Bonding in 1,2,4-Triazoles. Part VI.[1] Crystal Structure of 6-Mercapto-3-phenyl-*s*-triazolo[4,3-*b*]-*s*-tetrazine Pyridine Adduct

By **R. C. Seccombe** and **C. H. L. Kennard,*** Department of Chemistry, University of Queensland, Brisbane, Queensland 4067, Australia

The crystal structure of the title compound (V) has been determined from three-dimensional diffractometer data. Crystals are orthorhombic, space group *Pbcn*, with $z = 16$ in a unit cell of dimensions: $a = 1204{\cdot}56(7)$, $b = 1494{\cdot}23(9)$, and $c = 3153{\cdot}2(1)$ pm. The refinement was halted at R 0·044 for 3483 observed reflections. The triazole and tetrazine rings are planar with the phenyl groups rotated by 7 and 12·5° in the two molecules of an asymmetric unit.

Mean interatomic distances (pm; each ±0·3): C–S 167·2, N–N(ring) 137·2, N–N(side-chain), N(4)–N(9) 135·7, N(7)–N(8) 136·2; ring N(2)–C(3) 131·6; C(3)–N(4) 137·3; N(4)–C(5) 137·3, and C(5)–N(1) 162·1.

DICKINSON and Jacobsen[2] have found that 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (I) reacts with benzaldehyde in the presence of base to form an unstable monobenzylidene intermediate, either (II) or (III). This is rapidly converted into 1,2,3,4-tetrahydro-6-mercapto-*s*-triazolo[4,3-*b*]-*s*-tetrazine (IV) which will revert back to the monobenzylidene but in the opposite conformation, (*III*) or (*II*). At the liquid–air interface, (IV) is rapidly oxidized (*ca.* 1 min) by aerial oxygen to a purple 6-mercapto-3-phenyl-*s*-triazolo[4,3-*b*]-*s*-tetrazine (V). This contribution deals with the structure of (V).

DISCUSSION

The arrangement of the atoms in the molecules are shown in Figure 1.

Throughout this discussion, the mean for the two molecules in the asymmetric unit is given. In all cases, the two distances for a particular bond are very close to one another with the greatest deviation being for the C(15)–C(16) bond (1·3 pm).

In this structure, there is a six-membered tetrazine ring connected to the five-membered triazole ring along the C(3)–N(4) bond.

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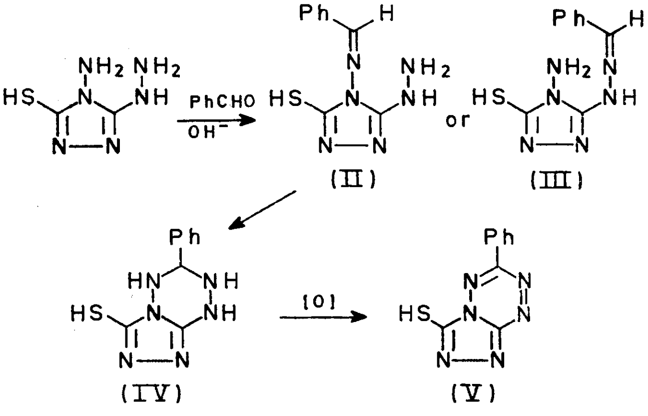
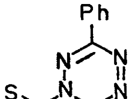
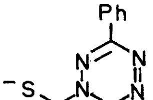
[1] Part V, R. C. Seccombe and C. H. L. Kennard, preceding paper.

[2] R. G. Dickinson and N. W. Jacobsen, *Chem. Comm.*, 1970, 1719.

