

## On the Preparation and Structure of Some *trans*-Fused Ureas: Perhydro-*trans*-thieno[3,4-*d*]imidazol-2-one SS-Dioxides

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Reaction of *trans*-3,4-dibromotetrahydrothiophen dioxide with methylamine affords *trans*-tetrahydro-3,4-bis-(methylamino)thiophen dioxide. Reaction with phosgene then gave perhydro-1,3-dimethyl-*trans*-thieno[3,4-*d*]imidazol-2-one SS-dioxide (3; R = Me), which was studied by X-ray crystallography. [Crystal data:  $a = 8.616(3)$ ,  $b = 15.280(5)$ ,  $c = 7.409(3)$  Å,  $\beta = 102.62(4)^\circ$ , space group C2/c, Z = 4]. Ammonia gave a similar product. Piperidine also reacted with the dibromide to give the corresponding diamine, whereas pyridine afforded a novel pyridinium salt.

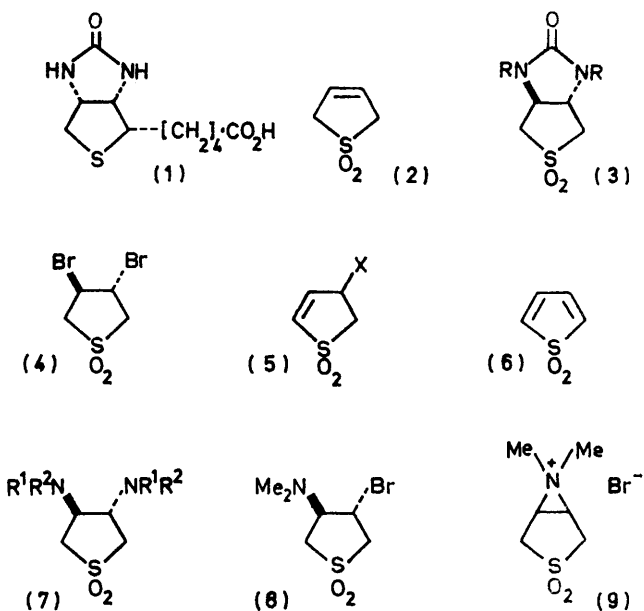
RECENTLY several interesting antimetabolites related to biotin (1) have been isolated.<sup>1</sup> Although several multi-stage routes to biotin and its analogues have been developed,<sup>2</sup> the potentially useful precursor, 2,5-dihydrothiophen dioxide (2)<sup>3</sup> has not been employed. This paper reports a simple route to the *trans*-fused cyclic ureas of the type (3), commencing from this precursor.

Reaction of 2,5-dihydrothiophen dioxide (2) with bromine afforded the known *trans*-dibromide (4).<sup>4</sup> The *trans*-orientation of the two bromine atoms is assigned by analogy with the mode of addition of bromine to cyclopentene.<sup>5</sup> The dibromide (4) eliminates hydrogen bromide with base to form the unsaturated sulphones (5)<sup>6</sup> and (6).<sup>7</sup> The latter, thiophen dioxide (6), appeared to be a useful precursor for the addition of amines. However, the addition of two molecules of an amine to thiophen dioxide (6) appears to be difficult. For example, ammonia reacted only slowly to give the diamine<sup>8</sup> (7; R<sup>1</sup> = R<sup>2</sup> = H), *via* the allylic amine (5; R = NH<sub>2</sub>). It is noteworthy that hydration of 2,3-dihydro-3-hydroxythiophen 1,1-dioxide yields tetrahydro-*trans*-3,4-dihydroxythiophen dioxide<sup>9</sup> and therefore the ammonia adduct of thiophen dioxide (7; R<sup>1</sup> = R<sup>2</sup> = H) would also be expected to have the *trans*-configuration. The addition of dimethylamine to thiophen dioxide (6) stops at the allylic amine (5; X = NMe<sub>2</sub>).<sup>6</sup>

In contrast, dimethylamine reacts with the dibromide (4) or with the allylic bromide (5; X = Br) to produce the diamine<sup>6</sup> (7; R<sup>1</sup> = R<sup>2</sup> = Me). These results suggest that the reaction of dimethylamine with the bromides proceeds *via* an intermediate (8),<sup>6</sup> which does not react further by prior elimination of hydrogen bromide followed by addition. Either direct substitution occurs on the intermediate (8), which would result in possible formation of a *cis*-diamine, or the

reaction proceeds *via* an aziridinium species (9) to give a *trans*-oriented diamine.

