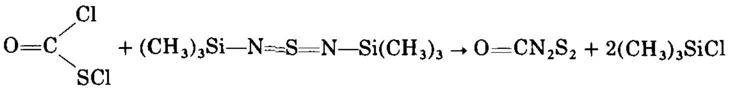
FIG. 8. Structure of $(CH_3)_2SnN_2S_2$.

SOF_2 and COF_2 react at room temperature with the tin compound with insertion and elimination of dimethyltin difluoride (*215*). $COCl_2$

$$(CH_3)_2SnN_2S_2 + COF_2 \rightarrow O{=}CN_2S_2 + (CH_3)_2SnF_2 \qquad (30)$$

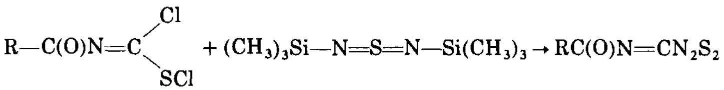
reacts similarly, but separation of the cyclic ketone from the dimethyltin dichloride proves to be difficult. The use of fluoro derivatives is favored by forming solid nonvolatile tin fluorides.

OCN_2S_2 (Fig. 9) is a yellow crystalline solid that melts at 40.5°C and can be sublimed under vacuum at room temperature. It may also be prepared from ClC(O)SCl and a silylated sulfur diimide (*168*).



$$O{=}C\begin{matrix}\diagup Cl\\ \diagdown SCl\end{matrix} + (CH_3)_3Si{-}N{=}S{=}N{-}Si(CH_3)_3 \rightarrow O{=}CN_2S_2 + 2(CH_3)_3SiCl \qquad (31)$$

According to this reaction scheme benzoyl-substituted isonitriles were prepared (*168*, *169*).



$$R{-}C(O)N{=}C\begin{matrix}\diagup Cl\\ \diagdown SCl\end{matrix} + (CH_3)_3Si{-}N{=}S{=}N{-}Si(CH_3)_3 \rightarrow RC(O)N{=}CN_2S_2 \qquad (32)$$

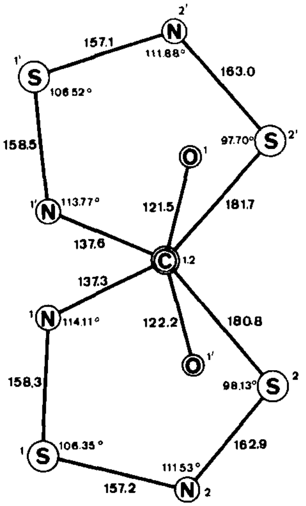


FIG. 9. Structure of OCN_2S_2.

OCN_2S_2 forms adducts with various Lewis acids (*216*)

$$OCN_2S_2 \left\{ \begin{array}{ll} +BF_3 & \rightarrow F_3BOCN_2S_2 \\ +SO_3 & \rightarrow O_3SOCN_2S_2 \\ +SbCl_5 & \rightarrow Cl_5SbOCN_2S_2 \\ +SbF_2Cl_3 & \rightarrow Cl_3F_2SbOCN_2S_2 \\ +SnCl_4 & \rightarrow Cl_4Sn(OCN_2S_2)_2 \\ +TiCl_4 & \rightarrow Cl_4Ti(OCN_2S_2)_2 \end{array} \right. \tag{33}$$

Infrared (IR) and Raman investigations support that the coordination of the Lewis acid to the ring occurs via the oxygen atom of the carbonyl group rather than a nitrogen atom of the ring. The adducts are decomposed on heating at elevated temperatures.

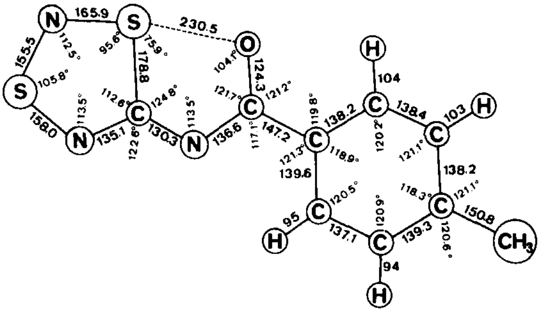
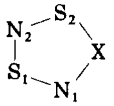


FIG. 10. Structure of $CH_3C_6H_4C(O)N{=}CN_2S_2$.

The molecule $CH_3C_6H_4C(O)N{=}CN_2S_2$, except for the hydrogen atoms of the methyl group, is planar (Fig. 10). The most noticeable feature of the structure is the S—O distance of 230.5 pm. It is a rare example of an SO bond longer than the "single bond" distance calculated from either Pauling's covalent radii (170 pm) or the Schomaker–Stevenson rule (169 pm) (*185*, *231*), but on the other hand the SO distance is appreciably shorter than a van der Waals contact (325 pm). This can be considered as a "frozen" nucleophilic attack of the carbonyl oxygen on the sulfur atom.

For the discussion of the sulfur–nitrogen bonding properties within the five-membered rings, the structural data are collected in the accompanying tabulation.



X	S_1N_1	S_1N_2	S_2N_2	Average SN	Angle $N_1S_1N_2$
$(CH_3)_2Sn$	155.2	160.2	167.3	160.9	116.8°
FSO_2NS	157.8	156.5	163.5	159.3	109.4°
$P_3N_3F_5NS$	157.3	154.0	162.8	158.0	109.7°
$O{=}C$	158.3	157.2	162.9	159.5	106.4°
$CH_3C_6H_4C(O)NC$	158.0	155.5	165.9	159.8	105.8°

It is quite obvious that, with decreasing size of X, the angle $N_1S_1N_2$ also should be diminished. A value of 116° is found for the tin compound, compared to 109° for the sulfur derivatives and 106° for the carbon compounds. Therefore the *s* character of S_1 should decrease when the angle increases and the bond length of the adjacent bonds N_1—S_1 and S_1—N_2 should become shorter. This trend cannot be observed because the N_2S_2 skeleton is a delocalized 6π-electron system, as is demonstrated by the nearly equal average S—N bond distance of the various compounds. This means that a change in electron density in the SN_2 part of the ring will be compensated by the remaining sulfur atom. The different S—N bond length can be explained best by resonance structures.

Calculations for S—N compounds have so far not given an answer to the different bond orders whereas resonance structures (Fig. 11)

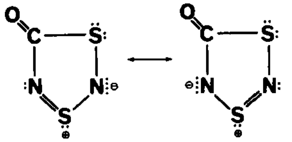
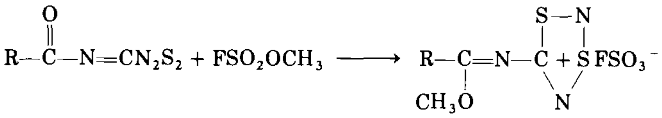


FIG. 11. Resonance structures of OCN_2S_2.

show a fairly good agreement (*1*, *18*, *65*, *71*, *164a*). The alkylation of R—C(O)—N=CN_2S_2 with the methyl ester of fluorosulfonic acid yields a cation with the following structure:



$$R{-}\overset{\overset{O}{\|}}{C}{-}N{=}CN_2S_2 + FSO_2OCH_3 \longrightarrow R{-}\underset{\underset{CH_3O}{|}}{C}{=}N{-}CN_2\overset{+}{S}_2\,FSO_3^- \quad (34)$$

The easy alkylation of the carbonyl oxygen is a support for the argument of a partial negative charge on the oxygen atom. An alkylation of the nitrogen atom was not observed (*169*). $N_3S_3Cl_3$ reacts with nitriles or azines to give dithiadiazolium chlorides, $RCN_2S_2{}^+Cl^-$ (*5, 211*).

$$3RCH{=}NN{=}CHR + 4N_3S_3Cl_3 \rightarrow 6[R{-}CN_2S_2]^+Cl^- + 3N_2 + 6HCl \qquad (35)$$

$$R = C_6H_5,\ C(CH_3)_3$$

According to this equation, the yield of the phenyl derivative is quantitive. The reaction with nitriles was not completely investigated; no equation or by-products were reported. The compounds contain a cation, confirmed by an X-ray structure determination (*6*), which has an S—S bond instead of an alternating NS arrangement shown in OCN_2S_2 and RC(O)—N=CN_2S_2 (Fig. 12).

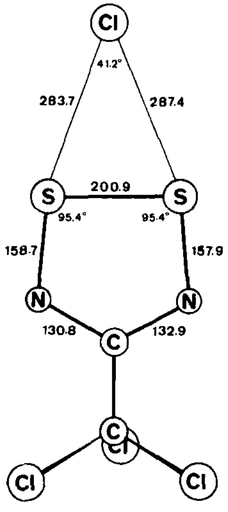


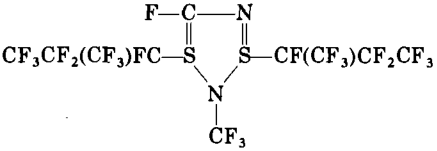
FIG. 12. Molecular structure of $[CCl_3CN_2S]^+Cl^-$.

To some extent this is surprising, because in such a structure it is not possible to write a resonance form with a carbenium center. Another striking feature is the close approach of the Cl^- ion to both sulfur atoms of the S_2 group. This triangular arrangement may be an important factor for the present structure. In $[C_6H_5CN_2S_2]^+Cl^-$ the chlorine ion can be replaced by various anions, and this is another proof of the ionic nature of this compound (*211*).

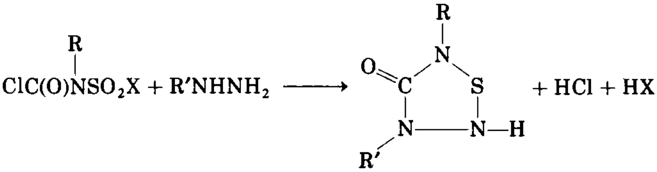
$$\mathrm{C_6H_5CN_2S_2{}^+Cl^-}\left\{\begin{array}{ll} +\mathrm{CF_3SO_3H} & \rightarrow \mathrm{C_6H_5CN_2S_2{}^+CF_3SO_3{}^-} + \mathrm{HCl} \\ +\mathrm{HN(SO_2F)_2} & \rightarrow \mathrm{C_6H_5CN_2S_2{}^+(FSO_2)_2N^-} + \mathrm{HCl} \\ +\mathrm{(C_2H_5)_3OBF_4} & \rightarrow \mathrm{C_6H_5CN_2S_2{}^+BF_4{}^-} + \mathrm{C_2H_5Cl} + \mathrm{C_2H_5OC_2H_5} \\ +\mathrm{NOPF_6} & \rightarrow \mathrm{C_6H_5CN_2S_2{}^+PF_6{}^-} + \mathrm{NOCl} \\ +\mathrm{SbCl_5} & \rightarrow \mathrm{C_6H_5CN_2S_2{}^+SbCl_6{}^-} \end{array}\right. \tag{36}$$

The complexes can be recrystallized from acetonitrile, and all are intensely yellow or red.

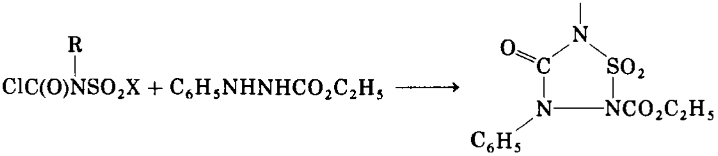
A five-membered dithiadiazole is formed, when $CF_3C{\equiv}CCF_3$ and $CF_3N{=}SF_2$ react in the presence of CsF (*117*).



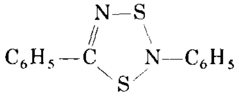
It was shown recently that chloro- and fluorosulfonylcarbamoyl chlorides undergo exclusive attack at the carbonyl group to give with hydrazines clean condensation products (*29*).



$R = CH_3, CH_3CH_2CH_2,\quad R' = CH_3, C_6H_5$ (37)
$X = Cl, F$

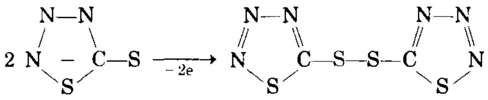


Thioarylisocyanates and diphenylsulfur diimide react to several products among which



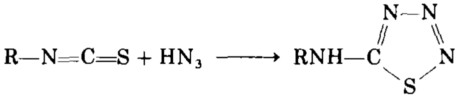
was isolated (*248a*).

