(a) $S_2O_5^{2-}$ (b) $S_2O_4^{2-}$

Figure 15.32   Structure of (a) the disulfite ion $S_2O_5^{2-}$ in $(NH_4)_2S_2O_5$, and (b) the dithionite ion $S_2O_4^{2-}$ in $Na_2S_2O_4.2H_2O$.

between $NaHSO_3$ and $NaBH_4$ (p. 167). Its main use is as a reducing agent in dyeing, bleaching of paper pulp, straw, clay, soaps, etc., and in chemical reductions (see below). Current world-wide demand is about 300 000 tonnes per annum.

The dithionite ion has a remarkable eclipsed structure of approximate C_{2v} symmetry (Fig. 15.32b). The extraordinarily long S–S distance (239 pm) and the almost parallel SO_2 planes (dihedral angle 30°) are other unusual features. Electron-spin-resonance studies have shown the presence of the $SO_2^{\cdot-}$ radical ion in solution (~300 ppm), suggesting the establishment of a monomer-dimer equilibrium $S_2O_4^{2-} \rightleftharpoons 2SO_2^-$. Consistent with this, air-oxidation of alkaline dithionite solutions at 30–60° are of order one-half with respect to $[S_2O_4^{2-}]$. Acid hydrolysis (second order with respect to $[S_2O_4^{2-}]$) yields thiosulfate and hydrogen sulfite, whereas alkaline hydrolysis produces sulfite and sulfide:

$$2S_2O_4{}^{2-} + H_2O \longrightarrow S_2O_3{}^{2-} + 2HSO_3{}^-$$

$$3Na_2S_2O_4 + 6NaOH \longrightarrow 5Na_2SO_3 + Na_2S + 3H_2O$$

Hydrated dithionites can be dehydrated by gentle warming, but the anhydrous salts themselves decompose on further heating. For example, $Na_2S_2O_4$ decomposes rapidly at 150° and violently at 190°:

$$2Na_2S_2O_4 \longrightarrow Na_2S_2O_3 + Na_2SO_3 + SO_2$$

Dithionites are strong reducing agents and will reduce dissolved O_2, H_2O_2, I_2, $IO_3{}^-$ and $MnO_4{}^-$.

Likewise Cr^{VI} is reduced to Cr^{III} and TiO^{2+} to Ti^{III}. Heavy metal ions such as Cu^I, Ag^I, Pb^{II}, Sb^{III} and Bi^{III} are reduced to the metal. Many of these reactions are useful in water-treatment and pollution control.

15.2.7 Sulfur–nitrogen compounds [206-210]

The study of S–N compounds is one of the most active areas of current inorganic research: many novel cyclic and acyclic compounds are being prepared which have unusual structures and which pose considerable problems in terms of simple bonding theory. The discovery in 1975 that the polymer $(SN)_x$ is a metal whose conductivity *increases* with decrease in

[206] M. BECKE-GOEHRING and E. FLUCK, Chap. 3 in C. B. COLBURN (ed.), *Developments in Inorganic Nitrogen Chemistry*, Vol. 1, pp. 150–240, Elsevier, Amsterdam, 1966.

[207] I. HAIDUC, *The Chemistry of Inorganic Ring Systems*, Part 2, (sulfur–nitrogen heterocycles), pp. 909–83, Wiley, London, 1970.

[208] H. G. HEAL, *The Inorganic Heterocyclic Chemistry of Sulfur, Nitrogen and Phosphorus*, Academic Press, London, 1981, 288 pp.

[209] H. W. ROESKY, *Adv. Inorg. Chem. Radiochem.* **22**, 239–301 (1979).

[210] *Gmelin Handbook of Inorganic Chemistry*, Sulfur–Nitrogen Compounds: Part 1, 288 pp (1977); Part 2, 333 pp (1985); Part 3, 325 pp (1987); Part 4, 272 pp (1987); Part 5, 276 pp (1990), Springer Verlag, Berlin.

temperature and which becomes superconducting below 0.33 K aroused tremendous additional interest and has stimulated still further the already substantial activity in this area of synthetic and structural chemistry. The field is not new. S_4N_4 was first prepared in an impure form by W. Gregory in 1835,[†] though the stoichiometry and tetrameric nature of the pure compound were not established until 1851 and 1896 respectively, and its cyclic, pseudo-cluster structure was not revealed until 1944.[211] Other important compounds containing S–N bonds that date from the first half of the nineteenth century include sulfamic acid $H[H_2NSO_3]$, imidosulfonic acid $HSO_3N{=}NH$, sulfamide $SO_2(NH_2)_2$, nitrilotrisulfonic acid $N(HSO_3)_3$, hydroxy nitrilosulfonic acids $HSO_3NH(OH)$ and $(HSO_3)_2N(OH)$, and their many derivatives (p. 743).

It will be convenient to describe first the binary sulfur nitrides S_xN_y and then the related cationic and anionic species, $S_xN_y{}^{n\pm}$. The sulfur imides and other cyclic S–N compounds will then be discussed and this will be followed by sections on S–N–halogen and S–N–O compounds. Several compounds which feature isolated S←N, S–N, S=N and S≡N bonds have already been mentioned in the section on SF_4; e.g. $F_4S{\leftarrow}NC_5H_5$, $F_5S{-}NF_2$, $F_2S{=}NCF_3$, and $F_3S{\equiv}N$ (p. 687). However, many SN compounds do not lend themselves to simple bond diagrams,[212] and formal oxidation states are often unhelpful or even misleading.
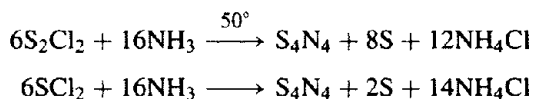
Nitrogen and sulfur are diagonally related in the periodic table and might therefore be expected to have similar electronic charge densities for similar coordination numbers (p. 76). Likewise, they have similar electronegativities (N 3.0, S 2.5) and these become even more similar when additional electron-withdrawing groups are bonded to the S atoms. Extensive covalent bonding into acyclic, cyclic and polycyclic molecular structures is thus not unexpected.
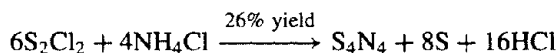
(i) Binary sulfur nitrides

There is little structural similarity between the sulfur nitrides and the oxides of nitrogen (p. 443). The instability of NS when compared with the great stability of NO, and the paucity of thionitrosyl complexes have already been mentioned (p. 453), as has the difference between diatomic O_2 and oligomeric or polymeric S_n. The compounds to be considered in this section are S_4N_4, cyclo-S_2N_2 and catena-$(SN)_x$ polymer, together with cyclo-S_4N_2, bicyclo-$S_{11}N_2$, and the higher homologues $S_{15}N_2$, $S_{16}N_2$, $S_{17}N_2$ and $S_{19}N_2$. More recently, crystalline S_5N_6 (the first binary sulfur nitride with more atoms of N than S) has been synthesized. The fugitive radicals $SN^\bullet$ and $S_3N_3^-$ have also been characterized.

(a) *Tetrasulfur tetranitride*, S_4N_4. This is the most readily prepared sulfur nitride and is an important starting point for the preparation of many S–N compounds. It is obtained as orange-yellow, air-stable crystals[†] by passing NH_3 gas into a warm solution of S_2Cl_2 (or SCl_2) in CCl_4 or benzene; the overall stoichiometries of the mechanistically obscure reactions are:

$$6S_2Cl_2 + 16NH_3 \xrightarrow{50°} S_4N_4 + 8S + 12NH_4Cl$$

$$6SCl_2 + 16NH_3 \longrightarrow S_4N_4 + 2S + 14NH_4Cl$$

Alternatively, NH_4Cl can be heated with S_2Cl_2 at 160°:

$$6S_2Cl_2 + 4NH_4Cl \xrightarrow{26\% \text{ yield}} S_4N_4 + 8S + 16HCl$$

[†] Disulfur dichloride was added to an aqueous solution of ammonia to give a yellow precipitate of sulfur contaminated with S_4N_4; *J. Pharm. Chim.* **21**, 315 (1835).

[211] CHIA-SI LU and J. DONOHUE, *J. Am. Chem. Soc.* **66**, 818–27 (1944). D. CLARK, *J. Chem. Soc.* 1615–20 (1952).

[212] R. GLEITER, *Angew. Chem. Int. Edn. Engl.* **20**, 444–52 (1981); R. D. HARCOURT and H. M. HÜGEL, *J. Inorg. Nuclear Chem.* **43**, 239–52 (1981); A. A. BATTACHARYYA, A. BATTACHARYYA, R. R. ADKINS and A. G. TURNER, *J. Am. Chem. Soc.* **103**, 7458–65 (1981); R. C. HADDON, S. R. WASSERMAN, F. WUDL and G. R. J. WILLIAMS, *J. Am. Chem. Soc.* **102**, 6687–93 (1980).
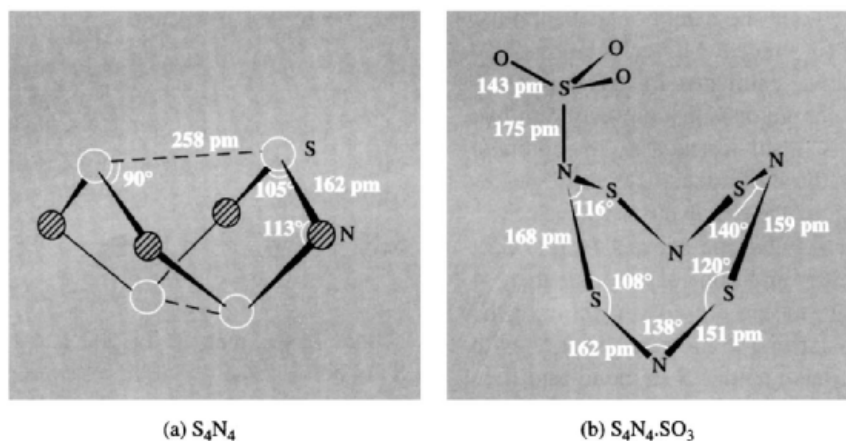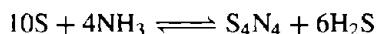
[†] Crystalline S_4N_4 is thermochromic, being pale yellow below about −30°; the colour deepens to orange at room temperature and to a deep red at 100° (cf. sulfur, p. 656).