In order to establish the configuration of such amine adducts, the dibromide (4) was treated with methylamine



to give a diamine (7; R<sup>1</sup> = H, R<sup>2</sup> = Me), which was characterized both as its hydrochloride, m.p. 193–195°, and as its bis-*N*-acetyl derivative (7; R<sup>1</sup> = Ac, R<sup>2</sup> = Me). Reaction of the diamine (7; R<sup>1</sup> = H, R<sup>2</sup> = Me) with phosgene in toluene afforded the cyclic urea (3; R = Me), which was subjected to X-ray analysis.

The successful analysis (see Experimental section) of the urea (3; R = Me) requires a two-fold axis in the molecule, indicative of a *trans*-fused structure (as in 3; R = Me); such *trans*-fused [3,3,0]-systems are rare.<sup>10</sup> The structure was solved and refined using the heavy-

<sup>1</sup> L. J. Hanka, M. E. Bergy, and R. B. Kelly, *Science*, 1966, **154**, 1667; D. G. Martin, L. J. Hanka, and L. M. Reineke, *Tetrahedron Letters*, 1971, 3791.

<sup>2</sup> For example, S. A. Harris, D. E. Wolf, R. Mazingo, G. E. Arth, R. C. Anderson, N. R. Easton, and K. Folkers, *J. Amer. Chem. Soc.*, 1945, **67**, 2096; M. W. Goldberg and L. H. Sternbach, U.S.P. 2,489,235/1949 (*Chem. Abs.*, 1951, **45**, 185).

<sup>3</sup> For a review on butadiene sulphone formation see S. D. Turk and R. L. Cobb, '1,4-Cycloaddition Reactions,' ed. J. Hamer, Academic Press, New York, 1967, p. 13.

<sup>4</sup> H. Staudinger and B. Ritzenthaler, *Ber.*, 1935, **68**, 470.

<sup>5</sup> W. D. Kumler, A. C. Huitric, and H. K. Hall, *J. Amer. Chem. Soc.*, 1956, **78**, 4345; cf. M. Prochazka and V. Horak, *Chem. Listy*, 1958, **52**, 1768.

<sup>6</sup> W. J. Bailey and E. W. Cummins, *J. Amer. Chem. Soc.*, 1954, **76**, 1932.

<sup>7</sup> W. J. Bailey and E. W. Cummins, *J. Amer. Chem. Soc.*, 1954, **76**, 1936.

<sup>8</sup> M. Prochazka and V. Horak, *Coll. Czech. Chem. Comm.*, 1959, **24**, 2278.

<sup>9</sup> M. Prochazka and V. Horak, *Coll. Czech. Chem. Comm.*, 1959, **24**, 1509.

<sup>10</sup> J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 1936, 611; L. N. Owen and A. G. Peto, *ibid.*, 1955, 2383; cf. S. A. Harris, R. Mazingo, D. E. Wolf, A. N. Wilson, and K. Folkers, *J. Amer. Chem. Soc.*, 1945, **67**, 2102.

atom method (sulphur). The final refinement was to an *R* factor of 0.0619 for the observed reflections. Table 1 lists the final positional and thermal parameters. Figure 1 shows the (001) projection of a single molecule, whilst Figure 2 details the intramolecular bond lengths and angles. The *trans*-fused bicyclic system is clearly

the expected values. Both rings are highly twisted (Figure 3) and do not have the normal envelope conformation such as associated, for example, with the *cis*-fused biotin derivative (10).<sup>13</sup> Table 2 lists the deviations of the atoms with respect to the plane perpendicular to Figure 3.