Free dithiocarbonic acid azide, $N_3CS(SH)$, was first described in 1915 (*73, 234*). It has been prepared by treating concentrated solutions of sodium azidodithioformate with hydrochloric acid at low temperatures. The complete absence of the strong absorptions characteristic of azide groups suggests that this acid has the structure of a thiatriazole (*136*). All alkali salts of $N_3CS_2^-$ are known (*73, 174*) and many heavy-metal salts. They are sensitive to mechanical shock. Much more stable are the salts of the thiatriazoles that are complexed with phosphines, π-allyl, or dienes. They can be prepared either by insertion of carbon disulfide into the azido complex of transition metals or by reaction of a mixture of the corresponding metal nitrate, NaN_3CS_2, and the phosphine (*73*). One of the major characteristics of $N_3CS_2^-$ anions is their susceptibility to oxidation, resulting in the formation of the disulfide (*73*)



(38)

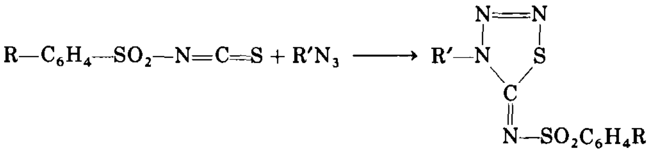
When $N_3CS_2^-$ is allowed to react with various organic dihalides of the type X—R—X, compounds of the following structure were prepared: $N_3CS_2—R—S_2CN_3$ (*186*). Esters of the type N_3CSSR are known (*73*). Attempts to obtain alkyl and aryl esters by direct condensation of the organic azides with carbon disulfide failed. The general method adopted for the preparation of the esters involves reaction of alkyl or aryl halide with NaN_3CS_2. The esters are crystalline solids that decompose more or less rapidly at elevated temperatures. The reaction of hydrazoic acid with isothiocyanates furnishes thiatriazoles (*116*).



(39)

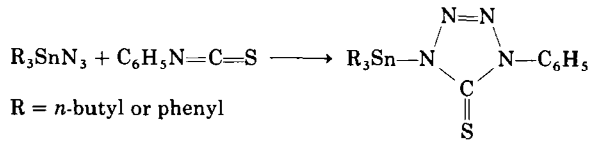
Despite the large number of investigations carried out with thiatriazoles, thiatriazolines have been mentioned in only a few reports (*135, 170*).

Arylsulfonylisothiocyanates react directly with organic azides to form thiatriazolines exclusively (*132, 253*).



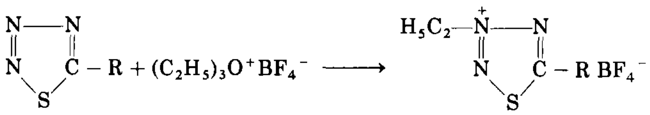
(40)

The reaction of tri-*n*-butyltin azide and triphenyltin azide with phenylisothiocyanate gives the 1:1 adduct (*128*).



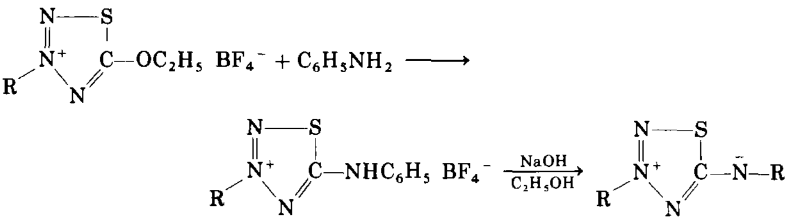
(41)

Other organometallic azides also produced C=N but not C=S, adducts. Esters of thiatriazoles can be alkylated with $(C_2H_5)_3O^+BF_4^-$ with formation of thiatriazolium salts (*103, 113*).



(42)

The conversion of the thiatriazolium salts with amines or $CH_2(CN)_2$ leads to new mesoionic heterocycles (*103*).



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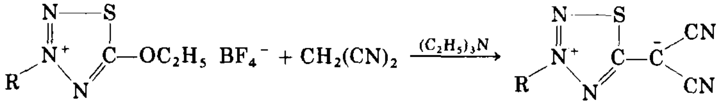
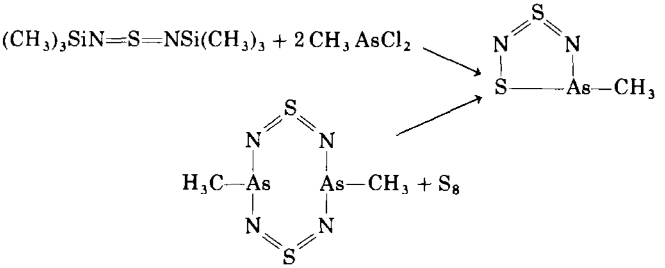


(44)

One five-membered sulfur–nitrogen–arsenic ring is known. The ring is obtained when *N,N'*-bis(trimethylsilyl)sulfur diimide is treated with CH_3AsCl_2 in the molar ratio of 1:2 (*225*). By using a different ratio of reactants, it is also possible to get a second product, in which there is a eight-membered ring (*224*). The eight-membered ring can be converted by elemental sulfur to the five-membered ring.

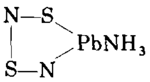


(45)

The product at room temperature is a red liquid that boils at 33°–35°C/0.05 Torr.

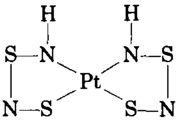
D. THE FUNCTION OF N_2S_2, HN_2S_2, AND NS_3 AS BIDENTATE LIGANDS

Already in 1904 Ruff and Geisel (*222*) observed a fragmentation of N_4S_4 when it is treated with lead iodide or nitrate in liquid ammonia. The product is an ammoniate of the composition $Pb(N_2S_2)NH_3$. The ammonia can be removed by heating. The structure was established by X-ray analysis (*264*).

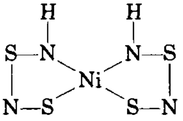


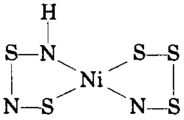
The thionitrosyl complexes of composition $Me(HN_2S_2)_2$, M = Ni, Co, Pt, Pd, Fe, are prepared from N_4S_4 and the metal chlorides, in the case of Pt from H_2PtCl_6 (*104a*). The iron, cobalt, and nickel derivates can also be obtained from the tetranitride and the carbonyls $Fe(CO)_5$, $Co_2(CO)_8$, and $Ni(CO)_4$ in a solvent (*43, 267*).

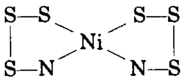
Compounds of this type were initially formulated as $M(SN)_4$, but later it was found on the basis of IR measurements that they contain hydrogen and should be formulated as $Me(HN_2S_2)_2$ (*187, 268*). These products are formed only in the presence of a solvent containing hydrogen, such as ethanol. The structure of the platinum complex was investigated by X-ray analysis.



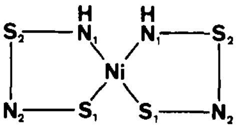
The molecule was found to be planar (*139*). The hydrogens are bonded to the nitrogen atoms next to the platinum, and the two chelate ligands are in cis configuration. The products of the reaction of N_4S_4 and nickel chloride in ethanol solution were separated by using alumina column chromatography. Three different compounds were isolated.







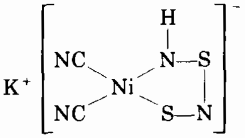
$Ni(HN_2S_2)(NS_3)$ and $Ni(NS_3)_2$ are readily soluble, but $Ni(HN_2S_2)_2$ is less soluble in benzene. Structural investigations by Weiss and Thewalt for $Ni(HN_2S_2)_2$ (Fig. 13) and $Pd(HN_2S_2)_2$ gave results similar to those for the platinum complex (*271*).



Ni—S_1	214.4
Ni—N_1	187.7
S_1—N_2	164.1
S_2—N_2	158.4
S_2—N_1	159.3

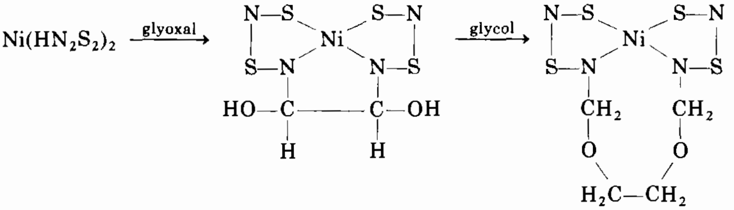
FIG. 13. Molecular structure of $Ni(HN_2S_2)_2$.

A sulfur atom is isoelectronic with an NH group. Therefore the replacement of the imido group by sulfur should not lead to a change in structure. It can be assumed that the other two derivatives are also planar. In contrast, the dimethyl derivative of $Ni(HN_2S_2)_2$, obtained by causing $Ni(HN_2S_2)_2$ to react with methyl iodide, possesses a trans configuration (*272*). The reason for this might be steric hindrance, because the monosubstituted methyl derivative has also a cis configuration. Of special interest is the mixed complex salt $K[Ni(CN)_2HN_2S_2]$, which can be prepared from $K_4[Ni_2(CN)_6]$ and N_4S_4 in alcoholic solution. It seems highly probable that the HN_2S_2 and NS_3 ligands could be used in a wider range for the preparation of metallic complexes (*267*).



The chemistry of the $Ni(HN_2S_2)_2$ compound is essentially that associated with the two imido groups, which undergo a number of cyclization reactions (*267*).

The NH group can be metallated with silver nitrate or organolithium reagents and caused to react further with organic halides. The reaction of $Ni(HN_2S_2)_2$ with glyoxal and a mixture of formaldehyde and methanol leads to cyclic derivatives (*102*).



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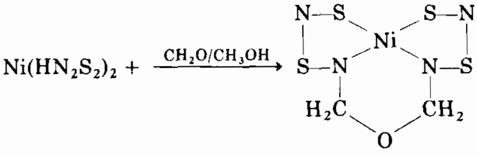
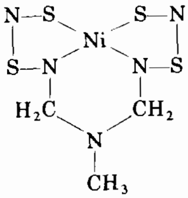
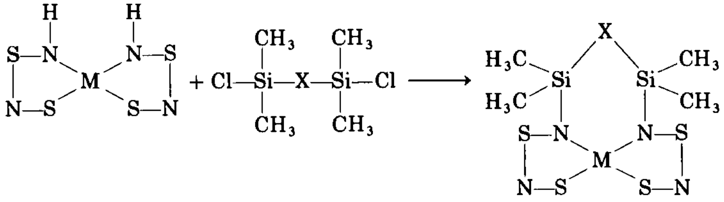


(47)

If methylamine is added in the reaction with formaldehyde, $Ni[C_3H_7N_5S_4]$ is formed.



New inorganic ring systems were obtained by the reaction of $Ni[HN_2S_2]_2$ and $Co[HN_2S_2]_2$ with 1,3-dichloropentamethyldisilazane and 1,3-dichlorotetramethyldisiloxane in tetrahydrofuran and in the presence of triethylamine (*261*).



(48)

$M = Ni$ $X = O$, $>NR$ $(R\colon —H, —CH_3, —C_2H_5)$

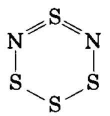
$M = Co$ $X = O$, $—N(CH_3)—N(CH_3)—$

The tricyclic structure has been confirmed by X-ray analysis for a nickel as well as for a cobalt derivative (*242*). The complexes are very soluble in organic solvents.

VI. Six-Membered Rings

A. DOUBLY COORDINATED SULFUR AND NITROGEN

Tetrasulfur dinitride has been known for over 70 years, and the molecular formula N_2S_4 has been accepted since Meuwsen's determination of the molecular weight in 1951 (*158*). Its dipole moment, ^{14}N-NMR spectrum, mass spectrum, IR spectrum, electronic spectrum, and Raman spectrum have been determined. This physical evidence shows that the compound has a cyclic structure with the nitrogen atoms in the 1,3-position (*172*). No evidence for other isomers was reported.



