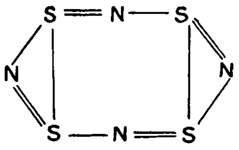
297. *The Structure of Sulphur Nitride.*

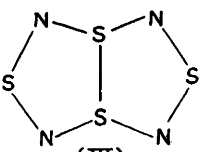
By D. Clark.

The crystal structure of sulphur nitride has been determined by *X*-ray analysis. The monoclinic cell contains four molecules S_4N_4, each consisting of a distorted tetrahedron of sulphur atoms with nitrogen atoms along four edges. The distance between sulphur atoms not joined through nitrogen is 2·58 Å which is much shorter than the normal van der Waals separation. Resonance formulæ are suggested to account for this short S–S distance.

Sulphur nitride is one of the few relatively simple inorganic compounds whose molecular structure has not been determined with certainty. The molecular formula S_4N_4 is known from cryoscopic measurements, but neither methods of preparation nor properties provide conclusive evidence for its structure. Early formulations by Schenck (*Annalen*, 1896, **290**, 171), Muthmann and Clever (*Z. anorg. Chem.*, 1896, **13**, 200), Ruff and Geisel (*Ber.*, 1904, **37**, 1573), and Meuwsen and Holch (*Ber.*, 1931, **64**,2 301) were directed primarily to satisfying the then-accepted valencies of the constituent atoms, and led to assemblages of three- and four-membered rings which are inherently improbable, *e.g.*, Ruff and Geisel's formula (I).



(I)



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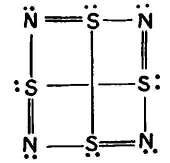

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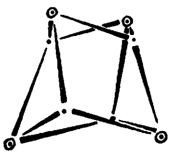
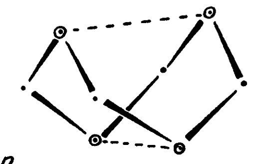


(II)

⊙Sulphur • Nitrogen



(IV)

Jaeger and Zanstra (*Proc. K. Akad. Wetensch. Amsterdam*, 1931, **34**, 782), as a result of an *X*-ray investigation, published structure (II), consisting of two interpenetrating bisphenoids of nitrogen and sulphur, which required an improbably short N–S distance of 1·2 Å, compared with 1·54 Å and 1·74 Å for double and single bonds respectively, calculated from known atomic radii. Further doubt is cast upon this work since the crystals are treated as orthorhombic, whereas their true symmetry is monoclinic. Buerger (*Amer. Min.*, 1936, **21**, 575) published a unit-cell and space-group determination, $a = 8·74$, $b = 7·14$, $c = 8·64$ Å, $\beta = 87° 39'$, space group $P2_1/n$ containing four molecules of S_4N_4 per unit cell, but no account of further structure work is given. Arnold, Hugill, and Hutson (*J.*, 1936, 1645) proposed configuration (III), consisting of two fused five-membered rings involving resonance among several different bond structures. Chia-Si Lu and Donohue (*J. Amer. Chem. Soc.*, 1944, **66**, 818) investigated the vapour by electron diffraction (the substance sublimes easily below 100° *in vacuo*) and were led to a configuration consisting of a bisphenoid of sulphur atoms with nitrogen atoms along four edges in square configuration (IV). They suggested resonance forms such as (V) to account for the short S–S distances across the two opposite edges of the bisphenoid not occupied by nitrogen atoms.

X-Ray Measurements and Space-group Determination.—The specimen was prepared by the action of ammonia on sulphur dichloride in an inert solvent, according to the method of Arnold, Hugill, and Hutson (*loc. cit.*). After crystallisation from carbon tetrachloride the substance formed needles elongated along the *b* axis, all of which were twinned. After recrystallisation by slow evaporation of the solvent at room temperature, a few untwinned crystals were obtained suitable for *X*-ray analysis.

Complete sets of overlapping, 15° oscillation photographs were taken about each of the three principal axes, filtered copper radiation being used. Intensities were estimated visually from a calibrated scale of intensities, additional short-exposure photographs being taken where necessary to obtain the intensities of outstandingly strong reflections. Polarisation and Lorentz corrections were applied in the usual way, giving a series of F^2 values on an arbitrary scale. No correction was made for absorption.

FIG. 1. *Patterson projection on* (010).