TABLE 1  
Final positional and thermal parameters ( $\times 10^4$ ). Standard deviations are in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
S	0000 *	2312(1)	2500 *	193(4)	32(1)	233(5)	000 *	-69(3)	000 *
N(1)	1302(6)	4782(3)	2432(7)	227(9)	43(2)	220(11)	-21(4)	-8(8)	-1(4)
O(1)	0593(6)	1823(2)	4179(6)	282(9)	42(2)	257(10)	1(4)	-87(7)	27(4)
O(2)	0000 *	6113(4)	2500 *	483(20)	33(3)	281(16)	000 *	26(14)	000 *
C(1)	1478(7)	3092(4)	2104(8)	140(9)	50(3)	258(14)	4(4)	22(9)	-6(5)
C(2)	0892(6)	390(3)	2921(7)	190(9)	33(3)	204(13)	-10(4)	-33(8)	-1(4)
C(3)	2919(11)	5102(6)	3187(12)	294(17)	82(5)	294(21)	-81(8)	-19(14)	6(8)
C(4)	0000 *	5304(6)	2500 *	320(22)	51(5)	168(18)	000 *	-11(15)	000 *
H(11)	1537(81)	3127(43)	0381(108)		64(18) †				
H(21)	2451(69)	2879(34)	2679(77)		29(13)				
H(32)	0876(58)	3871(31)	4439(73)		24(11)				
H(43)	2930(96)	5215(50)	4766(134)		78(22)				
H(53)	3843(112)	4581(62)	2558(160)		109(34)				
H(63)	3193(89)	5465(48)	2569(110)		52(22)				

\* Parameters fixed during the refinement. † Isotropic thermal parameters (*B*'s), in  $\text{\AA}^2 \times 10^3$ . The anisotropic thermal parameters are in the form:  $f_i = f_i^0 \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . The second digit in each hydrogen atom identification number refers to the carbon atom to which it is attached. The average carbon-hydrogen bond length is 1.07(8)  $\text{\AA}$ .

seen in Figure 3. Bond lengths compare well with the expected values. Thus the sulphur-oxygen bond length

By analogy with the methylamine derivative (3; R = Me), the unsubstituted cyclic urea (3; R = H) was also prepared from *trans*-3,4-diaminotetrahydrothiophen

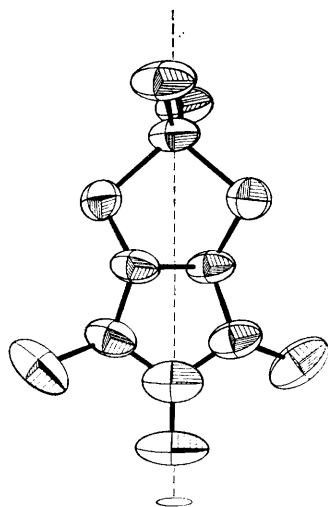


FIGURE 1 The (001) projection of the molecule. The thermal ellipsoids are scaled to include 50% probability

of 1.445(4)  $\text{\AA}$  is in good agreement with that, for example, in dimethyl sulphone<sup>11</sup> (1.473  $\text{\AA}$ ) and methanesulphonanilide<sup>12</sup> (1.438  $\text{\AA}$ ). The ring strain of the urea (3; R = Me) due to the *trans*-fusion causes a number of intramolecular bond angles to deviate markedly from

<sup>11</sup> D. A. Langa, J. V. Silverton, and W. M. Bright, *Chem. Comm.*, 1970, 1653.

<sup>12</sup> H. P. Klug, *Acta Cryst.*, 1968, **B24**, 792.