(a) S₄N₄   (b) S₄N₄.SO₃

Figure 15.33   Structure of (a) S_4N_4, and (b) $S_4N_4.SO_3$.

The compound also results from the reversible equilibrium reaction of sulfur with anhydrous liquid ammonia:

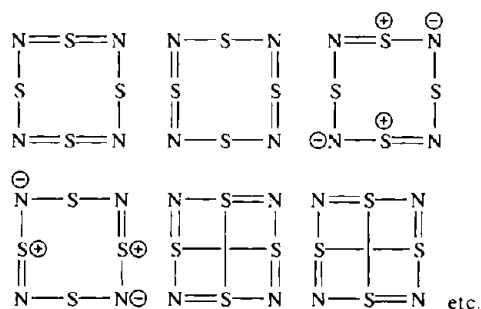$$10S + 4NH_3 \rightleftharpoons S_4N_4 + 6H_2S$$

The H_2S, of course, reacts with further ammonia to form ammonium sulfides but the reaction can be made to proceed in the forward direction as written by addition of (soluble) AgI to precipitate AgS and form NH_4I.

S_4N_4 is kinetically stable in air but is endothermic with respect to its elements (ΔH_f° 460 ± 8 kJ mol⁻¹) and may detonate when struck or when heated rapidly. This is due more to the stability of elementary sulfur and the great bond strength of N_2 rather than to any inherent weakness in the S–N bonds. On careful heating S_4N_4 melts at 178.2°. The structure (Fig. 15.33a) is an 8-membered heterocycle in the extreme cradle configuration; it has D_{2d} symmetry and resembles that of As_4S_4 (p. 579) but with the sites of the Group 15 and Group 16 elements interchanged. The S–N distance of 162 pm is rather short when compared with the sum of the covalent radii (178 pm) and this, coupled with the equality of all the S–N bond distances in the molecule, has been attributed to some electron delocalization in the heterocycle. The trans-annular S···S distances (258 pm) are intermediate between bonding S–S (208 pm) and

nonbonding van der Waals (330 pm) distances; this suggests a weak but structurally significant bonding interaction between the pairs of S atoms. A study by gas-phase electron diffraction yields similar dimensions except that the trans-annular S···S distance is slightly longer (266.6 pm) probably because of the absence of constraining crystal packing forces.[213]

It is not possible to write down a single, satisfactory, classical bonding diagram for S_4N_4 and, in valence-bond theory, numerous resonance hybrids must be considered of which the following are typical:

The extent to which each hybrid is incorporated into the full bonding description of the molecule will depend on the extent to which 3d orbitals
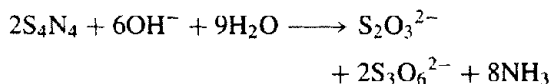
213 A. J. DOWNS, T. L. JEFFERY and K. HAGEN, *Polyhedron* **8**, 2631–6 (1989).

on S are involved and the extent of trans-annular S–S bonding. More recent MO-calculations lead to semiquantitative estimates of these features and to electron charge densities on the individual atoms.[212] It is also instructive to compare the structure of the 44-(valence)electron species S_4N_4 with those of the 46-electron species S_8^{2+} (p. 665) and the 48-electron species S_8 (p. 655): successive formal addition of 2 and then 4 electron results in the progressive opening of the S_4N_4 pseudocluster first to the *bicyclic*-S_8^{2+} with a single weak trans-annular S–S bond and then to the open-crown structure of S_8 with no trans-annular bonding at all.
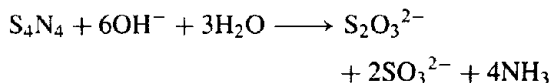
Interestingly, in the N-donor adducts $S_4N_4.BF_3$ and $S_4N_4.SbCl_5$ the S_4N_4 ring adopts the alternative D_{2d} configuration of As_4S_4, with the 4 S atoms now coplanar instead of the 4 N atoms; the mean S–N distance increases slightly to 168 pm but the (nonbonding) trans-annular S···S distances are 380 pm. The same interchange occurs in $S_4N_4.SO_3$ and Fig. 15.33b shows the substantial alternations in S–N distances and angles that are concurrently introduced into the ring. Likewise in the burgundy red salt $[S_4N_4H]^+[BF_4]^-$, formed by direct protonation of S_4N_4 by $HBF_4.Et_2O$ (S–N 157 pm, S–NH$^+$ 165 pm).[214] By contrast, in $S_4N_4.CuCl$ the heterocycle acts as a bridging ligand between zigzag chains of $(-Cu-Cl-)_\infty$; the S_4N_4 retains the same conformation and almost the same dimensions as in the free molecule, with 2 of the 4 planar N atoms acting as a *cisoid* bridge and the 2 trans-annular S···S distances remaining short (259 and 263 pm).[215] It is not yet clear in detail what factors determine the ring conformation adopted (see also p. 656). Other complexes are mentioned below.

S_4N_4 is insoluble in and unreactive towards water but readily undergoes base hydrolysis with dilute NaOH solutions to give thiosulfate,
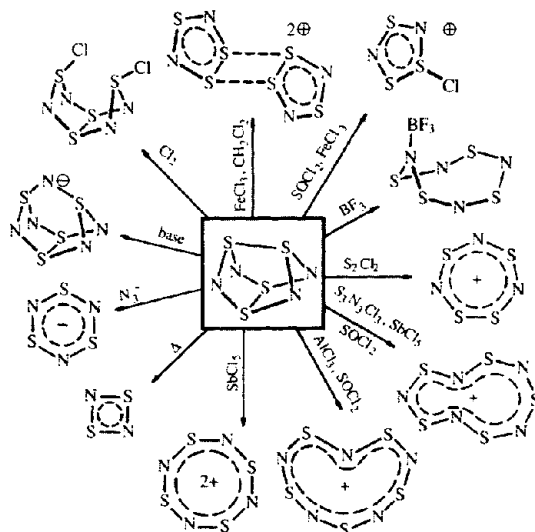
trithionate and ammonia:

$$2S_4N_4 + 6OH^- + 9H_2O \longrightarrow S_2O_3^{2-} + 2S_3O_6^{2-} + 8NH_3$$

More concentrated alkali yields sulfite instead of trithionate:

$$S_4N_4 + 6OH^- + 3H_2O \longrightarrow S_2O_3^{2-} + 2SO_3^{2-} + 4NH_3$$

Milder bases such as Et_2NH leave some of the S–N bonds intact to yield, for example, $S(NEt_2)_2$. The value of S_4N_4 as a synthetic intermediate can be gauged from the representative reactions in the Scheme below[210] and in Table 15.22. It can be seen that these reactions embrace:

(a) conservation of the 8-membered heterocycle and attachment of substituents to S or N (or subrogation of N by S);

(b) ring contraction to a 7-, 6-, 5- or 4-membered heterocycle with or without attachment of substituents;

(c) ring fragmentation into non-cyclic S–N groups (which sometimes then coordinate to metal centres);

(d) complete cleavage of all S–N bonds;

(e) formation of more complex heterocycles with 3 (or more) different heteroatoms.

[214] A. W. CORDES, C. G. MARCELLUS, M. C. NOBLE, R. T. OAKLEY and W. T. PENNINGTON. *J. Am. Chem. Soc.* **105**, 6008–12 (1983).

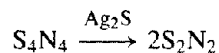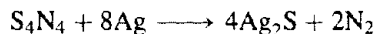[215] U. THEWALT, *Angew. Chem. Int. Edn. Engl.* **15**, 765–6 (1976).

