THE SULFUR NITRIDES

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I. Introduction

Although tetrasulfur tetranitride, S_4N_4, was first prepared about 1835 (*53*, *54*), the chemistry of the sulfur nitrides progressed slowly until the middle of the twentieth century. In 1940 the structure of S_4N_4 was not known and could not even be reliably postulated. Of the eight other sulfur nitrides described as individual chemical species in the present review, only two were known, and these had not been fully characterized. Since then, there have been great advances and the whole subject has been put on a systematic footing. Some key contributions have come from the schools of Donohue, who correctly determined the structure of S_4N_4; Becke-Goehring and Meuwsen, whose wide-ranging and meticulous experimental work and original thinking have extended our knowledge in many directions; and Weiss, whose introduction of chromatography to this area of chemistry has proved to be one of the most significant of the many advances made by him. At present, several research groups in Europe, North America, nd Asia are working on sulfur nitrides, and the subject is still in a lively state, though the effort is on a much smaller scale than in more fashionable fields of inorganic chemistry.

There has been no review devoted entirely to sulfur nitrides since 1959 (*8*), but the subject has been covered in three more recent reviews of broader scope (*14*, *16b*, *57*). "Gmelin's Handbuch" (*47*) covers the literature up to 1961.

In the present review, the literature has been examined up to September 1971. The main emphasis is on recent work, and an attempt is made to point out promising lines for future research.

II. Thiazyl, SN, and Its Polymers

A. SULFUR NITRIDE, SN

Sulfur nitride, SN, or thiazyl monomer, is a radical with one unpaired electron. In contrast to its homolog, nitric oxide, it polymerizes so readily that it cannot be isolated as a monomeric solid or liquid and has only a transient existence in the gaseous phase. Nevertheless, much is known about its formation and properties, mainly from its emission spectrum.

The band spectrum of SN was first observed in 1933 in the light emitted by an electric discharge through a mixture of nitrogen and sulfur vapor, and was recognized as coming from SN by its resemblance to the spectrum of NO (*34*). There have been several subsequent investigations of the SN spectrum, in the course of which emissions involving three electronically excited states ($^2\Sigma$, $^2\Delta$, and $^2\Pi$), as well as the ground state ($^2\Pi$), have been observed (*52*, *67*, *94*). The ESR spectrum of SN has been described (*26*).

SN is formed by the passage of an electric discharge through sulfur vapor and nitrogen (*34*, *67*, *81*) or SF_6 and nitrogen (*94*), from the reaction of "active nitrogen" with sulfur vapor (*17*), H_2S (*52*, *67*, *88*), or SCl_2 (*52*), or from flash photolysis of a mixture of COS and NF_3 (*75*).

The bond length of SN, 149.7 pm, calculated from its spectroscopic moment of inertia (*118*), is shorter by 24–28 pm than the sum of single-bond covalent radii, which indicates a bond order between 2 and 3. This parallels the situation for NO and is as expected for the electronic structure of both molecules, viz., three bonding MO's fully occupied and an odd electron in an antibonding MO. The dissociation energy of this strong S–N bond is estimated from spectroscopic data at 463 kJ (*87*). Nevertheless, the compound is endothermic and unstable with respect to its elements, like the other sulfur nitrides; ΔH^0_f is 281 kJ (*87*). The ionization potential has been estimated as 950 kJ from these thermochemical values coupled with the experimental electron-impact appearance potential of SN^+ from NSF (*87*).

The experimental dipole moment of SN is 1.8 ± 0.02 Debye units in either the ground ($^2\Pi_{1/2}$) or first excited ($^2\Pi_{3/2}$) states (*87*), corresponding to "24% ionic character."

Ab initio calculations of several properties of this molecule have been carried out (*87*), using the matrix Hartree–Fock method and the experimental internuclear distance. Good results were obtained for the dipole moment and the ionization potential, but the calculated binding energy (a small difference between two large quantities) was seriously in error.

The polymerization of SN has not been studied in detail, but a deposit of S_4N_4 has been observed in the exit pumping system of the apparatus used for the reaction of active nitrogen with H_2S or SCl_2 (*52*).

Salts of the SN^+ ion, analogous to the nitrosonium salts, have recently been prepared (*46a*) by the reaction of thiazyl fluoride, NSF, with arsenic and antimony pentafluorides.

B. TETRASULFUR TETRANITRIDE, S_4N_4

This is the best known nitride of sulfur, and has formed the starting point of most investigations in sulfur–nitrogen chemistry. One cannot work for long with sulfur–nitrogen compounds without encountering S_4N_4, for it is formed as a by-product of many reactions.

1. *Preparation*

The most convenient method of preparation of S_4N_4 is still the traditional one, from a sulfur chloride and ammonia in an inert solvent, usually carbon tetrachloride. This preparation has recently been investigated (*110*) with the object of maximizing yields; the findings largely supersede earlier scattered information on the effects of procedural variations. The oxidation state of sulfur in S_4N_4 is +3, so, in principle, it would be desirable to start from a sulfur(III) chloride if one existed. Since none does exist, the use of a CCl_4 solution of S_2Cl_2, saturated with chlorine, is recommended. It is not certain that the chlorine actually raises the oxidation state of the sulfur; the reaction of S_2Cl_2 with chlorine to give SCl_2 is known to be slow in absence of a catalyst. However, saturation with chlorine doubles the yield of S_4N_4. Excess ammonia is passed into the mixture, keeping the temperature between 20° and 50°. At 0° the yield of S_4N_4 is 65% lower; there is a 40% increase in the yield of the other main sulfur–nitrogen compound formed, S_7NH. The S_4N_4 is mostly precipitated in the reaction mixture together with ammonium chloride, from which it can be extracted with dioxane to give a yield of 28% based on sulfur.

S_4N_4 explodes when subjected to percussion, friction, or sudden heating. The above preparation is safe, but care is needed with the crystalline end product. Its sensitivity to shock or heat is stated to increase with purity (*110*). No serious accidents with S_4N_4 have been reported, but a research worker in our laboratory was badly cut on the hand when 0.5 gm of the compound which she was crushing with a glass rod in a small beaker detonated violently. The mishandling of quantities of a few grams could cause devastating explosions and endanger life. Obviously one should not leave stocks of S_4N_4 lying about or prepare more than is needed for the purpose in hand.

The course of this S_4N_4 synthesis is now partly understood (*13*, *15*). Whether the starting material is S_2Cl_2 or SCl_2, the volatile and rather unstable NSCl monomer is formed when the flow of ammonia starts; it can be driven out of the reaction mixture by a stream of nitrogen and identified by its infrared spectrum (*15*). NSCl is known to react with S_2Cl_2 (*73*) according to the equation

$$2NSCl + S_2Cl_2 \rightarrow [S_3N_2Cl]^+Cl^- + SCl_2$$

giving the red-brown crystalline compound $[S_3N_2Cl]^+Cl^-$; in the reaction mixture this reaction goes much more quickly than the competing trimerization of NSCl. The $[S_3N_2Cl]^+Cl^-$ has not been isolated from the mixture, as it transforms rapidly in the presence of excess sulfur chlorides and ammonia to the next intermediate, the golden-yellow crystalline thiotrithiazyl chloride, $[S_4N_3]^+Cl^-$. This precipitates and can be isolated in 45% yield (based on sulfur) by interrupting the ammonia stream at the right stage. Finally, as has been shown by separate experiments (*13*), the $[S_4N_3]^+Cl^-$ reacts with more ammonia to give S_4N_4.

A variant of this synthesis, handy for small-scale preparations but giving poor percentage yields, is to pass S_2Cl_2 vapor through pelleted ammonium chloride at 160° (*65*).

An adaptation of Herring's "azide synthesis" of phosphonitrilics is worth mentioning for the principle involved, although it has not yet been developed into a reliable S_4N_4 synthesis (*45*). S_2Cl_2 is added to a suspension of lithium azide in an inert solvent. Nitrogen is evolved. The reactions postulated are as follows:

$$4LiN_3 + 2S_2Cl_2 \rightarrow \underset{\text{(unstable)}}{2S_2(N_3)_2} + 4LiCl$$

$$2S_2(N_3)_2 \rightarrow 4SN + 4N_2$$

$$4SN \rightarrow S_4N_4$$

In the experiments reported, the S_4N_4 was not isolated, but underwent its known reaction with more S_2Cl_2 (Section II, B, 10) to give $[S_4N_3]^+Cl^-$ in 60% yield based on S_2Cl_2.

2. *General Description*

Tetrasulfur tetranitride forms monoclinic (*24*, *29*), strongly birefringent (*105*) crystals of density 2.20 to 2.23 gm/ml at room temperature (*47*), which are usually twinned. It is orange-yellow at room temperature, becoming almost colorless at −190°, orange-red at 100°, and red at higher temperatures. The melting points of well-crystallized specimens range from 178° to 187° (*110*). Since the compound in solution in molten sulfur decomposes completely between 130° and 190° (*101*), the melting point is probably affected by incipient decomposition and, consequently, by the rate of heating. S_4N_4 cannot readily be vaporized even in a high vacuum at room temperature, but it sublimes below 130° at 0.1 mm Hg (*78*). No vapor pressures have been reported, but various qualitative observations (*47*) suggest that the vapor pressure reaches 1 mm Hg somewhere between 80° and 130°. It is insoluble in, and not quickly affected by, water, but soluble in a wide range of organic solvents, in most cases without decomposition. Quantitative solubility data are available for four solvents (Table I). In addition, it is stated (*47*) to be

TABLE I

SOLUBILITIES OF TETRASULFUR TETRANITRIDE

Solvent	Temperature (°C)	Solubility (moles of S_4N_4 per kg of solvent)
Carbon disulfide	0	0.0160
	10	0.0295
	20	0.0404
	30	0.0568
	46.25	0.0810
Benzene	0	0.0140
	10	0.0263
	20	0.0389
	30	0.0536
	40	0.0686
	50	0.0847
	60	0.1056
Ethanol	0	0.0044
	10	0.0057
	20	0.0072
	30	0.0087
	40	0.0102
	50	0.0113

appreciably soluble in carbon tetrachloride, chloroform, aniline, benzaldehyde, formic acid, acetic acid pyridine, quinoline, thiophene, and naphthalene, and to be "almost insoluble" in nitromethane, acetonitrile, nitrobenzene, and n-pentane. In the laboratory S_4N_4 is easily recognized by its characteristic infrared spectrum in CS_2 solution, with two strong bands at 705 and 938 cm^{-1} (Fig. 1). Its X-ray powder diffraction pattern has also been published (*56*).