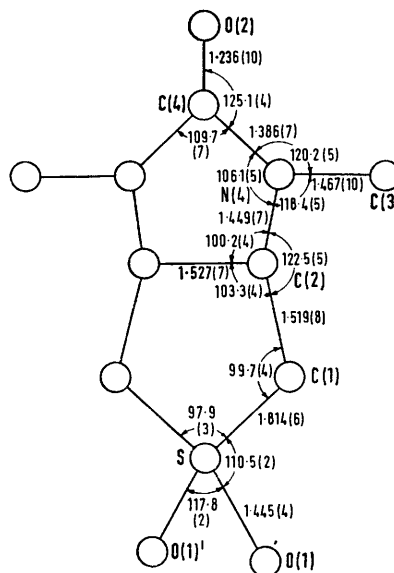


FIGURE 2 Intramolecular bond lengths and angles with standard deviations in parentheses. O(1)' refers to the two-fold axis atom related to O(1). The C(1)-(S)-O(1)' angle is  $109.2 \pm 0.3^\circ$

dioxide (7; R<sup>1</sup> = R<sup>2</sup> = H).<sup>9</sup> A brief examination of the reaction of the dibromide (4) with piperidine and

<sup>13</sup> C. Bonnemere, J. A. Hamilton, L. K. Steinrauf, and J. Knappe, *Biochemistry*, 1965, **4**, 240.

pyridine was also made. Piperidine reacts rapidly with the dibromide to give a bispiperidino-derivative [7;  $R^1R^2 = (CH_2)_6$ ], identified as its monomethiodide. On the basis of the above results it was also assigned the

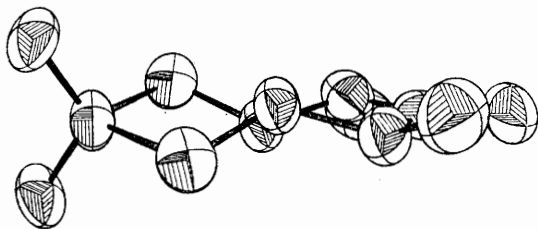


FIGURE 3 The (100) projection of the molecule

*trans*-configuration. An unusual reaction was observed with pyridine. Whereas a stoichiometric quantity of pyridine eliminated hydrogen bromide from the dibromide (4),<sup>14</sup> use of a large excess of pyridine afforded

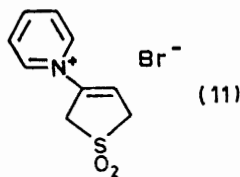
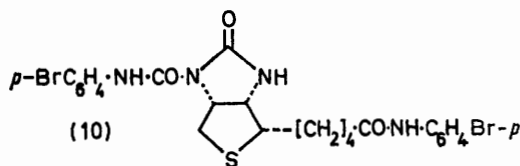
TABLE 2

Displacements from the least-squares plane parallel to the *a*-axis, and through the atoms S, O(2), and C(4)

	S *	C(1)	C(2)	C(3)
Displacement (Å)	0.000	-0.286	0.304	0.497
	C(4) *	N(1)	O(1)	O(2) *
Displacement (Å)	0.000	-0.049	1.214	0.000

\* Only these atoms were included in the calculation of the plane.

a crystalline salt (11). That the pyridinium salt had the  $\Delta^3$ -double bond was shown by <sup>1</sup>H n.m.r. spectroscopy. Its spectrum showed a broadened singlet at  $\tau$  2.9 ( $W_{\frac{1}{2}}$  7 Hz), assigned to the vinylic proton, and a



multiplet at 5.3–5.7, associated with the four protons of the methylene groups adjacent to the sulphone function. This salt probably forms by reaction of pyridine with the allylic bromide (5; X = Br), which is initially produced,<sup>14</sup> followed by base-catalysed migration of the remaining double bond to the 3(4)-position, an isomerisation with considerable precedent.<sup>15</sup>

Of interest was the purple colour of this salt (11).

Repeated recrystallization did not remove the colour, which was retained in solution. Measurement of its e.s.r. spectrum ruled out the presence of free radicals. The exact cause of the colour remains unexplained, but it may be due to an intramolecular charge-transfer interaction between the sulphone and pyridinium functions. With base a brilliant yellow colour formed, attributed to the formation of an ylide.