Table 15.22 Some further reactions of $S_4N_4^{(206-210)}$

Reagents and conditions	Products	Ref. for structure, etc.
Vacuum thermolysis (Ag wool 300°)	S_2N_2, $(SN)_x$	pp. 726, 727
$SnCl_2$ (boiling C_6H_6 + EtOH)	$S_4(NH)_4$	p. 735
NH_3	$S_2N_2.NH_3$	
$N_2H_4/SiO_2(C_6H_6, 46°)$	$S_{8-n}(NH)_n$, $n = 1-4$	p. 735
S/CS_2 (heat in autoclave)	S_4N_2	
S_2Cl_2	$[S_4N_3]^+Cl^-$	
AgF_2 (cold CCl_4)	$N_4(SF)_4$	
AgF_2 (hot CCl_4)	NSF, NSF_3	
$Cl_2(CCl_4)$	$N_3(SCl)_3$	
Br_2 (neat, heat in sealed tube)	$[S_4N_3]^+Br_3^-$	100% yield[216]
$HX(CCl_4)$ X = F, Cl, Br	$[S_4N_3]^+X^-$	
HI	H_2S, NH_3, I_2	
$OSCl_2$	$S_3N_2O_2$	Fig. 15.34a
$NiCl_2/MeOH$	$[Ni(S_2N_2H)_2]$ (also Co, Pd)	Fig. 15.34b
H_2PtCl_6	$[Pt(S_2N_2H)_2]$	Fig. 15.34b
PbI_2/NH_3	$[Pb(NSNS)(NH_3)]$	Fig. 15.34c

The molecular structures of the products are described as indicated at appropriate points in the text. $S_3N_2O_2$ was at one time thought to be cyclic but X-ray diffraction analysis has revealed an open chain structure (Fig. 15.34a).[217] The structure of $[Pt(S_2N_2H)_2]$ (Fig. 15.34b) is typical of several such compounds. When S_4N_4 reacts with metal carbonyls in aprotic media, the products are the structurally similar $[M(S_2N_2)_2]$ (M = Fe, Co, Ni). The pyramidal Pb^{II} complex (Fig. 15.34c) is also notable, and features unequal S–N distances consistent with the bonding indicated. Still further reaction types are continually being discovered. For example, with the diphosphines $Ph_2P(X)PPh_2$ (X = CH_2CH_2 or NC_4H_8N), S_4N_4 yields (N_3S_3)–$NPPh_2(X)$-PPh_2N–$(S_3N_3)^{(218)}$ whereas with platinum-metal complexes it forms adducts of the tridentate S,S,N-ligand *catena*-$S_4N_4^{2-}$, e.g. *fac*-$[Ir(CO)Cl(\eta^3$-$S_4N_4)(PPh_3)]$, Fig. 15.34d,[219]

fac-$[PtX_3(\eta^3$-$S_4N_4)]^-$ (X = Cl, Br, I)[220] and *mer*-$[PtCl_2(\eta^3$-$S_4N_4)(PMe_2Ph)]$, (Fig 15.34e).[220]

(b) *Disulfur dinitrogen*, S_2N_2. When S_4N_4 is carefully depolymerized by passing the heated vapour over Ag wool at 250–300° and 0.1–1.0 mmHg, the unstable cyclic dimer S_2N_2 is obtained. The main purpose of the silver is to remove sulfur generated by the thermal decomposition of S_4N_4; the Ag_2S so formed then catalyses the depolymerization of further S_4N_4:

$$S_4N_4 + 8Ag \longrightarrow 4Ag_2S + 2N_2$$

$$S_4N_4 \xrightarrow{Ag_2S} 2S_2N_2$$

In the absence of Ag/Ag_2S the product is contaminated with S_4N_2 (p. 728) formed by the reaction of the excess sulfur with either S_4N_4 or S_2N_2. (See next subsection for discussion of possible mechanisms.) S_2N_2 forms large colourless crystals which are insoluble in water but soluble in many organic solvents. The molecular structure is a square-planar ring (D_{2h}) analogous to the isoelectronic cation

[216] G. Wolmershäuser and G. B. Street, *Inorg. Chem.* **17**, 2685–6 (1978).

[217] J. Weiss, *Z. Naturforsch.* **16b**, 477 (1961); J. Weiss, *Fortsch. Chem. Forsch.* **5**, 635–62 (1966).

[218] C. J. Thomas and M. N. S. Rao, *Z. anorg. allg. Chem.* **619**, 433–6 (1993), and references cited therein.

[219] F. Edelmann, H. W. Roesky, C. Spang, M. Nolte-meyer and G. M. Sheldrick, *Angew. Chem. Int. Edn. Engl.* **25**, 931 (1986).

[220] V. C. Ginn, P. F. Kelly, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *Polyhedron* **12**, 1135–9 (1993). P. F. Kelly, R. N. Sheppard and J. D. Woollins, *Polyhedron* **11**, 2605–9 (1992). See also P. F. Kelly and J. D. Woollins, *Polyhedron* **8**, 2907–10 (1989).
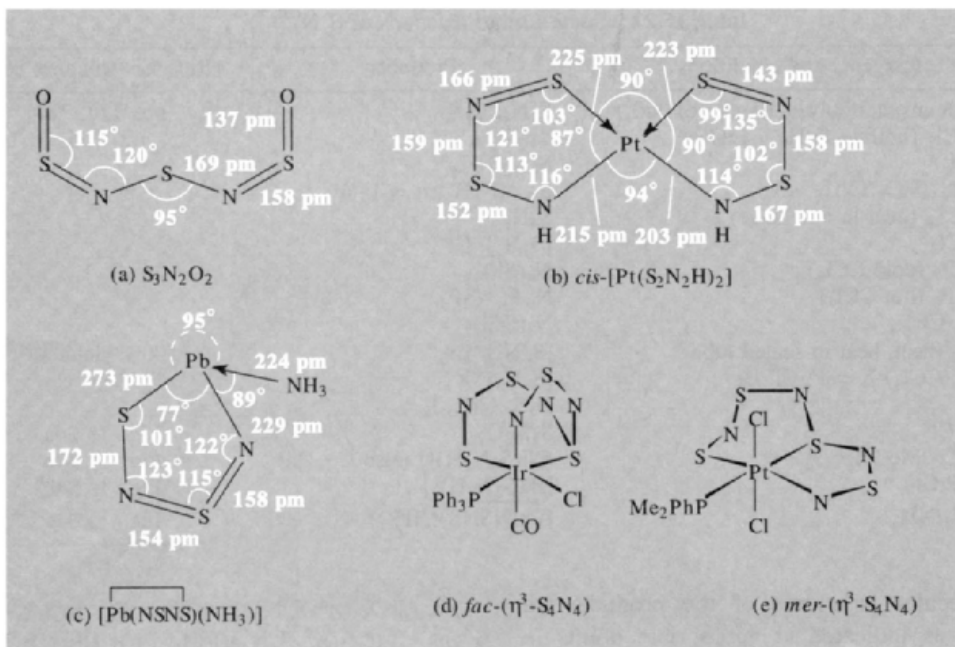
Figure 15.34   Structures of some SN compounds mentioned in Table 15.22 and the text.

S_4^{2+} (D_{4h}, p. 665). Figure 15.35 shows the structure obtained by X-ray diffraction at -130°[221] together with typical valence-bond representations.[212]
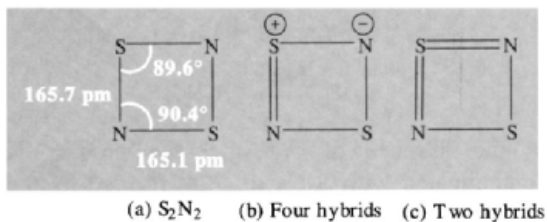

(a) S_2N_2 (b) Four hybrids   (c) Two hybrids

Figure 15.35   (a) Molecular structure and dimensions of S_2N_2,[220] together with (b) minimal valence-bond representation and (c) additional valence-bond representation involving 3d S orbitals. (Note that the molecule has 6 π electrons and 4 unshared electron-pairs superimposed on the square-planar σ-bonded structure.)

S_2N_2 decomposes explosively when struck or when warmed above 30°. Its chemistry

has therefore not been extensively studied. Reactions with NH_3 and with aqueous alkali are similar to those of S_4N_4. It also forms adducts with Lewis bases, e.g. $S_2N_2(SbCl_5)_2$; this latter is a yellow crystalline N-bonded complex which reacts with further S_2N_2 to give the orange crystalline monoadduct $S_2N_2.SbCl_5$. The heterocycle remains planar and the S–N distances are almost the same as in the free S_2N_2 molecule.

Undoubtedly the most exciting reaction of S_2N_2 is its slow spontaneous polymerization in the solid state at room temperature to give crystalline $(SN)_x$. Crystals up to several millimetres in length can be grown. Not only is this an unusually facile topochemical reaction for a solid at low temperature but it results in an unprecedented metallic superconducting polymer, as discussed in the following subsection.

[221] A. G. MacDiarmid,   C. M. Mikulski,   P. J. Russo, M. S. Saran, A. F. Garito and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 476–7 (1975).
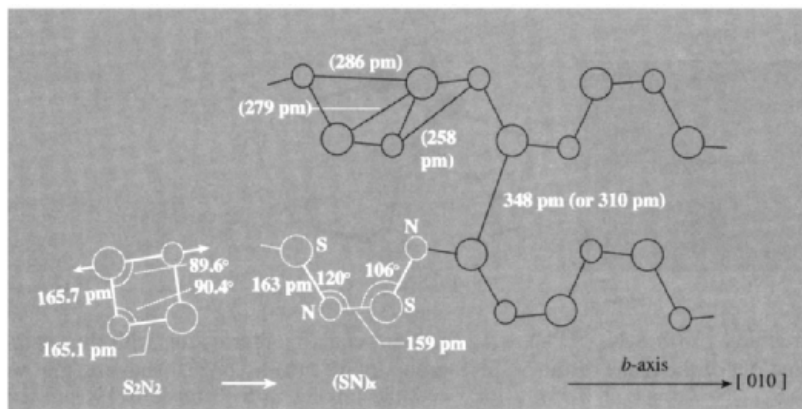
Figure 15.36   Structure of fibrous $(SN)_x$ and its relation to S_2N_2.