Of the three N–N distances in the molecule N(7)–N(8) (129·7 pm) is shorter than N(4)–N(9) (135·7 pm) in the tetrazine ring and N(1)–N(2) (137·2 pm) in the triazole ring. This compares with the N(1)–N(2) length in 1,2,4-triazole [3] (135·9 pm). The S–C bond length (167·2 pm) is shorter than the single S–C bond in methanesulphonanilide [4] (174·6 pm) and similar to that in 4-amino-3-(β-benzoylhydrazino)-5-mercapto-1,2,4-triazole [5] (166·8 pm) and in (I) [6] (168·1 pm). This suggests that the tetrazine ring has no influence on the S–C bond. One C–N distance within the triazole ring, [N(2)–C(3) 131·6 pm], is significantly shorter than the other three [N(1)–C(5) 135·7, C(5)–N(4) 137·3, and N(4)–C(3) 137·3 pm]. The C(5)–N(1) bond is longer than observed in other triazoles.[1,5-8] This lengthening may be due to the influence of the tetrazine ring although it has no apparent effect on the N(2)–C(3) bond. The C(3)–N(4) and N(4)–C(5) bond lengths are equivalent although the C(3)–N(4) bond is common to both ring systems. Apart from this bond, there are two other C–N distances in the tetrazine ring: C(10)–N(8) (141·8 pm) which is close to a single-bond and C(10)–N(9) (130·4 pm) which is close to a double-bond distance. Of the possible canonical forms, (A) comes closest to describing the bonding scheme.




(A)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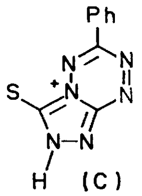
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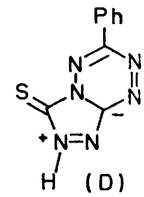
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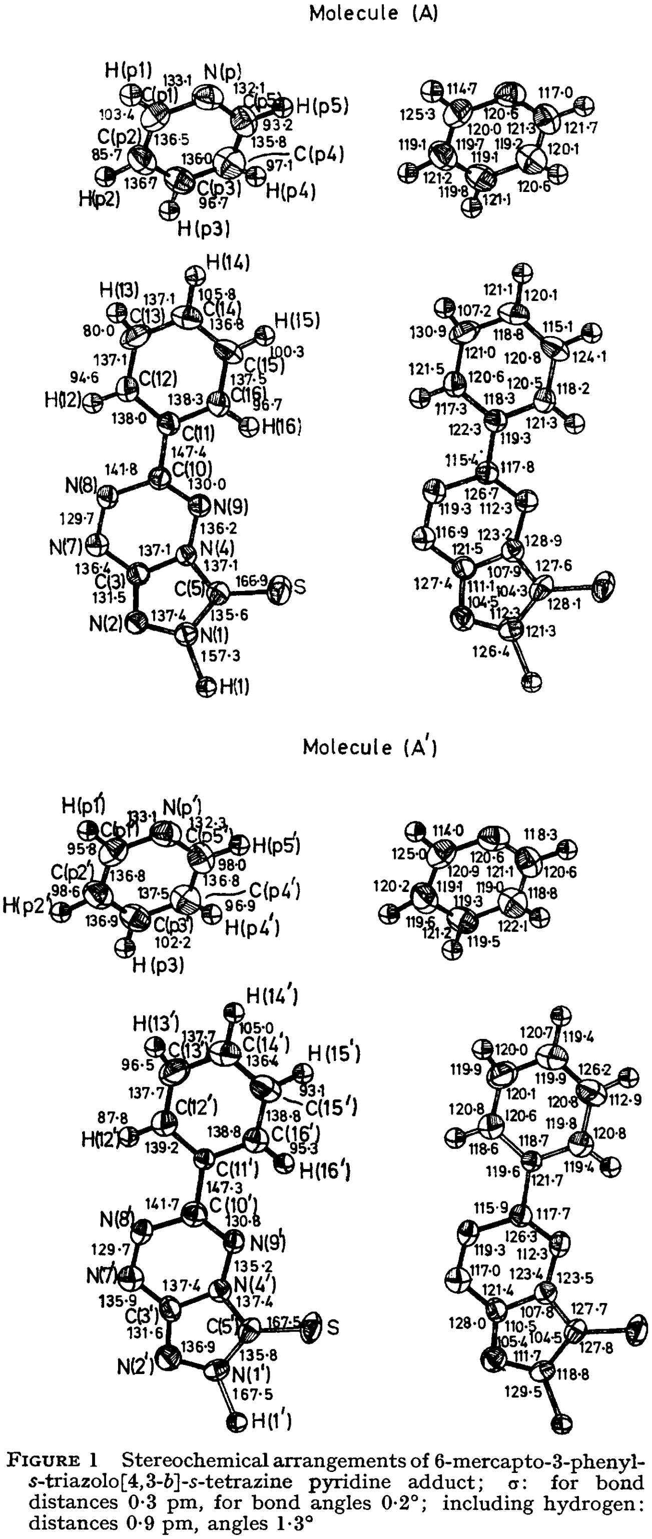