An attempt to isomerize the *trans*-urea (3; R = Me) into its *cis*-isomer by treatment with strong base failed. An alternative route to the corresponding *cis*-fused cyclic ureas will be reported on shortly.

#### EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were determined for Nujol mulls and <sup>1</sup>H n.m.r. spectra were recorded with a Varian T60 instrument for solutions in deuteriochloroform containing tetramethylsilane as internal reference. Light petroleum refers to the fraction of b.p. 60–80°.

*trans*-Tetrahydro-3,4-bis(methylamino)thiophen 1,1-Dioxide (7; R<sup>1</sup> = H, R<sup>2</sup> = Me).—Methylamine gas was slowly passed through a solution of 3,4-dibromotetrahydrothiophen 1,1-dioxide (16.5 g) in chloroform (325 ml) with stirring at <10°. After 1 h, the flask was sealed and the mixture was stirred overnight at room temperature. The solution was evaporated to small volume and aqueous 1N-sodium hydroxide (30 ml) was added. The aqueous phase was continuously extracted with chloroform for 72 h. The extracts were dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to give an oil, which slowly crystallized to give the *diamine* (9.5 g; 90%), m.p. 67–69° (from benzene–light petroleum),  $\nu_{\max}$  3320, 1295, and 1110 cm<sup>-1</sup>,  $\tau$  6.1–7.1 (6H, m), 7.50 (6H, s), and 8.50br (2H, exchanged with D<sub>2</sub>O) (Found: C, 40.3; H, 7.8; N, 15.7. C<sub>6</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S requires C, 40.4; H, 7.9; N, 15.7%). With hydrochloric acid a *bishydrochloride* formed, m.p. 193–195° (from aqueous ethanol) (Found: C, 28.8; H, 6.3; Cl, 28.4; N, 11.1. C<sub>6</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S·2HCl requires C, 28.7; H, 6.4; Cl, 28.2; N, 11.15%). The bismethylamino-compound was further characterized as its *acetyl derivative*, m.p. 251–253° (from water),  $\nu_{\max}$  1645, 1360, and 1115 cm<sup>-1</sup> (Found: C, 45.9; H, 6.9; N, 10.85. C<sub>10</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>S requires C, 45.8; H, 6.9; N, 10.7%).

*Perhydro*-1,3-dimethyl-*trans*-thieno[3,4-d]imidazol-2-one SS-Dioxide (3; R = Me).—*trans*-Tetrahydro-3,4-bis(methylamino)thiophen 1,1-dioxide (6.25 g) in 10% w/v aqueous sodium carbonate solution (100 ml) was treated with phosgene (17.4 g) in toluene (12.6 g) whilst stirring at room temperature. Ether (100 ml) was added and stirring continued overnight so that most of the excess of phosgene evaporated off. The aqueous phase was extracted with dichloromethane and the combined organic layers then evaporated to dryness to yield a white solid (3.1 g; 44%). Recrystallization from water gave the *trans*-urea, m.p. 198–199°,  $\nu_{\max}$  1710, 1320, and 1140 cm<sup>-1</sup>,  $\tau$  7.2 (6H, s) and 6.2–7.0 (6H, m). After heating the compound with 4N-NaOD in D<sub>2</sub>O for 78 h, the n.m.r. spectrum showed  $\tau$  7.2 (6H, s) and 6.75 (2H, s) (Found: C, 41.3; H, 6.0; N, 13.6; S, 15.85. C<sub>7</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>S requires C, 41.2; H, 5.9; N, 13.7; S, 15.7%).

<sup>14</sup> H. J. Backer and J. L. Melles, *Proc. h. ned. Akad. Wetenschap.*, 1951, **54B**, 340 (*Chem. Abs.*, 1953, **47**, 6932).

<sup>15</sup> D. E. O'Connor and W. I. Lyness, *J. Amer. Chem. Soc.*, 1964, **86**, 3840.

