Tetrasulphur Dinitride; Its Preparation, Crystal Structure, and Solid-state Decomposition to give Poly(sulphur nitride) †

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The reaction between cyclotetrathiatriazenium chloride (S_4N_3Cl) and zinc sulphide induced by zinc is a convenient small-scale method of preparing tetrasulphur dinitride. A second method was used to obtain crystals for *X*-ray analysis; vapours from S_4N_3Cl, thermolysed at 130 °C, were passed over silver selenide at 180 °C. The condensed product (after polymerisation of the S_2N_2 content at −5 °C) gave transparent red crystals of S_4N_2, space group $P4_2nm$ with a = 11.25(1), c = 3.836(4) Å, and Z = 4. The molecules are non-planar rings with m symmetry; S(1) and S(2) lie on the mirror plane. Distances are S(2)–S(3) 2.055(3), S(1)–N 1.561(8), and S(3)–N 1.661(8) Å. There is a close intermolecular contact, S ··· N 3.015 Å. The slow decomposition of S_4N_2 crystals at 263 K is accompanied by polymerisation to fibrous $(SN)_x$. The likely mechanism of the polymerisation is identified.

TETRASULPHUR dinitride is usually obtained [1,2] from tetrasulphur tetranitride and sulphur in an autoclave at 100—120 °C. The reaction between S_4N_3Cl and ZnS activated by zinc is a more convenient laboratory preparation. Another reaction, between S_4N_3Cl and Ag_2Se, was used to obtain pure transparent crystals suitable for *X*-ray analysis.

The molecular parameters of S_4N_2 show that all bond angles are under compression. This strain, the significant intermolecular attractions, and the (space-group) symmetry facilitate the novel solid-state decomposition/polymerisation to form $(SN)_x$.

EXPERIMENTAL

Tetrahydrofuran was dried by refluxing with potassium and then fractionally distilled.[3] Cyclotetrathiatriazenium chloride (S_4N_3Cl) was prepared by the method of Jolly and Maguire [4] and recrystallised from thionyl chloride. The silver selenide was prepared from pure elements in a vapour–solid reaction (silver pellets at 900 °C, and selenium pellets at 300 °C, in an evacuated sealed quartz tube). This method produced large millimetre-sized crystals of α-Ag_2Se. Since pure crystals do not pulverise easily, they were mixed with crushed fused silica (in a 1 : 1 weight ratio) and the mixture was milled under methanol in a tungsten carbide centrifugal ball-mill for 6 h; this product was used in reaction (*iii*).

(*i*) *Reduction of Cyclotetrathiatriazenium Chloride with Zinc Sulphide initiated by Zinc Metal.*—Cyclotetrathiatriazenium chloride (1.4 g, 6.805 mmol), zinc sulphide in the form of a fine powder (0.5 g, 5.13 mmol), and zinc dust (0.05 g, 0.76 mmol) in dry tetrahydrofuran (30 cm³) were stirred at −5 °C for 60 h under an atmosphere of dry nitrogen in a two-necked 250-cm³ flask with a water condenser. The originally pale yellow suspension started to develop a brown colour in *ca.* 15 min. After *ca.* 30 min a dark green solution formed (when the solid particles were allowed to settle). After *ca.* 1 h from the beginning of the reaction the supernatant solution turned a dark red colour which persisted for the duration of the experiment. The condenser was then connected to a refrigerated bath circulator (Haake F2-C) adjusted to −15 °C and the tetrahydrofuran (thf) was pumped off to dryness through the refrigerated condenser. The flask containing the solid reaction products was allowed to warm up to room temperature and the pumping was continued for 6 h until all S_4N_2 sublimed into the condenser. A small quantity of S_4N_2 was lost into the traps. The apparatus was then filled with dry nitrogen and the reaction flask was quickly exchanged for a pre-weighed 50-cm³ collection flask into which S_4N_2 was transferred by vacuum sublimation.

The total amount of pure final product (0.112 g) represented a *ca.* 7% yield (based on nitrogen) and *ca.* 30% based on equation (1) which appears best to summarise the

$$8S_4N_3Cl + 2ZnS \xrightarrow[-5°C]{thf} 2[S_4N_3]_2[ZnCl_4] + 3S_4N_2 + \tfrac{3}{2}S_4N_4 \quad (1)$$

reaction. Cyclotetrathiatriazenium tetrachlorozincate and tetrasulphur tetranitride were the only other two sulphur–nitrogen compounds found in the solid residue after S_4N_2 was sublimed off. It is noteworthy that after the vacuum transfer of S_4N_2 into the weighing flask a blue ' replica '-like residue [$(SN)_x$] of the original crystalline deposit was left behind in the condenser.