Figure 1 Stereochemical arrangements of 6-mercapto-3-phenyl-*s*-triazolo[4,3-*b*]-*s*-tetrazine pyridine adduct; σ: for bond distances 0·3 pm, for bond angles 0·2°; including hydrogen: distances 0·9 pm, angles 1·3°

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[3] P. Goldstein, J. Ladell, and G. Abowitz, *Acta Cryst.*, 1969, *B*, **25**, 135.

[4] H. P. Klug, *Acta Cryst.*, 1968, *B*, **24**, 792.

[5] R. C. Seccombe and C. H. L. Kennard, *J.C.S. Perkin II*, 1973, 4.

[6] N. W. Isaacs and C. H. L. Kennard, *J. Chem. Soc.* (*B*), 1971, 1270.

[7] R. C. Seccombe and C. H. L. Kennard, *J.C.S. Perkin II*, 1973, 1.

[8] R. C. Seccombe, J. V. Tillack, and C. H. L. Kennard, *J.S.C. Perkin II*, 1973, 6.

In the unit cell the tetrazine molecules are stacked in two sheets almost perpendicular to the *bc* plane and arranged at *ca.* 130° to each other (Figure 2). The pyridine molecules are also arranged parallel to the tetrazine molecules, along the *c* axis: at $y = 0,\frac{1}{2}$, as an unconnected string of pyridine molecules, while the triazole molecules occur at $y = \frac{1}{4},\frac{3}{4}$. Intermolecular distances are not <330 pm, *e.g.* S · · · N(7′) 347, S′ · · · N(8) 345, and N(9) · · · C(5′) 332 pm.