*Perhydro-trans-thieno*[3,4-*d*]imidazol-2-one SS-Dioxide (3; R = H).—3,4-Dibromotetrahydrothiophen 1,1-dioxide (30 g) and liquid ammonia (500 ml) were sealed in a stainless steel autoclave at room temperature for 1 month. The excess of ammonia was then evaporated off and the residue was taken up in aqueous sodium carbonate solution (90 g in 500 ml). A solution of phosgene (30 g) in benzene (100 ml) was slowly added to the stirred ice-cooled solution. After leaving the mixture overnight, when the excess of phosgene evaporated off, the precipitated solid was filtered off and recrystallized from water to give needles of the *urea* (4.5 g; 24%), m.p. (sealed tube) 298°,  $\nu_{\max}$  3290, 1705, 1690, 1310, and 1110  $\text{cm}^{-1}$ ,  $\tau$  ( $\text{CF}_3\text{CO}_2\text{H}$ ) 5.0 (2H, m) and 5.6–6.4 (4H, m) (Found: C, 34.2; H, 4.7; N, 15.8; S, 18.4.  $\text{C}_5\text{H}_8\text{N}_2\text{O}_3\text{S}$  requires C, 34.0; H, 4.6; N, 15.9; S, 18.2%).

*Tetrahydro-trans-3,4-dipiperidinothiophen 1,1-Dioxide* [7; R<sup>1</sup>R<sup>2</sup> = (CH<sub>2</sub>)<sub>5</sub>].—Freshly distilled piperidine (2.46 g) was added to a suspension of 3,4-dibromotetrahydrothiophen dioxide (2.0 g) in water (30 ml) at room temperature with stirring. A thick, white suspension formed. After 15 min aqueous 2N-sodium hydroxide (10 ml) was added and the suspension was cooled at 0° for 24 h and filtered. The solid was washed with cold water, and crystallized from ethanol to give needles (1.75 g), m.p. 122–123°,  $\nu_{\max}$  1310 and 1130  $\text{cm}^{-1}$ . A sample (250 mg) was warmed with methyl iodide for 15 min. The excess of the reagent was evaporated off and the residue was crystallized from acetonitrile to give prisms of the *monomethiodide*, m.p. 177–179° (Found: C, 42.0; H, 6.6; I, 29.6; N, 6.4.  $\text{C}_5\text{H}_{20}\text{IN}_2\text{O}_2\text{S}$  requires C, 42.1; H, 6.8; I, 29.6; N, 6.5%).

*2,5-Dihydro-3-(1'-pyridinium)thiophen 1,1-Dioxide Bromide* (11).—The dibromide (4) (10.0 g) in dry pyridine (100 ml) was left at room temperature for 48 h. The purple crystals that formed were collected, washed with benzene, and recrystallized from hot ethanol-methanol (3 : 2) to give purple needles of the *salt* (3.8 g; 38%), m.p. 177–179°,  $\nu_{\max}$  1630, 1320, and 1135  $\text{cm}^{-1}$ ,  $\tau$  ( $[\text{C}_5\text{H}_5]\text{Me}_2\text{SO}$ ) 0.7 (2H), 1.25 (1H), 1.75 (2H), 2.9 (1H), 5.3 (2H), and 5.7 (2H) (Found: C, 39.1; H, 3.65; N, 5.1; S, 11.6.  $\text{C}_9\text{H}_{10}\text{BrNO}_2\text{S}$  requires C, 39.3; H, 4.0; N, 5.0; S, 11.7%).

*Crystal Data for the trans-Urea* (3; R = Me).— $\text{C}_7\text{H}_{12}\text{N}_2\text{O}_3\text{S}$ , Monoclinic prismatic,  $a = 8.616(3)$ ,  $b = 15.280(5)$ ,  $c = 7.409(3)$  Å,  $\beta = 102.62(4)^\circ$ ,  $U = 951.85$  Å<sup>3</sup>,  $D_c = 1.423$ ,  $Z = 4$ ,  $D_m = 1.42(2)$  (flotation). Space group  $C2/c$ . Cu- $K_\alpha$  radiation (nickel-filtered);  $\lambda = 1.54178$  Å,  $\mu(\text{Cu-}K_\alpha) = 27.72$   $\text{cm}^{-1}$ .