(c) *Polythiazyl, $(SN)_x$.*[222] Polymeric sulfur nitride, also known as polythiazyl, was first prepared by F. B. Burt in 1910 using a method that is still often used today — the solid-state polymerization of crystalline S_2N_2 at room temperature (or preferably at 0°C over several days). Despite the bronze colour and metallic lustre of the polymer, over 50 y were to elapse before its metallic electrical conductivity, thermal conductivity and thermoelectric effect were investigated. By 1973 it had been established that $(SN)_x$ was indeed a metal down to liquid helium temperatures, and in 1975 the polymer was shown to be a superconductor below 0.26 K. (For higher-quality crystals the transition temperature rises to 0.33 K.) Values of the conductivity σ depend on the purity and crystallinity of the polymer and on the direction of measurement, being much greater along the fibres (b-axis) than across them. At room temperature typical values of $\sigma_{\|}$ are $1000–4000\,\text{ohm}^{-1}\,\text{cm}^{-1}$, and this increases by as much as 1000-fold on cooling to 4.2 K. Typical values of the anisotropy ratio $\sigma_{\|}/\sigma_{\perp}$ are ~50 at room temperature and ~1000 at 40 K.

The mechanism of formation of S_2N_2 from S_4N_4 and of the subsequent polymerization to $(SN)_x$ have been much studied and are very

sensitive to the exact conditions employed.[223] The use of the explosive intermediates S_4N_4 and S_2N_2 can be avoided by various alternative high-yield syntheses employing nonaqueous solvents. For example, $(SN)_x$ can be made in 65% yield by the reaction of $SiMe_3(N_3)$ with $N_3S_3Cl_3$, $N_2S_3Cl_2$ or N_2S_3Cl (pp. 738, 739) in MeCN solution at $-15°C$ or by the reaction of $N_3S_3Cl_3$ with an excess of NaN_3.[224] More recently still, the electrolytic reduction of $S_5N_5{}^+Cl^-$ (p. 732) in liquid SO_2 using a silver electrode has been used to deposit thin films of $(SN)_x$ on a variety of surfaces.[225]

$(SN)_x$ is much more stable than its precursor S_2N_2. When heated in air it decomposes explosively at about 240°C but it sublimes readily in vacuum at about 135°. The crystal structure reveals an almost planar chain polymer with the dimensions shown in Fig. 15.36. The S and N atoms deviate by about 17 pm from the mean plane. The structure should be compared

[222] M. M. Labes, P. Love and L. F. Nichols, *Chem. Revs.* **79**, 1–15 (1979). A definitive review with 150 references.

[223] H. Bock, B. Solouki and H. W. Roesky, *Inorg. Chem.* **24**, 4425–7 (1985); E. Besenyei, G. K. Eigendorf and D. C. Frost, *Inorg. Chem.* **25**, 4404–8 (1986); M. J. Almond, A. J. Downs and T. L. Jeffery, *Polyhedron* **7**, 629–34 (1988).

[224] F. A. Kennett, G. K. MacLean, J. Passmore and M. N. S. Rao, *J. Chem. Soc., Dalton Trans*, 851–7 (1982); A. J. Banister, Z. V. Hauptman, J. Passmore, C-M. Wong and P. S. White, *J. Chem. Soc., Dalton Trans.*, 2371–9 (1986).

[225] A. J. Banister, Z. V. Hauptman, J. M. Rawson and S. T. Wait, *J. Materials Chem.*, **6**, 1161–4 (1996).
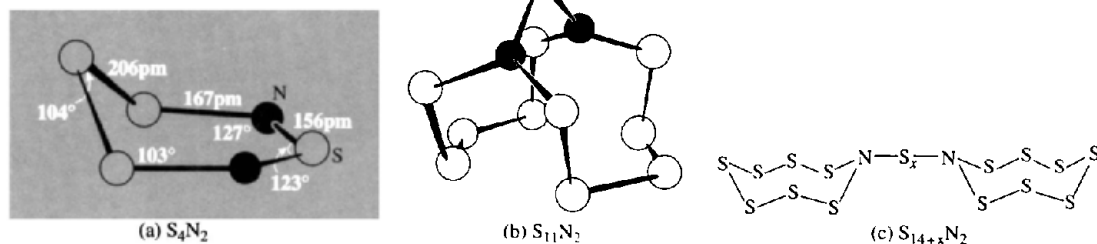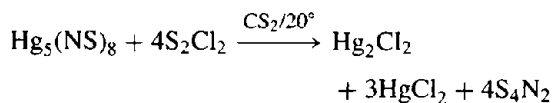
Figure 15.37 Structures of (a) S_4N_2[226] showing the "half-chair" conformation with the central S of the S_3 unit tilted out of the plane of the SNSNS group by 55°; (b) $S_{11}N_2$[227] showing the two planar N atoms; (c) $S_{14-x}N_2$ ($x = 1, 2, 3, 5$) — for $x = 2$ the linking S–S distance is 190 pm and S–N is 170 pm; for $x = 3$ the linking S–S is 204 pm and S–N 171 pm[228].

with that of helical S_∞ (p. 660), the (formal) replacement of alternate S atoms by N resulting both in a conformational change in the position of the atoms and an electronic change whereby 1 valence electron is removed for each SN unit in the chain. Polymerization is thought to occur by a one-point ring cleavage of each S_2N_2 molecule followed by the formation of the *cis-trans*-polymer along the *a*-axis of the S_2N_2 crystal which thereby transforms to the *b*-axis of the $(SN)_x$ polymer.

There is intense current interest in these one-dimensional metals and several related partially halogenated derivatives have also been made, some of which have an even higher metallic conductivity, e.g. partial bromination of $(SN)_x$ with Br_2 vapour yields blue-black single crystals of $(SNBr_{0.4})_x$ having a room-temperature conductivity of 2×10^4 ohm^{-1} cm^{-1} i.e. an order of magnitude greater than for the parent $(SN)_x$ polymer. An even more facile preparation involves *direct bromination* of S_4N_4 crystals ($\sigma \sim 10^{-14}$ ohm^{-1} cm^{-1} at 25°) with Br_2 vapour at 180 mmHg over a period of hours; subsequent pumping at room temperature gives *stoichiometries in the range* $(SNBr_{1.5})_x$ to $(SNBr_{0.4})_x$ and further pumping at 80°C for 4 h reduces the halogen content to $(SNBr_{0.25})_x$. Similar highly conducting nonstoichiometric polymers can be obtained by treating S_4N_4 with ICl, IBr and I_2, the increase in conductivity being more than 16 orders of magnitude.

(d) *Other binary sulfur nitrides.* Six further sulfur nitrides can be briefly mentioned: S_4N_2, $S_{11}N_2$ and $(S_7N)_2S_x$ ($x = 1,2,3,5$); as can be seen from Fig. 15.37, these belong to three distinct structural classes. (For a fourth structure class, exemplified by S_5N_6, see p. 729.)

S_4N_2 is usually prepared by heating S_4N_4 with a solution of sulfur in CS_2 under pressure at 100–120°, though a more convenient laboratory preparation is now available by the reaction of activated Zn on N_3S_4Cl.[226] The compound also results from the thermolytic loss of N_2 from S_4N_4 which occurs when S_4N_4 is heated under reflux in xylene for some hours. An alternative preparation (42% yield), which involves neither high pressure or high temperature, is the smooth reaction of solutions of $Hg_5(NS)_8$ and S_2Cl_2 in CS_2:

$$Hg_5(NS)_8 + 4S_2Cl_2 \xrightarrow{CS_2/20°} Hg_2Cl_2$$
$$+ 3HgCl_2 + 4S_4N_2$$

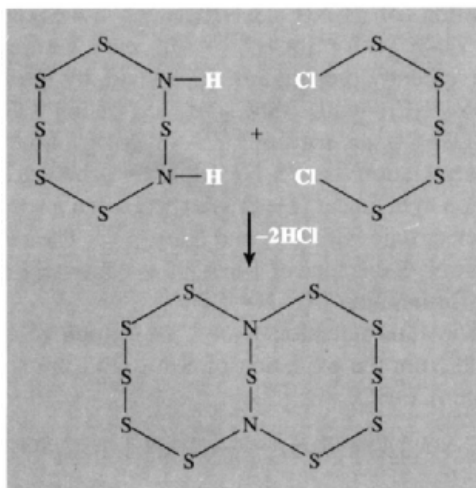In all these reactions only the 1,3-diazahetero-cycle (Fig. 15.37a) is obtained: the 1,1- and

[226] R. W. H. SMALL, A. J. BANISTER and Z. V. HAUPTMAN, *J. Chem. Soc., Dalton Trans.*, 2188–91 (1981). T. CHIVERS, P. W. CODDING and R. T. OAKLEY, *J. Chem. Soc., Chem. Commun.*, 584–5 (1981). T. CHIVERS, P. W. CODDING, W. G. LAIDLAW, S. W. LIBLONG, R. T. OAKLEY and M. TRSIC, *J. Am. Chem. Soc.* **105**, 1186–92 (1983).

[227] H. GARCIA-FERNANDEZ, H. G. HEAL and G. TESTE DE SAGEY, *Compt. Rend.* **C275**, 323–6 (1972).

[228] H. GARCIA-FERNANDEZ, H. G. HEAL and G. TESTE DE SAGEY, *Compt. Rend.* **C282**, 241–3 (1976).
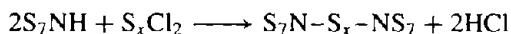
1,4-heterocycles and acyclic isomers are unknown (cf. N_2O_4, p. 455). S_4N_2 forms opaque red-grey needles or transparent dark red prisms which melt at 25° to a dark-red liquid resembling Br_2. It decomposes explosively above 100°. S_4N_2 appears to be a weaker ligand than either S_4N_4 or S_2N_2: it does not react with BCl_3 in CS_2 solution, and $SbCl_5$ gives a complex reaction mixture which contains $S_4N_4.SbCl_5$ and $[S_4N_3]^+[SbCl_6]^-$ in addition to a poorly defined 1:1 adduct.