(*a*) Atomic positions (fractional co-ordinates) and temperature factors with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*/Å^2
S	0·02386(5)	0·29871(5)	0·10143(2)	
S′	0·37671(5)	0·06542(5)	0·15855(2)	
C(3)	0·3320(2)	0·3247(2)	0·1310(1)	
C(5)	0·1594(2)	0·3192(2)	0·1068(1)	
C(3′)	0·0692(2)	0·0491(2)	0·1253(1)	
C(5′)	0·2396(2)	0·0525(2)	0·1522(1)	
N(1)	0·2298(2)	0·3555(1)	0·0780(1)	
N(2)	0·3370(2)	0·3593(2)	0·0927(1)	
N(4)	0·2256(1)	0·2999(1)	0·1410(1)	
N(7)	0·4169(2)	0·3150(1)	0·1593(1)	
N(8)	0·3922(2)	0·2818(1)	0·1961(1)	
N(9)	0·1964(2)	0·2646(1)	0·1792(1)	
N(1′)	0·1646(2)	0·0226(2)	0·1810(1)	
N(2′)	0·0595(2)	0·0200(2)	0·1645(1)	
N(4′)	0·1777(2)	0·0708(1)	0·1166(1)	
N(7′)	−0·0111(2)	0·0547(1)	0·0951()1	
N(8′)	0·0185(2)	0·0852(1)	0·0583(1)	
N(9′)	0·2117(2)	0·1040(1)	0·0789(1)	
C(10)	0·2810(2)	0·2567(2)	0·2047(1)	
C(11)	0·2606(2)	0·2200(2)	0·2474(1)	
C(12)	0·3457(2)	0·2017(2)	0·2754(1)	
C(13)	0·3233(3)	0·1681(2)	0·3149(1)	
C(14)	0·2162(2)	0·1536(2)	0·3279(1)	
C(15)	0·1313(2)	0·1730(2)	0·3006(1)	
C(16)	0·1526(2)	0·2058(2)	0·2606(1)	
C(10′)	0·1300(2)	0·1123(2)	0·0518(1)	
C(11′)	0·1551(2)	0·1517(2)	0·0101(1)	
C(12′)	0·2574(2)	0·1928(2)	0·0034(1)	
C(13′)	0·2840(2)	0·2278(2)	−0·0356(1)	
C(14′)	0·2086(2)	0·2240(2)	−0·0684(1)	
C(15′)	0·1078(3)	0·1846(2)	−0·0622(1)	
C(16′)	0·0799(2)	0·1481(2)	−0·0232(1)	
N(p) †	0·2682(2)	0·4649(1)	0·2579(1)	
N(p′)	0·3385(2)	0·0901(2)	0·5013(1)	
C(p1)	0·1597(2)	0·4583(2)	0·2654(1)	
C(p2)	0·1230(2)	0·4231(2)	0·3028(1)	
C(p3)	0·1979(2)	0·3963(2)	0·3327(1)	
C(p4)	0·3083(2)	0·4050(2)	0·3246(1)	
C(p5)	0·3411(2)	0·4405(2)	0·2870(1)	
C(p1′)	0·4429(2)	0·1040(2)	0·4892(1)	
C(p2′)	0·4793(2)	0·0761(2)	0·4502(1)	
C(p3′)	0·4065(3)	0·0340(2)	0·4235(1)	
C(p4′)	0·2985(2)	0·0214(2)	0·4363(1)	
C(p5′)	0·2669(2)	0·0507(2)	0·4756(1)	
H(1)	0·187(2)	0·389(2)	0·034(1)	3·5
H(12)	0·419(2)	0·205(2)	0·265(1)	4·7
H(13)	0·363(2)	0·146(2)	0·332(1)	5·0
H(14)	0·199(2)	0·131(2)	0·359(1)	4·0
H(15)	0·055(2)	0·162(2)	0·312(1)	4·9
H(16)	0·090(2)	0·218(2)	0·242(1)	4·5
H(1′)	0·209(2)	−0·007(2)	0·229(1)	3·6
H(12′)	0·305(2)	0·196(2)	0·025(1)	3·7
H(13′)	0·355(2)	0·257(2)	−0·040(1)	4·0
H(14′)	0·228(2)	0·251(2)	−0·098(1)	4·1
H(15′)	0·053(2)	0·176(2)	−0·083(1)	4·8
H(16′)	0·009(2)	0·121(2)	−0·019(1)	3·5
H(p1)	0·110(2)	0·483(2)	0·242(1)	4·7
H(p2)	0·053(2)	0·417(2)	0·307(1)	5·1
H(p3)	0·172(2)	0·371(2)	0·359(1)	3·9
H(p4)	0·363(2)	0·390(2)	0·346(1)	4·3
H(p5)	0·416(2)	0·448(2)	0·280(1)	4·4
H(p1′)	0·488(2)	0·132(2)	0·510(1)	4·2
H(p2′)	0·552(2)	0·097(2)	0·439(1)	4·0
H(p3′)	0·431(2)	0·012(2)	0·394(1)	4·5
H(p4′)	0·245(2)	−0·011(2)	0·419(1)	4·5
H(p5′)	0·190(2)	0·043(2)	0·485(1)	4·1

(*b*) Anistropic temperature factors ($\times 10^4$; those for β_{13}, β_{23}, and $\beta_{33} \times 10^5$) *