(*ii*) *Thermolysis of Cyclotetrathiatriazenium Chloride and Reaction with Silver Selenide.*—The gaseous products of pyrolysis of S_4N_3Cl were passed over finely dispersed silver selenide at 180 °C. The reaction was carried out in a simple all-glass apparatus (described earlier [5]) consisting of a straight pyrolysis tube and a train of three fractionating U tubes with two sealing-off constrictions for each U tube.

In a typical experiment, S_4N_3Cl (0.30 g, 1.46 mmol) was placed at the bottom of the pyrolysis tube heated in an oil-bath (130 °C). The reaction zone (5 cm above the S_4N_3Cl) consisted of silver selenide (0.65 g, 2.21 mmol, admixed with silica) supported on densely coiled fused silica wool [type A (Vitreosil), Thermal Syndicate Ltd.]. The line vacuum fluctuated between 10^{-4} and 10^{-5} Torr.‡ The U tubes were kept at −17, −78.5, and −196 °C. The reaction was complete within 15 h. The S_4N_2 and S_2N_2 were quantitatively trapped at −17 °C while the −78.5 °C trap condensed a negligible amount of a beige unidentified deposit containing silver. No selenium was detected in any of the U tubes. A small amount of intermixed selenium, S_4N_4, and $(SN)_x$ formed a ring just above the reaction zone.

† More systematic names for compounds mentioned in this paper are as follows: S_4N_2, cyclo-3,5-diaza-1,2,4,6-tetrathia-3,4-diene; S_4N_3Cl, cyclo-3,5,7-triaza-1,2,4,6-tetrathienium chloride; S_4N_4, cyclotetra-azathiene.

‡ Throughout this paper: 1 Torr = (101 325/760) Pa.

(*iii*) *Preparation of the Tetrasulphur Dinitride Crystal.*—The crystal specimen for the *X*-ray structure analysis was prepared by cleavage from a large prism grown from the vapour phase. The original prism comprised the forms {100}, {101}, {001} and in transmitted light showed a clear dark red garnet-like colour (not opaque red-grey as usually found).[2] The surfaces were highly reflecting with a slight metallic appearance and the crystals had a hard texture.

Crystal cleaving and the encapsulation into a thin-walled quartz capillary tube was carried out in a glove-box; because of its low melting point (23 °C) the S_4N_2 was manipulated on an aluminium block cooled by solid carbon dioxide. Approximately 0.5-mm sections were cleft with a pre-cooled razor blade along (001) which appeared to be a plane of well defined cleavage. During handling, the surface of the crystal tarnished a little.

(*iv*) *Decomposition/Polymerisation of Tetrasulphur Dinitride.*—Crystals of S_4N_2 which had been stored in unsealed tubes at −10 °C were found to have been converted into fibrous polymeric material with a metallic lustre. Under these conditions the polymerisation occurred within 3 or 4 weeks; the same effect was noted to occur also *in vacuo* at −15 °C after a period of 12 months. Observations of single crystals exposed to air at 10 °C showed that formation of the polymer fibres was preceded by striation and deepening of the red colour. Once initiated, in a single crystal, the change proceeded quite rapidly (within a few hours). The fibres developed parallel to *c* in the original crystals.

(*v*) *Crystal Structure of* S_4N_2.—*Crystal data.* S_4N_2, Tetragonal, $a = 11.25(1)$, $c = 3.836(4)$ Å, $U = 485.5$ Å^3, $D_c = 2.14$ g cm^{-3}, $F(000) = 318$, $Z = 4$, space group $P4_2nm$, $\mu = 1.65$ mm^{-1} for Mo-K_α, $\lambda = 0.710\ 69$ Å. Intensity data from a crystal having dimensions 1.0 × 0.8 × 0.55 mm maintained at 278 ± 3 K were collected for the layers $l = 0$—4 on a Stoe STADI-2 automatic two-circle diffractometer using graphite-monochromatised Mo-K_α radiation. After absorption corrections, 763 measured reflections were merged to give 425 unique values; the internal agreement over the equivalent reflections was $R = 0.046$. One reflection, for which $I < 3\sigma(I)$, was omitted from the structure determination.