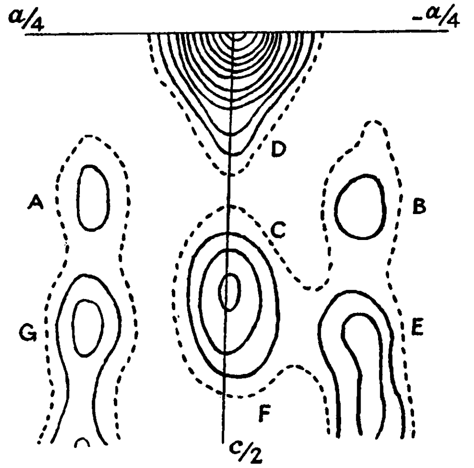
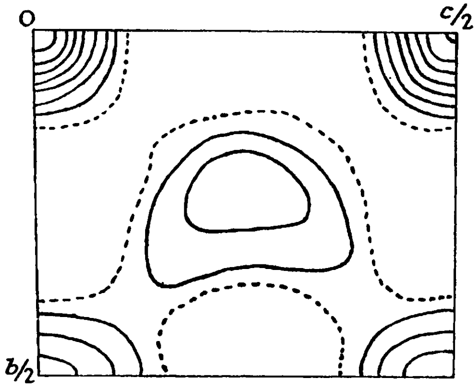


FIG. 2. *Patterson projection on* (100).



The orientation originally proposed by Buerger (*loc. cit.*), which gives an almost tetragonal cell, being retained, the following dimensions for the monoclinic unit cell were obtained: $a = 8{\cdot}75$, $b = 7{\cdot}16$, $c = 8{\cdot}65$ Å, $\beta = 87\frac{1}{2}°$, in very good agreement with those of Buerger. The space-group $P2_1/n$ was confirmed. The general position is fourfold—$\pm(x, y, z)$; $\pm(\frac{1}{2} - x)(\frac{1}{2} + y)(\frac{1}{2} - z)$. The unit-cell from the observed density (2·20 g./c.c.) contains 16 SN, or assuming a structure of discrete S_4N_4 molecules, $4S_4N_4$, which must therefore occupy a general position in the unit cell.

Structure Determination.—The (010) and (100) Patterson projections were calculated from the observed F^2 values and proved to be relatively simple. It was found possible to extract considerable information from them even in the absence of predominantly heavy atoms in the unit cell. The intramolecular distance, sulphur to sulphur bonded through nitrogen, S–(N)–S, from electron-diffraction data (Lu and Donohue, *loc. cit.*) as well as from known atomic radii and bond angles, must be in the region 2·6—2·7 Å. Two peaks *A* and *B* in the (010) Patterson projection (Fig. 1) can provisionally be identified as this vector, with possibly two others at *C* and *D*. All other peaks represent distances considerably greater than 2·7 Å even in projection. At the same time it was noted that the structure amplitudes F_{h0l} and $F_{h0\bar{l}}$ were very nearly equal, especially for low-order reflections. The simplified structure factor for those reflections is $F_{h0l} = 4 \cos 2\pi(hx + lz)$. If $F_{h0l} = F_{h0\bar{l}}$ then for every atom at (x, z) there must be a similar atom at $(x, \bar{z})$. Since the monoclinic angle β is very close to 90°, this is equivalent to two vertical planes of symmetry *mm* mutually at right angles in this projection, in addition to the symmetry required by the space-group. The outstanding feature of the (100) Patterson projection (Fig. 2) is the very large peak at $b = 0$, $c = \frac{1}{2}$, almost equal in height to the peak at the origin. This can be accounted for if there is a pseudo-plane of symmetry in this projection at $b = \frac{1}{4}$ in addition to the *n* glide plane.

