

# Hydrogen Bonds involving Polar CH Groups. Part 8.<sup>1</sup> The Synthesis and X-Ray Crystal Structure of 2-(2,2-Dimethyl-3-piperidinopropyl)-1,3-dithian 1,1,3,3-Tetraoxide; a Sterically Crowded Cyclic Disulphone

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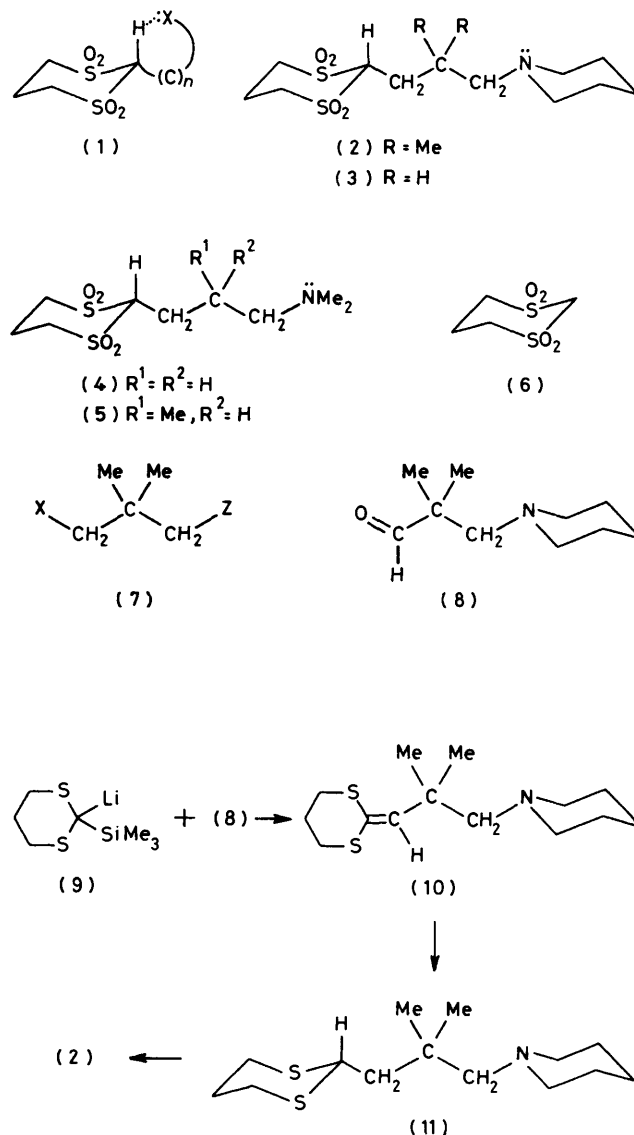
Reaction between 2,2-dimethyl-3-piperidinopropanal (8) and lithio-2-trimethylsilyl-1,3-dithian gives a keten dithioacetal (10), which is reduced to a dithioacetal (11) with trimethylsilane in trifluoroacetic acid, and oxidised to the title compound (2) with potassium permanganate in acetic acid. The advantages of trimethylsilane as a reducing agent are discussed. Crystal structure analysis of the disulphone (2), designed as a model for intramolecular C-H...N interactions, shows it to have an extended conformation, the desired cyclic conformation being disfavoured by steric effects. The structure was solved by direct methods, and refined to  $R$  0.039 for 2 232 independent reflections. The crystals are monoclinic,  $a = 7.107(2)$ ,  $b = 25.373(4)$ ,  $c = 9.929(2)$  Å,  $\beta = 108.55(2)^\circ$ , space group  $P2_1/c$ , and  $Z = 4$ .