Structure determination. Packing considerations led quite easily to a model of the structure which was confirmed by the use of the program MULTAN;[6] two sulphur atoms lay on a symmetry plane and one nitrogen and one sulphur were on general positions. Refinement by full-matrix least-squares with anisotropic temperature factors led to a final R of 0.057. It was found necessary to omit the 111 reflection from the refinement on the grounds of extinction ($F_o = 94$, $F_c = 104$). In the final cycle, shifts on all parameters were less than 0.005 estimated standard deviations. Atomic scattering factors were taken from ref. 7. The final atomic positions are given in Table 1; structure factors and anisotropic temperature factors have been desposited as Supplementary Publication No. SUP 23103 (5 pp.).*

TABLE 1

Fractional atomic co-ordinates (× 10^4)

Atom	*x*	*y*	*z*
S(1)	1 115(2)	1 115(2)	1 000 *
S(2)	3 200(2)	3 200(2)	1 525(24)
S(3)	3 530(2)	1 505(2)	3 278(24)
N	2 425(7)	707(6)	1 616(43)

* Restrained.

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

The expected ring structure of the molecule is confirmed, the dimensions being given in Table 2 (Figure 1). Molecules

TABLE 2

Bond distances and angles

(*a*) Distances (Å)

S(2)–S(3)	2.055(3)	S(3)–N	1.661(8)
		N–S(1)	1.561(8)

(*b*) Angles (°)

N–S(1)–N	122.1(6)	S(1)–N–S(3)	127.3(5)
N–S(3)–S(2)	103.9(4)	S(3)–S(2)–S(3)	103.2(2)

(*c*) Torsion angles (°)

S(2)–S(3)–N–S(1)	−34.3(5)
S(3)–N–S(1)–N′	5.7(5)
S(3)–S(2)–S(3′)–N′	−56.2(5)

(*d*) Dihedral angles (°) *

NN′S(3)S(3′)–S(3)S(2)S(3′)	54.6(5)
NN′S(3)S(3′)–NS(1)N′	4.6(5)

(*e*) Distances (Å) from NN′S(3)S(3′) plane

$-3.100x - 3.100y + 3.533z = -0.4035$

S(1) 0.066 S(2) −1.040

* Symmetry code: (′) = y,x,z.

are linked by close intermolecular contacts S(3) • • • N^{II} (where superscript II represents $\frac{1}{2} + y$, $\frac{1}{2} - x$, $\frac{1}{2} + z$) of 3.015(8) Å to 4_2 screw-axis-related neighbours (Figure 2).

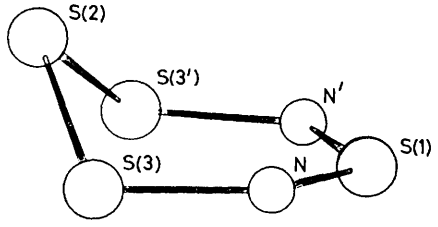


FIGURE 1 The S_4N_2 molecule with atom numbering

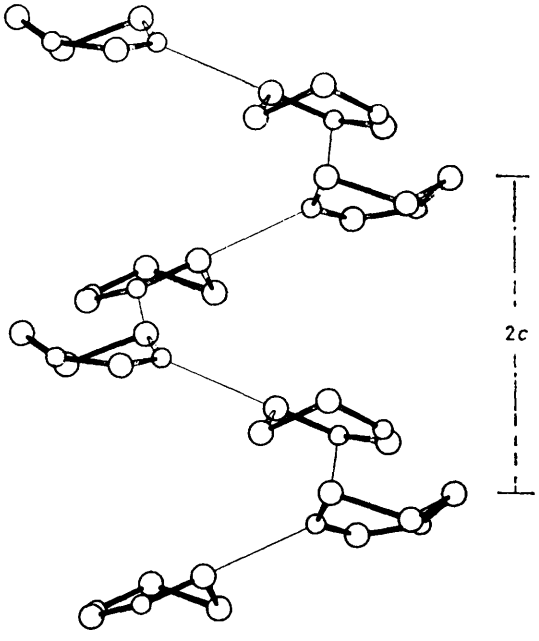


FIGURE 2 Helix around 4_2 screw axis formed by S • • • N intermolecular contacts (second helix omitted for clarity)

These contacts, which are less than the expected van der Waals distance, 3.35 Å, bind the molecules in three dimensions by a series of linked helices, each molecule being involved in two separate helices around different four-fold screw axes. A slightly closer intermolecular association (2.890 Å) in the structure of S_2N_2 has been reported.[8,*]