Thus in addition to the space-group symmetry, there are, in the two projections, three planes of pseudo-symmetry mutually at right angles, some of which must be satisfied by internal symmetry. Consider Lu and Donohue's tetrahedral model. If the nitrogen atoms of relatively low scattering power are neglected, we are left with an approximately tetrahedral arrangement of sulphur atoms, with six symmetry planes grouped in three pairs of mutually perpendicular planes but no centre of symmetry. Two planes of pseudo-symmetry in the unit cell can therefore be accommodated by symmetry planes of the tetrahedron, leaving the third to be satisfied by the actual arrangement of molecules in the unit cell. Peaks *E*, *F*, and *G* of the (010) Patterson projection suggested that (001) was the symmetry plane determining the arrangement of molecules. The orientation of the sulphur tetrahedron is therefore practically fixed by the other two symmetry planes, leaving *z* co-ordinates only to be determined by peaks *E*, *F*, and *G*. It was at once apparent that the resulting arrangement was very reasonable spatially and, at the same time, gave

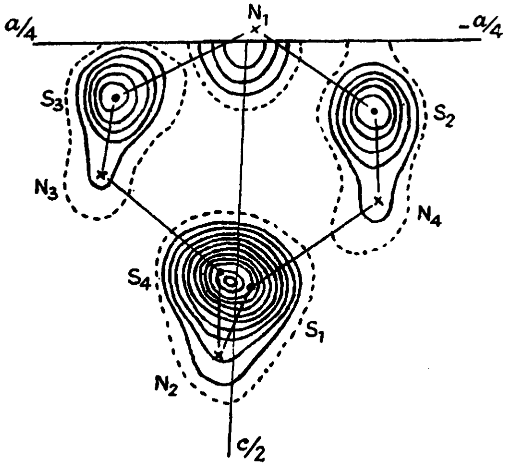


FIG. 3. *Electron density projected on* (010).

FIG. 4. *Electron density projected on* (100).

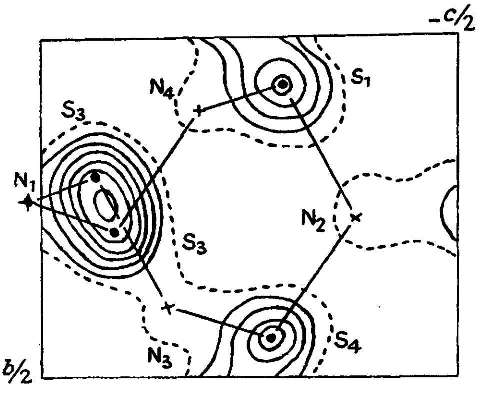
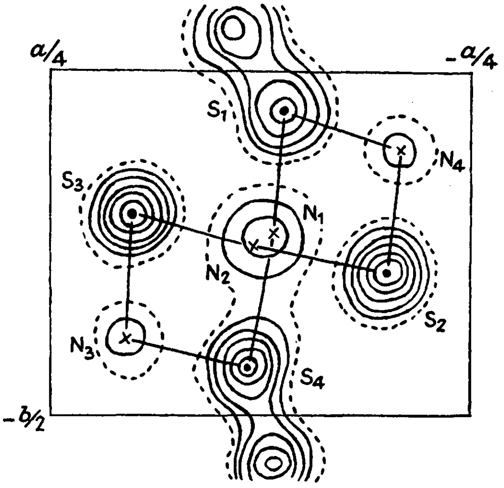


FIG. 5. *Electron density projected on* (001).



encouraging agreement between observed and calculated structure factors for low-angle reflections. Two alternative positions were left for the nitrogen atoms, of which the more likely, from considerations of available space, was characterised by two overlapping nitrogen atoms at the origin in the (010) projection. The signs of all the structure factors F_{h0l} were computed, only the four sulphur atoms being taken into account. A Fourier synthesis on (010) was then carried out by use of Beevers and Lipson strips. The resulting projection showed unmistakable signs of a fairly large peak at the origin, together with indications of two other nitrogen atoms (the fourth nitrogen would be masked by overlapping sulphur atoms). A preliminary synthesis on (100) confirmed the general correctness of the structure. The atomic parameters derived from these two projections were refined by successive syntheses in the usual way. It was necessary to compute all three projections (Figs. 3, 4, 5) before the atomic parameters could be completely determined. The (001) projection (Fig. 5) shows clearly the four tetrahedral sulphur atoms, together with the square of nitrogen atoms viewed along a diagonal, so leading to two overlapping nitrogen atoms N_1N_2 at the centre of the molecule. Table 1 gives the final parameters expressed as fractions of the corresponding lattice translations—the co-ordinates of the sulphur atoms can be determined unambiguously from one or other of the projections, but those of the nitrogen atoms are a little less certain owing to imperfect resolution, particularly in the case of N_1 which is not completely resolved in any projection.