$S_{11}N_2$ is obtained as pale amber-coloured crystals by the double condensation of $1,3-S_6(NH)_2$ with an equimolar amount of S_5Cl_2 in the presence of pyridine:

Some polymer is also formed but this can be converted into the bicyclic $S_{11}N_2$ by refluxing in CS_2. The X-ray crystal structure (Fig. 15.37b) shows that the 2 N atoms are planar.[227] This has been interpreted in terms of sp^2 hybridization at N, with some delocalization of the p_π lone-pair of electrons into S-based orbitals, thus explaining the considerably diminished donor power of the molecule. $S_{11}N_2$ is stable at room temperature but begins to decompose when heated above 145°.

The sulfur nitrides $S_{15}N_2$ and $S_{16}N_2$ are (formally) derived from *cyclo*-S_8 (or S_7NH) and can be prepared by reacting S_7NH with SCl_2 and S_2Cl_2 respectively:

$$2S_7NH + S_xCl_2 \longrightarrow S_7N-S_x-NS_7 + 2HCl$$

Both are yellow crystalline materials, stable at room temperature, and readily soluble in CS_2 (Fig. 15.37c).[228] Compounds with $x = 3$ and 5 can be prepared similarly.

Finally, in this subsection we mention the discovery of S_5N_6 which is best prepared (73% yield) by the reaction of $S_4N_5^-$ (p. 733) with Br_2 in CH_2Cl_2 at 0°C for several hours[229] Iodine reacts similarly but chlorine affords S_4N_5Cl (p. 731). S_5N_6 forms orange crystals which are stable for prolonged periods at room temperature in an inert atmosphere, though they immediately blacken in air. It can be sublimed unchanged at 45° (10^{-2} mmHg) and decomposes above 130°. The structure (Fig. 15.38) features a molecular basket in which an $-N{=}S{-}N-$ group bridges 2 S atoms of an S_4N_4 cradle. Comparison with S_4N_4 itself (p. 723) shows little change in the S–N distances in the cradle (161 pm) but the trans-annular S$\cdots$S distances are markedly different: one is opened up from 258 pm to 394 pm (nonbonding) whereas the other contracts to 243 pm suggesting stronger trans-annular bonding between these 2 S atoms and the incipient formation of 2 fused 5-membered S_3N_2 rings.
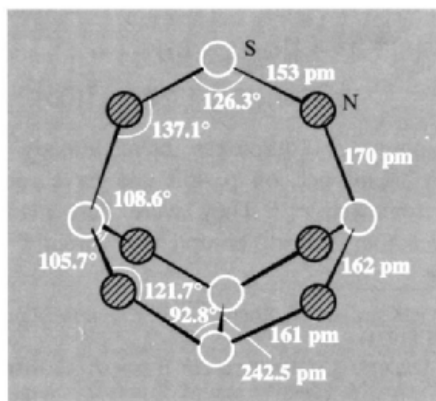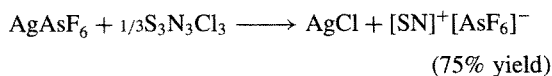

Figure 15.38 Structure of S_5N_6.

229 T. CHIVERS and J. PROCTOR, *J. Chem. Soc., Chem. Commun.*, 642–3 (1978) and *Can. J. Chem.* **57**, 1286–93 (1979). See also W. S. SHELDRICK, M. N. S. RAO and H. W. ROESKY, *Inorg. Chem.* **19**, 538–43 (1980).
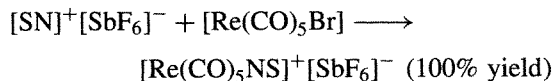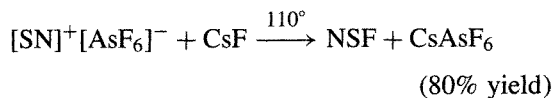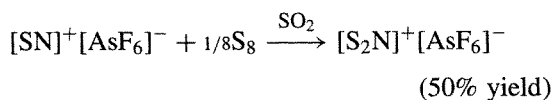
(ii) Sulfur–nitrogen cations and anions

Numerous charged sulfur–nitrogen species have been synthesized in recent years, particularly those having an odd number of N atoms which would otherwise be paramagnetic. However, thio analogues of nitrites (NO_2^-, p. 461) and nitrates (NO_3^-, p. 465) are unknown.

The simplest stable sulfur–nitrogen species is the cation $[SN]^+$ which was first prepared by the direct fluoride-ion transfer reaction between NSF and AsF_5 or SbF_5.[230] $[NS]^+[AsF_6]^-$ can also be prepared by reaction of an excess of AsF_5 with $S_3N_3F_3$ or by thermal decomposition of $[S_3N_2F_2]^+[AsF_6]^-$, but the simplest high-yield synthesis is by the reaction of $S_3N_3Cl_3$ with an excess of $AgAsF_6$ in liquid SO_2:[231]

$$AgAsF_6 + 1/3 S_3N_3Cl_3 \longrightarrow AgCl + [SN]^+[AsF_6]^-$$

(75% yield)

The cation has considerable synthetic potential for a wide range of S/N compounds, e.g.[231,232]

$$[SN]^+[AsF_6]^- + 1/8 S_8 \xrightarrow{SO_2} [S_2N]^+[AsF_6]^-$$

(50% yield)

$$[SN]^+[AsF_6]^- + CsF \xrightarrow{110°} NSF + CsAsF_6$$

(80% yield)

$$[SN]^+[SbF_6]^- + [Re(CO)_5Br] \longrightarrow$$
$$[Re(CO)_5NS]^+[SbF_6]^- \text{ (100% yield)}$$

Thionitrosyl complexes have already been briefly mentioned on p. 453 and have recently been reviewed.[233] They were first made[234] by reacting azido complexes directly with sulfur {e.g. $[(Et_2NCS)_3Mo\equiv N] + 1/8 S \longrightarrow [(Et_2NCS)_3Mo(NS)]$}, but this reaction is not general. An alternative to direct metathesis with $[SN]^+$ is dissociative oxidative addition {e.g. $[MCl_2(PPh_3)_2] + 1/3(S_3N_3Cl_3) \longrightarrow [MCl_3(NS)(PPh_3)_2]$}. In the few complexes for which X-ray structural data are available the M–N–S group is essentially linear (170–177°) (see p. 453 and refs. 233, 235) but spectroscopic data on others suggest that bent and even η^1-bridging modes may be possible.

The dithionitronium cation $[S_2N]^+$, which is the sulfur analogue of the nitronium cation (p. 458), was first prepared as the crystalline salt $[S_2N]^+[SbCl_6]^-$ by the complex oxidative reaction of S_7NH, S_7NBCl_2 or $1,4-S_6(NH)_2$ (p. 735) with $SbCl_3$.[236] It can be more conveniently prepared, in 30% yield, by reaction of $S_3N_3Cl_3$ with $3SbCl_5 + 3/8 S_8$ using $OSCl_2$ or CH_2Cl_2 as solvent.[237] An X-ray structure determination on $[S_2N]^+[SbCl_6]^-$ showed the cation to be linear ($D_{\infty h}$) as expected for a species isoelectronic with CS_2 and NO_2^+.[236] The rather short N–S distance of 146.4 pm is consistent with the formulation $[S=N=S]^+$.

The radical cation $S_3N_2^+$ is formed in high yield from the oxidation of S_4N_4 with the anhydride $(CF_3SO_2)_2O$:[238]

$$(CF_3SO_2)_2O + S_4N_4 \longrightarrow [S_3N_2]^+[CF_3SO_3]^- + CF_3SO_2S_3N_3$$

The product is a black-brown solid that is very sensitive to oxygen. The same cation can be obtained by oxidation of S_4N_4 with AsF_5 and is unusual in being the only sulfur–nitrogen (paramagnetic) radical that has been obtained as a stable crystalline salt. X-ray diffraction analysis shows the structure to be a planar 5-membered ring with approximate

[230] O. GLEMSER and W. KOCH, *Angew. Chem. Int. Edn. Engl.* **10**, 127 (1971).

[231] A. APBLETT, A. J. BANISTER, D. BIRON, A. G. KENDRICK, J. PASSMORE, M. SCHRIVER and M. STOJANAC, *Inorg. Chem.* **25**, 4451–2 (1986).

[232] G. HARTMANN and R. MEWS, *Angew. Chem. Int. Edn. Engl.* **24**, 202–3 (1985).
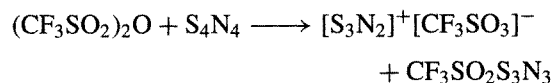
[233] J. D. WOOLLINS, Chap. 18 in R. STEUDEL (ed.), *The Chemistry of Inorganic Ring Systems*, Elsevier, Amsterdam, 1992, pp. 349–72.

[234] J. CHATT and J. R. DILWORTH, *J. Chem. Soc., Chem. Commun.*, 508 (1974).

[235] J. BALDAS, J. BONNYMAN, M. F. MACKAY and G. A. WILLIAMS, *Aust. J Chem.* **37**, 751–9 (1984).

[236] R. FAGGIANI, R. J. GILLESPIE, C. J. L. LOCK and J. D. TYRER, *Inor. Chem.* **17**, 2975–8 (1978).

[237] A. J. BANISTER and A. G. KENDRICK, *J. Chem. Soc., Dalton Trans.*, 1565–7 (1987).

