Hydrogen Bonds Involving Polar CH Groups. Part 11.[1] Further Confirmation of Intramolecular Bonds to Nitrogen in 2-Aminoalkyl-1,3-dithiane 1,1,3,3-Tetraoxides by *X*-Ray Crystal Structure Analysis

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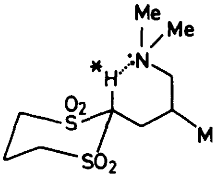
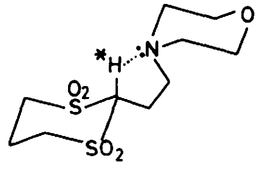
Crystal structures have been determined for 2-(3-dimethylamino-2-methylpropyl)-1,3-dithiane 1,1,3,3-tetraoxide (1) and 2-(2-morpholinoethyl)-1,3-dithiane 1,1,3,3-tetraoxide (2), two compounds having C–H · · · · N intramolecular hydrogen bonds in solution. Crystals of both are monoclinic, space group $P2_1/n$, and have unit cell dimensions, a = 19.144(4), b = 9.372(3), c = 16.561(5) Å, β = 108.74(2)°, Z = 8, and a = 9.534(1), b = 20.563(3), c = 6.936(1) Å, β = 99.81(1)°, Z = 4, respectively. Both structures were solved by direct methods, refinements being to R = 0.052 for 3 432 independent reflections in (1), and to R = 0.079 for 2 168 in (2). Two conformations of (1) exist per asymmetric unit, one having an intramolecular C–H · · · · N hydrogen bond as confirmed by an N · · · · H distance of 2.41 Å and appropriate geometry about nitrogen; the second is in an open conformation with an intermolecular C–H · · · · O hydrogen bond (2.39 Å) to a sulphone oxygen of the other molecule. There is some disorder in the side chain. Compound (2) is highly disordered, but the conformation also suggests an intramolecular C–H · · · · N hydrogen bond with an N · · · · H distance of 2.57 Å.

In the preceding two parts of this series, we presented unequivocal evidence for intramolecular C–H · · · · N and C–H · · · · O interactions of the hydrogen bonding type in solutions of certain 2-substituted 1,3-disulphones in [$^2H_2$]-dichloromethane by ^{1}H n.m.r. spectroscopy.[1,2] Very few interactions of this type had been known previously, and none had been demonstrated in solution. We now report that such interactions are also present in at least two of the disulphones in the crystalline state, as revealed by *X*-ray crystallography.

The largest interactions, as measured by the associated shift to lower field of the ^{1}H n.m.r. signal for the SO_2–CHR–SO_2 methine proton, were found in 2-(3-aminopropyl)-1,3-disulphones having a 2-methyl substituent in the side chain. In compound (1), the indicated proton (*) was shifted 1.28 p.p.m. downfield relative to a model compound.[2] A series of 2-(2-aminoethyl)-1,3-disulphones all had methine ^{1}H signals 0.62—0.66 p.p.m. to lower field than that of a model compound; structure (2) is one example.[2] In compounds (1) and (2), the geometry favours intramolecular hydrogen bonds within six- and five-membered rings, respectively.


(1)


(2)

Experimental

Compounds (1) and (2) were prepared as described previously;[2] crystals were grown by slow evaporation of $CHCl_3$–CCl_4 solutions.

Crystal Data.—These were collected on a Syntex P3 diffractometer at 173 K, using graphite-monochromatised Mo–K_α radiation, λ 0.710 69 Å.

Compound (1). $C_{10}H_{21}NO_4S_2$, M = 283.41, monoclinic, space group $P2_1/n$ (No. 14), Z = 8. At 173 K: a = 19.144(4), b = 9.372(3), c = 16.561(5) Å, β = 108.74(2)°, U = 2 814 Å^3, D_c = 1.338 g cm^{-3}. μ(Mo-K_α) = 3.74 cm^{-1}.

Unit cell dimensions were refined from the setting angles of 47 computer centred reflections obtained from a crystal measuring 0.40 × 0.06 × 0.45 mm.

Intensity data for 6 148 independent reflections ($4° < 2\theta < 54°$) were collected by the ω-scan technique. Scans of 1° were used, with rates ranging from 4.0—10.0° min^{-1}; the ratio of scan time to background counting time was 1.0. Intensities were corrected for Lorentz and polarisation effects, and also for absorption (ψ-scan); the amount of variance in the transmission factors was 91.0—99.7.

Compound (2). $C_{10}H_{19}NO_5S_2$, M = 297.39, monoclinic, space group $P2_1/n$ (No. 14), Z = 4. At 173 K: a = 9.534(1), b = 20.563(3), c = 6.936(1) Å, β = 99.81(1)°, U = 1 339.9 Å^3, D_c = 1.474 g cm^{-3}. μ(Mo-K_α) = 4.03 cm^{-1}.