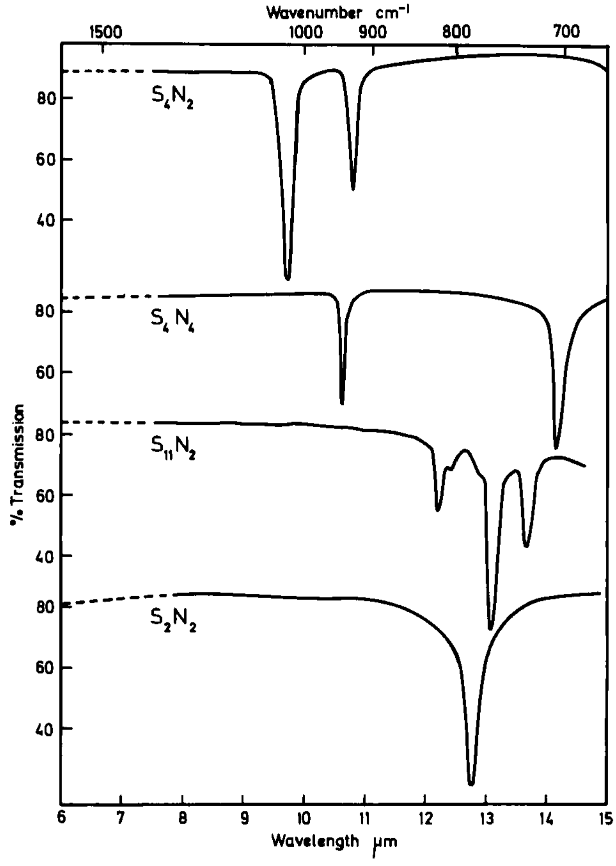


FIG. 1. Infrared spectra of CS_2 solutions of sulfur nitrides. 2–5% Solutions in CS_2; 0.2-mm cell. Dotted lines in regions of strong solvent absorption.

3. *Molecular Structure*

The molecular formula S_4N_4 has been established by analysis and cryoscopic and ebullioscopic determinations of the molecular weight

(*1, 99*). Diffraction studies of the vapor (*71*) and crystal (*104*) show the molecule to have the shape of Fig. 2 in both states of aggregation, with D_{2d} ($\bar{4}2m$) symmetry. The nitrogen atoms form a square and the sulfur atoms a bisphenoid. The S–N bond lengths are all the same, 161.6 ± 1.0 pm (*108*), and correspond to about a 1.65 bond order (*27a*). The distances S-1 to S-3 and S-2 to S-4 are 258 pm, longer than a S–S single bond (205 pm), but shorter than the sum of van der Waals' radii (about 330 pm). This suggests weak S–S bonding, supported by MO calculations (*108*). A molecule with the shape shown in Fig. 2 should have a zero dipole moment. Nonzero values, 0.52 and 0.72 D, have, however, been calculated from the experimental dielectric constants and refractive indices of solutions in benzene and CS_2, respectively (*96*). These values may be spurious, arising from failure to correct adequately for the atomic polarization, which is likely to be abnormally high in this molecule (*74, 96*). The infrared and Raman spectra of S_4N_4, in the solid state and in solution, have been explained in terms of the structure given in Fig. 2 (*19, 55*), with assignments shown in Table II. Fourteen vibrational fundamentals are expected for this structure, of which two (those of A_2 species) would be inactive in both the infrared and Raman spectra, while seven (species B_2 and E) would be active in the infrared. A valence force field has been calculated (*19*) in good agreement with the observed frequencies.

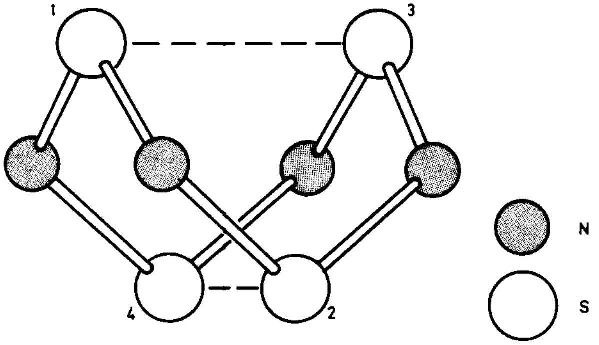


FIG. 2. Molecular structure of S_4N_4. After Sharma and Donohue (*104*).

The structure of S_4N_4 does now seem to be virtually settled, although an alternative to that shown in Fig. 2, with the sulfur and nitrogen atoms interchanged and N–N bonds present, was being discussed as recently as 1966 (*108*). MO calculations (*108*) show that this alternative

TABLE II

FUNDAMENTAL VIBRATIONS OF THE MOLECULE OF TETRASULFUR TETRANITRIDE[a]

Wavenumber (cm^{-1})	Infrared or Raman spectra[b]	Assignment
		A_1
716	Raman only, polarized (2)	S–N
529.7	Raman only[c]	SSN
213	Raman only, polarized (10)	S–S
		A_2
	Inactive in both modes	S–N
	Inactive in both modes	SSN
		B_1
888	Raman only (2)	S–N
615	Raman only (3)	SSN
		B_2
705	Infrared (vs) and Raman	S–N
564	Infrared (m) and Raman (2)	SSN
177.5	Infrared (m) and Raman, depolarized (6)	S–S
		E
938	Infrared (s) and Raman (2)	S–N
766	Infrared (vw) and Raman	S–N
519.3	Infrared (w) and Raman	SSN
314	Infrared (m) and Raman (1.5)	SSN

[a] From Bragin and Evans.

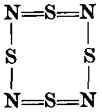
[b] Numbers in parentheses represent relative Raman intensities. Letters in parentheses represent infrared intensities (very weak, weak, medium, strong, or very strong).

[c] So far not actually observed in the Raman spectrum, but only as a weak band in the infrared spectrum of the solid.

should be considerably less stable than the structure given in Fig. 2. Moreover, the chemical behavior of S_4N_4 is always compatible with Fig. 2 and sometimes inconsistent with the alternative (inasmuch as hydrazine is not formed by hydrolysis or reduction).

4. *Electronic Structure*

The facts relating to the electronic structure of S_4N_4 are as follows. All S–N bonds have the same length, corresponding to a bond order of about 1.65 (*27a*). The bond distances (Section II,B,3) suggest weak S–S bonding. The electronic absorption spectrum shows poorly resolved vibronic bands of medium intensity at about 420 and 327 nm, which are responsible for the color; a very strong band at 257 nm; and a strong band beyond 185 nm with a shoulder at 204 nm (*20*). S_4N_4 is diamagnetic, with $\chi = -102 \times 10^{-6}$ mole^{-1}; this value exceeds the value for $S_4(NH)_4$ and is considered evidence of a diamagnetic ring current (*20*). The ^{14}N NMR spectrum of S_4N_4 (*74*) consists of a single line at 485 ± 20 ppm upfield from aqueous nitrite ion; a value nearer to typical values for singly bonded nitrogen than for doubly bonded nitrogen, although the bond lengths, and Lewis structures (I) to (III), point to a degree of multiple bonding.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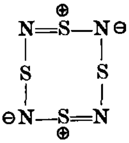
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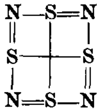
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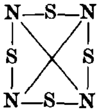

(IV)

There have been three theoretical models of the electronic structure, all with delocalized π electrons as a feature. In the earliest and simplest, the "electron-on-a-sphere" model of 1962 (*27a*), these electrons were assumed to move in a sphere of uniform potential coterminous with the molecule. Subsequently, two fuller MO treatments have been published (*20*, *108*). The interpretation of the experimental data in terms of these models is complicated and not entirely settled (*74*). Reference should be made to the original papers for details. The more recent MO treatments do, however, support the evidence of the bond lengths that there is appreciable S–S bonding but negligible N–N bonding; in other words, structure (III) contributes but (IV) does not. The main ultraviolet band at 257 nm may well represent an $n \rightarrow \pi^*$ transition into a π orbital which the NMR data suggest must be spherically symmetrical (*74*).

5. *Thermochemistry*

Although the S–N bonds in S_4N_4 are quite strong (~307 kJ; the exact value depends on the strength assumed for the S–S bonds), the compound has a positive enthalpy of formation from its elements. This, of course, is a consequence of the high dissociation energy of the nitrogen molecule. ΔH^0_f has recently been determined by decomposition of the nitride to its elements in a calorimeter [*5*]; it is given as 460 ± 8 kJ/mole. This replaces a value of 536 kJ determined in the last century.

6. *General Reactions*

The reactions of S_4N_4 are very diverse. It is convenient to classify them along conventional lines as thermal decomposition and dissociation, oxidation, reduction, reactions with electrophiles, reactions with nucleophiles, and addition reactions.

The eight-membered ring of S_4N_4 is not to be compared to organic rings which persist essentially unchanged through a variety of substitutions, couplings, and ring fusions. It is better to think of it as a labile polymer of four thiazyl, SN, units, which are individually fairly stable, but are as likely to appear in the reaction products of S_4N_4 in groups of two, three, or five, as in fours.

7. *Thermal Decomposition and Dissociation*

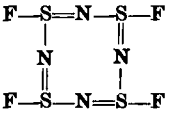
When heated to 130° (*51*) or higher at ordinary pressures, S_4N_4 decomposes wholly to nitrogen and sulfur, usually with an explosion. Differential thermal analysis of samples diluted with a large excess of octasulfur (*102*) shows that under these conditions decomposition proceeds quietly, though exothermically, between 120° and 190°.