The compound can be prepared by several routes:

1. Heating N_4S_4 with sulfur in CS_2 at 120°C in an autoclave (*91*)
2. Causing $Hg_5(NS)_8$ to react with disulfur dichloride in CS_2 (*158*)

$$Hg_5(NS)_8 + 4S_2Cl_2 \rightarrow 4N_2S_4 + 3HgCl_2 + Hg_2Cl_2 \qquad (49)$$

3. Reaction of disulfur dichloride with aqueous ammonia (*175*)
4. Reduction of $[N_3S_4]Cl$ with metallic zinc (*102*)

5. Treating S_7NH with $N_3S_3Cl_3$ in benzene at 80°C in the presence of pyridine (*94*)

$$S_7NH + N_3S_3Cl_3 \rightarrow N_2S_4 + N_4S_4 \tag{50}$$

6. Decomposition of $Hg(NS_7)_2$ at room temperature (*107a*)

The reaction according to route 3 seems to be a simple route to tetrasulfur dinitride. The yield is 8.2%, and isolated by-products are S_7NH and N_4S_4. N_2S_4 is a red-brown liquid with an unpleasant odor, mp. 23.5°C. The pure liquid decomposes within a few hours at room temperature. N_2S_4 is reduced with $LiAlH_4$ or $SnCl_2$ in ether, which results in the formation of $N_2S_4H_2$ (*72*). A product of the composition $N_3S_3SbCl_6$ was reported from the reaction of N_4S_4 with $SOCl_2$ and $SbCl_5$. The structure of $N_3S_3^+$ is not known (*26*). N_3S_3Cl was obtained from the reaction of chlorine with excess N_4S_4 (*278*). $N_3S_3^-$, a 10-π-electron system, was prepared from N_4S_4 and a tetraalkylammonium azide or CsN_3 in ethanol. On the basis of spectroscopic investigations a cyclic structure with C_{3v} symmetry was assigned for this anion (*39a*).

B. Structural Investigations of Six-Membered Rings with the Coordination Number Two at the Sulfur and Nitrogen Atoms

The structures of six-membered rings with an NSN unit have been established with the emphasis on investigating the influence of adjacent atoms with high coordination numbers. In detail, compounds with carbon and phosphorus (*209*) of coordination number four and compounds of sulfur with coordination numbers three and four were studied (*75, 76, 204, 270*) (Fig. 14).

The first three compounds demonstrate that the N—S bond (153 pm) as well as the NSN angle in all compounds is, within experimental error, the same. The π-electron density of the NSN-unit is not influenced by the adjacent atoms when they have a high coordination number. Atoms with high coordination numbers function as a barrier for π electrons, even if there is an additional charge, as demonstrated in $SN_2NS_2O_4^-$. The negative charge is localized on the SO_2—N—SO_2 part of the molecule. Also the electron-withdrawing property of a fluorine atom in $SN_2N_4P_4F_6$ does not influence the electron density. Although conjugation is not observed, hyperconjugation might be possible. In $SN_2S_2N_3PF_2$ the adjacent sulfur atoms to the NSN unit have a coordination number three. In this case it has already be seen that a small change in the NS-bond distance (155 pm) occurred. The

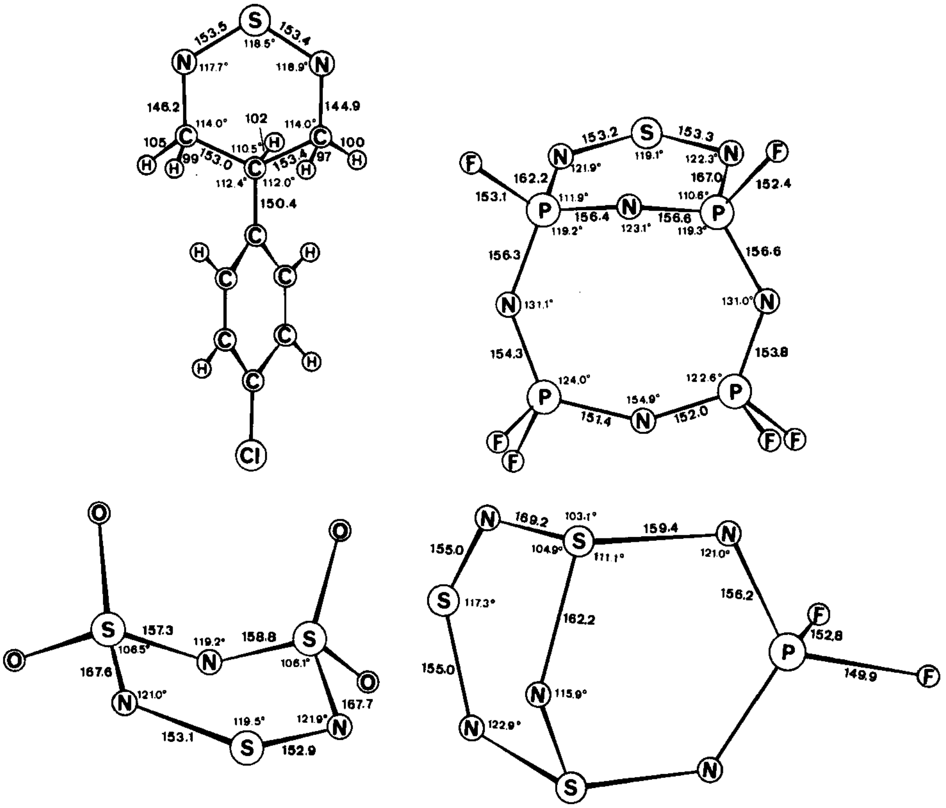


FIG. 14. Molecular structures of (a) $SN_2C_9H_9Cl$; (b) $SN_2N_4P_4F_6$; (c) $SN_2NS_2O_4^-$; (d) $SN_2S_2N_3PF_2$.

electron density of the NSN part is to a small extent influenced by sulfur atoms of coordination number three. In addition, it might be interesting to note that $SN_2S_2N_3PF_2$ and phenyl-substituted derivatives are prepared from $(CH_3)_3SiNSNSi(CH_3)_3$ and fluorophosphoranes (*12*, *131*, *212*).

A combination of the thirteen building units of sulfur in Table I results in 180 different six-membered rings. Only a small number of them have so far been synthezised (*102a*).

C. SULFUR AND NITROGEN WITH COORDINATION NUMBERS TWO AND/OR THREE

$N_3S_3Cl_3$ is obtained as large yellow needles when N_4S_4 is dissolved in CCl_4 and treated with chlorine. Instead of chlorine, SO_2Cl_2 can be used as a chlorinating agent. Another method uses $N_2S_3Cl_2$ and SO_2Cl_2 for the preparation of $N_3S_3Cl_3$ (*4*, *91*). On heating $N_3S_3Cl_3$ to 110° under high vacuum, NSCl may be obtained as a greenish-yellow gas. NSCl polymerizes again to $N_3S_3Cl_3$. The compound (Fig. 15) is freely soluble in organic solvents and is stable in dry air. It is a nearly flat ring where all N—S bonds are of the same length. The addition of SO_3 to $N_3S_3Cl_3$ leads to the adduct $N_3S_3Cl_3 \cdot 6SO_3$, which decomposes at 100°C to give $N_3S_3Cl_3 \cdot 3SO_3$; at higher temperatures $(NSOCl)_3$ is formed (*93*).

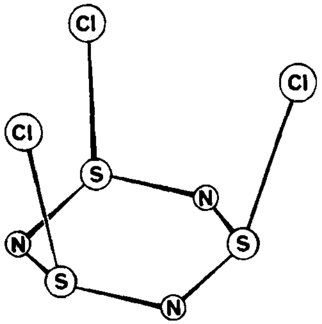


FIG. 15. Molecular structure of $N_3S_3Cl_3$.

$Mo(CO)_6$ and $N_3S_3Cl_3$ react in dichloromethane with formation of a brown crystalline solid.

$$Mo(CO)_6 + N_3S_3Cl_3 \rightarrow MoN_3S_3Cl_3 + 6CO \qquad (51)$$

The pyrolysis of $MoN_3S_3Cl_3$ under vacuum yields a sublimable solid of composition $MoN_3S_9Cl_6$. The structures of both compounds are unknown (*276*). The corresponding fluorine compound $N_3S_3F_3$ is obtained either from the fluorination of $N_3S_3Cl_3$ with AgF_2 or the direct fluorination of N_4S_4 with elemental fluorine at low temperatures (*82*, *83*, *151*). X-ray determination shows a slightly puckered six-membered N—S ring with bond distances of 158.7 and 159.8 pm, respectively. All fluorine atoms are in axial positions similar to $N_3S_3Cl_3$ (*127*). The Lewis acids BF_3, SbF_5, and AsF_5 form stable adducts with $N_3S_3F_3$ (*161*) with formation of the cation $N_3S_3F_2^+$. Three adducts of $N_3S_3Cl_3$ are known with the following composition: $N_3S_3Cl_3 \cdot SbCl_5$, $N_3S_3Cl_3 \cdot TiCl_4$, and $(N_3S_3Cl_3)_2 \cdot SnCl_4$ (*161*). Nitrogen-substituted organic derivatives of N_2S_4 are known. The 1,3-diaza as well as the 1,4-diaza isomers have been prepared.

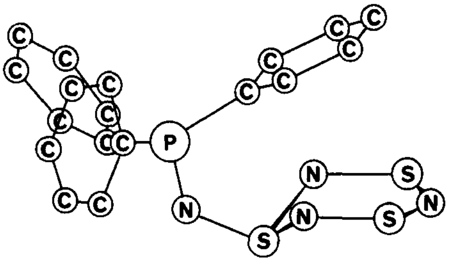
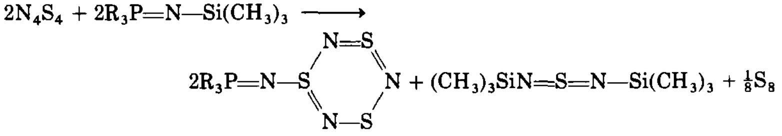


FIG. 16. Molecular structure of $(C_6H_5)_3PN_4S_3$.

The compound $(C_6H_5)_3PN_4S_3$ has been shown by X-ray single-crystal studies to have a six-membered N_3S_3 ring, five members of which are coplanar (N_3S_2) (Fig. 16). The third sulfur of the ring is tervalent and 139° out of the plane. The bonds between sulfur and nitrogen are not equal (*114*). $(C_6H_5)_3PN_4S_3$ is prepared from N_4S_4 and triphenylphosphine or methylentriphenylphosphorane or triorganylimino-*N*-(trimethylsilyl)phosphorane, respectively (*67*, *125*, *223*).

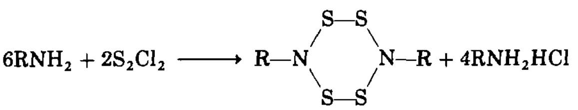


(52)

R = C_6H_5 and/or CH_3

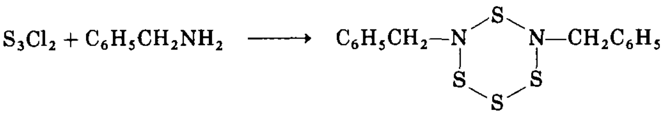
The structure of triphenylarsine trisulfur tetranitride is similar to that of the analogous phosphine compound. The triphenyl substituent group is bonded through nitrogen to the sulfur of an N_3S_3 group, the remaining five members of which are planar (*115*).

The 1,4-diazatetrasulfanes are prepared from primary amines and disulfur dichloride (*102*, *244*).



(53)

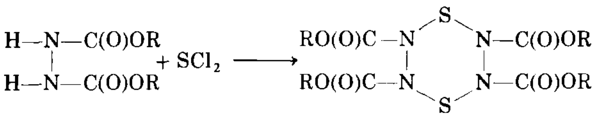
The 1,3-isomer has been obtained from S_3Cl_2 and benzylamine (*41*).



(54)

The cyclic structure of these compounds is assumed on the basis of molecular weight determinations. Their kinetic stability depends upon the nature of the organic substituents.

Six-membered hydrazine compounds were obtained by the condensation of sulfur dichloride with esters of hydrazine dicarbonic acid (*263*).



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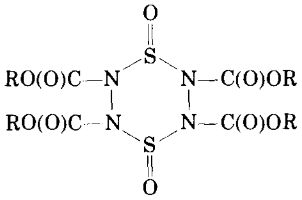
These compounds react with *m*-chloroperbenzoic acid. Among the products isolated, a bissulfoxide was found.