As part of a programme designed to determine the optimum structural requirements for intramolecular C-H...X hydrogen bonds using models of general structure (1), we required the disulphone (2). Spectroscopic measurements on a number of compounds (1) having different side-chain lengths  $n$  and basic groups X have shown that the intramolecular interaction was optimised when it could lead to a six-membered ring, and when X was a tertiary amino-group as in structure (4).<sup>2</sup> Further, the introduction of a methyl group into the side chain as in structure (5) was found to enhance the interaction, apparently as a result of reduced conformational mobility.<sup>2</sup> It thus seemed likely that a structure analogous to (5), but having  $R^1 = R^2 = \text{Me}$  might show a still stronger interaction.

## Results and Discussion

**Synthesis of the Disulphone (2).**—Compounds of type (1) have been prepared by reaction between the anion derived from the disulphone (6) and appropriately substituted alkyl halides.<sup>2</sup> However, difunctionalised derivatives (7) of 2,2-dimethylpropane are sterically hindered towards  $S_N2$  displacement reactions, and attempts to prepare compound (2) from structures of this type and the disulphone (6) failed. An attractive alternative approach was to condense the aldehyde (8) from a Mannich reaction between piperidine, methanal, and 2-methylpropanal<sup>3</sup> with the disulphone (6), and to reduce the resulting double bond to give (2). However, attempts to carry out the condensation under a wide variety of conditions failed, owing again to excessive steric crowding. Seebach and co-workers have prepared keten dithioacetals in high yields by reaction between lithio trimethylsilyl dithioacetals, such as (9), and carbonyl compounds, including sterically crowded aldehydes and ketones.<sup>4</sup> The approach shown in the Scheme was thus attempted.

Reaction between compounds (8) and (9) gave a moderate yield of the expected product (10), a type of structure which has been reduced effectively by triethylsilane in trifluoroacetic acid (TFAA).<sup>5</sup> Although this reagent reduced compound (10) in moderate yield, the product (11) could not be freed completely from triethylsilanol either by fractional distillation or by column chromatography. The alternative triphenylsilane<sup>5</sup> gave only a very low yield of (11). In contrast, the sterically smaller trimethylsilane effected the reduction in good yield in TFAA, and the lower boiling (31–34 °C/26



Scheme.

Torr) trimethylsilanol was readily removed together with the solvent under reduced pressure, leaving the product (11) essentially pure. We thus suggest trimethylsilane as a convenient alternative reagent to its triethyl analogue in reductions of this type. For the final oxidation step we used potassium permanganate in acetic acid, this being one of the few reagents available for the oxidation of sulphides to sulphones in the presence of tertiary amines.<sup>6</sup> Disulphone (2) was formed in good yield.

The <sup>1</sup>H n.m.r. chemical shift of the disulphone ring methine proton has proved to be the most sensitive probe for intramolecular C-H...X interactions as in structure (1).<sup>2</sup> Thus, for compounds (3), (4), and (5) in which interactions were indicated, values respectively of δ(CD<sub>2</sub>Cl<sub>2</sub>) 5.03, 4.62, and 5.53 were observed, as compared with δ 4.23 found in the homologue of (4) having six methylene groups in the side chain.\* In the disulphone (2) the methine signal was found at δ 4.83, an ambiguous result, but one which showed clearly that the introduction of a second side-chain methyl group reduced, rather than enhanced, the interaction apparent in compound (5).

To establish the molecular conformation adopted by compound (2) in the solid state, crystals were examined by X-ray diffraction methods. The structure determination was of additional interest since there have been no reports to date giving crystal structures of monocyclic disulphones, although the conformations of such systems have been inferred from dipole-moment measurements.<sup>7</sup>