When the vapor of S_4N_4 at low pressure is passed through a region heated to 300°, S_2N_2 is formed (Section II,C). There is some accompanying decomposition of S_4N_4 to its elements, and if steps are not taken to remove the sulfur so formed, S_4N_2 (Section III) is produced by reaction of this sulfur with S_4N_4 or S_2N_2.

8. *Oxidation, including Halogenation*

S_4N_4 is little affected by air, dry or moist, at room temperature, but it burns vigorously when slowly heated. Rapid heating in air causes detonation (*47*). It reacts with ozone and hydrogen peroxide, but the reactions are not understood (*47*). Nitrogen dioxide in carbon tetrachloride or carbon disulfide oxidizes S_4N_4 to nitrosyl disulfate, $(NO)_2S_2O_7$ (*77*). Chloramine-T in acidified dioxane converts it quantitatively to sulfuric acid and ammonia (*79*).

The direct reaction of S_4N_4 with fluorine has not been investigated, but electrochemical fluorination breaks the molecule down completely, giving NF_3 and SF_6 as major products (*33*). Milder fluorination can be effected by metal fluorides in high oxidation states. Under the mildest conditions, when a CCl_4 solution of the nitride is warmed with silver(II) fluoride and then allowed to cool, colorless needles of tetrathiazyl tetrafluoride (V) crystallize out (*46*). This compound contains the S_4N_4 ring intact, but flattened (*114*). It depolymerizes to thiazyl fluoride



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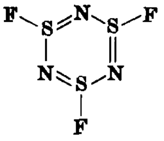

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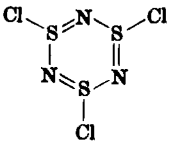


(VII)

monomer, NSF, when heated to 300° *in vacuo* (*44*). NSF, a colorless gas boiling at 0.4°, can also be made in good yield by fluorination of S_4N_4 under more vigorous conditions, viz., refluxing with HgF_2 in carbon tetrachloride (*46*). The cyclic trimer, $N_3S_3F_3$ (VI), also exists, but it is made by fluorination of $N_3S_3Cl_3$ (VII), not directly from S_4N_4 (*46*). $N_3S_3Cl_3$ (m.p. 162.5°) results from the action of chlorine on a solution or suspension of S_4N_4 in CS_2 or CCl_4 (*100*). In this standard preparation, the $N_3S_3Cl_3$ only crystallizes hours after the chlorine has been passed into the vessel. This is because, as recently shown (*82*), the primary chlorination product is not $N_3S_3Cl_3$, but $N_4S_4Cl_4$, the chlorine analog of (V). The $N_4S_4Cl_4$ has not been isolated; it decomposes according to the equation

$$N_4S_4Cl_4 \rightarrow N_3S_3Cl_3 + NSCl$$

with a half-reaction time of about 1 hr in CS_2 at room temperature. $N_3S_3Cl_3$ can be depolymerized to gaseous NSCl *in vacuo* at 110°, whereas at room temperature NSCl trimerizes easily (*43*, *82*). These reactions of the chlorine and fluorine compounds illustrate the lack of kinetic stability of the polythiazyl ring systems and the importance of thermodynamics in determining the reaction products under practical conditions.

Bromine and S_4N_4 in CS_2 react to give bronze crystals, insoluble in nonpolar solvents, which until recently were thought to be poly(thiazyl bromide), $(NSBr)_x$. In our own investigations, however, we have not been able to get analyses in good agreement with this formula, and we suspect that the bronze compound may really be $S_3N_2Br_2$. It gives a conducting solution in nitromethane, which $N_3S_3Cl_3$ does not. There is infrared evidence of the formation of NSBr as a soluble intermediate in the bromination reaction (*84*).

When S_4N_4 reacts at room temperature with bistrifluoromethyl nitroxide, $(CF_3)_2NO$, a white crystalline compound is formed with the tetrameric formula $[NSON(CF_3)_2]_4$; X-ray diffraction shows it to have a structure like (V), with the S_4N_4 ring intact although altered in shape (*32a*).

S_4N_4 dissolves in concentrated sulfuric acid to give an orange solution. At the same time it is oxidized in a complex reaction (*66*, *70*). One of the early products is $S_2N_2^+$, the identity of which has been established by ESR spectroscopy. The end products include sulfur dioxide and sulfamic acid.

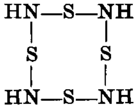
9. *Reduction*

The MO calculations on S_4N_4 (Section II, B, 4) show that there should be low-lying vacant orbitals; the presence of these is confirmed by the ability of the molecule to add an electron. Electrolysis in tetrahydrofuran solution, or treatment with potassium in the same solvent, gives the paramagnetic species $S_4N_4^-$ (*76*), recognized by its ESR spectrum and stable only below −25°. Potassium in dimethoxyethane at room temperature reduces S_4N_4 to a series of colored ions, two of them paramagnetic, which were formerly thought to be the result of simple electron addition to S_4N_4, but must now be attributed to unidentified decomposition products (*27*, *76*). There is not yet convincing evidence for the direct addition of more than one electron to the S_4N_4 molecule. However, an orange-red sodium salt thought to contain the anion $S_4N_4^{4-}$ has been obtained from tetrasulfur tetraimide (VIII) by the reaction

$$S_4(NH)_4 + 4[Ph_3C]^-Na^+ \xrightarrow[\text{dioxane}]{\text{ether-}} 4Ph_3CH + [S_4N_4]^{4-}Na_4^+$$

and the lithium salt can be obtained similarly using butyllithium (*4a*).

S_4N_4 can easily be reduced to sulfur imides. In the fast reaction with tin(II) chloride in boiling methanol/benzene (*51*), a hydrogen atom is simply added to each nitrogen of the ring. The product (VIII) is a colorless crystalline compound melting at 156°, with a puckered ring molecule very like that of octasulfur (*98*). By contrast, the slow reduction of S_4N_4 with hydrazine adsorbed on silica gel in benzene at 46° (*39–41*) gives a mixture of cyclic sulfur imides $S_{8-n}(NH)_n$ ($n = 1$, 2, 3, or 4) as well as sulfur. Examples of these imides are shown in formulas (VIII) to (XII) (*109*).



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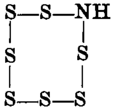

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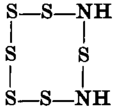

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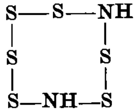

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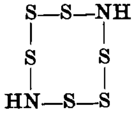

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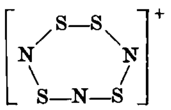


(XIII)

Hydrogen iodide in CCl_4 completely reduces S_4N_4 to H_2S and ammonia (*80*).

10. Reactions with Electrophiles

The reactions of S_4N_4 with Lewis acids are a topic of current interest. Surprisingly, however, little attention has been given to the hydrogen ion. A dark red precipitate thought to be $S_4N_4 \cdot HCl$ is formed (*72*) initially from the nitride and HCl in carbon tetrachloride, and reacts with more HCl according to the equation

$$S_4N_4 \cdot HCl + 3HCl \longrightarrow [S_4N_3]^+Cl^- + NH_4Cl + Cl_2$$

The reactions with HBr (*72*) and HF (*93*) are similar in their end results.

TABLE III

ADDUCTS OF TETRASULFUR TETRANITRIDE WITH MAIN GROUP HALIDES AND SULFUR TRIOXIDE

S_4N_4 plus:	Reference	S_4N_4 plus:	Reference
BF_3	*116*	$2SbI_3$	*97*
BCl_3	*92, 116*	$2SO_3$	*51*
$2BCl_3$	*92*	$4SO_3$	*51*
BBr_3	*116*	Se_2Cl_2(?)	*115*
$\frac{1}{2}SnCl_4$	*116*	$SeCl_4$	*92*
$\frac{1}{2}SnBr_4$	*4a*	$SeCl_4 \cdot SO_3$	*92*
$2SbF_5$	*97*	$TeCl_4$	*92*
$4SbF_5$	*30*	$TeCl_4 \cdot BCl_3$	*92*
$SbCl_5$	*92, 116*	$TeCl_4 \cdot SbCl_5$	*92*
$2SbCl_5$	*92*	$TeCl_4 \cdot SO_3$	*92*
$2SbBr_3$	*97*		

The halides of the ion $[S_4N_3]^+$ (XIII) (thiotrithiazyl halides) are well characterized crystalline salts (*57*). S_4N_4 probably acts as a base toward H^+ in these reactions, but a more direct investigation of its Brønsted base character in the absence of complications is obviously needed.