FIG. 6. *General arrangement of* $4S_4N_4$ *molecules in unit cell.*

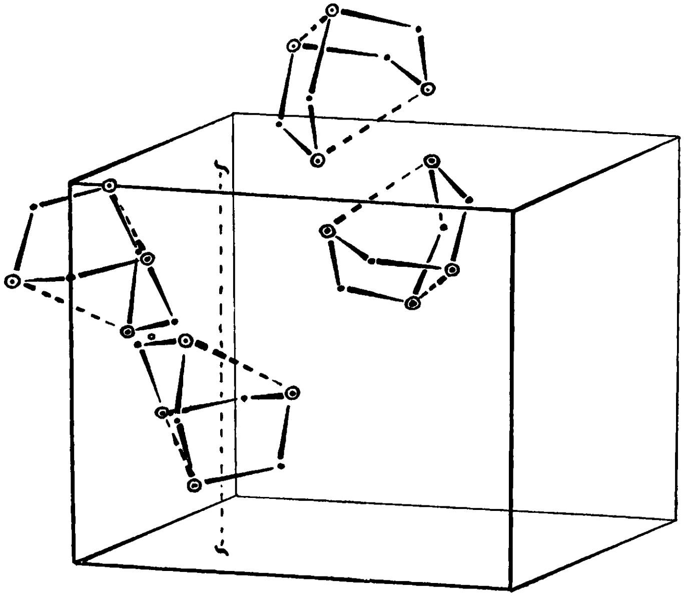


TABLE 1.

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
S_1	0·984	0·932	0·296	N_1	0·995	0·763	0·980
S_2	0·849	0·711	0·087	N_2	0·010	0·739	0·383
S_3	0·148	0·800	0·067	N_3	0·167	0·610	0·160
S_4	0·029	0·555	0·276	N_4	0·840	0·893	0·193

Calculated F values were obtained by using these co-ordinates and scattering factors taken from " International Tables for the Determination of Crystal Structure; " $F_{obs.}$ and $F_{calc.}$ were put on the same scale, and $F_{calc.}$ corrected by a temperature factor with $B = 4{\cdot}0$. Table 2 shows the agreement between observed and calculated values, the discrepancy calculated using the conventional expression $100\ \Sigma(F_{obs.} - F_{calc.})/\Sigma F_{obs.}$ being 20%.

Discussion of the Structure.—The molecular structure fully confirms that proposed by Lu and Donohue (*loc. cit.*), from electron-diffraction data, the bond lengths and angles being as follows :

	Electron diffraction	Crystal structure
S–N, Å	1·62	1·60
>N bond angle	112°	115°
>S bond angle	106°	102°

The four sulphur atoms (Fig. 6) form a slightly distorted tetrahedron, the pairs of sulphur atoms linked through nitrogen being separated by 2·71 Å compared with 2·58 Å for unbonded pairs (Lu and Donohue give *ca.* 2·70 Å for both these distances). Within experimental error the nitrogen atoms lie at the corners of a square. All sulphur–nitrogen

TABLE 2. *Observed and calculated structure factors for the principal zones*

(in approximate order of increasing sin θ).