(56)

D. Compounds of Coordination Number Two at Nitrogen and Four at Sulfur

The sulfanuryl chlorides and fluorides belong to this class of compounds. There are four different possibilities for the preparation of $N_3S_3O_3Cl_3$:

1. Pyrolysis of $ClSO_2N{=}PCl_3$, obtained from the reaction of PCl_5 and H_2NSO_3H (*122*)

$$3ClSO_2N{=}PCl_3 \rightarrow (NSOCl)_3 + 3OPCl_3 \qquad (57)$$

2. Reaction of thionyl chloride with sodium azide (*124*)

$$3SOCl_2 + 3NaN_3 \rightarrow (NSOCl)_3 + N_2 + 3NaCl \qquad (58)$$

3. Oxidation of $N_3S_3Cl_3$ with SO_3 (*93*)

$$N_3S_3Cl_3 + 3SO_3 \rightarrow (NSOCl)_3 + 3SO_2 \qquad (59)$$

4. Ammonolysis of SO_2Cl_2 in the presence of $SOCl_2$ (*92*).

Kirsanov obtained two products by pyrolysis, the α- and β-isomers (m.p. 144°–145° and 46°–47°C). Separation could be achieved by vacuum sublimation. The structure of the α-isomer is known (*24, 274*). All N—S bonds were found to be of the same length (156.4 pm), the molecule exhibiting a chair form. All chlorine atoms are in axial positions. $(NSOCl)_3$ is converted to the corresponding fluoride by means of KF in carbon tetrachloride (*232*) or under reduced pressure with SbF_3 (*137*). The two isomers differ in the position of their fluorine and oxygen atoms with respect to the nonplanar ring (*86*).

PHYSICAL PROPERTIES OF THE *cis*- AND *trans*-ISOMER

	cis-$(NSOF)_3$	*trans*-$(NSOF)_3$
Melting point	17.4°C	−12.5°C
Boiling point	138.4°C	130.3°C
Density (g/ml)	1.92	1.92
Heat of vaporization (joule/mol)	39.8	40.7
^{19}F NMR	A type	AB_2 type

Numerous sulfur oxide difluorides, such as $CsNSOF_2$, $Hg(NSOF_2)_2$, $(CH_3)_3SnNSOF_2$, and $B(NSOF_2)_3$, have been found to decompose with liberation of $(NSOF)_3$ (*83*).

Substitution reactions of sulfanuryl halides have been described in the literature (*19, 86, 166, 259a*). $N_3S_3O_3(C_6H_5)_3$ is accessible both from C_6H_5SOCl and azide (*152*) and from $(NSOF)_3$ and C_6H_6 in the presence of $AlCl_3$ (*166*).

Mixed chloro, fluoro compounds have been obtained by the fluorination with SbF_3 under reduced pressure (*137*). $(NSOF)_2(NSOCl)$ as well as $(NSOCl)_2NSOF$ form mixtures of three isomers each, which can be separated by gas chromatography. Assuming the ring to be planar, the isomers of $(NSOF)_2(NSOCl)$ might be pictured as shown in Fig. 17 (*83, 137*).

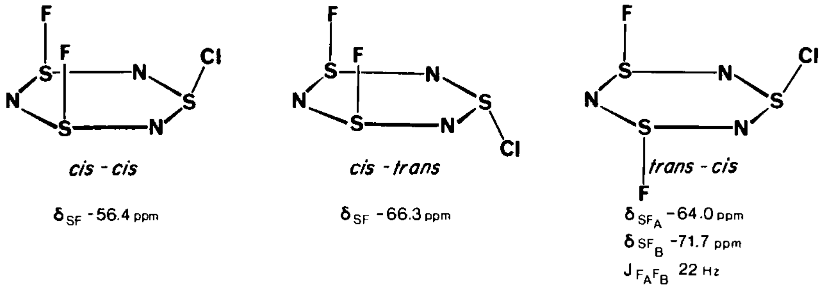


FIG. 17. Isomers of $(NSOF)_2(NSOCl)$.

An interesting compound is $N_3S_3O_3F_2NH_2NH_3$, which is prepared from $(NSOF)_3$ and ammonia in diethyl ether. $N_3S_3O_3F_2NH_2$ is formed by treatment of the ammoniate with HCl gas. $N_3S_3O_3F_2NH_2NH_3$ can be used to prepare a series of derivatives where the two protons of the amino group have been replaced by $=SF_2$, $=SCl_2$, $=SOF_2$, $=PCl_3$, and $=CHC_6H_5$. Oxalyl chloride forms a bridged derivative, $(N_3S_3F_2NHCO)_2$ (*138, 240, 260*). The reaction of $(NSF)_3$ with various amines was studied in detail (*260*).

With *N,N′*-dimethylethylendiamine, a bridged as well as a bicyclic compound is obtained (*260*). The anion $N_3S_3O_3F_2^-$ has been prepared by reaction of $(NSOF)_3$ with CH_3SH (*255*) and $C_6H_5NHNH_2$ (*260*).

$$\begin{aligned}&(NSOF)_3 + 2CH_3SH + 2N(CH_3)_3 \rightarrow \\ &\qquad N_3S_3O_3F_2^-HN(CH_3)_3^+ + CH_3SSCH_3 + HFN(CH_3)_3\end{aligned} \tag{60}$$

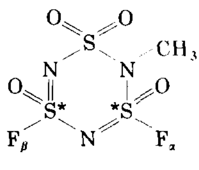
$$(NSOF)_3 + H_2NNHC_6H_5 + 2N(CH_3)_3 \rightarrow N_3S_3O_3F_2^-HN(CH_3)_3^+ + HFN(CH_3)_3 \tag{61}$$

$N_3S_3O_3F_2N(CH_3)_2$ reacts with $H_2NNHC_6H_5$ with formation of the $N_3S_3O_3FN(CH_3)_2^-$ anion.

The use of CH_3OH instead of CH_3SH leads to the anion $N_3S_3O_3F_2O^-$ (*255*).

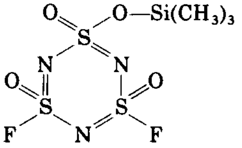
$$(NSOF)_3 + CH_3OH + 2N(CH_3)_3 \rightarrow N_3S_3O_3F_2O^-N(CH_3)_4^+ + HFN(CH_3)_3 \tag{62}$$

The free acid can be isolated by means of a cation exchanger, evaporation of the aqueous solutions yields the monohydrate $N_3S_3O_3F_2OH \cdot H_2O$. The silver salt and two alkylated products were reported (*255–257*). On the basis of ^{19}F NMR for the methyl derivate, the following structure was proposed:



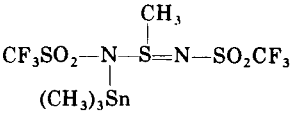
This compound has two asymmetric sulfur atoms, which are marked by asterisks (*). The optical activity was demonstrated by ^{19}F NMR in the presence of butanol-2 in an inert solvent. The alcohol coordinates to the sulfur atom adjacent to the α-fluorine, thus forming a pair of diastereoisomers. As a result, in the ^{19}F NMR spectrum all resonance lines are doubled (*83*). $N_3S_3O_3FN(CH_3)_2O^-$ was prepared from $N_3S_3O_3F_2N(CH_3)_2$ and methanol in the presence of triethylamine

(*258*). If $N_3S_3O_3F_2O^-Ag^+$ is subjected to reaction with $(CH_3)_3SiCl$ or $(CH_3)_3SnCl$, then the metal adds to an oxygen atom of the anion (*258*)



E. BONDING PROPERTIES OF SULFUR WITH COORDINATION NUMBERS THREE AND FOUR

From bond angles and bond lengths (Fig. 18) it is understandable that the $>$SX can be exchanged for an $>$SOX group (*83*). Within experimental error the bond angles at nitrogen are identical. The same applies to the angles at sulfur. The differences in bond length can be interpreted on the basis of different coordination numbers. Recently it was found that coordination numbers and bond lengths can be correlated. In the case of



$$CF_3SO_2-\underset{(CH_3)_3Sn}{\underset{|}{N}}-\overset{CH_3}{\overset{|}{S}}=N-SO_2CF_3$$

it was found that the shortest SN bond (S_2—N_2: 155 pm) belongs to sulfur of coordination number four and nitrogen of coordination

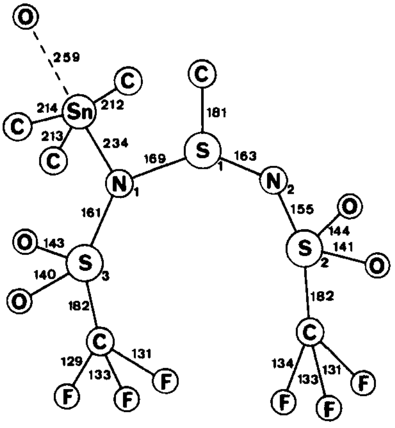


FIG. 18. Molecular structure of $CF_3SO_2(CH_3)_3SnN\underset{CH_3}{\underset{|}{S}}NSO_2CF_3$.

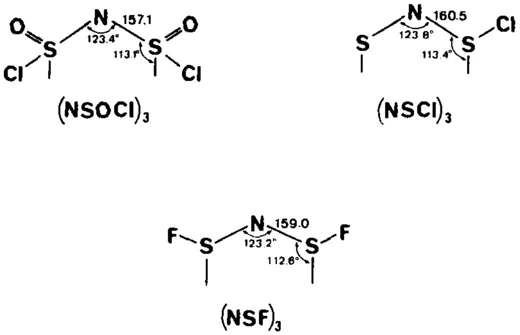


FIG. 19. Bond angles and bond lengths of $(NSOCl)_3$, $(NSCl)_3$, and $(NSF)_3$.

number two. An increase in coordination number of the atom N_1 leads to a lengthening of the S_3—N_1 distance to 161 pm (Fig. 18).

A similar effect is observed for the sulfur atom S_1 having coordination number three. S_1—N_2 is shorter then S_1—N_1 (*198*). In general, for sulfur of coordination numbers (CN) three and four, the following series of increasing bond lengths may be valid:

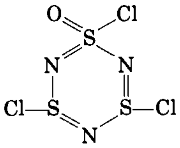
$$\begin{aligned}&S(CN = 4)\text{—}N(CN = 1) < S(CN = 4)\text{—}N(CN = 2) < S(CN = 4)\text{—}N(CN = 3)\\&\qquad\approx S(CN = 3)\text{—}N\text{—}(CN = 2) < S(CN = 3)\text{—}N(CN = 3)\end{aligned}$$

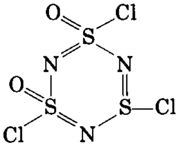
Sulfurs of coordination number two cannot be included, because, as shown earlier, these compounds take part in the delocalization. According to this series, the shortest SN-bond will be observed when the difference of the coordination numbers is high. In fact, the polarity of such a bond is high, and this results in a decrease of the bond length. Therefore, the change in the SN-bond length from —N—S(=O)—Cl (157.1 pm) to N—S—Cl (160.5 pm) is understandable (Fig. 19). Another example is N≡SF and $N{\equiv}SF_3$ with NS bond lengths of 144.6 and 141.6 pm, respectively.

F. DOUBLY COORDINATED NITROGEN, THREE- AND/OR FOUR-COORDINATED SULFUR

The interconversion of NS(O)X and NSX results in the formation of various ring compounds. The chlorination of $S(NSO)_2$ yields $(NSOCl)_3$

and (*228, 269*) two compounds with mixed coordination numbers at sulfur.





By means of AgF_2 or SbF_3 the chlorine atoms can be exchanged for fluorine under proper conditions

$$2(NSCl)_2NSOCl + AgF_2 \rightarrow (NSF)_2NSOCl + (NSF)_2NSOF \tag{63}$$

$$(NSOCl)_2NSCl + AgF_2 \rightarrow (NSOCl)_2NSF \tag{64}$$

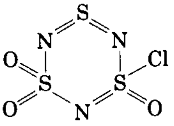
$$(NSOCl)_2NSCl + SbF_3 \rightarrow (NSOF)_2NSCl \tag{65}$$

$$(NSOCl)_2NSCl + SbF_3\ \text{exc.} \rightarrow (NSOF)_2NSF \tag{66}$$

All compounds are distillable liquids without decomposition in vacuum. $(NSOF)_2NSCl$ was also obtained from the reaction of $N_3S_3O_3F_2NH_2$ with $SOCl_2$ (*138*) and from the reaction of $N_3S_3O_3F_2O^-$ with PCl_5 (*255*). The corresponding $(NSOF)_2NSF$ is accessible from $N_3S_3O_3F_2O^-$ and PF_5 (*255*).

G. TWO- AND FOUR-COORDINATED SULFUR

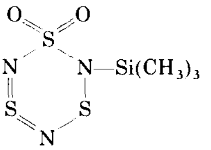
Compounds of this class are rare. The reaction of $FSO_2N{=}S{=}O$ and BCl_3 yields $ClSO_2N{=}S{=}O$ which is not stable and eliminates SO_2. The resulting $ClSO_2N{=}S{=}NSO_2Cl$ could not be isolated and made to react with excess $ClSO_2N{=}S{=}O$ with formation (*191, 192*) of $N_3S_3O_3Cl$.