*Intensity Measurements.*—Intensity data were collected for a crystal of the *trans-urea* (3; R = Me) of approximate dimensions 0.10 × 0.15 × 0.60 mm, mounted about the  $c^*$  axis, using a General Electric XRD6 diffractometer, equipped with a manual goniometer, pulse height analyser,

\* Supplementary Publication No. SUP 20392 (4 pp., 1 microfiche), lists the final observed and calculated structure factors. For details of Supplementary Publications see Notice to Authors, No. 7, in *J. Chem. Soc. (A)*, 1970, Issue no. 20.

<sup>16</sup> R. H. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 1966, **5**, 411.

<sup>17</sup> E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

and scintillation counter. The stationary-crystal-stationary-counter method of intensity estimation was used throughout, with a 4° take-off angle and a counting time of 10 s. Individual backgrounds ( $2\theta_{hkl} + 1$ )° were measured for all reflections. The 204 and 112 reflections were used as reference reflections to check on crystal stability; in neither case was there any significant decline in the course of the data collection. The intensities of 700 reflections with  $2\theta \leq 120^\circ$  were measured, of which 519 were considered to be statistically significant (net counts were  $\geq 3\sigma(I)$ , where  $\sigma$ , the standard deviation in the intensity, was taken as  $[I + 2B + (0.03I)^2]^{1/2}$ , and  $B$  is the background count.<sup>16</sup> The 181 'unobserved' reflections were excluded from any subsequent least-squares calculations. No correction for absorption was applied. The intensity statistics were as expected for the space group  $C2/c$ . The position of the sulphur atom was readily deduced from a 3-dimensional ( $E^2 - 1$ ) sharpened Patterson synthesis. With the sulphur on the position (O, Y, 1/4), *i.e.* on the two-fold axis, a structure factor calculation gave an  $R$ -factor of 0.531. The resulting difference Fourier map revealed the complete structure. Full-matrix least-squares refinement of the positional and isotropic thermal parameters for the atoms, all of which had been assigned their correct scattering factors, resulted in an  $R$  factor of 0.161 after four cycles. The  $x$  and  $z$  co-ordinates of the sulphur, carbon, and oxygen atoms, assumed to lie on the two-fold axis were kept invariant. All bond lengths and angles had acceptable values after refinement. Conversion of the temperature factors into their anisotropic ( $\beta_{ij}$ ) equivalents, followed by four more cycles of refinement, reduced  $R$  to 0.103. Inspection of a difference Fourier map at this stage revealed the presence of the 6 hydrogen atoms in the asymmetric unit. Further refinement with the positional and isotropic thermal parameters of the hydrogen atoms also being varied gave an  $R$  factor of 0.064. Inclusion of a Hughes-type weighting scheme<sup>17</sup> followed by four more cycles of refinement gave an  $R$  factor of 0.0619 for the 519 observed reflections (an  $R$  factor of 0.0929 for all 700 measured reflections). All parameter shifts were less than 0.1 of their corresponding standard deviations and refinement was judged to be complete.\*

All calculations were performed on the University of London CDC6600 computer using the XRAY 70 crystallographic computing system.<sup>18</sup> The scattering factors were taken from ref. 19. Figures 1 and 3 were drawn with the aid of ORTEP.<sup>20</sup>

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<sup>18</sup> A revision of X-RAY 67, 'Program System for X-ray Crystallography,' University of Maryland Technical Report, 1967, no. 67–58.

<sup>19</sup> International Tables for X-ray Crystallography, 1962, Kynoch Press, Birmingham, Vol. III.

<sup>20</sup> C. K. Johnson, ORTEP, ORNL-3794, Oak Ridge National Laboratory, 1965.