With the halides of the main-group elements, in inert solvents, S_4N_4 often gives donor–acceptor complexes in which nitrogen is the donor atom (Table III). The adduct $S_4N_4 \cdot BF_3$ is obtained (*116*) as dark burgundy-red crystals by passing BF_3 into a CH_2Cl_2 slurry of S_4N_4. In its crystal structure (*32*) one nitrogen of the S_4N_4 ring is coordinated to boron, and the ring is flatter than in S_4N_4, with the four sulfur atoms coplanar (cf. Fig. 3). The orange-red $S_4N_4 \cdot BCl_3$, formed similarly, is believed, on infrared evidence, to be similarly constituted (*116*). $S_4N_4 \cdot BBr_3$ exists (*116*), but has not been obtained pure. Following the usual order of Lewis acid strengths toward donor nitrogen, the BF_3 adduct is less stable than the BCl_3 adduct, losing BF_3 easily on warming or *in vacuo*, with an enthalpy of dissociation of only 62.8 kJ/mole, and being converted to $S_4N_4 \cdot BCl_3$ by treatment with BCl_3. The red, crystalline, and rather stable $S_4N_4 \cdot SbCl_5$, formed by bringing the components together in CCl_4, $CHCl_3$, or CH_2Cl_2 (*116*), has been shown by X-ray diffraction (*86*) to have the structure given in Fig. 3, with one donor nitrogen atom and the ring flattened. There has been some discussion whether the S_4N_4 molecule can add molecules of Lewis acid to more than one of its nitrogen atoms. There is no clear structural proof that it can, although such behavior would not be surprising in view of the proven behavior of S_2N_2 as a bidentate ligand (Section II,C,4). Diadducts of S_4N_4 with BCl_3 or $SbCl_5$ are reported to be formed in liquid SO_2 at $-40°$ (*92*), but their infrared spectra point to the ionic structures $[S_4N_4 \cdot BCl_2]^+[BCl_4]^-$ and $[S_4N_4 \cdot SbCl_4]^+[SbCl_6]^-$, with unidentate S_4N_4. The mixed adduct $S_4N_4 \cdot BCl_3 \cdot SbCl_5$ is likewise believed (*116*) on infrared evidence to be $[S_4N_4 \cdot BCl_2]^+[SbCl_6]^-$, and the mixed adduct $S_4N_4 \cdot BCl_3 \cdot SO_3$ has been formulated as $[S_4N_4 \cdot BCl_2]^+[SO_3Cl]^-$ on the evidence of infrared and conductance data (*92*). Adducts with two or four molecules of SO_3 (*51*) or SbF_5 (*30*) have been reported, but considering the tendency of SO_3 and SbF_5 to polymerize, these adducts may well

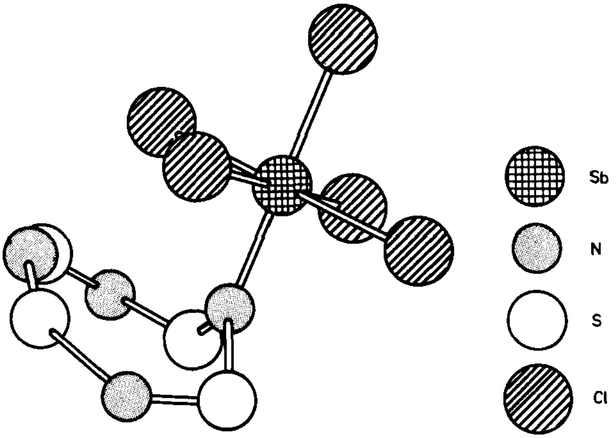


FIG. 3. Molecular structure of $S_4N_4 \cdot SbCl_5$. After Neubauer and Weiss (*86*).

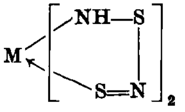
consist of clusters of Lewis acid molecules coordinated to one nitrogen atom of the S_4N_4 ring. 1 : 1 Complexes with $SeCl_4$ and $TeCl_4$ have been given (*92*) an ionic formulation $[S_4N_4 \cdot MCl_3]^+Cl^-$, and they yield adducts formulated ionically as $[S_4N_4 \cdot MCl_3]^+[ACl]^-$ ($A = BCl_3$, $SbCl_5$, or SO_3) with a second Lewis acid. But the evidence cited for these formulations (conductance data in acetonitrile) does not establish the constitution in the solid state, and X-ray crystallographic studies are needed.

An important reaction of S_4N_4 with a Lewis acid is the standard preparation of thiotrithiazyl chloride [cation (XIII)]. It is tempting to

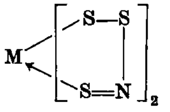
$$3S_4N_4 + 2S_2Cl_2 \xrightarrow[CCl_4]{\text{boiling}} \underset{(90\%\ \text{yield})}{4[S_4N_3]^+Cl^-}$$

postulate addition of S_4N_4 to S_2Cl_2 as the first step in this reaction. However, tracer results with ^{35}S are not easily reconciled with this view (*51*), and another mechanism, involving the dissociation of S_4N_4 to $2S_2N_2$, has been suggested. The corresponding reaction with Se_2Cl_2 is more complicated (*2*, *38*). In CCl_4, the products are thiotrithiazyl chloride and selenium. In thionyl chloride, a yellow compound, recrystallizable from formic acid, is produced which has the empirical formula $SeS_2N_2Cl_2$ and which may be the hexachloroselenate of the selenotrithiazyl cation $[SeS_3N_3]^+$, analogous in structure to (XIII).

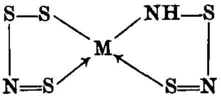
Many reactions of S_4N_4 with the compounds of transition and post-transition metals give rise to complexes in which there are S–N ligands, but probably not intact molecules of S_4N_4. These have been well reviewed (*112*) and only the main results will be described here. Some of the reactions have been carried out in inert solvents and seem relatively simple. With iron, cobalt, and nickel carbonyls in benzene, for example, S_4N_4 gives strongly colored crystalline compounds $M(SN)_4$, of unknown constitution, but monomeric in some solvents. $Mo(CO)_6$ gives the explosive $Mo(SN)_5CO$ (*117*). The ligands in these complexes are probably unidentate SN or bidentate S_2N_2. The same holds for the complexes $CuCl_2 \cdot S_2N_2$ and $CuBr_2S_2N_2$, obtained from S_4N_4 and the halide in dimethylformamide. In the other reactions of complex formation described in the literature, the solvents participate chemically in obscure ways. The nickel, cobalt, and palladium complexes (XIV), (XV), and (XVI), obtained by heating methanol or dimethylformamide solutions of the metal halide with S_4N_4, are colored, crystalline compounds with definite melting points (*112*), the structures of which have been well established crystallographically and otherwise. The hydrogen atoms in the NH groups must come from the solvent; their presence was recognized by infrared spectroscopy and their substitution reactions have been studied.



(XIV)



(XV)



(XVI)

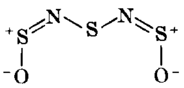
The reactions of S_4N_4 with various metal halides in thionyl chloride have recently been investigated (*4*). They are complicated reactions, because S_4N_4 is known to react with thionyl chloride in the absence of other Lewis acids to give thiotrithiazyl chloride [cation (XIII)] and thiodithiazyl dioxide (XVII) (*2*). The products usually have the stoichiometry of adducts of SN or S_2N_2, but most of them are insoluble in nonpolar solvents and probably polymeric. Exceptionally, the reaction with $AlCl_3$ gives a yellow, soluble, crystalline salt $[S_5N_5]^+[AlCl_4]^-$, the cation of which is a heart-shaped nearly planar ring (*3*).

11. Reactions with Nucleophiles

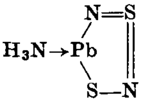
S_4N_4 and S_2N_2 (Section II,C) both dissolve in liquid ammonia to give (after a few minutes standing in the case of S_4N_4) the same red solution, which on evaporation leaves a cinnabar-red solid formulated as $(SN)_2 \cdot NH_3$ or $S_4N_4 \cdot 2NH_3$ or $H_3N_3S_2$ (*6, 7, 85, 119*). Its molecular weight has not been reported. The suggestion that it is an acid with the structure $H{-}N{=}S{=}N{-}S{-}NH_2$ has been made (*6*) on the evidence of its sodium salts. Titration of the ammonia solution with triphenylmethylsodium gives a brown monosodium salt and then a yellow, explosive trisodium salt, probably because the imide hydrogen and the two amide hydrogens are successively replaced. Only one H atom readily ionizes in ammonia solution, however, and the compound behaves as a 1 : 1 electrolyte (*119*). $H_3N_3S_2$ might be expected to behave as a chelating ligand, and if it did so, would give six-membered chelate rings with metal ions. Actually, however, it reacts with "b" class metal ions to give complexes which seem to be derived, not from $H_3N_3S_2$ itself, but from another ligand $H_2N_2S_2$ resulting from disproportionation.

$$2H_3N_3S_2 \rightarrow H_2N_2S_2 + S(NH)_2$$

Addition of lead nitrate or iodide, for example, to the ammonia solution of $H_3N_3S_2$ precipitates green $Pb(NS)_2 \cdot NH_3$, which has been shown by X-ray diffraction to contain the chelate structure (XVIII) (*112*). The drive for the postulated disproportionation probably comes from the superior stability of five-membered chelate rings and the preference of



(XVII)



(XVIII)

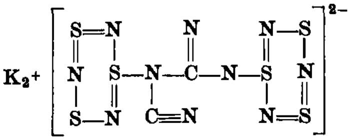
"b" ions for sulfur over nitrogen as a ligand atom. There is evidence for the other product of the disproportionation, $S(NH)_2$; a "salt" of this compound, $HgN_2S \cdot NH_3$, precipitates when mercury(II) iodide is added to the filtrate from precipitation of the lead salt. Thallium, silver, and copper salts can be made in the same manner as the lead salt(XVIII). The formulation usually given for the copper and silver salts, $M(NS)_2$ indicates a +2 oxidation state for the metal, although the copper salt can only be made from Cu(I). It has been suggested (*112*) that these salts are really MS_2N_2H derived from the +1 oxidation state. Air oxidation of a pyridine solution of the compound $(SN)_2 \cdot NH_3$ gives rise to the ammonium salt of the anion $[S_4N_5O]^-$, tetrasulfur tetranitride oxide imide (*16a*, *105a*), a yellow, well-crystallized compound forming stable solutions in polar solvents. The structure of this anion is not known; its infrared spectrum is complex and suggests that a $\rangle S{=}O$ group is present.

The hydrolysis of S_4N_4 has been studied under heterogeneous (*48*) and homogeneous (*80*) conditions. The time required in a homogeneous, aqueous–organic solvent medium containing 0.5 *N* alkali is about 2 hr at room temperature. Reaction in acid solutions is generally slower, but the rate increases with acidity. The nitrogen is always completely converted to ammonia (*48*), confirming the physical–structural deduction that there are no N–N bonds in the molecule and justifying the usual assignment of oxidation number −3 to nitrogen and +3 to sulfur. On this view of the sulfur oxidation state, reasonable mechanisms have been suggested to explain the complex mixture of sulfur oxidation numbers found in the end products of hydrolysis (*18*, *80*, *95*). In the presence of excess sulfite ion, the overall reaction of "hydrolysis" becomes relatively simple, but it is not clear whether the thiophilic sulfite ion attacks the

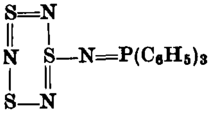
$$S_4N_4 + 6H_2O + 2H_2SO_3 \rightarrow 2H_2S_3O_6 + 4NH_3$$

S_4N_4 ring itself or its primary hydrolysis products (*80*). Hydrolysis of S_4N_4 with aqueous ammonia (*104a*) gives similar products and also sulfamate, probably formed via trithionate.