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	48·0(4)	62·7(5)	101(1)	3·9(4)	−45(2)	−22(2)
S′	55·1(5)	68·2(5)	87(1)	5·7(4)	−2(2)	18(2)
C(3)	45(2)	46(2)	74(3)	−6(1)	10(6)	2(5)
C(5)	55(2)	37(1)	72(3)	4(1)	−29(6)	−25(5)
C(3′)	48(2)	37(2)	80(3)	3(1)	40(6)	4(6)
C(5′)	57(2)	37(1)	67(3)	7(1)	27(6)	8(5)
N(1)	57(2)	51(1)	66(2)	−1(1)	−17(5)	11(5)
N(2)	56(2)	53(1)	77(3)	−8(1)	11(6)	20(5)
N(4)	41(2)	38(1)	61(2)	2(1)	5(4)	7(4)
N(7)	48(2)	51(1)	87(3)	−8(1)	−17(5)	31(5)
N(8)	44(2)	52(1)	82(3)	−6(1)	−23(5)	22(5)
N(9)	41(1)	43(1)	66(2)	−3(1)	−3(5)	4(4)
N(1′)	66(2)	46(1)	72(1)	3(1)	25(6)	22(5)
N(2′)	59(2)	46(2)	91(3)	3(1)	61(6)	29(5)
N(4′)	45(1)	37(1)	62(2)	2(1)	27(5)	10(4)
N(7′)	53(2)	51(1)	96(3)	−4(1)	16(5)	9(4)
N(8′)	49(2)	51(1)	91(3)	−4(1)	−15(5)	8(5)
N(9′)	48(2)	38(1)	63(2)	3(1)	31(5)	15(4)
C(10)	45(2)	36(1)	73(3)	3(1)	−7(6)	−2(5)
C(11)	48(2)	34(1)	66(3)	−2(1)	3(6)	1(5)
C(12)	50(2)	69(2)	87(3)	3(2)	8(7)	34(7)
C(13)	86(3)	64(2)	84(3)	13(2)	−57(8)	39(7)
C(14)	93(3)	44(2)	76(3)	−9(2)	19(7)	12(6)
C(15)	70(2)	71(2)	98(3)	−16(2)	31(8)	87(7)
C(16)	51(2)	66(2)	89(4)	−10(2)	−26(7)	65(7)
C(10′)	49(2)	34(1)	71(3)	4(6)	7(6)	−8(5)
C(11′)	50(2)	40(2)	66(3)	7(1)	7(6)	−3(5)
C(12′)	56(2)	44(2)	73(3)	8(2)	7(6)	13(6)
C(13′)	71(3)	44(2)	90(3)	7(2)	68(7)	26(6)
C(14′)	99(3)	52(3)	65(3)	17(2)	50(7)	15(6)
C(15′)	83(3)	72(2)	72(3)	7(2)	−50(8)	1(7)
C(16′)	61(2)	55(2)	84(3)	2(2)	−22(7)	5(6)
N(p)	74(2)	46(1)	63(2)	−9(1)	−15(6)	21(4)
N(p′)	78(2)	43(1)	71(2)	6(1)	30(5)	−2(5)
C(p1)	70(2)	68(2)	117(4)	3(2)	−64(8)	50(7)
C(p2)	62(2)	75(2)	137(2)	6(2)	45(8)	66(8)
C(p3)	86(2)	43(2)	81(3)	1(2)	35(7)	21(5)
C(p4)	75(2)	64(2)	80(3)	−3(2)	−43(7)	35(6)
C(p5)	57(2)	65(2)	95(3)	−14(2)	−12(7)	25(7)
C(p1′)	73(2)	49(2)	96(3)	−1(2)	−47(7)	−12(6)
C(p2′)	70(2)	58(2)	100(3)	−4(2)	47(7)	−2(6)
C(p3′)	95(3)	52(2)	87(2)	−2(2)	75(8)	−32(6)
C(p4′)	90(3)	47(2)	101(3)	−14(2)	7(8)	−55(6)
C(p5′)	64(2)	44(2)	118(3)	−6(2)	47(8)	6(6)

* In the form $\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$. † p Denotes pyridine atom.