**Structure of the Disulphone (2).**—Selected bond lengths, valency angles, and torsion angles are given in Table 1. An ORTEP drawing (Figure) shows the molecule to have an extended conformation which prohibits an intramolecular H(1)...N interaction. Both rings are in chair conformations, and the part of the molecule including C(6), C(7), C(13), C(14), and the piperidine ring is almost symmetrical about a plane through C(6), C(7), N, and C(10), though the ring is rotated about the N-C(7) bond by nearly 2°. The other half of the molecule deviates from symmetry about this plane in two senses: first there is a twist of nearly 4° about the C(5)-C(6) bond, apparently to relieve O(2)...H(14) and O(4)...H(13) interactions (Table 2), and second the disulphone ring is itself distorted about an axis through C(1) and C(3). This latter distortion is apparent from a comparison of the torsion angles C(1)-S(1)-C(2)-C(3) with C(1)-S(2)-C(4)-C(3) and O(2)-S(1)-C(2)-C(3) with O(4)-S(2)-C(4)-C(3) (Table 1c), and from Table 3 in which S(1) and C(4) are seen to lie below, and S(2) and C(3) above, a plane defined by these four atoms. This distortion probably helps to relieve interactions among O(1), O(3), H(3), H(5A), and H(5B) (Table 2a). Adjacent axial atoms deviate less than 6° from an antiperiplanar conformation (Table 1c).

An examination of space-filling models suggests that the conformation adopted by the disulphone (2) in the crystal is the most stable, a conformation as in structure (1) being higher in energy owing to a serious steric interaction between one methyl group and a sulphone oxygen atom. This interaction is lacking in the analogous conformation of the monomethyl compound (5), thus permitting a C-H...N close approach and accounting for the lower field chemical shift of the disulphone ring methine proton.

Bond lengths and angles appear to be normal from a comparison with molecules having related structural units.

\* Smaller incremental shifts were found in analogues having OMe in place of the NR<sub>2</sub> group, showing that the electronegativity of X was not the major contributor to the downfield shift of the methine proton.