[238] R. J. GILLESPIE, J. P. KEMT and J. F. SAWYER, *Inorg. Chem.* **20**, 3784–99 (1981).
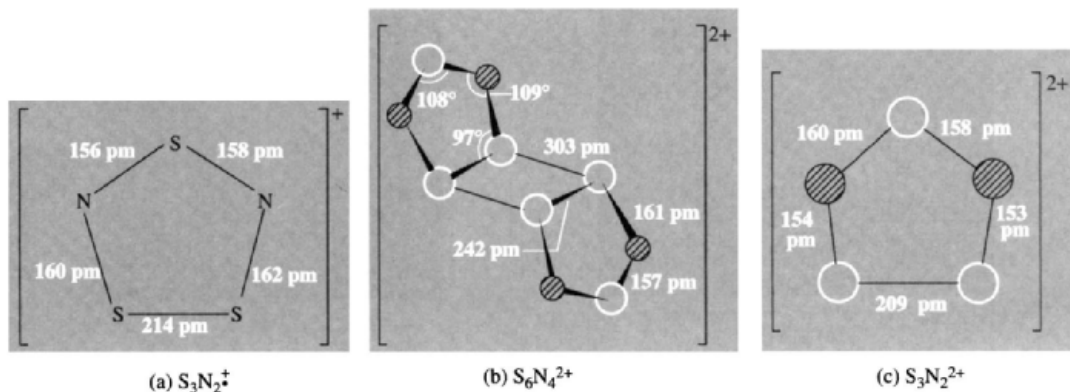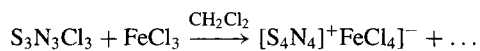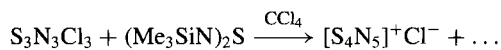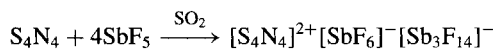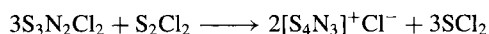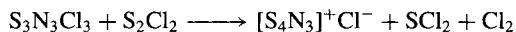
Figure 15.39 Structures of (a) the planar radical cation $S_3N_2^{+}$, (b) its dimer $S_6N_4^{2+}$ and (c) the corresponding planar diamagnetic dication $S_3N_2^{2+}$.

C_{2v} symmetry (Fig. 15.39a). The corresponding diamagnetic dimer $S_6N_4^{2+}$ was obtained in low yield by oxidation of S_3N_2Cl with $ClSO_3H$: its structure (Fig. 15.39b) consists of 2 symmetry-related planar $S_3N_2^+$ units linked by 2 very long S–S bonds. Alternatively, the central S_4 unit can be thought of as being bound by a 4-centre 6-electron bond. Even more remarkably, a diamagnetic 6π-electron dication, $[S_3N_2]^{2+}$, which is less stable than its paramagnetic 7π-electron analogue $[S_3N_2]^+$, has been prepared and characterized as the crystalline salt $[S_3N_2]^{2+}[AsF_6]_2^{-}$.[239] The planar conformation of the ring is retained, but the dimensions are significantly different (Fig. 15.39(c)) most notably in the shortening of the S–S and adjacent S–N bonds. The dication is only stable in the crystalline phase; in SO_2 solutions it reversibly dissociates into the paramagnetic species $[SN]^+$ and $[SNS]^+$, the cycloaddition in the solid state apparently being driven by the high lattice energy of the 1:2 salt.

Cations containing 4 S atoms include $S_4N_3^+$, $S_4N_4^{2+}$ and $S_4N_5^+$, as well as the unique radical cation $S_4N_4^+$. The structures are in Fig. 15.40 and typical preparative routes are:[210, 240–241]

$$S_3N_3Cl_3 + S_2Cl_2 \longrightarrow [S_4N_3]^+Cl^- + SCl_2 + Cl_2$$

$$3S_3N_2Cl_2 + S_2Cl_2 \longrightarrow 2[S_4N_3]^+Cl^- + 3SCl_2$$

$$S_4N_4 + 4SbF_5 \xrightarrow{\;SO_2\;} [S_4N_4]^{2+}[SbF_6]^-[Sb_3F_{14}]^-$$

$$S_3N_3Cl_3 + (Me_3SiN)_2S \xrightarrow{\;CCl_4\;} [S_4N_5]^+Cl^- + \ldots$$

$$S_3N_3Cl_3 + FeCl_3 \xrightarrow{\;CH_2Cl_2\;} [S_4N_4]^+FeCl_4^- + \ldots$$

These compounds contain some fascinating and subtle structural and bonding problems. For example, the compound $[S_4N_4]^{2+}[SbF_6]^-$-$[Sb_3F_{11}]^-$ shows two structurally distinct cations, one with essentially equal S–N distances around the planar ring (Fig. 15.40b) and the other, also planar, but with alternating S–N distances of *ca.* 153 and 162 pm and with bond angles at S and N of 127° and 143°, respectively. By contrast, a non-planar boat-shaped structure was found for the dication in $[S_4N_4]^{2+}[SbCl_6]_2^{-}$.[240] The unusual radical cation $[S_4N_4]^{+}$ occurs in the brown, moisture-sensitive compound $[S_4N_4]^+[FeCl_4]^-$ and features a puckered 8-membered ring in which the four S atoms form an almost perfect square and all the S–N

239 W. V. F. BROOKS, T. S. CAMERON, F. GREIN, S. PARSONS, J. PASSMORE and M. J. SCHRIVER, *J. Chem. Soc., Chem. Commun.*, 1079–81 (1991).

240 R. J. GILLESPIE, D. R. SLIM and J. D. TYRER, *J. Chem. Soc., Chem. Commun.*, 253–5 (1977). R. J. GILLESPIE, J. P. KENT, J. F. SAWYER, D. R. SLIM and J. D. TYRER, *Inorg. Chem.* **20**, 3799–812 (1981).

241 T. CHIVERS, L. FIELDING, W. G. LAIDLAW and M. TRSIC, *Inorg. Chem.* **18**, 3379–87 (1979).

242 U. MÜLLER, E. COMRADI, U. DEMANT and K. DEHNICKE, *Angew. Chem. Int. Edn. Engl.* **23**, 237–8 (1984).

(a) $S_4N_3^+$

(b) $S_4N_4^{2+}$

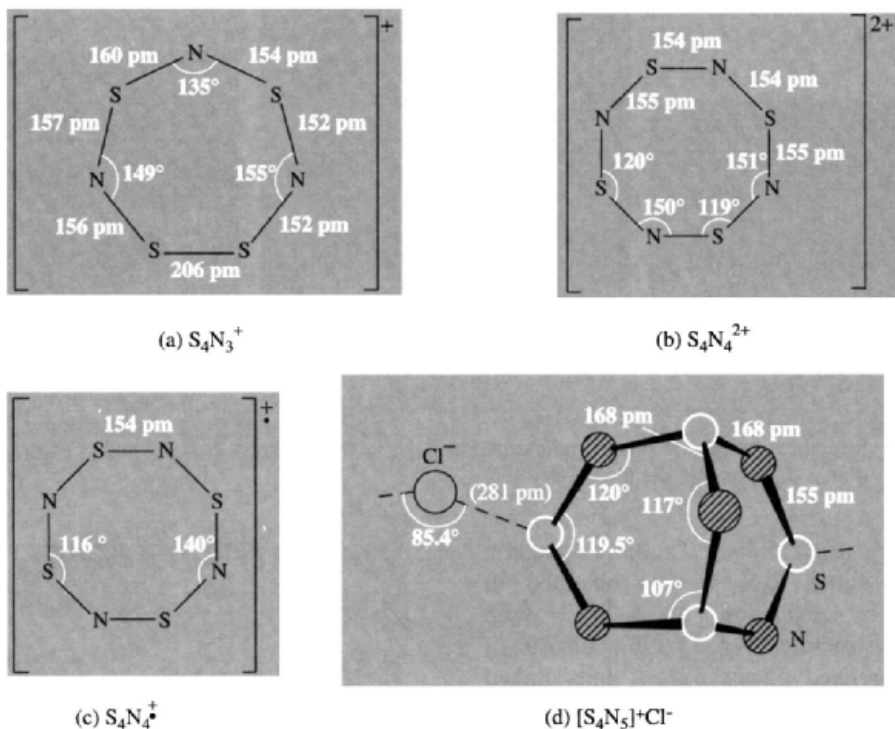(c) $S_4N_4^{+\bullet}$

(d) $[S_4N_5]^+Cl^-$

Figure 15.40   Structure of (a) planar $S_4N_3^+$; (b) planar $S_4N_4^{2+}$ (see text); (c) puckered $S_4N_4^{+\bullet}$; (d) a portion of the polymeric structure of $[S_4N_5]^+Cl^-$ showing the trans-annular bridging N atom.

distances are essentially equal at 154 pm, but in which the four N atoms are located alternately 34, −59, 45 and −38 pm above and below the plane of the four S atoms. The original papers should be consulted for further details.

An interesting structural problem also emerges from the study of the final sulfur–nitrogen cation to be considered, $S_5N_5^+$. First made in 1972, this was originally thought to contain a planar, heart shaped 10-membered heterocycle on the basis of X-ray diffraction studies on $[S_5N_5]^+[AlCl_4]^-$; however, it now seems likely that this is an artefact of disorder within the crystals and that the structure of the cation is as in Fig. 15.41[243] which is the
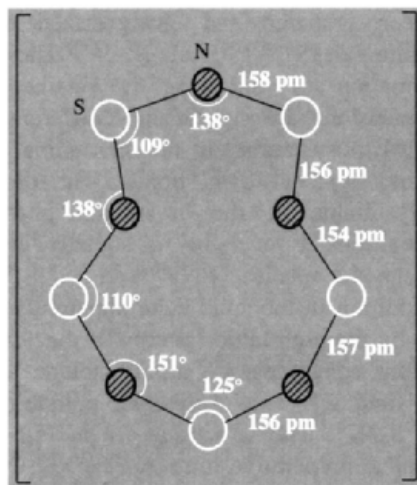

Figure 15.41   Structure of $S_5N_5^+$.