The atoms of the triazole ring and the sulphur atom constitute a plane, with tetrazine and phenyl rings bent away. The phenyl groups are rotated by *ca.* 7° in one molecule and 12·5° in the other.

EXPERIMENTAL

Crystal Data.—$C_{14}H_{11}N_7S$, $M = 309·35$. Orthorhombic $a = 1204·56(7)$, $b = 1494·23(9)$, $c = 3153·2(1)$ pm, $U = 5·6775$ nm^3, $D_m = 1·40$ (by flotation), $Z = 16$, $D_c = 1·45$, $F(000) = 2560$. Cu-K_α radiation, $\lambda = 154·18$ pm; $\mu(\text{Cu-}K_\alpha) = 20·96$ cm^{-1}. Space group $Pbcn$ (D_{2h}^{14}, No. 60). Unit-cell parameters were refined by least-squares from high-angle reflections. Data were obtained from a crystal measuring 0·15 × 0·175 × 0·25 mm on a Siemens automatic single-crystal diffractometer.[9,10] The integrated intensities were recorded by the θ-2θ scan using a five value method.[11] Scan speed was preset with an upper limit of 0·6 s per step of 0·01°. Nickel attenuators were selected so that the total

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[9] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1967, **22**, 457.

[10] D. C. Craig, personal communication, 1969.

[11] U. W. Arndt and B. T. M. Willis, 'Single Crystal Diffractometry,' Cambridge University Press, Cambridge, 1966, pp. 265—267.