The thiophiles, cyanide ion and triphenylphosphine, attack S_4N_4 in dimethylformamide solution (*35*). One sulfur atom is removed from the molecule in each case. The product from cyanide attack is thought to be a derivative of the dimer of cyanamide in which the hydrogens have been replaced by S_3N_3 rings (XIX) (*35*). It has not been obtained pure.



(XIX)



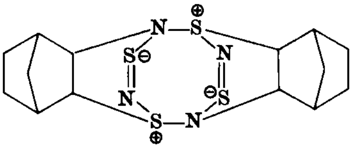
(XX)

The product from triphenylphosphine (*35*, *68*) forms red monoclinic crystals, and X-ray diffraction (*64*) shows it to have the structure (XX). The corresponding cyclohexyl compound has also been made (*68*). Phenyldichlorophosphine probably attacks the S_4N_4 ring similarly, but an excess of the phosphine was used in the reported experiments, leading to total breakdown of the ring with the formation of phosphonitrilic chlorides and phenyldichlorophosphine sulfide (*36*).

Nucleophilic ring opening of S_4N_4 by arylmagnesium bromides gives rise to an interesting series of stable, colored, well-crystallized compounds, Ar–S–N=S=N–S–Ar (*113*), which deserve further investigation.

12. Additions

Some of the Lewis formulations of S_4N_4 [e.g., (II) and (III)] show the molecule with alternate S=N bonds. It is natural to ask whether S_4N_4 would behave as an "inorganic diene" and add to dienophiles in reactions of the Diels–Alder type. It does, in fact, readily form the colorless, crystalline adducts, $S_4N_4 \cdot 4C_5H_6$ (with cyclopentadiene), $S_4N_4 \cdot 2C_7H_{10}$ (with norbornene), and $S_4N_4 \cdot 2C_7H_8$ (with norbornadiene) (*16*, *16b*). The structures of the adducts have not been determined, but by analogy with organic Diels–Alder reactions the structure (XXI) has been suggested for the norbornene adduct.



(XXI)

C. DISULFUR DINITRIDE, S_2N_2

1. *Preparation*

Disulfur dinitride, S_2N_2, the dimer of thiazyl, can be made in good yield by passing the vapor of S_4N_4 at a pressure of about 1 mm Hg or less through silver wool at 300° (*11*, *19*, *21*, *89*). Better yields and safer working conditions are claimed if the operation is carried out at lower temperatures and pressures (*31*). The silver is converted to silver sulfide. Its main function is to remove sulfur generated by the decomposition of S_4N_4 to its elements; if this were not done, the product would be contaminated with too much S_4N_2 formed from this sulfur and S_4N_4 or S_2N_2. The silver sulfide may catalyze the depolymerization of S_4N_4.

2. *Description*

S_2N_2 forms large, colorless crystals which can be sublimed at 10^{-2} mm Hg at room temperature (*50*). It is insoluble in water, but soluble in benzene, carbon tetrachloride, ether, acetone, and especially tetrahydrofuran and dioxane (*50*); it can be recrystallized from ether. It has a repulsive smell and is the least stable of the thiazyl polymers, detonating with friction, shock, or heating above 30°. It polymerizes rapidly at room temperature in the solid state or in solution (*19*).

3. *Molecular Structure*

The cryoscopic molecular weight in benzene corresponds to the formula S_2N_2 (*50*). The infrared spectra of the solid, vapor, and solution indicate a planar, nearly square ring structure with alternating sulfur and nitrogen atoms and D_{2h} symmetry (*19*, *111*), but the instability of the compound has so far prevented a structure determination by X-ray or electron diffraction.

4. *Reactions*

As S_2N_2 is not very easy to prepare or purify, its reactions have not been as extensively investigated as those of S_4N_4.

Rapid and quantitative polymerization to S_4N_4 takes place when traces of alkalis or potassium cyanide are added to solutions of S_2N_2 in organic solvents (*21*). However, when dry, purified S_2N_2 is stored for 30 days in an evacuated desiccator, nearly 100% conversion to polythiazyl $(SN)_x$ (Section II,D) is observed. In moist air, S_2N_2 changes quickly to a mixture of S_4N_4, hydrolysis products, and a little $(SN)_x$ (*31*, *50*). When heated to 250° in a sealed tube, it decomposes quantitatively to its elements (*89*).

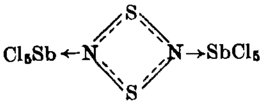
The reactions of S_2N_2 with Lewis acids are a subject of current interest. Adducts of S_2N_2 can be formed, but in some circumstances adducts of S_4N_4 or $(SN)_x$ are obtained. When S_2N_2 is gradually added to $SbCl_5$ in dichloromethane at room temperature (*89*), the following sequence of reactions takes place:

$$S_2N_2 + 2SbCl_5 \rightarrow S_2N_2(SbCl_5)_2 \text{ (yellow crystalline precipitate)}$$

$$S_2N_2 + S_2N_2(SbCl_5)_2 \text{ (dissolves)} \rightarrow S_2N_2\cdot SbCl_5 \text{ (orange, crystallizes on evaporation)}$$

$$S_2N_2\cdot SbCl_5 + S_2N_2 \rightarrow S_4N_4\cdot SbCl_5 \text{ (orange-red precipitate)}$$

Any further S_2N_2 added is quickly changed to S_4N_4, apparently because of catalysis by some unidentified component of the mixture. The adduct $S_2N_2(SbCl_5)_2$ has been shown by X-ray crystallography to have the structure (XXII), with two donor nitrogen atoms and a planar S_2N_2 ring almost the same in dimensions as the free S_2N_2 molecule (*91*).



(XXII)

Mono- and diadducts are also formed with BCl_3 at −78° (*90*). The diadduct easily loses BCl_3. The monoadduct readily polymerizes to a brown solid $[(S_2N_2)(BCl_3)]_x$, which almost certainly does not contain intact S_2N_2 rings. It resembles, and may be identical with, the adduct of $(SN)_x$ with BCl_3 (Section II,D,4). With excess BF_3 (*90*), S_2N_2 gives only the known $S_4N_4\cdot BF_3$ (Section II,B,10). This may be a result of the weakness of BF_3 as a Lewis acid; even in the presence of excess BF_3, there would be a relatively high concentration of free S_2N_2 in equilibrium with the presumed primary adduct $S_2N_2\cdot BF_3$, permitting the secondary reaction

$$S_2N_2 + S_2N_2\cdot BF_3 \rightarrow S_4N_4\cdot BF_3$$

to take place quickly.

The nucleophilically catalyzed dimerization of S_2N_2 has been mentioned above. There is little further information on its behavior with nucleophiles. With liquid ammonia (*6*, *7*, *85*) and aqueous alkali (*50*) it gives the same products as S_4N_4.

D. POLYTHIAZYL, $(SN)_x$

1. Preparation

This compound, of special interest because it conducts electricity, was first observed in 1910 as a blue film with bronzy reflex, accompanying the pyrolysis of S_4N_4 vapor (*25*). We now know that it originates from the polymerization of S_2N_2. The only way to make it in quantity is to store S_2N_2 in an evacuated desiccator, or in a dry, inert atmosphere, for about 30 days at room temperature (*31*, *50*). According to the size of the S_2N_2 crystals used, the $(SN)_x$ crystals in the resulting mass may be very small or up to 3 mm long. They look like brass and have a fibrous makeup.

2. Molecular Structure

The molecular structure of polythiazyl is unknown. It is sometimes assumed to consist of zigzag chains of alternating sulfur and nitrogen atoms. Perhaps this assumption should be questioned, in view of an observation (*31*) that the compound can be sublimed almost unchanged at 100° and 10^{-3} mm Hg, giving in the process no S_4N_4 and very little S_2N_2. It is diamagnetic, with susceptibility equal to the sum of the Pascal constants (*50*), which suggests, but does not prove, that ring currents and rings are absent. It has not been possible so far to form good single crystals for X-ray diffraction. Nevertheless, some progress is being made with X-ray and electron diffraction studies (*18a*, *28*, *31*, *50*); the dimensions of the unit cell have been determined, and it is known to contain four SN radicals (*18a*).

3. Electrical Properties

The resistivity of pelleted samples is of the order of 10^{-2} ohm-cm, and drops with rising temperature (*28*, *50*, *69*). Although this suggests semiconduction, the plot of log of resistivity against $1/T$ is not linear (*28*, *31*), and its slope gives very low activation energies for conduction, <0.02 eV. The Seebeck coefficient shows conduction to be mainly by electrons, and the Hall effect is undetectable, showing that the current carriers have very low mobility (*69*). Although $(SN)_x$ is sometimes called a semiconductor, it has been suggested (*69*) that the conduction may really be metallic, the effect of rising temperature being to increase the mobility of the carriers rather than their number. The optical spectrum contains intense bands peaking at 1.77 eV and about 4 eV (*8*, *31*). Neither of these could correspond to the <0.02 eV activation of the "dark" conductance. It has been impractical, however, to examine the material for photoconductivity in these bands because of its low "dark" resistance (*28*).

Obviously, we must still admit to considerable ignorance of the molecular and electronic structure of polythiazyl.

4. Chemical Behavior

Polythiazyl is not explosive. It ignites in air near 130°. It is insoluble in all ordinary solvents, but can be hydrolyzed with concentrated sodium hydroxide solution to ammonia, sulfite, and thiosulfate (*50*). It is slowly hydrolyzed in moist air (*31*) and forms an adduct $[(S_2N_2)(BCl_3)]_x$ on standing at 20° with BCl_3 (*90*).