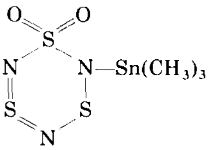


m.p. 105°-108°C

The yield of $N_3S_3O_3Cl$ is increased, when $ClSO_2N{=}S{=}NSO_2Cl$ is irradiated with ultraviolet light. If $N_4S_4O_2$ is treated with $N[Si(CH_3)_3]_3$

or $N[Sn(CH_3)_3]_3$,





$(CH_3)_3SiN_3S_3O_2$ as well as $(CH_3)_3SnN_3S_3O_2$ were isolated as red crystalline compounds (*221*). The same compounds were obtained from the reaction of FSO_2NSO with the sulfur diimides of trimethyl tin and trimethyl silicon; whether these compounds are six-membered or five-membered rings was established by X-ray analysis. These compounds are the first examples containing three different sulfur atoms of formal oxidation numbers two, four, and six (Fig. 20).

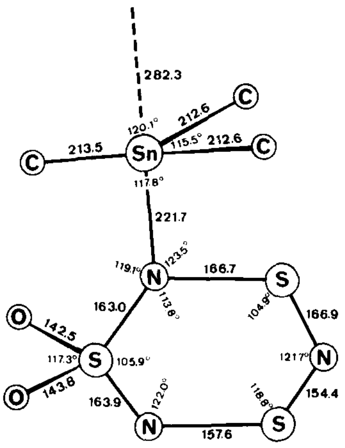
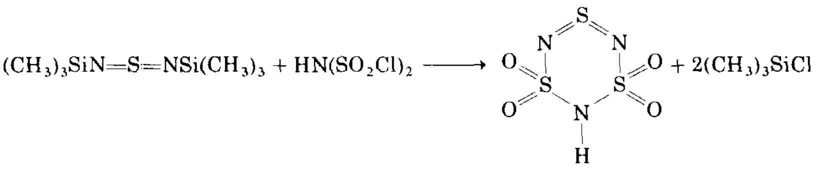


FIG. 20. Molecular structure of $(CH_3)_3SnN_3S_3O_2$.

It has been shown that $(CH_3)_3SiN{=}S{=}NSi(CH_3)_3$ and $HN(SO_2Cl)_2$ reacted to form $HN_3O_4S_3$.



(67)

The structure was established by means of the mass spectrum (*210*). The same compound is formed when $HN(SO_2Cl)_2$ is treated with $(CH_3)_3SiNSO$ (*44*).

H. THREEFOLD COORDINATED NITROGEN AND FOUR-COORDINATED SULFUR

Compounds of this type have been known since 1892 (*102, 247*). Recent X-ray analysis confirmed the six-membered cyclic structure (*56, 105*). $(CH_3NSO_2)_3$ reacts with trimethylamine to form the tetramethylammonium salt, which can be converted to the acid by means of an ion-exchange resin; this is caused to react with silver–carbonate to yield $(CH_3NSO_2)_2(NSO_2)^-Ag^+$. The reaction of the silver salt with C_2H_5I gave $(CH_3NSO_2)_2(NSO_2C_2H_5)$ (*259*).

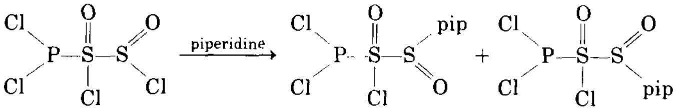
I. COMPOUNDS HAVING ONE ELEMENT IN THE RING OTHER THAN SULFUR AND NITROGEN

From the preparation of $(NSOCl)_3$ and $(NPCl_2)_3$ it follows that ring systems containing both $NPCl_2$ and NSOCl units should also exist. If the thermolysis of $ClSO_2N{=}PCl_3$ is carried out under ultraviolet light, the mixed ring *cis*-$(NPCl_2)$-$(NSOCl)_2$ is formed (*251*). This compound and $(NPCl_2)_2NSOCl$ can be synthezized by thermolysis of the reaction mixture of $[Cl_3PNPCl_3]^+[PCl_6]^-$ and sulfamic acid (*16, 17, 52, 104*). Fluorination of (*cis*-$NPCl_2$)-$(NSOCl)_2$ by AgF_2 yields the fluorine analog. By allowing $(NPCl_2)(NSOCl)_2$ to react with SbF_3, a mixture of two isomers of $(NPCl_2)(NSOF)_2$ is obtained (*16, 123*). The crystal structures of (*cis*-$NPCl_2$)$(NSOCl)_2$ and of the fluorine analog $(NPCl_2)\cdot(NSOF)_2$ (*249, 252*) have been investigated by X-ray analysis. Both molecules are six-membered rings, which show some deviation from planarity. The rings possess a chair conformation. The oxygen atoms are in equatorial position with respect to the mean plane of the ring. The sulfur-bonded halogen atoms are in an axial position. In contrast to $(NSOCl)_3$, the N—S bond lengths in the mixed systems appear to be different:

	NS (pm)
(*cis*-$NPCl_2$)$(NSOCl)_2$	154.0; 157.8
(*cis*-$NPCl_2$)$(NSOF)_2$	152.7; 156.8
(*cis*-$NSOCl$)$_3$	157.1

In contrast to the aminolysis of $(NPCl_2)_2NSOCl$ by morpholine and pyrrolidine, it is observed that in the reaction of *cis*-$NPCl_2(NSOCl)_2$

with piperidine in acetonitrile the first substitution takes place at one of the sulfur atoms. This results in a 1 : 1 mixture of two isomers (*250*).



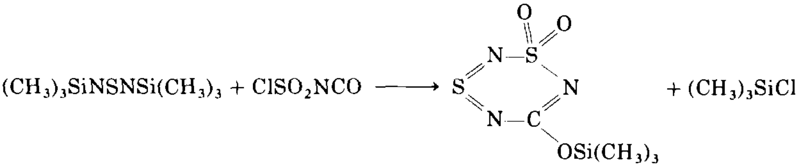
(68)

In both isomers, the PCl_2 center appears to be more reactive toward further substitution than the SOCl center.

In ether, if the reaction takes place the phosphorus atom is attacked predominantly. This has been observed for the amines NH_3, CH_3NH_2, $C_2H_5NH_2$, *n*- and *i*-propylamine. Introducing a relatively small amino group, the reaction in acetonitrile also takes place at phosphorus. However, in acetonitrile the substitution at phosphorus decreases with increasing bulk of the nucleophile, whereas the substitution at sulfur increases (*123*).

The substitution at sulfur requires a very polar solvent. Tetrakis- as well as tris-substituted piperidine derivatives of $NPCl_2(NSOCl)_2$ are known (*250*). $NPCl_2(NSOF)_2$ reacted with silicon–nitrogen compounds and ammonia with monosubstitution at the phosphorus (*111*).

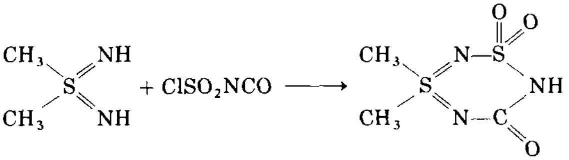
When equimolar amounts of chlorosulfonyl isocyanate and $(CH_3)_3 \cdot SiNSNSi(CH_3)_3$ are combined, a carbon-containing six-membered ring is formed (*13, 210*).



(69)

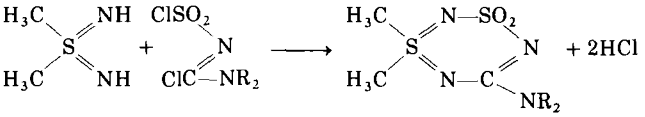
Using $(CH_3)_3SiNS(O)NSi(CH_3)_3$ in the reaction with chlorosulfonyl isocyanate leads to the analogous oxidized compound with coordination number three at one of the sulfur atoms (*13*).

S,S-Dimethyl sulfodiimide has been reported to give in a condensation addition reaction with the bifunctional chlorosulfonylisocyanate a cyclic compound in low yield (*99*).

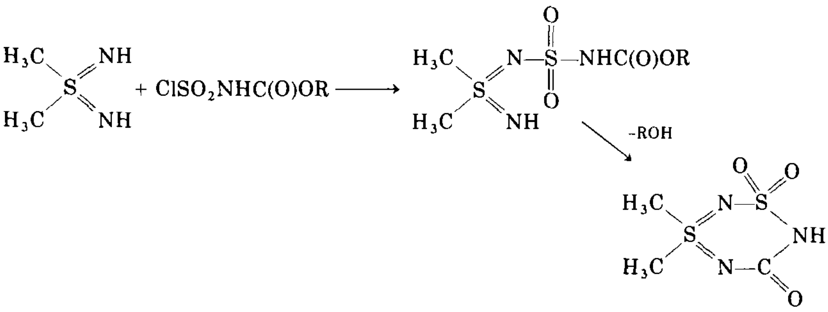


(70)

A series of such compounds have been synthesized either by the reaction of bifunctional imidoyl halides or *N*-chlorosulfonyl carbamates with *S*,*S*-dimethyl sulfodiimide (*100*).

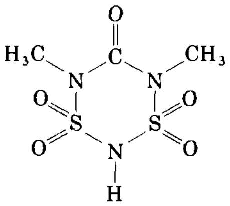


(71)



(72)

When $HN(SO_2Cl)_2$ reacts with *N*,*N'*-dimethylurea, a compound with two SO_2 groups and one carbonyl group is isolated (*243*).



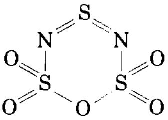
This compound can be converted to the silver salt, which reacts with CH_3I to yield the corresponding methyl derivative.

An oxygen-containing six membered ring of composition $N_2S_3O_5$ is readily available by reaction of either N_4S_4 or $N_2S_3O_2$ with excess of SO_3 (*102*).

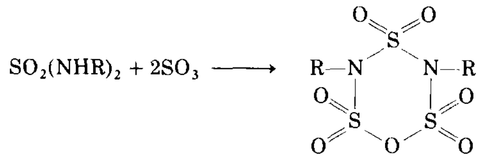
$$N_4S_4 + SO_3 \longrightarrow N_4S_4SO_3 \xrightarrow{SO_3} N_2S_3O_5 \qquad (73)$$

$$N_2S_3O_2 + 3SO_3 \longrightarrow N_2S_3O_5 + 3SO_2 \qquad (74)$$

The following structure was found by X-ray analysis (*189a*):



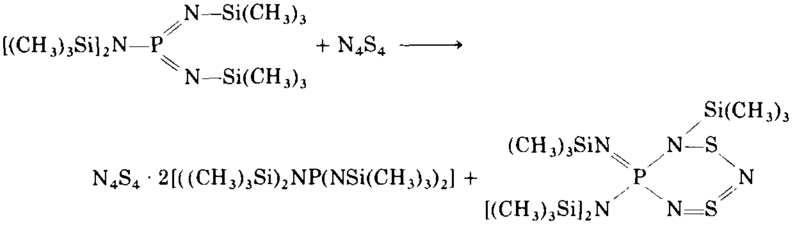
A cyclic six-membered ring is also formed when *N*,*N*′-dimethyl sulfamide or *N*,*N*′-dimethoxy sulfamide is made to react with SO_3 (*102*).



R = methyl, methoxy

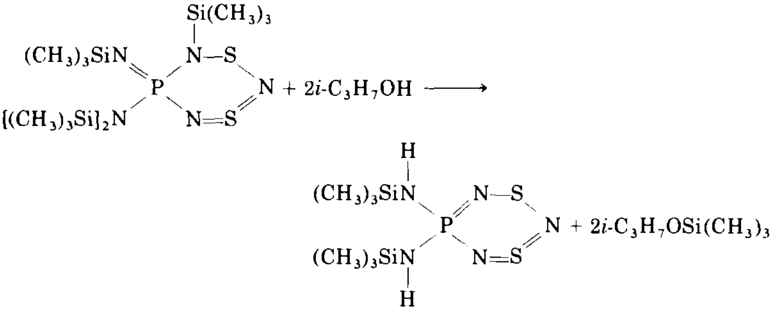
(75)

Probably a phosphorus-containing six-membered S—N ring is formed according to the following reactions:



(76)

In addition to the six-membered ring, a 1:2 adduct was isolated. When the six-membered ring is allowed to react with 2 mol of isopropanol, two of the four trimethylsilyl groups are replaced by hydrogen.