(*vi*) *Crystallography of the Polymerised Decomposition Product.*—Examination of the lustrous decomposition product by *X*-ray rotation and Weissenberg photographs showed it to be identical with $(SN)_x$ obtained by the solid-state polymerisation of S_2N_2. The *b* axis fibre direction of the polymer was parallel to the unique four-fold axis of the S_4N_2 crystal; in addition, the Weissenberg photographs showed preferred orientation of the other axes of the polymer crystallites. The ω spread of the 100 reflection is shown in Figure 3 in comparison with that observed in the

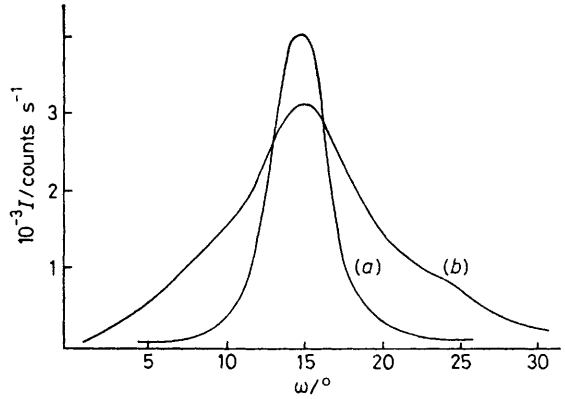


FIGURE 3 ω Scan through reflection 100 showing preferred orientation in: (*a*) $(SN)_x$ from S_2N_2; (*b*) $(SN)_x$ from S_4N_2

$(SN)_x$ polymer obtained from S_2N_2. Both of these polymer samples were completely twinned with *c* as the twinning axis. The *X*-ray photographs showed no evidence of crystalline sulphur.

RESULTS AND DISCUSSION

Synthesis.—Vapour-phase and solution reductions of sulphur–nitrogen–chlorine compounds commonly give S_4N_4 and smaller quantities of S_4N_2 and S_8.[9] We have found that a few reactions produce S_4N_2 as a major product. The new preparation from S_4N_3Cl and ZnS–Zn compares well with the three main published methods (from S_4N_4–S_8 in an autoclave,[1] decomposition of $Hg[NS_7]_2$,[10] and S_2Cl_2–NH_3).[11,12] It is a modification of a procedure ('N_2S_5' from S_4N_3Cl and Zn) described by Muthmann and Clever,[13] and is a rapid and convenient small-scale preparation. An alternative method is to heat 1 : 1 S_4N_3Cl and $(COONa)_2$ under refluxing nitromethane for 1 h.[14] The mixed products can be separated by gel permeation chromatography.[10] Thermal decomposition of S_4N_3Cl at the solvent boiling point also contributes to the formation of products (there is a reduced yield in the absence of oxalate).[14]

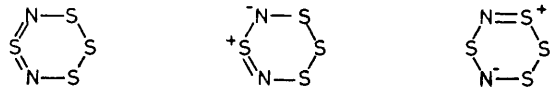
* *Note added at proof:* The ring geometry agrees closely with that described by T. Chivers, P. W. Codding, and R. T. Oakley, *J. Chem. Soc., Chem. Commun.*, 1981, 584.

The reaction between vaporised S_4N_3Cl and silver selenide was investigated as a possible route to a S–Se–N polymer or other S–Se–N compounds. No selenium compound was detected but the route produced pure and well faceted crystals of S_4N_2 suitable for *X*-ray study; the reaction appeared to be as in equation (2). The

$$2S_4N_3Cl + Ag_2Se \longrightarrow S_4N_2 + 2S_2N_2 + 2AgCl + Se \quad (2)$$

temperature (180 °C) of the finely divided silver selenide was kept well above the β ⟶ α transition point (133 °C),[15] and so the silver atoms (arranged at random within a body-centred cubic sub-lattice of selenium atoms) were particularly mobile and effective for dechlorination. The mixed condensate (S_2N_2 and S_4N_2) was stored at −5 °C for 2 months in an evacuated tube. Crystals of S_4N_2 and polymerising S_2N_2 developed at different sites and were easily separated when the tube was opened in a dry-box. Since S_4N_2 is a low melting solid (m.p. 23 °C) crystals were manipulated on a cold stage.