243 H. W. ROESKY,   W. G. BÖWING,   I. RAYMENT   and H. M. M. SHEARER, *J. Chem. Soc., Chem. Commun.*, 735–6 (1975); A. J. BANISTER, J. A. DURRANT, I. RAYMENT and H. M. M. SHEARER, *J. Chem. Soc., Dalton Trans.*, 928–30

(1976). See also R. J. GILLESPIE, J. F. SAWYER, D. R. SLIM and J. D. TYRER, *Inorg. Chem.* **21**, 1296–302 (1982).
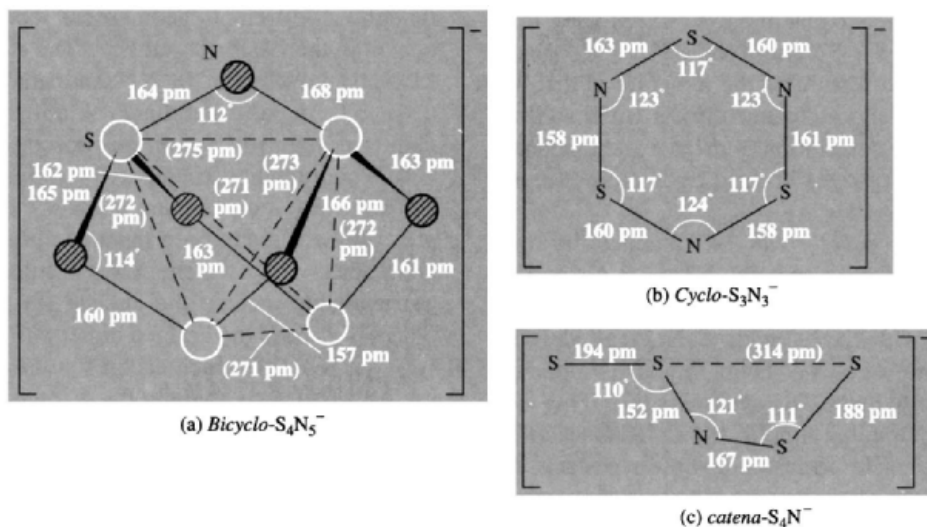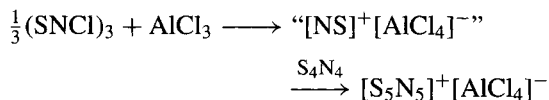
Figure 15.42 Structure of sulfur–nitrogen anions.

conformation observed in $[S_5N_5]^+[S_3N_3O_4]^-$ and $[S_5N_5]^+[SnCl_5(POCl_3)]^-$. Salts such as the yellow $[S_5N_5]^+[AlCl_4]^-$ and dark-orange $[S_5N_5]^+[FeCl_4]^-$ can readily be prepared in high yield by adding $AlCl_3$ (or $FeCl_3$) to $S_3N_3Cl_3$ in $SOCl_2$ solution and then treating the adduct so formed with S_4N_4; the overall stoichiometry can be represented as:

$$\tfrac{1}{3}(SNCl)_3 + AlCl_3 \longrightarrow \text{``}[NS]^+[AlCl_4]^-\text{''}$$

$$\xrightarrow{S_4N_4} [S_5N_5]^+[AlCl_4]^-$$

though the reaction is undoubtedly more complex and proceeds via the adduct $(SNCl)_3 \cdot 2AlCl_3$.[244] Treatment of $[S_5N_5]^+[AlCl_4]^-$ with thf yields pure $[S_5N_5]Cl$ from which $[S_5N_5]^+[BF_4]^-$ can readily be prepared.[245] The planar azulene-shaped cation also occurs in the crystalline adduct $[S_5N_5]^+{}_4[As_8Cl_{28}]^{4-} \cdot 2S_4N_4$.[246] Uncoordinated sulfur–nitrogen anions are less common than

S–N cations and all are of recent preparation:[247] *bicyclo*-$S_4N_5^-$ (1976), *cyclo*-$S_3N_3^-$ (1977) and *catena*-S_4N^- (1979), as well as the more fugitive species S_3N^- and S_7N^-. Structures are in Fig. 15.42. $S_4N_5^-$ occurs as the product in a variety of reactions of S_4N_4 with nucleophiles:[248] e.g. liquid NH_3 or ethanolic solutions of R_2NH, MN_3 (M = Li, Na, K, Rb), KCN or even Na_2S. The course of these reactions suggests the initial formation of $S_3N_3^-$ which then reacts with further S_4N_4 to give $S_4N_5^-$. The ammonium salt $[NH_4]^+[S_4N_5]^-$ is a ubiquitous product of the reaction of ammonia with S_4N_4, $(SNCl)_3$, S_2Cl_2, SCl_2 or SCl_4.[249] Yet another route is the methanolysis of $(Me_3SiN)_2S$:

$$Me_3Si-N=S=N-SiMe_3 \xrightarrow{MeOH} [NH_4]^+[S_4N_5]^-$$

Subsequent metathesis with Bu^n_4NOH yielded yellow crystals suitable for X-ray structure analysis. The structure of $[S_4N_5]^-$ (Fig. 15.42a)

[244] A. J. BANISTER and H. G. CLARKE, *J. Chem. Soc., Dalton Trans.*, 2661–3 (1972). See also A. J. BANISTER, A. J. FIELDER, R. G. HEY, and N. R. M. SMITH, *ibid.*, 1457–60.

[245] A. J. BANISTER, Z. V. HAUPTMAN, A. G. KENDRICK and R. W. H. SMALL, *J. Chem. Soc., Dalton Trans.*, 915–24 (1987).

[246] W. WILLING, U. MÜLLER, J. EICHER and K. DEHNICKE, *Z. anorg. allg. Chem.* **537**, 145–53 (1986).

[247] T. CHIVERS and R. T. OAKLEY *Topics in Current Chemistry. Vol. 102, Inorganic Ring Systems*, Springer Verlag, Berlin, 1982, pp. 117–47 (114 references).

[248] J. BOJES, T. CHIVERS, I. DRUMMOND and G. MACLEAN, *Inorg. Chem.* **17**, 3668–72 (1978).

[249] O. J. SCHERER and G. WOLMERSHÄUSER, *Chem. Ber.* **110**, 3241–4 (1977).

is closely related to that of S_4N_4 (and $S_4N_5^+$), one trans-annular $S\cdots S$ being bridged by the fifth N atom.[250] One feature of the structure is that all the $S\cdots S$ distances become almost equal so that an alternative description is of an S_4 tetrahedron with 5 of the 6 edges bridged by N atoms, angle S–N–S 112–114°.

The anion $S_3N_3^-$ can be obtained by the action of azides (or metallic K) on S_4N_4 or the reaction of KH on $S_4(NH)_4$.[251] Further reaction of $S_3N_3^-$ with S_4N_4 yields $S_4N_5^-$ (as above). The structure of $S_3N_3^-$ (Fig. 15.42b) is a planar ring of approximate D_{3h} symmetry.[251] This has interesting bonding implications. Thus each S in a heterocycle forms a σ bond to each of its neighbours (thereby using 2 electrons) and it also has an exocyclic lone-pair of electrons: this leaves 2 electrons to contribute to the π system of the heterocycle (which might or might not involve S 3d orbitals). Likewise, each N atom has 2 electrons in σ bonds, one exocyclic lone pair, and contributes one electron to the π system. Planar S–N heterocycles having 4–10 ring atoms are now known and all except the radical cation $S_3N_2^{+\cdot}$ have $(4n + 2)\pi$ electrons where $n = 1, 2,$ or 3 as shown below:

Ringe/size	4	5	6	7	8	10
Species	S_2N_2	$S_3N_2^{+\cdot}$	$S_3N_3^-$	$S_4N_3^+$	$S_4N_4^{2+}$	$S_5N_5^+$
Number of π electrons	6	[7]	10	10	10	14

Thermal decomposition of $[N(PPh_3)_2]^+$-$[S_4N_5]^-$ in MeCN yields sequentially the corresponding salts of $S_3N_3^-$ and S_4N^- (50% yield). An X-ray crystallographic analysis of the dark-blue air-stable product $[N(PPh_3)_2]^+[S_4N]^-$ revealed the presence of the unique acyclic anion $[SSNSS]^-$ whose structure is in Fig. 15.42c. The anion is planar with *cis-trans* configuration,

though a different geometrical configuration occurs in the $[AsPh_4]^+$ salt.[252] The existence of $[S_4N]^-$ as well as of $[S_7N]^-$ and small amounts of $[S_3N]^-$ in sulfur-ammonia solutions has been demonstrated by ^{14}N nmr spectroscopy.[253]

The coordination chemistry of sulfur–nitrogen anions is also a burgeoning field.[254] Some complexes have already been mentioned (pp. 725–6) and others for which X-ray structural data are available include the chelate $[Pt(PPh_3)_2(\eta^2\text{-}SNSN)]$[255] and the bridged dimer $[\{(Ph_3P)_2Pt\}_2\text{-}(\mu,\eta^2\text{-}S_2N_2)_2]$ in which each Pt atom is chelated by $-SNSN-$ and then bridged to the other Pt atom by the coordinated N atom to form a central planar Pt_2N_2 ring.[256] For coordinated $[S_3N_2]^{2-}$ and $[S_3N_4]^{2-}$ examples include the chelated titanocene derivatives $[Ti(\eta^5\text{-}C_5H_5)_2\text{-}(\eta^2\text{-}S_3N_2)]$ and $[Ti(\eta^5\text{-}C_5H_5)_2 (\eta^2\text{-}S_3N_4)]$ which feature the 6- and 8-membered ring systems $\overline{TiSSNSN}$ and $\overline{TiNSNSNSN}$, respectively.[257] The chelating trianion $[S_2N_3]^{3-}$ occurs in the 6-coordinate mixed ligand trisbidentate vanadium(V) complex $[V(dtbc)(phen)(\eta^2\text{-}N_3S_2)]$ (dtbc = di-*t*-butylcatecholate, $Bu_2^tC_6H_2O_2^{2-}$; phen = 1,10-phenanthroline)[258] and in the

[250] W. FLUES, O. J. SCHERER, J. WEISS and G. WOLMERSHÄUSER, *Angew. Chem. Int. Edn. Engl.* **15**, 379–80 (1976).