(77)

$[(CH_3)_3SiNH]_2PN_3S_2$ is blue-violet in color and melts at 104°C. An alternative four-membered ring has been discussed (*8*).

VII. Seven-Membered Rings

A. DOUBLY COORDINATED SULFUR AND NITROGEN

The $N_3S_4^+$ ion has been known for a long time. It is an almost planar seven-membered ring as shown in Fig. 21 (*55, 118, 265, 266*). The calculated charge distribution for this ion clearly indicates that the positive charge is extensively delocalized and largely located on the sulfur atoms. The fact that the S—N bond distances (155.0 pm) are equal within experimental error indicates that there is delocalization of the π bonding in this ring. $N_3S_4^+$ can be described as a 10-π-electron system. The question of the σ- and π-contribution in the sulfur–sulfur bond and the possibility of long-range S—S interactions are other points of interest in the structure of this cation (*1*).

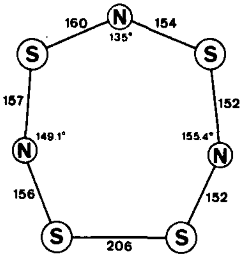


FIG. 21. Molecular structure of $N_3S_4^+$.

A number of methods used to prepare $N_3S_4^+$ are based on ring contraction of N_4S_4, which may be caused by S_2Cl_2, $SOCl_2$, $CH_3C(O)Cl$, HCl, and other acid chlorides (*102*). $N_3S_4^+$ may be obtained also by ring expansion of $N_3S_3Cl_3$ and $N_2S_3Cl_2$ with S_2Cl_2.

$$N_3S_3Cl_3 + S_2Cl_2 \rightarrow N_3S_4^+Cl^- + SCl_2 + Cl_2 \qquad (78)$$

$$3N_2S_3Cl_2 + S_2Cl_2 \rightarrow 2N_3S_4^+Cl^- + 3SCl_2 \qquad (79)$$

If S_2Cl_2 is allowed to react with ammonia, lithium azide, or ammonium chloride under controlled conditions, $N_3S_4^+Cl^-$ is also formed. The bromide of $N_3S_4^+$ is prepared by metathesis of the chloride with potassium bromide in formic acid, and the corresponding fluoride is produced by fluorination of the bromide with hydrogen fluoride. It has been found that these halides undergo both oxidation and reduction reactions (*102*). Both N_3S_4Cl and N_3S_4Br give N_4S_4 and NSCl and NSBr, respectively, on thermal decomposition. No NSI is formed on decomposition of N_3S_4I (*83*).

$$2N_3S_4Cl \xrightarrow{120°C} N_4S_4 + 2NSCl + 2S \tag{80}$$

$$2N_3S_4Br \xrightarrow{90°C} N_4S_4 + 2NSBr + 2S \tag{81}$$

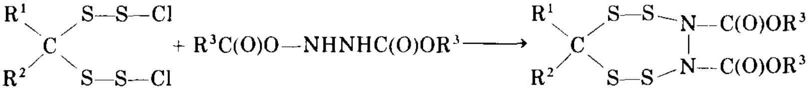
$$4N_3S_4I \xrightarrow{0-30°C} 3N_4S_4 + 2I_2 + 4S \tag{82}$$

In $N_3S_4{}^+Cl^-$ the chloride can be replaced by various anions, SO_3F^- (*182*), $SO_3CF_3{}^-$, $N(SO_2F)_2{}^-$, $N(SO_2CF_3)SO_2Cl^-$, $N(SO_2CF_3)SO_2F^-$ (*201*), $N(SO_2Cl)_2{}^-$ (*32, 102*). $N_3S_4{}^+Cl^-$ forms adducts with $CuCl_2$, $NiCl_2$, $CoCl_2$, $TeBr_4$, $SbCl_3$, $BiCl_3$, ICl, ICl_3 (*25, 130, 183, 184*), $SbCl_5$ (*129*), $InCl_3$ (*279*), and $HgCl_2$ (*262*).

B. Compounds Having One Element within the Ring Other Than Sulfur and Nitrogen

It is of interest that N_4S_4 and $SeCl_2$ react to give $N_3S_3Se^+$. A seven-membered ring was proposed (*25*), but no structural investigations were reported.

A seven-membered ring with a nitrogen–nitrogen bond was isolated from the following reaction (*144*).



(83)

The structure of the methyl compound was determined by X-ray analysis. The seven-membered ring exists in a twist conformation (*145*).

VIII. Eight-Membered Rings

Although the chemistry of N_4S_4 has been fully discussed in recent articles (*30, 60, 81, 82, 90, 91, 192*), for the general cohesion of this chapter it is necessary that its chemistry be dealt with briefly here. The main emphasis is placed on more recent work.

A. Structure and Bonding in N_4S_4, Its Adducts with Lewis Acids and in $N_4S_4{}^{2+}$

The spatial arrangement shown (Fig. 22) was proved by X-ray and electron diffraction (*50, 148, 233*). The cradlelike conformation showed that all sulfur atoms have coordination number three instead of two for a planar ring. An explanation for this was given on the basis

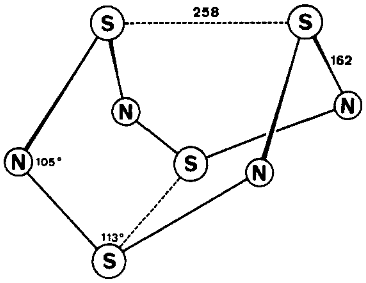


FIG. 22. Molecular structure of N_4S_4.

of an HMO model. The resultant π-orbital scheme is shown in Fig. 23. The π-system of the planar N_4S_4 model is occupied by 12 electrons. Therefore, the lowest five π-orbitals are doubly occupied, and the two higher e_g-orbitals each accommodate a single electron, according to Hund's rule. Thus, the D_{4h} model predicts a triplet ground state. It was shown that symmetry reduction by bond alternation or angle deformation does not yield a significant split of the originally degenerate levels and will not change the multiplicity. The cradle conformation can be described by bending the planar system in such a way that two opposite atoms are brought into close transannular contact. Their interaction is too small to yield a stable singlet ground state and therefore a second σ-bond is necessary to create a 4-centered 8π-system in the plane of the molecule and two σ-bonds, one below and one above this plane. These symmetry considerations show that only the cradle conformation gives a singlet ground state. Whether the nitrogen or sulfur atoms form this transannular interaction is not a question of symmetry, but rather of the total energy of the system. With the help of MO calculations it was shown that the stabilization of the singlet ground state is caused by the effective interaction of the $3p$-orbitals of sulfur over a distance of 258 pm. The $3p\sigma$–$3p\sigma$ overlap of

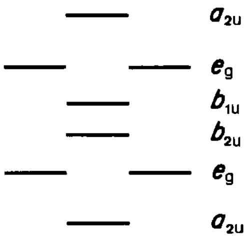


FIG. 23. Hückel molecular orbital diagram for planar N_4S_4 with D_{4h} symmetry.

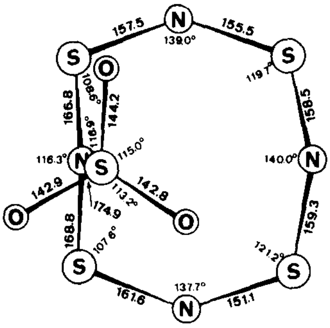


FIG. 24. Molecular structure of $N_4S_4{\cdot}SO_3$.

two sulfur orbitals is much larger than the $2p\sigma$–$2p\sigma$ overlap of two nitrogen orbitals.

N_4S_4 forms adducts with Lewis acids (*74, 173*). A comparison of the structure of these adducts with the structure of free N_4S_4 (Fig. 24) shows that the geometry of the molecule has been changed dramatically. The addition of a Lewis acid to N_4S_4 perturbs only one center of the eight-membered ring (Fig. 25). This perturbation removes the degeneracy of the two highest occupied levels of the planar D_{4h} system, so that a singlet ground state is obtained for this model without the necessity of postulating transannular bonds. From the MO model it follows that for $N_4S_4{}^{2+}$ a planar D_{4h} structure is to be expected, which can be described as a 10-π-electron delocalized system.

An X-ray crystallographic study has shown that the cyclic cation $N_4S_4{}^{2+}$ has different structures in the compounds $[N_4S_4][SbCl_6]_2$ and $[N_4S_4][SbF_6][Sb_3F_{14}]$, which were prepared by the reactions of $(NSCl)_3$

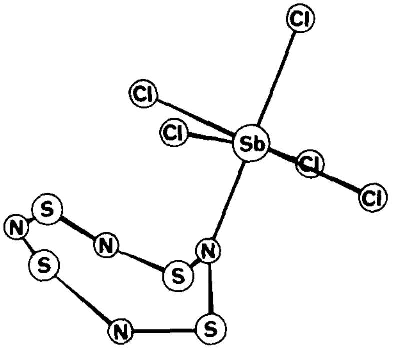


FIG. 25. Molecular structure of $N_4S_4{\cdot}SbCl_5$.

or N_4S_4 with $SbCl_5$ and of N_4S_4 with SbF_5, respectively, in SO_2 solution (*79*).

$$N_4S_4 + 3SbCl_5 \rightarrow [N_4S_4][SbCl_6]_2 + SbCl_3 \tag{84}$$

$$N_4S_4 + 4SbF_5 \rightarrow [N_4S_4][SbF_6][Sb_3F_{14}] \tag{85}$$

The cell of $[N_4S_4][SbF_6][Sb_3F_{14}]$ contains two crystallographically nonequivalent $N_4S_4^{2+}$ ions (A) and (B). Structure (A) is planar and has equal bond lengths and bond angles; structure (B) is also planar but has alternating bond lengths; and structure (C) is nonplanar and has S_4 symmetry and a very pronounced alternation in bond lengths, while the bond angles are all equal (Fig. 26). All three forms have similar energies and the presumably weak interactions with neighboring ions in the crystal lattice appear to be sufficient to cause a rather drastic change in the structure of the cation.

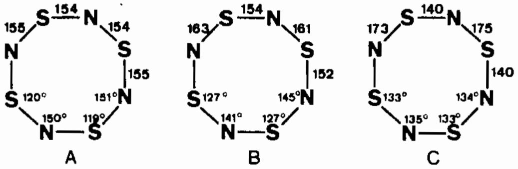


FIG. 26. Molecular structures of $N_4S_4^{2+}$. Structure of ring (A) in $[N_4S_4][SbF_6][Sb_3F_{14}]$; (B) structure of ring (B) in $[N_4S_4][SbF_6][Sb_3F_{14}]$; (C) structure of ring (C) in $[N_4S_4][SbCl_6]_2$, viewed down the S_4 axis.

B. COMPOUNDS WITH COORDINATION NUMBERS TWO AND THREE

N_4S_4 reacts in inert solvents with a wide variety of Lewis acids. Adducts with stoichiometries 2:1, 1:1, 1:2, and 1:4 have been isolated that contain, per mole of N_4S_4: $C_6H_5BCl_2$, TiI_4, $HfCl_4$, WCl_4, WBr_4 (*3*), BF_3 (*179*, *275*), X-ray structure (*59*), 1 or 2 BCl_3 (*14*, *179*, *181*, *275*), 1 or 2 $AlCl_3$ (*3*, *46*), 1 or 2 $AlBr_3$ (*3*, *46*), $GaCl_3$ (*3*), $InCl_3$ (*3*), $FeCl_3$ (*3*), 4 TiF_4 (*3*), 0.5 $SnCl_4$ (*14*, *102*), 0.5 $SnBr_4$ (*27*), 2 or 4 SbF_5 (*53*), 1 or 2 $SbCl_5$ (*14*, *173*, *275*), $SbBr_3$ (*106*), SbI_3 (*106*), 1,2, or 4 SO_3 (*74*), $SeCl_4$ (*181*), $TeCl_4$ (*181*), $TeBr_4$ (*15*), 1 or 2 $TiCl_4$ (*102*), $TiBr_4$ (*14*), $ZrCl_4$ (*14*), VCl_4 (*14*), $NbCl_5$ (*14*), $TaCl_5$ (*14*), $MoCl_5$ (*173*), WCl_4 (*3*), CuCl (*241*), CuBr (*241*), $CuCl_2$ (*241*).