**Table 1.** Selected bond lengths (Å), valency angles (°), and torsion angles (°), with e.s.d.s in parentheses

(a) Bond lengths			
S(1)-O(1)	1.442(1)	C(5)-C(6)	1.536(3)
S(1)-O(2)	1.430(2)	C(6)-C(7)	1.531(3)
S(1)-C(1)	1.799(2)	C(6)-C(13)	1.529(3)
S(1)-C(2)	1.765(2)	C(6)-C(14)	1.521(4)
S(2)-O(3)	1.436(1)	N-C(7)	1.467(3)
S(2)-O(4)	1.433(2)	N-C(8)	1.460(3)
S(2)-C(1)	1.813(2)	N-C(12)	1.459(3)
S(2)-C(4)	1.766(2)	C(8)-C(9)	1.520(4)
C(1)-C(5)	1.539(3)	C(9)-C(10)	1.494(5)
C(1)-H(1)	0.95(2)	C(10)-C(11)	1.508(5)
C(2)-C(3)	1.523(3)	C(11)-C(12)	1.514(4)
C(3)-C(4)	1.508(3)		
(b) Valency angles			
O(1)-S(1)-O(2)	118.2(1)	S(2)-C(4)-C(3)	113.8(2)
O(1)-S(1)-C(1)	108.7(1)	C(1)-C(5)-C(6)	116.2(2)
O(1)-S(1)-C(2)	108.6(1)	C(5)-C(6)-C(7)	105.6(2)
O(2)-S(1)-C(1)	107.3(1)	C(5)-C(6)-C(13)	111.0(2)
O(2)-S(1)-C(2)	109.7(1)	C(5)-C(6)-C(14)	110.7(2)
C(1)-S(1)-C(2)	103.3(1)	C(7)-C(6)-C(13)	109.9(2)
O(3)-S(2)-O(4)	118.5(1)	C(7)-C(6)-C(14)	109.4(2)
O(3)-S(2)-C(1)	106.8(1)	C(13)-C(6)-C(14)	110.1(2)
O(3)-S(2)-C(4)	109.5(1)	N-C(7)-C(6)	113.2(2)
O(4)-S(2)-C(1)	107.0(1)	C(7)-N-C(8)	112.1(2)
O(4)-S(2)-C(4)	109.3(1)	C(7)-N-C(12)	112.8(2)
C(1)-S(2)-C(4)	105.0(1)	C(8)-N-C(12)	110.3(2)
S(1)-C(1)-S(2)	111.9(1)	N-C(8)-C(9)	110.7(2)
S(1)-C(1)-C(5)	111.2(2)	C(8)-C(9)-C(10)	111.4(3)
S(2)-C(1)-C(5)	109.4(2)	C(9)-C(10)-C(11)	109.2(3)
S(1)-C(2)-C(3)	112.0(2)	C(10)-C(11)-C(12)	111.5(3)
C(2)-C(3)-C(4)	113.6(2)	N-C(12)-C(11)	110.8(2)
(c) Torsion angles			
S(1)-C(1)-S(2)-C(4)	-50.7		
S(1)-C(1)-C(5)-C(6)	117.0		
S(1)-C(2)-C(3)-C(4)	68.9		
S(2)-C(1)-S(1)-C(2)	53.9		
S(2)-C(1)-C(5)-C(6)	-118.8		
S(2)-C(4)-C(3)-C(2)	-65.0		
O(1)-S(1)-C(1)-H(1)	-174.3		
O(1)-S(1)-C(2)-H(2A)	179.3		
O(2)-S(1)-C(2)-C(3)	-174.7		
O(3)-S(2)-C(1)-H(1)	177.8		
O(3)-S(2)-C(4)-H(4B)	174.5		
O(4)-S(2)-C(4)-C(3)	168.0		
N-C(7)-C(6)-C(5)	-179.4		
N-C(7)-C(6)-C(13)	-59.6		
N-C(7)-C(6)-C(14)	61.5		
N-C(8)-C(9)-C(10)	-57.9		
N-C(12)-C(11)-C(10)	57.1		
C(1)-S(1)-C(2)-C(3)	-60.5		
C(1)-S(2)-C(4)-C(3)	53.7		
C(1)-C(5)-C(6)-C(7)	176.4		
C(6)-C(7)-N-C(8)	115.5		
C(6)-C(7)-N-C(12)	-119.3		
C(8)-C(9)-C(10)-C(11)	54.5		
C(9)-C(10)-C(11)-C(12)	-54.2		
H(2A)-C(2)-C(3)-H(3A)	-176.0		
H(3A)-C(3)-C(4)-H(4B)	176.4		

Thus for two structures having the fragment SO<sub>2</sub>-CH<sub>2</sub>-SO<sub>2</sub>,<sup>8,9</sup> relevant bond parameters are, respectively, C-S 1.79 and 1.798 Å, S=O 1.44 and 1.428 Å, S-C-S 111.5 and 112.9°, O-S-O 118.2 and 118.9°, and C-S-C 104.9 and 103.2°. Likewise, the parameters for the piperidine ring closely match those for an N-alkyl analogue,<sup>10</sup> though in other examples

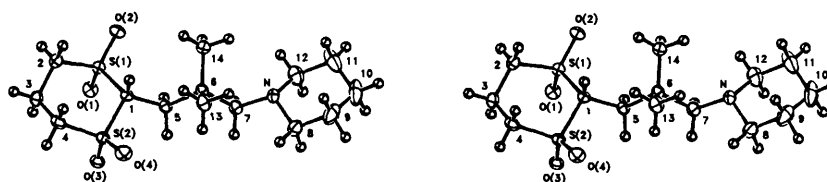


Figure. ORTEP drawing of the disulphone (2) showing the atom numbering system used