Unit cell dimensions were refined from the setting angles of 49 computer centred reflections obtained from a crystal measuring 0.27 × 0.20 × 0.30 mm.

Intensity data were collected for 3 068 independent reflections (ω-scan; $4° < 2\theta < 55°$), using scans of 1° with rates ranging from 3.0—6.0° min^{-1}. Intensities were corrected for Lorentz and polarisation effects, but not for absorption.

Solution and Refinement.—These were carried out as reported elsewhere.[3]

Compound (1). The structure was solved using QTAN. The positions of the hydrogen atoms were calculated; only those on the ring were refined. Full matrix least-squares refinement of positional and thermal parameters (anisotropic for C, N, O, and S; isotropic for H) using 3 432 reflections with $F_o^2 > 2\sigma(F_o^2)$ converged at $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ = 0.052 and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ = 0.051. The largest peaks in the final difference-Fourier map had magni-

Table 1. [a] Positional parameters for compounds (1) and (2)

	Compound (1), molecule A			Compound (1), molecule B			Compound (2)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
(a) Refined									
S(1)	0.318 94(5)	0.365 2(1)	0.265 22(6)	0.609 65(6)	0.347 6(1)	0.381 26(7)	0.226 3(2)	0.191 40(8)	0.308 0(2)
S(2)	0.356 16(6)	0.281 6(1)	0.109 61(6)	0.590 13(5)	0.073 8(1)	0.465 66(6)	0.381 4(1)	0.156 78(7)	−0.022(3).2
O(1)	0.242 4(1)	0.329 1(3)	0.226 8(2)	0.534 3(1)	0.341 5(4)	0.324 7(2)	0.350 4(5)	0.218 8(2)	0.425 6(5)
O(2)	0.337 3(2)	0.474 4(4)	0.329 6(2)	0.663 0(2)	0.420 9(4)	0.353 1(2)	0.117 5(4)	0.164 2(2)	0.403 1(5)
O(3)	0.281 1(2)	0.237 1(3)	0.067 4(2)	0.515 5(1)	0.059 7(3)	0.409 9(2)	0.515 5(4)	0.182 6(2)	0.074 0(6)
O(4)	0.398 9(2)	0.328 5(3)	0.057 7(2)	0.630 3(2)	−0.053 9(3)	0.499 5(2)	0.382 9(4)	0.104 9(2)	−0.159 3(6)
O(5)							0.043 4(4)	−0.125 4(2)	0.132 3(6)
N	0.474 2(2)	0.644 5(5)	0.195 7(3)	0.613 4(2)	0.058 0(5)	0.145 4(2)	0.223 7(7)	−0.014 2(3)	0.193(1)
C(1)	0.355 0(2)	0.422 8(5)	0.182 6(2)	0.642 3(2)	0.167 1(5)	0.407 9(2)	0.283 7(5)	0.127 2(3)	0.163 5(7)
C(2)	0.368 9(2)	0.209 6(6)	0.306 8(3)	0.610 5(2)	0.420 1(5)	0.480 7(3)	0.145 9(6)	0.250 4(3)	0.137 9(8)
C(3)	0.365 1(2)	0.097 0(5)	0.239 9(3)	0.562 2(2)	0.336 6(5)	0.520 9(2)	0.249 3(6)	0.274 3(3)	0.004 1(8)
C(4)	0.403 3(2)	0.141 7(5)	0.177 1(3)	0.592 7(2)	0.189 2(5)	0.550 8(2)	0.274 8(6)	0.220 9(3)	−0.140 4(7)
C(5)	0.309 5(2)	0.550 6(5)	0.136 7(3)	0.638 8(2)	0.080 4(5)	0.328 4(3)	0.374 4(7)	0.079 1(3)	0.298(1)
C(6)	0.343 3(3)	0.667 3(6)	0.106 5(4)	0.699 8(2)	0.110 8(7)	0.291 3(3)	0.378(1)	0.015 2(5)	0.226(2)
C(6A)							0.310(2)	0.023 9(7)	0.380(2)
C(7)	0.411 6(3)	0.725 4(7)	0.146 0(4)	0.686 0(3)	0.035 9(7)	0.207 9(3)	0.145(1)	−0.039 0(4)	0.347(1)
C(8)	0.520 0(3)	0.601 4(7)	0.145 9(5)	0.607 9(4)	−0.035 8(8)	0.072 6(4)	0.009 5(9)	−0.072 8(3)	0.249(1)
C(9)	0.518 6(5)	0.728 4(8)	0.267 0(5)	0.599 0(4)	0.204 1(8)	0.117 4(4)	0.118 6(7)	−0.102 2(3)	−0.014(1)
C(10)	0.285 1(3)	0.775 7(6)	0.056 6(3)	0.775 2(3)	0.075 8(10)	0.351 3(4)	0.255 6(8)	−0.069 3(4)	0.072(2)
H(1)	0.400(2)	0.446(4)	0.213(2)	0.688(2)	0.177(4)	0.443(2)	0.193(5)	0.105(2)	0.091(7)
H(2A)	0.411(2)	0.236(4)	0.330(2)	0.660(2)	0.415(4)	0.516(2)			
H(2B)	0.347(2)	0.180(4)	0.347(2)	0.597(2)	0.510(4)	0.468(2)			
H(3A)	0.314(2)	0.067(4)	0.211(2)	0.515(2)	0.328(4)	0.486(2)			
H(3B)	0.387(2)	0.017(4)	0.270(2)	0.562(2)	0.387(4)	0.571(2)			
H(4A)	0.445(2)	0.173(4)	0.197(2)	0.641(2)	0.188(4)	0.584(2)			
H(4B)	0.406(2)	0.069(4)	0.140(2)	0.560(2)	0.141(4)	0.577(2)			
(b) Calculated									
H(5A)	0.2718	0.5137	0.0891	0.6415	−0.0183	0.3435			
H(5B)	0.2882	0.5923	0.1756	0.5930	0.0991	0.2861			
H(6)	0.3531	0.6197	0.0587	0.6987	0.2106	0.2799			
H(7A)	0.4036	0.7958	0.1839	0.7220	0.0683	0.1828			
H(7B)	0.4264	0.7719	0.1032	0.6925	−0.0636	0.2183			
H(8A)	0.4900	0.5445	0.0983	0.5614	−0.0268	0.0304			
H(8B)	0.5371	0.6819	0.1242	0.6459	−0.0146	0.0490			
H(8C)	0.5593	0.5449	0.1790	0.6141	−0.1338	0.0920			
H(9A)	0.4916	0.7603	0.3015	0.6021	0.2639	0.1650			
H(9B)	0.5606	0.6741	0.3007	0.6332	0.2349	0.0909			
H(9C)	0.5384	0.8112	0.2459	0.5501	0.2114	0.0775			
H(10A)	0.2397	0.7297	0.0304	0.7828	0.1225	0.4036			
H(10B)	0.2789	0.8448	0.0968	0.7795	−0.0230	0.3612			
H(10C)	0.3014	0.8230	0.0156	0.8116	0.1068	0.3268			