III. Tetrasulfur Dinitride, S_4N_2

Traces of this nitride, recognizable by its dark red color, are formed in many reactions involving sulfur–nitrogen compounds. S_4N_2 was first properly characterized in 1951 (*78*), although it had been known, in an impure state, since 1896.

1. Preparation

S_4N_2 is best prepared by heating S_4N_4 with sulfur to 100°–120° in CS_2 solution in an autoclave (*12*). The mechanism of this synthesis is complicated and little understood. The solvent must participate, because much thiocyanogen polymer, $(CNS)_x$, is formed; also, experiments with ^{35}S have shown that 30–35% of the sulfur in the S_4N_2 produced comes from the solvent (*8*). The use of an autoclave can be avoided. S_4N_2 is formed, with loss of nitrogen, when a benzene (or better, xylene) solution of S_4N_4 is refluxed for some hours (*8*, *78*); but yields are smaller, and the method has not been fully investigated. Another very interesting preparation (*78*) not requiring an autoclave

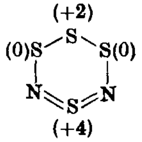
$$Hg_5(NS)_8 + 4S_2Cl_2 \xrightarrow[20^\circ]{CS_2} Hg_2Cl_2 + 3HgCl_2 + 4S_4N_2$$

(42% yield)

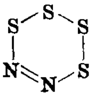
employs one of the mercury salts of $S_4(NH)_4$ (VIII). The idea of this preparation could be further exploited. There are many other salts and complexes of "b" class metals (Section II,B) with sulfur–nitrogen ligands which would probably react with chlorosulfanes to give sulfur nitrides. It is conceivable that new sulfur nitrides, including perhaps isomers of S_4N_2 (below), might be formed in this way. Such reactions would probably go at low temperatures and might therefore be made to yield, by kinetic control, products which are thermodynamically unstable.

2. *Isomerism*

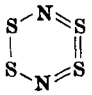
Physical and chemical evidence described below show that S_4N_2 has the structure (XXIII). Many hypothetical isomers of S_4N_2 can be



(XXIII)



(XXIV)



(XXV)

written, such as those represented by formulas (XXIV) and (XXV). None, however, is known. They are probably thermodynamically unstable with respect to (XXIII), for, as shown by chromatography (*83*), only one form of S_4N_2 is present in the products of the autoclave preparation. The same holds true for the products of the $Hg_5(NS)_8$ method (above); the reason in this case may be thermodynamic or structural.

3. *General Description*

Tetrasulfur dinitride forms opaque, red-gray needles which melt at 23° to a dark red liquid looking like bromine (*8*, *83*). In the pure state it decomposes in a few hours at room temperature, and decomposition becomes explosive at 100° (*8*). It keeps much better in solution in CS_2. The vapor pressures have not been measured, but the nitride can easily be sublimed at room temperature at about 1 mm Hg or lower pressures. Vacuum sublimation, or chromatography in CS_2 solution on silica gel, are good ways of purifying it (*83*). It is insoluble in and slowly hydrolyzed by water. It dissolves readily without decomposition in many organic solvents, including CS_2, benzene, chloroform, ether, acetone, ethanol, formic acid, nitrobenzene, and hexane (*49*, *78*).

4. *Molecular Structure*

The molecular formula S_4N_2 has been established by analysis and cryoscopic determination of the molecular weight in benzene (*78*). Determination of the molecular structure has been more difficult. An astonishing number of Lewis structures can be written for the formula S_4N_2. Excluding unlikely features such as three-membered rings and adjacent charges of the same sign, the number is of the order of sixty. Only a few of these have ever been discussed in the literature. There are, unfortunately, no X-ray crystallographic data on S_4N_2, and the instability of the crystals would make an X-ray study difficult. However, the following physical evidence makes it possible to rule out the great majority of hypothetical structures at once, and then to select (XXIII) as the most likely structure among the few remaining contenders (*83*). First, the ^{14}N NMR spectrum contains a single resonance 105 ppm upfield from aqueous nitrate ion, indicating that the two nitrogen atoms are equivalent and doubly bonded. Most of the hypothetical structures have either nonequivalent nitrogen atoms or nitrogen atoms at bridgeheads (i.e., singly bonded), so these need not be further considered. Second, the dipole moment, 1.74 ± 0.28 Debye units, is unmistakably nonzero, and there are coincidences between Raman and infrared spectral frequencies, so that centrosymmetric structures [including planar and chair form (XXV)] can be ruled out. Third, linear structures with equivalent nitrogen atoms cannot be reconciled with the mass spectral fragmentation pattern (*83*). This leaves only (XXIII), (XXIV), and boat form (XXV) to be discussed. There is no frequency in the vibrational spectrum high enough for an N=N bond. Hence (XXIV) can be ruled out. Finally, there are four fundamental S–N stretching vibrations (*83*), the number expected for (XXIII); boat form (XXV) would give only three. The physical evidence, then, is consistent with (XXIII). This structure is also supported by chemical evidence. Hydrolysis (*49*, *78*) converts all the nitrogen in the compound to ammonia; no hydrazine or molecular nitrogen is formed as would perhaps be expected from (XXIV). Detailed studies of the hydrolysis products in the presence and absence of HSO_3^- (*49*) have shown that the sulfur in S_4N_2 behaves as if it were in three oxidation states. This can be understood in terms of

$$S_4N_2 \rightarrow S(+4) + S(+2) + 2S(0) + 2N(-3)$$

(XXIII), by assigning reasonable oxidation states to the different sulfur atoms as shown; but it would be difficult to reconcile with (XXV), in which all the sulfur atoms must have the same oxidation number.

It is noteworthy that S_4N_2 has an entirely different structure from N_2O_4. N_2O_4 is in equilibrium with the paramagnetic NO_2. S_4N_2, in contrast, gives no evidence of dissociation to radicals. It is diamagnetic, with susceptibility near the sum of the Pascal constants (*49*).

5. *Chemical Behavior*

Apart from the hydrolysis just described, the chemistry of S_4N_2 has not been adequately investigated.

S_4N_2 appears to be less strongly basic than S_4N_4 or S_2N_2, undergoing no reaction with BCl_3 in CS_2 solution at room temperature (*84*). In contrast to organic nitrogen bases such as pyridine it does not hydrogen-bond to phenol. It does, however, combine with $SbCl_5$ to give a moisture-sensitive compound with approximately the composition of a 1 : 1 adduct. At the same time, $SbCl_5$ oxidatively destroys some of the S_4N_2, giving rise to $S_4N_4 \cdot SbCl_5$ (Section II, B, 10) and $[S_4N_3]^+[SbCl_6]^-$.

Its sensitivity to oxidative ring opening is also apparent in its reactions with chlorine and bromine, which still have to be fully worked out (*84*). Simple halogenation products containing the intact S_4N_2 ring do not appear to be formed; reaction with chlorine produces instead S_4N_4, $[S_4N_3]^+Cl^-$, and $[S_6N_4]^{2+}Cl_2^-$.

Like other sulfur nitrides, S_4N_2 is easily reduced by HI in anhydrous

$$S_4N_2 + 6H^+ + 6I^- \rightarrow 3I_2 + 4S + 2NH_3$$

formic acid (*49*). Reduction with hydrogen and palladium, potassium borohydride, sodium dithionite, lithium aluminum hydride, or hydrazine (*84*) gives a mixture of cyclic sulfur imides with eight-membered rings, including compounds (VIII) to (XII). A literature report (*37*) of the formation of cyclo-1,3-$S_4(NH)_2$ by reduction of S_4N_2 with tin(II) chloride could not be confirmed, repetition of the experiment giving mainly (IX) (*84*).

IV. Saturated Sulfur–Nitrogen Frameworks, Coupled and Fused Rings, and Polymers

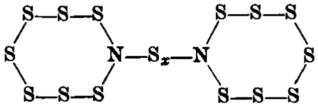
A. GENERAL

The analogy between the sulfanes and the alkanes has often been pointed out, and there is a similar analogy between the cycloalkanes and the various sulfur ring molecules S_x ($x = 6, 7, 8, 9, 10, 12$, or 18) present in different crystalline sulfur allotropes. But sulfur is always divalent in polysulfur chains, and branching seems not to occur. Thus, the branched chains, fused or coupled rings, and cages of organic chemistry can have no analogs among structures composed wholly of sulfur atoms. The situation changes if a few tervalent heteroatoms, such as nitrogen, are introduced as branching points (*62*). An infinite variety of sulfur–nitrogen frameworks can then be postulated, with corresponding structural features to known carbon frameworks. These sulfur nitrides differ from those so far discussed in being "formally saturated"; i.e., they can be written with all single bonds. It is for the experimenter to find out which of them are stable under practical conditions. Only a small fraction of the vast range of conceivable structures has actually been realized. Four coupled-ring nitrides of the homologous series $S_7N–S_x–NS_7$ have been characterized. One fused-ring nitride, $S_{11}N_2$, is very stable and has been extensively studied. In addition, there are incompletely characterized sulfur–nitrogen polymers—some regular and others with more random structures.

B. THE COUPLED-RING NITRIDES, $S_7N–S_x–NS_7$

1. *Preparation*

The members of this series (formula XXVI) with $x = 1$, 2, 3, and 5 have been isolated. Those with $x = 1$ ($S_{15}N_2$) and $x = 2$ ($S_{16}N_2$) were the first saturated sulfur nitrides to be discovered. Their synthesis has set the pattern for all later investigations in the field.