Table 2. Significant O...H contacts

(a) Intramolecular <3.0 Å	(b) Intermolecular <2.6 Å
O(1)···H(3A) 2.67(2)	O(1)···H(1) 2.54(2)
O(3)···H(3A) 2.88(2)	O(1)···H(2A) 2.54(2)
O(1)···H(5A) 2.71(2)	O(2)···H(4B) 2.59(2)
O(3)···H(5B) 2.60(2)	O(3)···H(2A) 2.42(2)
O(2)···H(14A) 2.88(2)	O(3)···H(4B) 2.45(2)
O(2)···H(14C) 2.97(3)	O(3)···H(9B) 2.57(3)
O(4)···H(13B) 2.84(2)	

the C(9)–C(10) and C(10)–C(11) distances are *greater* than those for C(8)–C(9) and C(11)–C(12).<sup>11,12</sup>

The nitrogen atom makes no close intermolecular approaches to hydrogen atoms in other molecules, probably for steric reasons. However, it is noteworthy that the sulphonyl oxygen atoms make several such close approaches, most being to the more polar axial hydrogens H(1), H(2A), and H(4B). Those less than 2.6 Å are given in Table 2b; it is possible that interactions of this type are responsible for the observed high m.p. of many cyclic disulphones [*e.g.*, 308 °C for compound (6)].

### Experimental

I.r. spectra were recorded in Nujol on a Perkin-Elmer 577 spectrophotometer, using polystyrene in calibration, <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra on a JEOL FX 90Q instrument in CDCl<sub>3</sub>, using SiMe<sub>4</sub> as internal reference, and mass spectra on a Hitachi RMS-4 spectrometer.

2,2-Dimethyl-3-piperidinopropanal (8),<sup>3</sup> 2-trimethylsilyl-1,3-dithian,<sup>4</sup> and trimethylsilane<sup>13</sup> were prepared by published procedures.

**Preparation of the Disulphone (2).**—2-Methyl-3-piperidinopropan-2-ylketen trimethylene dithioacetal (10). 2-Trimethylsilyl-1,3-dithian (3.84 g, 0.020 mol) was dissolved in dry tetrahydrofuran (THF) (40 ml) at –78 °C, and Bu<sup>n</sup>Li (12.8 ml; 15% solution in pentane) was added. After 1 h at –50 °C, the solution was treated dropwise with the amino-aldehyde (8) (3.74 g, 0.022 mol), the temperature was raised slowly to –20 °C, and the mixture was stirred at this temperature for 2 h and overnight at 25 °C. Water (10 ml) was added, the mixture was evaporated under reduced pressure, the residue was extracted with CHCl<sub>3</sub> (50 ml), and the extract dried (MgSO<sub>4</sub>) and evaporated to give the dithioacetal (10) (2.05 g, 38%), b.p. 124 °C/0.2 Torr; *M*<sup>+</sup> 271; δ(CDCl<sub>3</sub>) 5.99 (1 H, s, =CH), 3.0–2.7 (4 H, m, CH<sub>2</sub>S), 2.42 (4 H, m), and 2.30 (2 H, s) (CH<sub>2</sub>N), 2.08 (2 H, m, dithian CH<sub>2</sub>), 1.42 (6 H, m, piperidine CH<sub>2</sub>), and 1.16 (6 H, s, CH<sub>3</sub>).

2-(2-Dimethyl-3-piperidinopropyl)-1,3-dithian (11). Keten dithioacetal (10) (1.8 g, 0.0066 mol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 ml), TFAA (2.5 ml) was added, the solution was cooled to 0 °C, and Me<sub>3</sub>SiH (1.5 ml; precooled to <0 °C) was added in one portion. The mixture was stirred at 25 °C in a sealed flask for 48 h, the solvent and by-product Me<sub>3</sub>SiOH evaporated

Table 3. Least-squares mean plane equation, and distances (Å) from the plane for atoms in the disulphone ring<sup>a</sup>

Atom	x	y	z	Distance
S(1)*	1.1392	6.4706	3.8842	–0.026(1)
S(2)*	3.5768	4.9674	4.7515	0.026(1)
C(2)*	2.3272	7.7264	3.5262	0.031(3)
C(4)*	4.3803	6.4911	4.3602	–0.031(3)
C(1)	2.0839	4.9483	3.7228	0.783(2)
C(3)	3.4939	7.7025	4.5057	–0.709(3)