[a] In this and the following Tables ,e.s.d.s are given in parentheses.

tudes of 0.53 and 0.44 e Å^{-3}, and were located close to, and on opposite sides of C(6).

Compound (2). The structure was solved by MULTAN. The position of H(1) only was calculated, and then refined. Full matrix least-squares refinement, as for compound (1), using 2 168 reflections, converged at $R = 0.079$ and $R_w = 0.096$. The two largest peaks in the final difference-Fourier map had magnitudes of 1.04 and 0.95 e Å^{-3}, and were located near N.

Final positional parameters are in Table 1, and final observed and calculated structure factors, and thermal parameters are available as a Supplementary Publication (SUP No. 23804, 46 pp.).*

Results and Discussion

Ortep drawings of compounds (1) and (2) are displayed in Figures 1 and 2; selected interatomic distances and bond angles are given in Tables 2 and 3.

Compound (1).—Molecules exist in two different conformations in each asymmetric unit. One, molecule A, shows a very definite intramolecular C–H ···· N interaction, formed within a six-membered ring by the curling round of the side chain. The N ···· H(1) distance (2.41 Å; Table 4) is very significantly shorter than that recently suggested for the sum of the van-der-Waals radii (2.75 Å) in C–H ···· N hydrogen bonding interactions;[4] it also compares well with the 2.47 Å distance reported earlier by us in another six-membered ring C–H ···· N hydrogen bonded system.[5] Further, H(1) fills in the tetrahedral geometry about the nitrogen atom rather well, the C–N ···· H(1) angles all lying in the range 93.5—122.4° (Table 4).

The atom C(6) is disordered over a large volume of space, as evidenced by the additional peaks in the difference-Fourier

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* For details of the Supplementary Publications scheme, see Instructions for Authors (1984), *J. Chem. Soc., Perkin Trans. 1*, 1984, Issue 1.