(XXVI)

All these compounds are prepared by the condensation of two molecules of heptasulfur imide, S_7NH (IX) with a chlorosulfane S_xCl_2.

$$2S_7NH + S_xCl_2 \xrightarrow{-2HCl} S_7N–S_x–NS_7$$

Heptasulfur imide, a stable crystalline compound, is the simplest of a series of imides (*57*) exemplified by formulas (VIII) to (XII), all derived, in principle, from octasulfur, and all with puckered-ring molecules (*109*) like octasulfur. It can easily be prepared in quantity from ammonia and S_2Cl_2 in a polar solvent (*58*). Its condensation with chlorosulfanes is slow when the reactants are simply mixed in a solvent such as CS_2; with pyridine present, however, it reacts almost instantaneously at room temperature.

The nitrides of this group with $x = 1$ and $x = 2$ were prepared in 1959 (*9*, *10*), and those with $x = 3$ and $x = 5$ more recently (*42*).

2. *Purification; Molecular Exclusion Chromatography*

The easiest of these nitrides to prepare pure and in high yield is $S_{17}N_2$ ($x = 3$). When prepared as described above, $S_{15}N_2$ and to a lesser extent $S_{16}N_2$ are always contaminated with uncrystallizable sulfur nitrides, which may be other members of the same homologous series, formed in consequence of the disproportionation of the chlorosulfane during the reaction. The purification by crystallization of products thus contaminated is frustrating, because the impurities often separate as a second liquid phase (a red oil) into which the desired compound partitions very strongly. Adsorption chromatography on silica gel is also unsatisfactory because all the compounds are rather weakly adsorbed and tend to move with the solvent front. The stronger adsorbent, activated alumina, decomposes the sulfur–nitrogen rings. Vapor phase chromatography is out of the question because of the low vapor pressure and thermal instability of the compounds. A breakthrough in this purification problem has recently been achieved with the use of molecular exclusion chromatography on an inert polystyrene gel (*63*). Besides its application to the compounds under discussion, this advance has opened up the whole field of saturated sulfur–nitrogen frameworks to systematic investigation. Its advantages include the ability to handle thermodynamically unstable compounds with the least possible risk of rearrangement; the ability to separate nonpolar or weakly polar compounds not amenable to adsorption chromatography provided their molecules differ in size; and the fact that the elution volume of a sought-for compound can be accurately predicted by means of its simple relationship to molecular weight (*63*).

3. *Molecular Structure*

No structure determinations on the solid compounds by physical methods have been reported. The method of synthesis leaves little room for doubt that (XXVI) correctly represents the structural formulas. From the formation of S_7NH (IX) by reaction of $S_{15}N_2$ and $S_{16}N_2$ with piperidine (*9*), it has been argued that these nitrides must contain intact S_7N rings, but this is not proof, since S_7NH is also formed by the reduction of S_4N_4, $[S_4N_3]^+Cl^-$, and S_4N_2.

With all members of this homologous series except the first, a question arises as to the structure and conformation of the $-S_x-$ chain. The dipole moments (*101*) so far measured (in CS_2) are (Debye units): $S_{15}N_2$ ($x = 1$) 0.79; $S_{16}N_2$ ($x = 2$) 1.46; and $S_{17}N_2$ ($x = 3$) 0.88. To begin with, these values for $S_{16}N_2$ and $S_{17}N_2$ rule out branched chains, for a sulfur "side-chain" $>S \rightarrow S$ would introduce a relatively large moment. It seems reasonable to assume that the dihedral angles in the $-S_x-$ chains in $S_{16}N_2$ and $S_{17}N_2$ are near the usual values for polysulfur structures (90°–105°). If so, it follows from simple reasoning (*101*), which will not be given here, that $S_{17}N_2$ must exist in solution as a mixture of conformers.

4. *Properties and Reactions*

$S_{15}N_2$ (m.p. 137°), $S_{16}N_2$ (m.p. 122°), and $S_{17}N_2$ (m.p. 97°) are yellow, crystalline solids, stable in moist air for periods of a few days. Over many months they slowly decompose, giving CS_2-insoluble polymeric material. $S_{19}N_2$ ($x = 5$) could not be crystallized (*101*), but gave satisfactory analyses and molecular weight values, and has been proved chromatographically to be a single substance.

All these nitrides are fairly soluble in CS_2, but only slightly soluble in other nonpolar solvents. It is a curious property of these and saturated

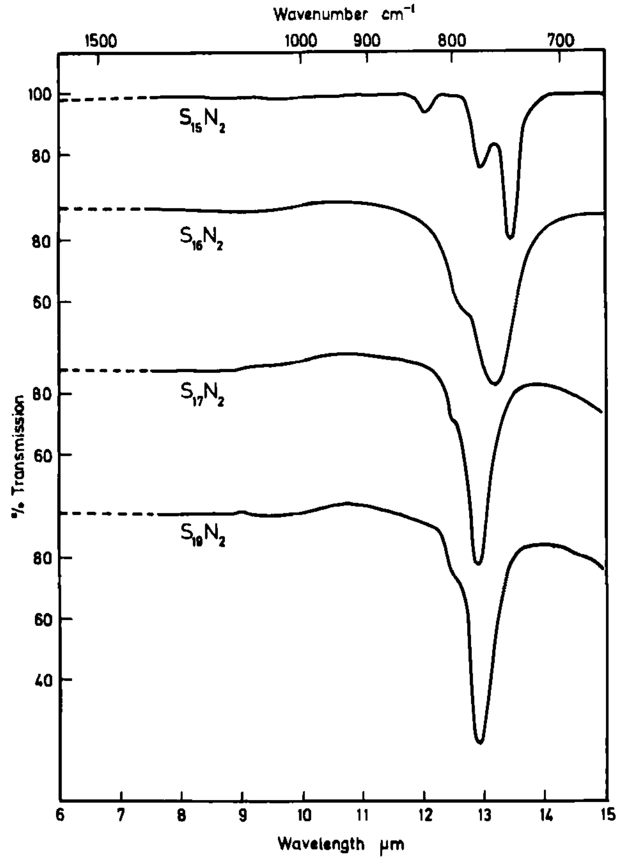


FIG. 4. Infrared spectra of nitrides of the homologous series $S_7N{-}S_x{-}NS_7$: 2-4% solutions in CS_2; 0.2-mm cell. Dotted lines in regions of strong solvent absorption.

polymeric sulfur nitrides (Section IV, E) that they are precipitated from solution in CS_2 by adding quite small amounts of CCl_4.

The infrared spectra of CS_2 solutions of these nitrides show a strong S–N stretch at 750–775 cm^{-1}. In $S_{19}N_2$ the nitrogen atoms are in a nearly symmetrical environment and the band is solitary and nearly symmetrical. On moving down the homologous series to $S_{15}N_2$, a shoulder, becoming a satellite band, develops as the nitrogen environment becomes less symmetrical (Fig. 4). This regularity would be a useful tool for investigating the structures of saturated sulfur–nitrogen polymers (Section IV, E).

On heating for a few minutes just above their melting points, $S_{15}N_2$, $S_{16}N_2$, and $S_{17}N_2$ decompose, giving S_4N_4, which subsequently breaks down to sulfur and nitrogen (*103*). The largest yield of S_4N_4 is obtained from $S_{15}N_2$, which alone of the three compounds has in its structure the –S–N–S–N– configuration present in S_4N_4.

C. THE FUSED-RING NITRIDE, $S_{11}N_2$

1. *General*

This compound, with structure (XXVII) (see also Fig. 5) is one of the most interesting recent developments in the chemistry of sulfur nitrides.

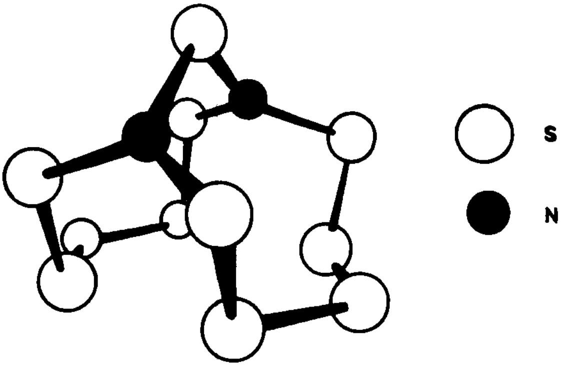
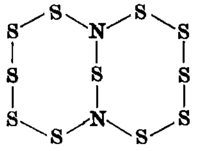


FIG. 5. Molecular structure of $S_{11}N_2$.

Its existence was expected, since molecular models show that two rings with the crown conformation of octasulfur can be fused at the 1,3-positions with little strain (Fig. 5). Experience has now shown $S_{11}N_2$ to be stable and easily handled. Its decomposition, which starts at about

145°, is exothermic but not explosive, at any rate with the small quantities hitherto made. It is not sensitive to shock or friction.



(XXVII)

2. *Preparation*

The best route to $S_{11}N_2$ is a double condensation of 1,3-hexasulfur diimide (X) with an equimolar quantity of S_5Cl_2 (*60*, *63*), in the presence of pyridine. This diimide isomer is formed in rather small yield from the S_2Cl_2–ammonia reaction (*58*) and from the reduction of S_4N_4 with hydrazine (*40*). It is difficult to separate it from its 1,5-isomer; the separation is easier when one prepares it from S_4N_4 and hydrazine, for this method gives relatively little of the 1,5-compound. There are indications that the crude mixture of 1,3- and 1,5-isomers may work nearly as well as pure 1,3-$S_6(NH)_2$ in the preparation of $S_{11}N_2$ (*63*), so separation may not be necessary.

The reaction between the 1,3-diimide and S_5Cl_2 is a polycondensation between two bifunctional molecules, to which the standard theory of polycondensations applies. The products to be expected are linear polymers and ring oligomers of the general formula $[-(S_6N_2)-S_5-]_x$. $S_{11}N_2$ (XXVII) can be thought of as a ring oligomer with $x = 1$. Primary ring closure should be promoted, relative to chain growth, by mixing the reactants under Ruggli–Ziegler dilution conditions. Experimentally, however, the dilution technique gave only a 9% yield of $S_{11}N_2$ from the initial work-up, the remainder of the product being a sticky mixture of polymers. Much more $S_{11}N_2$ was obtained by refluxing the polymers for a few hours with CS_2 (*63*). The polymer has evidently a thermodynamic tendency to eliminate molecules of $S_{11}N_2$. Consequently, the dilution technique is not really needed. It is more convenient and almost as productive to mix the reactants quickly and then decompose the resulting polymer by refluxing it with CS_2.