<sup>a</sup> The equation is of the form (0.1370)x + (–0.3481)y + (–0.9274)z + (–5.6720) = 0. x, y, and z are orthogonalised coordinates in Å. The atoms used in the plane calculation are indicated with an asterisk.

under reduced pressure, and the residue used directly in the next stage, crude yield 1.32 g (73%); *M*<sup>+</sup> 273; δ(CDCl<sub>3</sub>) 4.11 (1 H, t, *J* 5 Hz, dithian CH), 3.0–2.7 (4 H, m, CH<sub>2</sub>S), 2.44 (4 H, m) and 2.05 (2 H, s) (CH<sub>2</sub>N), 2.0 (2 H, m, dithian CH<sub>2</sub>), 1.58 (2 H, d, *J* 5 Hz, side-chain CH<sub>2</sub>), 1.41 (6 H, m, piperidine CH<sub>2</sub>), and 0.92 (6 H, s, CH<sub>3</sub>).

**Oxidation to disulphone (2).** A solution of the dithian (11) (1.0 g, 0.0037 mol) in glacial AcOH (30 ml) was treated with powdered KMnO<sub>4</sub> (0.29 g, 0.0018 mol). The mixture was stirred at 25 °C for 36 h, rendered colourless with SO<sub>2</sub> gas, adjusted to pH 10 with solid Na<sub>2</sub>CO<sub>3</sub>, and extracted continuously with Et<sub>2</sub>O overnight. The residue from evaporation of the Et<sub>2</sub>O was dissolved in 2M-HCl (50 ml), the solution was extracted with CHCl<sub>3</sub> (3 × 25 ml), and the aqueous phase was treated with excess of solid Na<sub>2</sub>CO<sub>3</sub>. The solution was again extracted with CHCl<sub>3</sub> (3 × 25 ml), and the extracts were dried (MgSO<sub>4</sub>) and evaporated. Recrystallisation of the residue (CHCl<sub>3</sub>–CCl<sub>4</sub>) gave the *disulphone* (2) (0.75 g, 60%) as plates, m.p. 205 °C (Found: C, 50.1; H, 8.2; N, 4.3. C<sub>14</sub>H<sub>27</sub>NO<sub>4</sub>S<sub>2</sub> requires C, 49.8; H, 8.1; N, 4.15%); *M*<sup>+</sup> 337; *v*<sub>max</sub> 2 805 (CH<sub>2</sub>N), 1 330, and 1 142 cm<sup>–1</sup> (SO<sub>2</sub>); δ(<sup>1</sup>H) (CD<sub>2</sub>Cl<sub>2</sub>) 4.86 [1 H, t, *J* 3.9 Hz, H(1)], 3.47–3.11 [4 H, m, H(2) and H(4)], 2.49–2.36 [6 H, m, H(3), H(8), and H(12)], 2.18 [2 H, s, H(7)], 2.14 [2 H, d, *J* 3.9 Hz, H(5)], 1.45 [6 H, m, H(9), H(10), and H(11)], and 0.94 [6 H, s, H(13) and H(14)]; δ(<sup>13</sup>C) (CD<sub>2</sub>Cl<sub>2</sub>) 78.11 [C(1)], 70.20 [C(7)], 57.67 [C(8) and C(12)], 51.27 [C(2) and C(4)], 35.38 [C(6)], 30.13 [C(5)], 27.10 [C(13) and C(14)], 25.99 [C(9) and C(11)], 24.53 [C(10)], and 17.78 p.p.m. [C(3)].