Structure.—The geometry found for the S_4N_2 molecule (with 1,3 nitrogen positions) is as expected from published physical and chemical evidence[16] and indicates one major canonical structure (I). The structure found



(I) (II) (III)

does not agree with the planar geometry found from CNDO/2 calculations; the authors did however assume rather unrealistic sulphur–nitrogen distances (all identical at 1.60 Å).[17] The short sulphur–nitrogen distances found (1.561 Å) are a little longer than in most sulphur di-imides [*e.g.* 1.545(9) and 1.529(5) Å in $S(NC_6H_4Me\text{-}p)_2$[18] and $S(NSPh)_2$[19] respectively]; this is perhaps due to ring strain. In the absence of strain, a sulphur–nitrogen distance of 1.56 Å is normally associated with an NSN bond angle of *ca.* 118.6° (calculated from the relationship[20] d_{SN} in pm = 213.14 − 0.4816 $\widehat{S}$) and so the found angle $\widehat{S}$ [122.1(6)°] indicates that ring buckling has incompletely relieved angular compression at NSN (buckling decreases average ring angles). Buckling also increases the NSSS dihedral angle (to 56°). The preferred dihedral angle between the two substituents attached to a sulphur(II)–sulphur(II) bond is close to 90°. Geometric constraints which force this angle to be appreciably smaller lead to significant torsional strain.[21,22] Hence buckling of the ring at S(3) relieves but does not eliminate this strain.

In each S=N–S unit the mean bond distance (1.611 Å) corresponds (from the equation:[23] d_{NS} = 176.97 − 0.1346 $\widehat{N}$ for unstrained species) to an expected SNS angle of *ca.* 115° (found SNS 127.3°), and so again loss of ring planarity has only partly relieved angular strain. It seems likely that buckling occurs at S(3) rather than at S(2) because this sacrifices less π-bond energy. If one

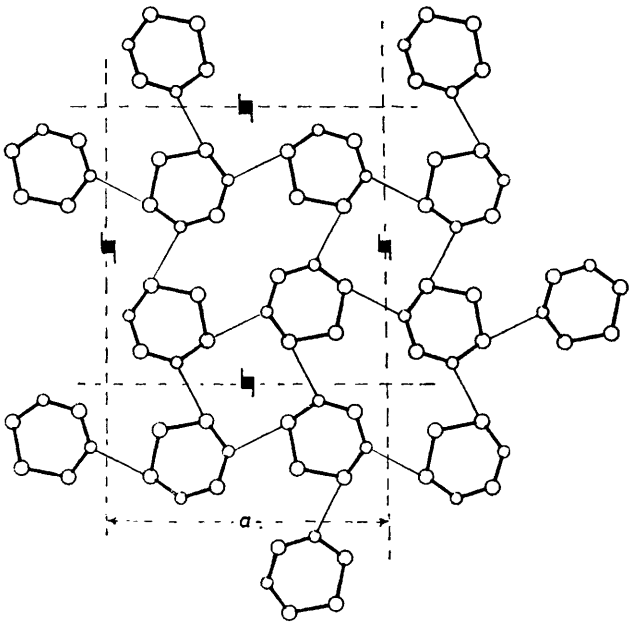


FIGURE 4 Projection of structure of S_4N_2 along *c*

assumes that, in S_4N_2, the preferred * SSS angle is 106° (as in S_∞ [24]) and the preferred SSN is *ca.* 109° (as in S_7NH [25]) then the sum of the preferred angles [119 + 2(115) + 2(109) + 106°] is 14° below the total angles found (687°). A similar set of angles (NSN, SNS, and SSN) in planar S_3N_2 would produce *ca.* 27° strain (in this case bonds would be compressed rather than expanded). Thus, S_3N_2 would be appreciably more strained than S_4N_2 (especially since the strain is distributed among fewer atoms). Nevertheless it looks as if S_3N_2 should be preparable at low temperatures. Since the preferred bond angle at selenium is lower than for sulphur [SSS in S_∞ is 106°, and $S^{II}SeS^{II}$ in $Se(SCN)_2$ [26] is 101°] it seems likely that SeS_3N_2 should also be preparable with selenium replacing the strongly out-of-plane sulphur in S_4N_2.

The structure of poly(sulphur nitride) $(SN)_x$ has been determined by *X*-ray [8] and neutron [27] diffraction and a model has been proposed [8] for the mechanism of the solid-state polymerisation of S_2N_2 to $(SN)_x$ involving the close intermolecular S · · · N contacts. A similar mechanism is possible for the polymer formation from the title compound, the basis being the double 4_2 helix formed by the sequence N–S(3) · · · N^{II}–$S(3^{II})$ · · · *etc.*, Figure 4. This process is clearly less direct than in the case of the polymer formation from S_2N_2 since here the atom movements required are greater and the elimination of sulphur is involved. This may account for the less pronounced preferred orientation of the polymeric material from the title compound (as shown in Figure 2).

It is intended to pursue a more detailed investigation of the mechanism of polymer formation in S_4N_2.

* A ' preferred ' angle is the angle which would be adopted in the absence of strain.

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