3. *Description*

$S_{11}N_2$ forms amber-colored crystals. The color of pure samples is very pale, but does seem to be intrinsic. There are two crystalline forms, both monoclinic and both with four molecules in the unit cell (*61*). Slow evaporation of CS_2 solutions gives unsymmetrical octahedra of the α form; rapid evaporation gives thin platelets of the β form. The transition temperature, deduced from the crossing of the solubility curves, is 21° approximately; below this temperature the α form is stable and less soluble than the β form. At 21°, the solubility of both forms is 2.8 gm/100 gm CS_2. α-$S_{11}N_2$ is only very slightly soluble in other common solvents, for example (gm per 100 gm solvent at 20°), ether 0.03, hexane 0.02, and chloroform 0.09. The α crystals melt at 149°–150° when heated quickly in a capillary, but this figure is not very reproducible because of the polymorphic transition and incipient decomposition near the melting point. ΔH for the $\alpha \rightarrow \beta$ transition near room temperature is approximately 10 kJ (deduced from the difference in slopes of the solubility curves).

Neither form is quickly affected by storage in moist air at room temperature, but a few β crystals have been observed to become opaque, presumably because of transition to the α form. CS_2 solutions keep well in the dark in absence of oxygen, but when evaporated in air and light they give some sticky, insoluble polymeric matter.

In the laboratory, $S_{11}N_2$ is easily recognized by its characteristic infrared spectrum in the S–N stretching region (Fig. 1).

4. *Molecular Structure*

X-Ray crystallographic studies on the α-form of $S_{11}N_2$ show that it has the structure of Fig. 5 (*42a*). Other physical evidence (*10*) is consistent with this structure, in which both rings have essentially the shape of the S_8 ring. The mass spectrum shows the molecular ion $S_{11}N_2^+$ and expected fragments. The vibrational spectrum is complicated and difficult to interpret, but the number of infrared-active S–N fundamentals and the number of infrared–Raman coincidences in the S–N stretching region seem consistent with the C_{2v} symmetry of Fig. 5. In CS_2 solution, α- and β-$S_{11}N_2$ give identical infrared spectra, although there are minor differences in their KBr disk spectra; hence, the difference between the forms is probably in the mode of packing in the crystal, not in the structure of the molecules themselves. The dipole moment in CS_2 solution (0.46 Debye) is nonzero as expected from Fig. 5.

5. *Bonding and Chemical Behavior*

The X-ray studies show that the three bonds from each nitrogen atom in α-$S_{11}N_2$ are coplanar. This implies sp^2 hybridization and suggests that the nitrogen lone pairs are used in $p\pi$–$d\pi$ bonding to sulfur, and so unavailable to confer basic properties on the molecule.

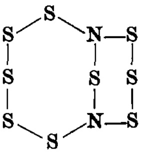
Several observations confirm this. In the first place, $S_{11}N_2$ is not strongly basic. It is insoluble in, and not affected by, concentrated sulfuric acid at room temperature, and it does not combine with BCl_3 at room temperature in CS_2 solution. Second, the dipole moment is much lower than would be expected from two lone pairs in partial reinforcement. Third, the average S–N bond energy term is 248 kJ, about right for a bond order of 1.33, which is what would be expected if the p_z electrons of each sp^2-hybridized nitrogen were fully utilized in $p\pi$–$d\pi$ bonding to its three neighbor sulfur atoms. This bond energy term has been deduced from data for the exothermic decomposition of $S_{11}N_2$ ($\Delta H = -262$ kJ) in solution in molten sulfur in a differential thermal analysis apparatus (*102*). Finally, the electronic absorption spectrum of $S_{11}N_2$ in hexane is remarkably like that of S_8, and contains no additional band attributable to an $n \rightarrow \pi^*$ transition of lone-pair electrons on nitrogen (*101*, *102*).

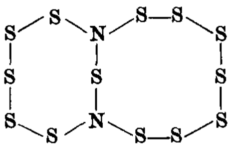
6. *Other Modes of Formation*

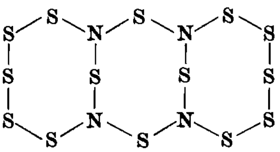
$S_{11}N_2$ is formed in condensation reactions of sulfur imides from which it would not be expected on obvious mechanistic grounds. Good yields are obtained from (X) and S_7Cl_2, poorer yields from (X) and S_3Cl_2. Still more surprisingly, it can be obtained in moderate yield from (XII) (with its imide groups apparently in the wrong relative positions) and S_7Cl_2. These facts are a warning against pressing the analogy between S–N chemistry and organic chemistry too far, and a challenge to the experimenter to try out "wild" ideas.

D. OTHER FUSED-RING NITRIDES

Models of other fused-ring nitrides such as S_9N_2 (XXVIII) and $S_{13}N_2$ (XXIX) can be made up with reasonable bond angles and dihedral angles. Attempts to make (XXVIII) and (XXIX) from (X) and S_3Cl_2 or S_7Cl_2, respectively, have however failed, probably because of kinetic obstacles which may eventually be overcome by using other methods of condensation (*63*). Just as S_6 and S_{10} are thermodynamically unstable


(XXVIII)


(XXIX)


(XXX)

relative to S_8, so compounds such as (XXVIII) and (XXIX) are likely to be unstable with respect to $S_{11}N_2$, and their preparation will call for reaction at low temperatures followed by mild methods of purification such as molecular exclusion chromatography (Section IV, B, 2).

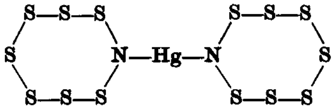
The unknown compound (XXX) may well be thermodynamically very stable. Attempts to make it by condensing (VIII) with S_5Cl_2 or (X) with SCl_2 have not so far succeeded (*101*).

E. Polymeric Saturated Sulfur Nitrides

In all condensation reactions of the bifunctional hexasulfur diimides (X, XI, and XII) with chlorosulfanes S_xCl_2, polymers of the general formula $[-(S_6N_2)-S_x-]_y$ are formed in quantity as tarry red materials.

When equimolar quantities of diimide and chlorosulfane are used, the polymers contain a negligible concentration of end groups and are true sulfur nitrides. Part of the polymer so obtained from (X) is soluble in CS_2, and, from its molecular weight, appears to be a mixture of dimer and trimer, presumably cyclic. The rest is insoluble and presumably consists of linear high polymers. Both kinds are labile at or near room temperature, each giving rise to some of the other when refluxed with CS_2 (*63*). As already mentioned, they eliminate $S_{11}N_2$ (Section IV, C, 2) at the same time.

Condensation of S_2Cl_2 with two moles of (X), (XI), or (XII) gives linear oligomers with NH end groups (*59*). These compounds are not strictly sulfur nitrides, but approximate thereto as the chains get longer. Complex possibilities of isomerism arise among them, which are worth discussing because they show some of the problems to be expected in the experimental study of large, complex saturated sulfur–nitrogen frameworks. The rings of (X), for example, can couple cis or trans to each other through a sulfur chain; the resulting isomers have been separated chromatographically and shown to transform to an equilibrium mixture with a half-reaction time of about 3 hr at room temperature. The rings of (XI) are optically active and give diastereoisomeric coupling products through a sulfur chain; the diastereoisomers have been separated chromatographically and shown to epimerize with a half-reaction time of, again, about 3 hr. Further, polysulfur chains exhibit conformational isomerism, because, with dihedral angles of about 90°, each successive sulfur atom can be added to a chain in a "right-handed" or a "left-handed" way (*107*). The energy barriers between conformations are low enough (*107*) to permit rapid isomerization at room temperature. Considering all these points, it is to be expected that a typical polysulfur nitride built up of a combination of rings, chains, and cages would be formed as a mixture of isomers with very similar gross properties, that would be very difficult to separate and would equilibrate among themselves within minutes to hours at room temperature. In some cases, too, there will be a labile equilibrium between different degrees of polymerization. It is not surprising, then, that the polymeric nitrides so far described (*22*, *23*, *63*), even the dimers and trimers, are uncrystallizable tars.



(XXXI)

Besides the condensation reactions already described, there is a second route to polymeric saturated sulfur nitrides. The mercury(II) "salt" of S_7NH (XXXI) is treated with iodine in CS_2 solution (*22*, *23*). The sequence of reactions is probably

$$Hg(S_7N)_2 + I_2 \rightarrow HgI_2 + 2S_7N\cdot \text{ (unstable)}$$

$$2S_7N\cdot \rightarrow \text{polymer}$$

The polymer, a CS_2-soluble red tar, is of unknown structure and has a molecular weight in the range of 2000–3000. It can be separated by chromatography on silica gel into fractions with varying elemental compositions, infrared spectra, and molecular weights. On standing for a few weeks it eliminates some S_8 and produces a polymer insoluble in CS_2. This may well prove to be typical of large, saturated polysulfur nitride molecules; as discussed above, they are labile at room temperature and therefore (cf. plastic sulfur) will gradually eliminate thermodynamically stable decomposition products such as S_8 and perhaps $S_{11}N_2$.

V. Conclusion

There is obviously a great deal more worthwhile work to be done in the field of sulfur nitrides. This includes studies of their behavior as bases; structural studies on the nitrides themselves, their adducts, and metal derivatives; and investigations of the stability and transformations of saturated polysulfur nitrides. One promising area of research is the use of S–N compounds of metals for the attempted synthesis of new sulfur nitrides (an aspect of the general topic of "reactions of coordinated ligands"). The recently investigated anions of the sulfur imides (*106*) are also attractive starting materials for new syntheses. The relatively new experimental technique of preparative-scale molecular exclusion chromatography opens up many opportunities for the experimenter.

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