Diadducts: $N_4S_4BCl_3SbCl_5$ (*275*), $N_4S_4AlCl_3SbCl_5$ (*46*), $N_4S_4SnCl_4$-$POCl_3$ (*23*), $N_4S_4BCl_3SO_3$ (*181*), $N_4S_4SbCl_5SO_3$ (*181*), $N_4S_4TeCl_4SO_3$, $N_4S_4TeCl_4BCl_3$ (*181*), $N_4S_4TeCl_4SbCl_5$, $N_4S_4TeCl_4{\cdot}SO_3$ (*181*).

Structural investigations of the adducts are rare (*59*, *173*, *241*). In the structure of $CuClN_4S_4$ (*241*), N_4S_4 functions as a bridging ligand. It is surprising that the N_4S_4 group in $CuClN_4S_4$ does not change its conformation. Bond distances and angles are close to those of the free N_4S_4 molecule. The complex $IrCl(CO)P(C_6H_5)_3N_4S_4$ is formed, together with other products, when N_4S_4 is treated with $IrCl(CO)[P(C_6H_5)_3]_2$. This complex is diamagnetic; the structure is not known (*153*).

Originally, it was reported that N_4S_4 in a Diels–Alder type of reaction functions as a diene, when it forms 1:2 adducts with cyclopentadiene, bicycloheptene, or bicycloheptadiene (*33*). A structural investigation showed that the organic ligands are not bonded to sulfur and nitrogen, but only to the sulfur atoms of the N_4S_4 ring. Therefore, these reactions cannot be formulated as Diels–Alder-type additions. The average SN distance is 162 pm (Fig. 27), the same as is that found in N_4S_4 (*64*, *97*). The transannular S—S-bond lengths are 400 pm compared to 258 pm in N_4S_4. The N_4S_4 ring also remained intact with adducts of *trans*-cyclooctene (*165*), norbornene, norbornadiene, and dicyclopentadiene (*42*).

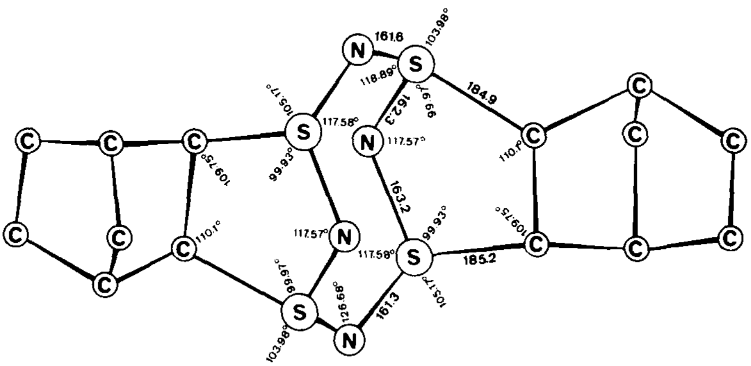


FIG. 27. Molecular structure of $N_4S_4 \cdot 2C_7H_8$, without hydrogen atoms.

Recently N_4S_4 has been used as an insertion reagent in metal–nonmetal bonds (*101*, *200*, *218*, *219*, *223*).

$$2(CH_3)_3SiNR_2 + N_4S_4 \rightarrow 2(CH_3)_3SiN{=}S{=}N{-}SNR_2 \qquad (86)$$

The resulting products are interesting starting materials for the reaction with halides.

$N_4S_4F_4$ was prepared by the direct fluorination of N_4S_4 with either elemental fluorine (*151*) or with AgF_2 in carbon tetrachloride (*87*). $N_4S_4F_4$ has a puckered compact structure (Fig. 28) with almost identical bond angles at the sulfur and nitrogen and a very pronounced

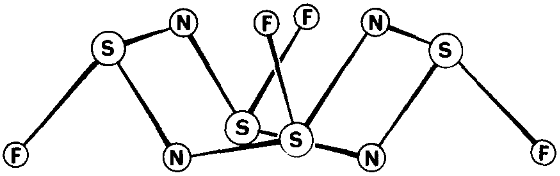


FIG. 28. Molecular structure of $N_4S_4F_4$.

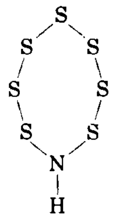
alternation in bond lengths of 154 and 166 pm. In contrast to the chair-shaped six-membered ring of $N_3S_3F_3$, only two fluorine atoms occupy axial positions (*273*). The electronic structure of $N_4S_4F_4$ and other cyclothiazenes has been investigated within the framework of the CNDO/2 approximation. The stability and preferred conformation of the molecules studied were discussed in terms of transannular energy bonding and antibonding terms. The results support Dewar's islands model (*45*). However, the average bond lengths in $N_4S_4F_4$ (160 pm) is essentially the same as in $N_3S_3F_3$ (159 pm) or $N_3S_3Cl_3$ (160 pm). The bond lengths of 160 pm seems to be characteristic of molecules having sulfur with coordination number three and nitrogen with coordination number two. Therefore, the energy differences of molecules with strongly alternating bond lengths and equal bond lengths should be small.

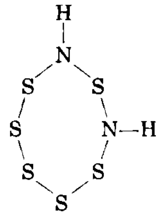
When $N_4S_4F_4$ is treated with the Lewis acids AsF_5 or SbF_5, a mixture of $N_3S_3F_2{}^+MF_6{}^-$ and $NS^+MF_6{}^-$ (M = As, Sb) is obtained (*161*). The $N_4S_4F_3{}^+$ cation seems not to be a stable one, but it is reported that BF_3 forms a stable adduct with $N_4S_4F_4$ (*85*).

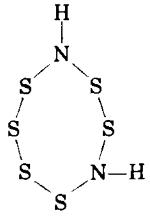
A chlorine analog of $N_4S_4F_4$ was detected as an unstable intermediate in the chlorination of N_4S_4 with elemental chlorine. $N_4S_4Cl_4$ is readily transformed into $N_3S_3Cl_3$ (*4*, *171*). $N_4S_4[ON(CF_3)_2]_4$ is obtained when the stable bistrifluoromethylnitroxide radical, $(CF_3)_2NO$, reacts with N_4S_4. A ring expansion is observed when $N_3S_3Cl_3$ reacts with $(CF_3)_2NO$ or with $Hg[(CF_3)_2NO]_2$ to give $N_4S_4[ON(CF_3)_2]_4$ (*61*, *62*). The SN ring structure can be compared with that of $N_4S_4F_4$ having SN bond distances of 156 and 162 pm (*70*). These data result in an average S—N bond length of 159 pm, which is characteristic for three-coordinated sulfur and two-coordinated nitrogen.

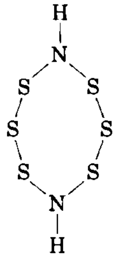
The reduction of N_4S_4 with alcoholic tin(II) chloride gives the tetraimide $N_4S_4H_4$. The ring of this molecule has a crown-shaped configuration very similar to that of the S_8 molecule. The sulfur bond angles in $N_4S_4H_4$ and S_8 are very close, being 108.4° in $N_4S_4H_4$ and 107.8° in S_8 (*102*). The NH group is isoelectronic with a sulfur atom (*106*). The ammonolysis of S_2Cl_2 in dimethylformamide produced a mixture of products, which may be regarded as derivatives of S_8

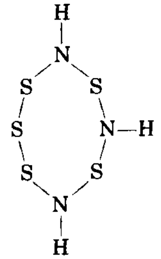
by replacing atoms of sulfur by the imino group. Separations were achieved by fractional crystallization and column chromatography (*106*). A convenient route to S_7NH is the reaction of elemental sulfur with sodium azide (*39b*, *39c*)

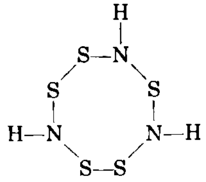

S_7NH


$1,3\text{-}S_6(NH)_2$


$1,4\text{-}S_6(NH)_2$


$1,5\text{-}S_6(NH)_2$


$1,3,5\text{-}S_5(NH)_3$


$1,3,6\text{-}S_5(NH)_3$

Structures have been confirmed by X-ray analysis (*187a*, *252a*, *254*) and also by a study of infrared, Raman (*170a*, *234a*, *237a*), and photoelectron spectra (*27a*). In the crown-shaped S_7NH molecule the nitrogen atom is nearly planar coordinated (*109*). The structure contains no N · · · H bond, but a weak S · · · H interaction. The similarities of $N_4S_4H_4$ along with S_7NH, $S_6(NH)_2$, and $S_5(NH)_3$ have led to their designation as pseudosulfurs. The chemistry of these compounds is mainly that associated with the imido group, which undergoes a number of normal reactions, such as metallization or substitution by inorganic and organic halides. S_7NH and $N_4S_4H_4$ have been studied in the greatest detail, as they are more accessible. NS_7^- was first reported as its sodium salt (*34*). It is a rather unstable yellow ion, best made by reaction (*87*) (*156*, *176*).

$$S_7NH + 2KOH\,(\text{solid}) \xrightarrow[-62°C]{THF} KOH \cdot H_2O + K^+NS_7^- \qquad (87)$$

It reacts as a strong nucleophile, e.g., with methyl iodide.

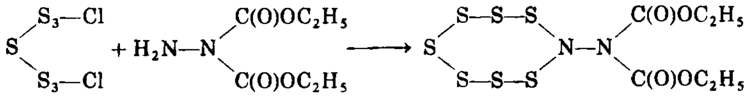
S_7NH was coupled with various sulfur dichlorides, SCl_2, S_2Cl_2, S_3Cl_2, and S_5Cl_2 in the presence of a stoichiometric amount of pyridine, giving $(S_7N)_2S$, $(S_7N)_2S_2$, $(S_7N)_2S_3$, and $(S_7N)_2S_5$, respectively (*106*). The same compounds were obtained according by following reactions (*107, 188*):

$$S_7NH + C_6H_5HgO(O)CCH_3 \rightarrow S_7NHgC_6H_5 + CH_3C(O)OH \qquad (88)$$

$$S_xCl_2 + 2S_7NHgC_6H_5 \rightarrow (S_7N)_2S_x + 2C_6H_5HgCl \quad (x = 1, 2) \qquad (89)$$

S_7NH and $[(CH_3)_2N]_3PO$ form a 2:1 adduct (*238a*) which is only stable below −25°C.

The mercury derivative $S_7NHgC_6H_5$ can also be caused to react with $(CH_3)_3SnCl$, BCl_3 and BBr_3 to yield $S_7NSn(CH_3)_3$ and $(S_7N)_mBX_{n-m}$, where $X = Cl$, $m = 2,3$ and $X = Br$, $m = 1,2$ (*107*). According to this route, pyridine·$B(NS_7)_3$, $CO(NS_7)_2$, $(C_6H_5)_2P(S)NS_7$, and R_3MNS_7 ($M = Sn$, Pb; $R = CH_3$, C_2H_5) were prepared (*189*). $(C_6H_5)_2P(S)NS_7$ was also obtained from $(C_6H_5)_2P(S)Cl$ and S_7NH (*121*). The reaction between diborane and S_7NH gives S_7NBH_2 and $(S_7N)_2BH$ (*157*). A hydrazine derivative of the S_7N ring was prepared from S_7Cl_2 and the hydrazine dicarbonic acid ester in the presence of triethylamine (*146*).



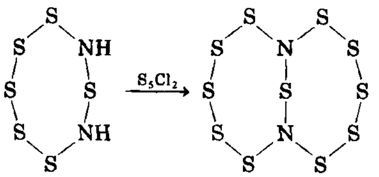
(90)

The X-ray structures of $S_7NC(O)CH_3$ and $1,3,5\text{-}S_5(NCH_2OH)_3$ were investigated (*254*). The S_7N ring is cleaved when S_7NH is treated with tetra-*n*-butylammonium hydroxide:

$$S_7NH + (n\text{-}C_4H_9)_4N^+OH^- \rightarrow (n\text{-}C_4H_9)_4N^+S_4N^- \qquad (91)$$

and the perthionitrate is formed (*48, 49*).

Anions of $1,5\text{-}S_6(NH)_2$ are obtained, when this compound is treated with C_2H_5Li. The resulting anions $S_6N_2H^-$ and $S_6N_2^{2-}$ may be allowed to react with alkyl iodides (*246*). The reaction between the 1,3-isomer and sulfur chlorides gives the first known fused-ring sulfur nitride, $S_{11}N_2$ (*106, 108*).