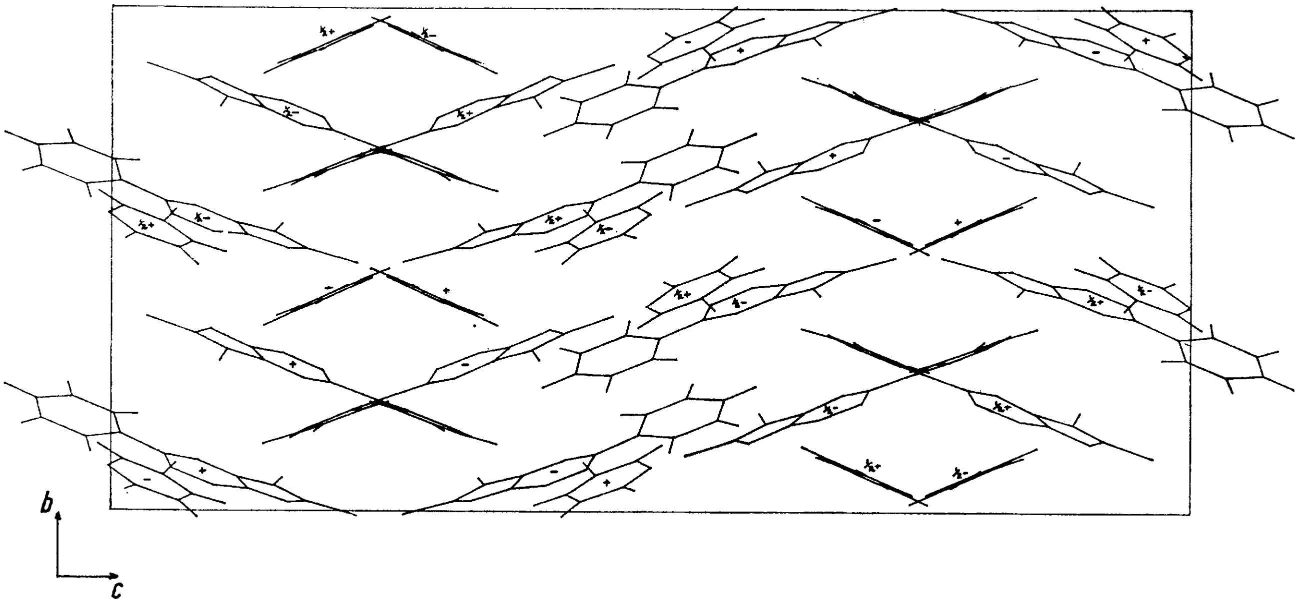

FIGURE 2 Packing in the unit cell

recorded counts for all reflections was of the same order of magnitude (*i.e. ca.* 10^5 counts min^{-1}). A standard reflection was monitored every 50 reflections. To prevent decomposition the crystal used was coated with a thin film of Vaseline, which was found to be effective, since the variation of the standard reflection was less than its standard deviation. 3843 of the 5397 independent reflections collected up to 2θ 82° were considered observed having $I > 2{\cdot}5\sigma(I)$. The data were corrected for Lorentz, polarisation, and absorption.

Structure Determination.—The structure was determined by the symbolic addition method. The largest 345 E values were used to generate Σ_2 relationships. Three origin-defining reflections were selected: 1,4,3, E 6·45; 1,4,4, E 4·91; and 1,5,6, E 3·26. Four other reflections were also chosen and given symbols: 0,4,3, E 5·35, A; 2,8,7, E 4·55, B; 8,1,19, E, 4·18, C; and 1,8,6, E 3·28, D. Signs or symbols were generated for the 345 largest E values by use of the Σ_2 relationships. A set of signs ($A-$, $B+$, $C-$, $D-$), giving the strongest indications of being correct, was chosen and an E map computed.

Because of the nature of the packing of the molecules in the unit cell, some reflections have very large E values (1,4,3, 6·45; 0,4,3, 5·35; 1,4,4, 4·92; and 2,8,7, 4·55). Other reflections involved will therefore have a high triplet product. The structure was solved by restricting the Σ_2 relationships used to expand the sign and symbol relationships to those which had a triple minimum value $>10{\cdot}0$. All the non-hydrogen atom positions were found from the E map. Full-matrix least-squares refinement reduced the residual R from an initial value of 0·497 to 0·097. A difference-Fourier synthesis revealed the positions of the hydrogen atoms. Full-matrix least-squares refinement with anisotropic temperature factors for all non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms reduced R to 0·044 and the weighted residual R' to 0·036 $\{R' = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{\frac{1}{2}}\}$.

Although the refinement had not yet converged, it was halted at this stage because of excessive computing time involved. Three reflections were seen to be affected by extinction from a plot of I_c/I_o *vs.* I_c [12] but no correction to the data was made. A final difference electron-density map revealed no features. None of the 345 phases determined during the symbolic addition procedure changed sign during the refinement stages. A weighting scheme using the σ values calculated from counting statistics was chosen. The final atomic parameters together with their standard deviations are in the Table. Observed and calculated structure factor amplitudes are listed in Supplementary Publication No. SUP 20508 (7 pp., 1 microfiche).* Atomic scattering factors for carbon and nitrogen were taken from ref. 13, for sulphur from ref. 14, and for hydrogen from ref. 15; those for sulphur were corrected for anomalous dispersion.[13]

All computations [16] were made on an IBM 360/50 at the University of New South Wales, Sydney.

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* See note about Supplementary Publications in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[12] G. H. Stout and L. H. Jensen, '*X*-Ray Structure Determination: A Practical Guide,' Macmillan, New York, 1968, p. 411.

[13] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, pp. 201—227.

[14] B. Dawson, *Acta Cryst.*, 1960, **13**, 403.

[15] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[16] ABSCOR (Absorption Correction), W. R. Busing and H. A. Levy, modified by D. C. Craig; FOURIER, J. White and D. C. Craig; LSAM (Logical Symbolic Addition Method), G. Germain, P. Main, and M. M. Woolfson, modified by C. T. Grainger; LSTSQS (ORFLS, W. R. Busing and H. A. Levy) modified by D. C. Craig.