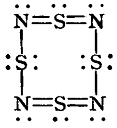
*h*0*l*	$F_{\text{obs.}}$	$F_{\text{calc.}}$	*h*0*l*	$F_{\text{obs.}}$	$F_{\text{calc.}}$	*h*0*l*	$F_{\text{obs.}}$	$F_{\text{calc.}}$	*h*0*l*	$F_{\text{obs.}}$	$F_{\text{calc.}}$	*h*0*l*	$F_{\text{obs.}}$	$F_{\text{calc.}}$
101	12	12	$50\bar{1}$	5	3	107	1	1	$70\bar{5}$	3	$\bar{4}$	608	2	$\bar{3}$
$10\bar{1}$	11	12	105	12	$\overline{13}$	$10\bar{7}$	6	5	507	7	8	$60\bar{8}$	2	$\bar{2}$
200	22	22	$10\bar{5}$	8	$\overline{10}$	604	1	1	$50\bar{7}$	0	0	10·00	4	$\bar{3}$
002	10	$\bar{9}$	404	6	9	$60\bar{4}$	1	$\bar{1}$	804	0	0	00·10	2	2
202	12	$\overline{13}$	$40\bar{4}$	6	9	406	7	6	$80\bar{4}$	1	1	905	0	$\bar{1}$
$20\bar{2}$	15	$\overline{17}$	503	8	8	$40\bar{6}$	2	3	408	0	4	$90\bar{5}$	2	2
301	22	$\overline{25}$	$50\bar{3}$	4	4	703	4	4	$40\bar{8}$	0	2	509	1	$\bar{1}$
$30\bar{1}$	19	$\overline{20}$	305	2	$\bar{3}$	$70\bar{3}$	2	3	901	3	$\bar{4}$	$50\bar{9}$	1	$\bar{2}$
103	21	15	$30\bar{5}$	2	2	307	10	12	$90\bar{1}$	3	$\bar{2}$	10·02	1	$\bar{1}$
$10\bar{3}$	20	18	600	28	22	$30\bar{7}$	10	11	109	4	$\bar{6}$	$10\cdot0\bar{2}$	1	$\bar{1}$
400	2	2	006	8	$\bar{7}$	800	5	5	$10\bar{9}$	2	$\bar{3}$	20·10	2	2
004	1	2	602	0	$\bar{1}$	008	4	$\bar{5}$	903	2	3	$\overline{20}\cdot\overline{10}$	0	1
303	18	18	$60\bar{2}$	0	$\bar{2}$	802	2	1	$90\bar{3}$	2	2	10·04	1	1
$30\bar{3}$	18	16	206	0	0	$80\bar{2}$	0	0	309	2	$\bar{2}$	$10\cdot0\bar{4}$	1	1
402	10	$\overline{12}$	$20\bar{6}$	3	3	208	2	$\bar{2}$	$30\bar{9}$	0	0	40·10	1	2
$40\bar{2}$	13	$\overline{14}$	505	2	$\bar{3}$	$20\bar{8}$	4	5	707	1	0	$40\cdot\overline{10}$	1	1
204	6	8	$50\bar{5}$	2	$\bar{3}$	606	0	$\bar{2}$	$70\bar{7}$	2	$\bar{2}$	808	3	$\bar{2}$
$20\bar{4}$	11	13	701	5	5	$60\bar{6}$	4	$\bar{3}$	806	2	$\bar{2}$	907	3	2
501	6	$\bar{5}$	$70\bar{1}$	9	8	705	6	$\bar{6}$	$80\bar{6}$	0	0	709	1	$\bar{3}$

*hk*0	$F_{\text{obs.}}$	$F_{\text{calc.}}$	*hk*0	$F_{\text{obs.}}$	$F_{\text{calc.}}$	*hk*0	$F_{\text{obs.}}$	$F_{\text{calc.}}$	*hk*0	$F_{\text{obs.}}$	F_{calc}	*hk*0	$F_{\text{obs.}}$	F_{calc}
110	0	0	240	3	4	060	7	$\bar{7}$	830	0	1	280	1	$\bar{2}$
200	22	22	510	1	1	450	2	2	270	1	1	380	0	$\bar{1}$
210	1	1	430	0	0	160	7	6	560	9	$\bar{9}$	760	0	$\bar{1}$
020	12	$\overline{11}$	520	8	$\bar{8}$	720	5	$\bar{4}$	370	0	$\bar{1}$	850	0	0
120	1	$\bar{1}$	340	8	$\bar{8}$	260	5	$\bar{6}$	910	2	2	940	6	$\bar{5}$
220	10	10	600	28	22	640	2	2	750	1	$\bar{1}$	10·20	4	2
310	0	0	610	1	1	800	5	5	840	0	2	670	0	0
130	3	$\bar{2}$	530	0	0	360	0	0	920	1	$\bar{1}$	480	0	$\bar{1}$
320	1	$\bar{2}$	150	2	$\bar{2}$	550	1	$\bar{1}$	470	0	0	10·30	0	0
400	2	2	440	1	1	730	0	0	660	3	$\bar{3}$	580	2	1
230	2	2	250	1	$\bar{1}$	810	0	1	080	4	$\bar{4}$	860	1	$\bar{1}$
410	1	1	620	6	$\bar{4}$	820	1	$\bar{1}$	180	2	$\bar{2}$	950	0	$\bar{1}$
420	12	13	350	2	$\bar{2}$	460	4	$\bar{4}$	930	0	0	10·40	1	$\bar{1}$
330	0	0	540	4	3	650	1	2	570	0	0			
040	6	6	630	1	1	740	5	$\bar{6}$	10·00	4	$\bar{3}$			
140	14	$\overline{13}$	710	4	2	170	0	0	10·10	0	0			