(92)

X-Ray analysis has shown that there are two puckered eight-membered rings with three coplanar bonds around each nitrogen. Organic derivatives of the eight-membered sulfur nitrogen ring may be obtained by the reaction of S_xCl_2 ($x = 1, 2, 3, 5, 7$) with primary amines (*5a, 40, 95*):

$$S_7Cl_2 + 3CH_3NH_2 \rightarrow S_7NCH_3 + 2CH_3NH_2HCl \tag{93}$$

$$4SCl_2 + 12RNH_2 \rightarrow (SNR)_4 + 8RNH_2 \cdot HCl \tag{94}$$

where $R = CH_3, C_2H_5, C_6H_5CH_2, C_6H_5CH_2CH_2$,

$$2S_3Cl_2 + 6CH_3NH_2 \rightarrow (CH_3NS_3)_2 + 4CH_3NH_2HCl \tag{95}$$

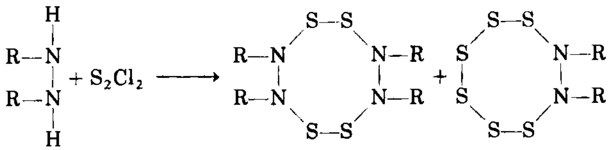
or by the reaction of tetrasulfurimide with organic reagents that react with secondary amines (*102*):

$$N_4S_4H_4 + 4C_6H_5NCO \rightarrow (NSC(O)NHC_6H_5)_4 \tag{96}$$

$$N_4S_4H_4 + 4CH_2O \rightarrow (NSCH_2OH)_4 \tag{97}$$

The most fully investigated was the tetramethyl derivative, for which infrared, Raman, and NMR spectra and an X-ray investigation were reported in support of its cyclic structure (*150*).

Hydrazine and disulfur dichloride in ether produce nitrogen and elemental sulfur. However, a more intensive study of the reaction of 1,2-dimethylhydrazine and other substituted hydrazines with S_2Cl_2 showed two types of compounds to be formed (*141, 142*):



(98)

$R = CH_3, C(O)OCH_2CH_3, C(O)OC(CH_3)_3$

The latter is obtained also from RNHNHR and S_6Cl_2 (*143*). $(OSNH)_4$ has been prepared by air oxidation of $N_4S_4H_4$ or by heating a mixture of 80% elemental sulfur and 20% $N_4S_4H_4$ in the presence of air as an oxidant. $(OSNH)_4$ can be stored at room temperature for several days, but it slowly polymerizes to $(OSNH)_x$ (*66, 68*).

A short note has been published on the preparation of $(NSOF)_4$, which was obtained by pyrolysis of $Hg(NSOF)_2$ (*137*).

The syntheses of $S_4N_5^-$ was achieved by methanolysis of *N*-trimethylsilyl-*N′*-*tert*-butyl sulfodiimide or by reaction of sodium azide with N_4S_4 (*39, 39d, 226*).

$$3NaN_3 + 4N_4S_4 \rightarrow 3NaS_4N_5 + 0.5S_8 + 5N_2 \qquad (99)$$

$NH_4S_4N_5$ is formed by the reaction of S_2Cl_2, SCl_2, SCl_4, $(NSCl)_3$, and N_4S_4 with ammonia (*227*).

The geometric structure (Fig. 29) of the $S_4N_5^-$ anion may be compared with that of N_4S_4, where in one S—S bond a nitrogen has been inserted. This nitrogen bridge levels the distances between the sulfur atoms in such a way that each nitrogen has a nearly undistorted tetrahedral surrounding (*69*).

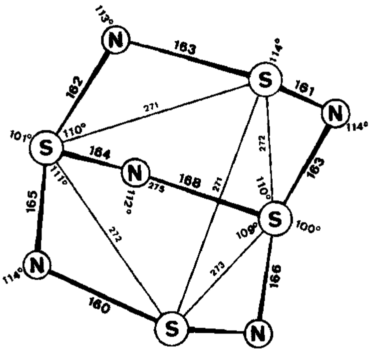


FIG. 29. Molecular structure of $S_4N_5^-$.

C. COMPOUNDS WITH COORDINATION NUMBERS TWO, THREE, AND FOUR

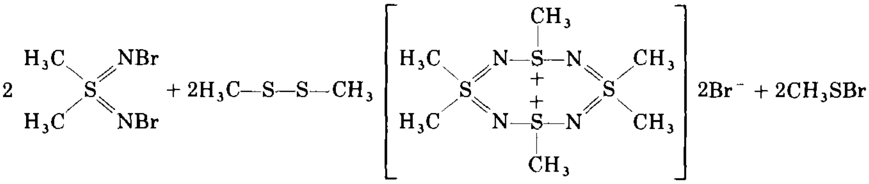
One of the products of the reaction of thionyl chloride with liquid ammonia is the salt $NH_4^+S_4N_5O^-$. This anion is clearly related to $S_4N_5^-$, but one sulfur atom has an additional oxygen atom, which was shown by an X-ray analysis (*31, 149, 235, 236*).

There have been several attempts to prepare the neutral compound $(O_2SNH)_4$ (*102*). The best method of preparing derivatives of the tetrameric ring appears to be the condensation of sulfamide with sulfuryl chloride in acetonitrile.

$$2O_2S(NH_2)_2 + 2SO_2Cl_2 \rightarrow (NH_4)_4(O_2SN)_4 + 4HCl \qquad (100)$$

The ammonium salt can easily be converted into barium, potassium, or silver salts. The ammonium salt is only slightly soluble in water and can be recrystallized from it. A characteristic reaction is the substitution of the metal attached to the nitrogen sites by an organic group (*37, 102*).

When *N,N′*-dibromo-*S,S*-dimethyl sulfodiimines and dialkyl disulfides react in nitromethane, methanol, or methylene chloride, an eight-membered ionic ring system is formed containing alternating sulfur and nitrogen atoms (*7, 194*):



(101)

The saltlike compounds can be derived from N_4S_4 by adding two methyl groups each to two sulfur atoms, and one methyl group each to the two remaining sulfur atoms.

Oxides of N_4S_4 may be prepared from *N,N′*-bis(trimethylsilyl) sulfodiimide and $FSO_2N{=}S{=}O$, $FSO_2N{=}S{=}NSO_2F$, or FSO_2OSO_2F. However, the yields of $N_4S_4O_2$ and $N_4S_4O_4$ are low. $N_4S_4O_2$ is best prepared from condensation of sulfamide with $N_2S_3Cl_2$ (*204, 213, 214, 220, 221*). This procedure gives $N_4S_4O_2$ in yields of 80%. The unit cell contains two crystallographically independent sets of molecules. One set is situated on the mirror planes at $y = \frac{1}{4}$ and $\frac{3}{4}$, and the other around 2-fold axes. Individual molecules do not possess 2-fold shaped symmetry, and disordering of the molecules is required to give rise to the observed symmetry. The dimensions shown in Fig. 30 refer to the

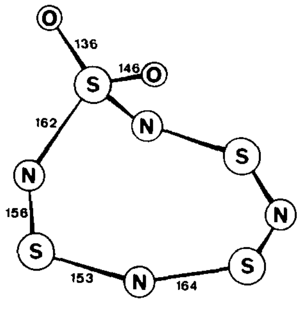
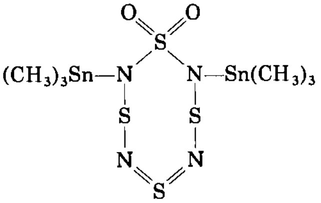


FIG. 30. Molecular structure of $N_4S_4O_2$.

ordered molecule lying on the mirror plane. The molecule contains an eight-membered N_4S_4 ring with both oxygens attached to the same sulfur atom. This atom lies 152 pm and the two adjacent nitrogen atoms 41 pm above the mean plane of the other ring atoms, which are coplanar to within 1.4 pm. The bonding can be described in terms of two sulfodiimide fragments linked by S and SO_2 bridges or, in view of the approach to planarity of the N_4S_3 part of the ring, as a 10-π delocalized system linked into a ring by the SO_2 group.

$N_4S_4O_2$ reacts with $N[Sn(CH_3)_3]_3$ without ring contraction. The formula for this product, shown below, is recognizably related to that of $N_4S_4O_2$ (*220*). The structure was investigated by an X-ray analysis.



IX. Ten-Membered Rings

One of the compounds known so far in this class is the $N_5S_5{}^+$ cation. Salts of this cation have been prepared by three different methods: (a) from the reaction between $S[NSi(CH_3)_3]_2$ and FSO_2NSO; (b) from N_4S_4 or $N_3S_3Cl_3$ with a metal chloride in $SOCl_2$; (c) by insertion of the thionitrosyl cation, NS^+, into one NS bond of N_4S_4 (*20, 22, 23, 160, 204*).

On the basis of X-ray structural investigations two different structures were reported for the $N_5S_5{}^+$ cation: A heart-shaped configuration

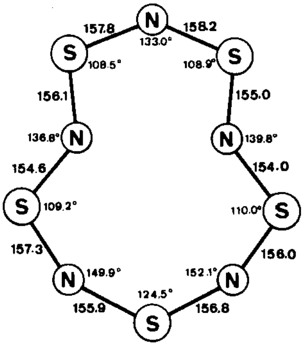
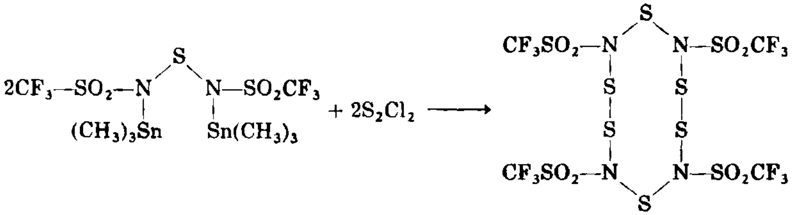


FIG. 31. Molecular structure of $N_5S_5{}^+$.

and an azulene-like configuration. In a localized picture (Fig. 31) the bonding of $N_5S_5^+$ can be described as follows. The σ-skeleton consists of 10 N—S σ-bonds, each center is furthermore carrying a lone pair, n. This accounts for 10 σ- and 20n-electrons and leaves 14 π-electrons. Semiempirical calculations on the heart-shaped structure of $N_5S_5^+$ confirm this picture (*1*). X-Ray data from other SN rings indicate that the sulfur centers adopt angles between 90° and 120° while for the nitrogen centers values between 115° and 125° are found. On the average we obtain about the same value as for carbon π-systems, namely 120°. Taking angle strain and lone-pair interactions into account, it is hard to understand why a heart-shaped structure should be preferred over the others. The comparison of six possible structural isomers of $N_5S_5^+$ within an MO framework leads to the conclusion that an azulenelike structure of $N_5S_5^+$ is to be preferred (*28*). A ten-membered ring can be prepared by the action of S_2Cl_2 on $[CF_3SO_2NSn\cdot(CH_3)_3]_2S$ in the molar ratio of 1:1.



(102)

^{19}F-NMR studies show all the fluorine atoms to be in the same environment. A proof for the ring size was given by mass spectra (*199*).

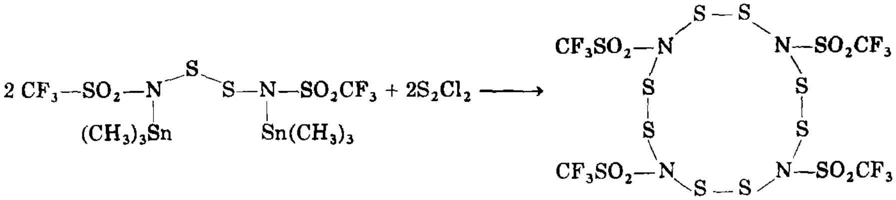
It seems highly probable that larger S—N rings could be made in a similar way, when electron-withdrawing groups are attached to nitrogen and other heteroatoms are incorporated into the rings. There is thus the prospect of considerable development of this particular aspect of sulfur–nitrogen chemistry in the future.

X. Twelve-Membered Rings

A twelve-membered ring has been reported, as a product of thermal condensation of $ClSO_2NH_2$ (*133a*):

$$6ClSO_2NH_2 \rightarrow (SO_2NH)_6 + 6HCl \qquad (103)$$

$[CF_3SO_2NSn(CH_3)_3S]_2$ reacts with S_2Cl_2 to yield the twelve-membered ring $[CF_3SO_2NS_2]_4$.



(104)

It was shown by X-ray analysis that the molecule has a chair conformation (*126a*), which is different in structure from the isoelectronic S_{12} skeleton (*237*).

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