[251] J. BOJES, T. CHIVERS, W. G. LAIDLAW and M. TRSIC, *J. Am. Chem. Soc.* **101**, 4517–22 (1979), and references therein. See also R. JONES, P. F. KELLY, D. J. WILLIAMS and J. D. WOOLLINS, *Polyhedron* **6**, 1541–6 (1987); and P. N. JAGG, P. F. KELLY, H. S. RZEPA, D. J. WILLIAMS, J. D. WOOLLINS and W. WYLIE *J. Chem. Soc., Chem. Commun.*, 942–4 (1991).

[252] N. BUFORD, T. CHIVERS, A. W. CORDES, R. T. OAKLEY, W. T. PENNINGTON and P. N. SWEPSTON, *Inorg. Chem.* **20**, 4430–2 (1981). See also T. CHIVERS and C. LAU. *Inorg. Chem.* **21**, 453–5 (1982).

[253] T. CHIVERS, D. D. McINTYRE, K. J. SCHMIDT and H. J. VOGEL, *J. Chem. Soc., Chem. Commun.*, 1341–2 (1990); see also T. CHIVERS and K. J. SCHMIDT, *ibid.* pp. 1342–3, for $S_2N_2H]^-$.

[254] P. F. KELLY and J. D. WOOLLINS, *Polyhedron* **5**, 607–32 (1986); T. CHIVERS and F. EDELMANN, *Polyhedron* **5** 1661–99 (1986); H. W. ROESKY, in H. W. ROESKY (ed.), *Rings Clusters and Polymers of Main Group and Transition Elements*, Elsevier, Amsterdam, 1989, pp. 369–408; J. D. WOOLLINS, in R. STEUDEL (ed.), *The Chemistry of Inorganic Ring Systems*, Elsevier, Amsterdam, 1992, pp. 349–72.

[255] R. JONES, P. F. KELLY, D. J. WILLIAMS and J. D. WOOLLINS, *Polyhedron* **4**, 1947–50 (1985). See also P. A. BATES, M. B. HURSTHOUSE, P. F. KELLY and J. D. WOOLLINS, *J. Chem. Soc., Dalton Trans.*, 2367–70 (1986).

[256] R. JONES, P. F. KELLEY, D. J. WILLIAMS and J. D. WOOLLINS, *J. Chem. Soc., Chem. Commun.*, 1325–6 (1985).

[257] C. G. MARCELLUS, R. T. OAKLEY, W. T. PENNINGTON and A. W. CORDES, *Organometallics* **5**, 1395–400 (1986).

[258] T. A. KABANOS, A. M. Z. SLAWIN, D. J. WILLIAMS and J. D. WOOLLINS, *J. Chem. Soc., Chem. Commun.*, 193–4

anionic complex $[WCl_2F_2(\eta^2\text{-}N_3S_2)]^-$.[259] Copper(I) and silver complexes of the $[S_3N]^-$ ion are of older vintage, e.g. $[Cu(PPh_3)_2(\eta^2\text{-}SSNS)]$ and $[Cu(\eta^2\text{-}SSNS)_2]^-$.[260]
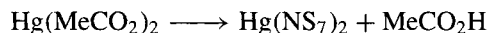
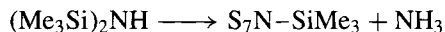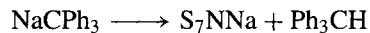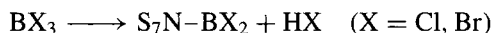### (iii) Sulfur imides, $S_{8-n}(NH)_n$ [206]

The NH group is "isoelectronic" with S and so can successively subrogate S in *cyclo*-S_8. Thus we have already seen that reduction of S_4N_4 with dithionite or with $SnCl_2$ in boiling ethanol/benzene yields $S_4(NH)_4$. Again, whereas reaction of S_2Cl_2 or SCl_2 with NH_3 in non-polar solvents yields S_4N_4, heating these 2 reactants in

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(1990). See also P. F. Kelly, A. M. Z. Slawin, D. J. Williams and J. D. Woollins *Polyhedron* **10**, 2337–40 (1991).
[259] H. Borgholte, K. Dehnicke, H. Goesmann and D. Fenske, *Z. anorg. allg. Chem.*, **586**, 159–65 (1990).
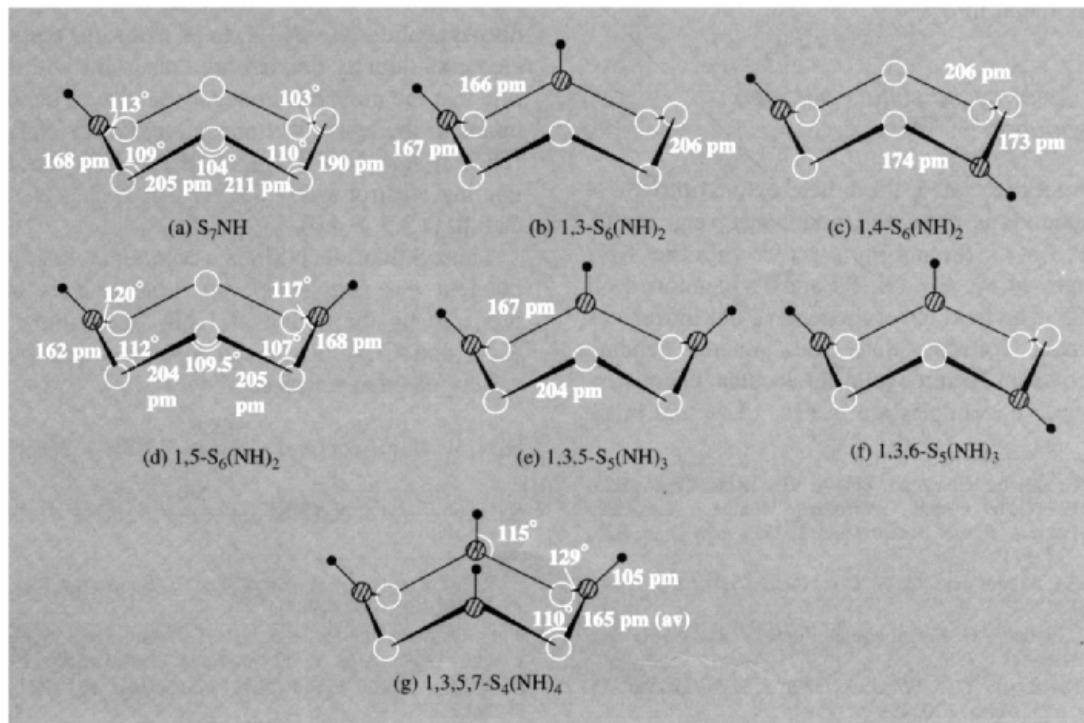[260] J. Bojes, T. Chivers and P. W. Codding, *J. Chem. Soc., Chem. Commun.*, 1171–3 (1981).

polar solvents such as dimethylformamide affords a range of sulfur imides. In a typical reaction 170 g S_2Cl_2 and the corresponding amount of NH_3 yielded:

S_8 (32 g)	1,3-$S_6(NH)_2$ (0.98 g)	1,3,5-$S_5(NH)_3$ (0.08 g)
S_7NH (15.4 g)	1,4-$S_6(NH)_2$ (2.3 g)	1,3,6-$S_5(NH)_3$ (0.32 g)
	1,5-$S_6(NH)_2$ (0.82 g)	

In no case have adjacent NH groups been observed.

S_7NH is a stable pale-yellow compound, mp 113.5°; the structure is closely related to that of *cyclo*-S_8 as shown in Fig. 15.43a. The proton is acidic and undergoes many reactions of which the following are typical (see also p. 729):

$$BX_3 \longrightarrow S_7N\text{-}BX_2 + HX \quad (X = Cl, Br)$$

$$NaCPh_3 \longrightarrow S_7NNa + Ph_3CH$$

$$(Me_3Si)_2NH \longrightarrow S_7N\text{-}SiMe_3 + NH_3$$

$$Hg(MeCO_2)_2 \longrightarrow Hg(NS_7)_2 + MeCO_2H$$

Figure 15.43 Structures of the various cyclo sulfur imides.