0*kl*	$F_{\text{obs.}}$	$F_{\text{calc.}}$	0*kl*	$F_{\text{obs.}}$	$F_{\text{calc.}}$	0*kl*	$F_{\text{obs.}}$	$F_{\text{calc.}}$	0*kl*	$F_{\text{obs.}}$	$F_{\text{calc.}}$	0*kl*	$F_{\text{obs.}}$	$F_{\text{calc.}}$
011	1	0	041	0	1	036	6	$\bar{7}$	056	4	$\bar{4}$	039	1	1
002	10	$\bar{9}$	042	8	7	017	2	$\bar{2}$	047	0	0	075	0	0
012	12	13	015	0	0	060	7	$\bar{7}$	071	0	0	00·10	2	2
020	12	$\overline{11}$	034	0	$\bar{1}$	054	4	6	038	5	6	01·10	2	$\bar{4}$
021	1	1	025	2	2	061	3	$\bar{2}$	072	0	0	082	0	1
022	30	$\overline{27}$	043	0	1	027	4	4	065	0	0	083	0	1
013	4	4	006	8	$\bar{7}$	062	2	4	073	1	$\bar{1}$	067	1	2
031	1	$\bar{2}$	016	0	0	046	4	$\bar{4}$	019	0	1	058	1	2
023	1	$\bar{1}$	035	0	$\bar{1}$	008	4	$\bar{5}$	057	0	0	049	1	$\bar{2}$
004	1	2	051	2	2	063	0	1	048	0	1	076	0	$\bar{1}$
032	8	$\bar{8}$	044	0	$\bar{1}$	055	2	2	029	0	$\bar{2}$	084	0	$\bar{1}$
014	15	14	052	1	$\bar{4}$	037	0	0	074	2	3	085	0	$\bar{1}$
024	11	11	026	4	5	018	1	$\bar{2}$	066	0	$\bar{1}$	068	0	0
033	3	$\bar{2}$	053	0	0	028	0	1	080	4	$\bar{4}$	059	1	$\bar{1}$
040	6	6	045	3	4	064	0	$\bar{2}$	081	0	0			

distances are equal, and the bond length 1·60 Å may be compared with 1·57 Å for S–N in the sulphamate ion $[SO_3{\cdot}NH_2]'$ (Brown and Cox, *J.*, 1940, 1) and 1·63 Å in the dinitrososulphite ion $SO_3{\cdot}N{<}^{NO}_{O}$ (Cox, Jeffrey, and Stadler, *J.*, 1949, 1783).

One point of interest in the molecule is the short distance between pairs of sulphur atoms not linked through nitrogen. The observed value is 2·58 Å compared with 3·7 Å for the normal van der Waals separation and 2·1 Å for an ordinary single bond. This was explained by Lu and Donohue on the basis of resonance forms, some of which contain a single bond between these two atoms, *e.g.*,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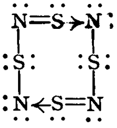
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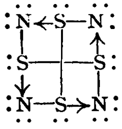
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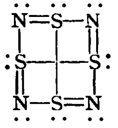
(IX)

Of these, (VI) is probably the most important, containing sulphur with a decet of electrons, but the importance of the cross-bonded structures is shown by the short S–S distances across the other two sides of the tetrahedron. It should be noted that the observed distance is only about 0·1 Å shorter than the separation of sulphur atoms linked through nitrogen, where they are forced together by the fixed N–S distances and bond angles. Purely geometrical considerations may therefore play a part, although cross-bonded structures confer some additional stability to account for the existence of the present structure rather than of other forms of puckered ring containing similar bond lengths and angles. The angle between this third " bond " and the other two bonds formed by the sulphur atom is approximately 90°.

The packing of the molecules in the unit cell (Fig. 6) is purely molecular, as already indicated by the low melting point and the volatility of the crystals. The distances of closest approach of neighbouring molecules are S–N 3·3 Å and S–S 3·7 Å, in good agreement with the accepted van der Waals radii of these atoms. The abundant formation of twin crystals follows from the pseudo-symmetry of the unit cell and the closeness of the monoclinic angle to 90°.

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