**Crystal Data for the Disulphone (2).**—C<sub>14</sub>H<sub>27</sub>NO<sub>4</sub>S<sub>2</sub>, *M* = 337.50, monoclinic, space group *P*2<sub>1</sub>/*c* (No. 14), *Z* = 4. At 173 K: *a* = 7.107(2), *b* = 25.373(4), *c* = 9.929(2) Å, β = 108.55(2)°, *U* = 1 697 Å<sup>3</sup>, *D*<sub>c</sub> = 1.321 g cm<sup>–3</sup>. Mo-*K*<sub>α</sub> radiation, λ = 0.710 69 Å, μ(Mo-*K*<sub>α</sub>) = 3.14 cm<sup>–1</sup>.

A crystal with approximate dimensions 0.45 × 0.05 × 0.50 mm was mounted on a Syntex P3 diffractometer equipped with a low-temperature apparatus which cooled the crystal to 173 K. The unit-cell dimensions at this temperature were refined from the setting angles of 44 computer-centred reflections in the range 22° < 2θ < 26°.

**Table 4.** Final positional parameters ( $\times 10^4$ ; for S,  $\times 10^5$ ) for the non-hydrogen atoms of disulphone (2), with e.s.d.s in parentheses

Atom	x	y	z
S(1)	34369(9)	25502(3)	41263(6)
S(2)	72762(9)	19577(3)	50477(6)
O(1)	3495(2)	2606(1)	5584(2)
O(2)	1541(3)	2544(1)	3048(2)
O(3)	7305(2)	1968(1)	6500(2)
O(4)	8227(3)	1527(1)	4588(2)
N	1089(3)	190(1)	2815(2)
C(1)	4690(3)	1950(1)	3955(2)
C(2)	4939(4)	3045(1)	3746(3)
C(3)	7043(4)	3036(1)	4787(3)
C(4)	8222(4)	2558(1)	4632(3)
C(5)	3657(4)	1467(1)	4338(3)
C(6)	2781(4)	1068(1)	3138(3)
C(7)	1976(4)	615(1)	3816(3)
C(8)	2187(5)	-304(1)	3198(3)
C(9)	1359(6)	-720(1)	2062(3)
C(10)	-794(6)	-817(1)	1831(2)
C(11)	-1900(5)	-301(2)	1507(4)
C(12)	-1006(4)	106(1)	2645(3)
C(13)	4375(4)	862(1)	2540(3)
C(14)	1088(4)	1314(1)	1958(3)

Intensity data for 2 841 independent reflections ( $4^\circ < 2\theta < 50^\circ$ , graphite monochromatised Mo- $K_\alpha$  radiation) were collected by the  $\omega$ -scan technique. Scans of  $0.8^\circ$  were used with scan rates in the range  $4.0\text{--}10.0^\circ \text{ min}^{-1}$ . Backgrounds were measured at both ends of the scan, with  $\omega$  displaced  $1^\circ$  from the  $K_\alpha$  peak. Intensities were corrected for Lorentz and polarisation effects and also for absorption, the amount of variance in transmission factors being 0.91–1.00.

**Solution and refinement.** These were carried out on a PDP-11 computer using local modifications of the programmes supplied by the Enraf-Nonius Corp.<sup>14</sup> The atomic scattering factors were taken from ref. 15.

The structure was solved in a straightforward fashion by direct methods (MULTAN). The positions of the hydrogen atoms were calculated. Full matrix least-squares refinement of all positional and thermal parameters (anisotropic for C,

N, O, and S; isotropic for H) using 2 232 reflections with  $F_o^2 > 2\sigma(F_o^2)$  converged at  $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.039$  and  $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.039$ . The largest peak in the final difference-Fourier map had a magnitude less than  $0.27 \text{ e } \text{ \AA}^{-3}$ .

Final positional parameters are given in Table 4, and final observed and calculated structure factors, and thermal parameters are available as a Supplementary Publication (SUP No. 23554, 21 pages).\*

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\* For details of the Supplementary Publications scheme, see Instructions to Authors (1983) in *J. Chem. Soc., Perkin Trans. 1*, 1983, Issue 1.

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