Table 2. Interatomic distances (Å) and bond angles (°) for compound (1)

	Molecule A [a]	Molecule B
(*a*) Distances		
S(1)–O(1)	1.437(2)	1.447(2)
S(1)–O(2)	1.437(2)	1.427(2)
S(1)–C(1)	1.803(3)	1.808(4)
S(1)–C(2)	1.758(4)	1.777(4)
S(2)–O(3)	1.442(2)	1.437(2)
S(2)–O(4)	1.433(2)	1.436(2)
S(2)–C(1)	1.797(3)	1.813(3)
S(2)–C(4)	1.771(4)	1.765(3)
C(1)–H(5)	1.532(4)	1.530(4)
C(1)–H(1)	0.88(3)	0.88(3)
C(2)–C(3)	1.515(5)	1.518(5)
C(3)–C(4)	1.511(5)	1.520(5)
C(5)–C(6)	1.439(5) *	1.512(5)
C(6)–C(7)	1.372(6) *	1.495(5)
C(6)–C(10)	1.538(5)	1.502(5)
N–C(7)	1.434(5)	1.456(5)
N–C(8)	1.441(6)	1.468(6)
N–C(9)	1.446(6)	1.444(6)
(*b*) Angles		
O(1)–S(1)–O(2)	117.8(1)	118.5(1)
O(1)–S(1)–C(1)	108.6(1)	108.4(2)
O(1)–S(1)–C(2)	109.1(2)	109.0(2)
O(2)–S(1)–C(1)	106.7(2)	107.6(2)
O(2)–S(1)–C(2)	109.1(2)	108.9(2)
C(1)–S(1)–C(2)	104.7(2)	103.4(2)
O(3)–S(2)–O(4)	118.0(1)	118.2(1)
O(3)–S(2)–C(1)	108.3(1)	107.9(1)
O(3)–S(2)–C(4)	108.6(2)	109.7(2)
O(4)–S(2)–C(1)	108.1(2)	106.9(2)
O(4)–S(2)–C(4)	109.4(2)	108.9(2)
C(1)–S(2)–C(4)	103.6(2)	104.3(2)
S(1)–C(1)–S(2)	112.4(2)	112.0(2)
S(1)–C(1)–C(5)	108.4(2)	111.8(2)
S(1)–C(1)–H(1)	101(2)	104(2)
S(2)–C(1)–C(5)	111.7(2)	108.6(2)
S(2)–C(1)–H(1)	110(2)	108(2)
C(5)–C(1)–H(1)	113(2)	112(2)
S(1)–C(2)–C(3)	113.5(2)	112.6(3)
C(2)–C(3)–C(4)	113.0(2)	112.8(3)
S(2)–C(4)–C(3)	112.2(3)	112.8(2)
C(1)–C(5)–C(6)	121.3(2) *	115.1(3)
C(5)–C(6)–C(7)	127.0(4) *	111.0(3)
C(5)–C(6)–C(10)	111.1(3)	113.2(4)
C(7)–C(6)–C(10)	114.1(4) *	110.8(4)
N–C(7)–C(6)	123.8(4) *	115.7(3)
C(7)–N–C(8)	111.7(4)	107.4(4)
C(7)–N–C(9)	110.2(4)	113.8(4)
C(8)–N–C(9)	108.3(4)	110.4(4)

[a] Values marked * are abnormal as a result of disorder at C(6) and C(7).

map, and the associated abnormal bond distances and angles (marked * in Table 2). Although this contributes to the apparently large thermal motions of a number of carbon atoms in the side chain, the position of the nitrogen atom seems to be little affected. Introduction of the methyl substituent at C(6) nevertheless appears to inhibit disorder. Thus, a 3-aminopropyl analogue, unsubstituted in the side chain, was too disordered to permit complete structure determination,[6] whereas an analogue with two methyl groups at C(6) showed no significant disorder.[3] The additional steric constraints in this latter compound, however, prevented formation of an intramolecular hydrogen bond.

Table 3. Selected interatomic distances (Å) and bond angles (°) for compound (2)

(*a*) Distances [a]			
S(1)–O(1)	1.433(2)	C(3)–C(4)	1.533(4)
S(1)–O(2)	1.434(2)	C(5)–C(6)	1.410(5) *
S(1)–C(1)	1.799(3)	C(5)–C(6A)	1.452(7) *
S(1)–C(2)	1.773(3)	N–C(6)	1.568(5) *
S(2)–O(3)	1.440(2)	N–C(6A)	1.616(7) *
S(2)–O(4)	1.431(2)	N–C(7)	1.493(7) *
S(2)–C(1)	1.818(2)	N–C(10)	1.471(6) *
S(2)–C(4)	1.777(3)	C(7)–C(8)	1.526(6)
C(1)–C(5)	1.523(4)	O(5)–C(8)	1.421(3)
C(1)–H(1)	1.02(2)	O(5)–C(9)	1.420(4)
C(2)–C(3)	1.544(4)	C(9)–C(10)	1.502(5)
(*b*) Angles [b]			
O(1)–S(1)–O(2)	118.9(1)	C(1)–S(2)–C(4)	104.7(1)
O(1)–S(1)–C(1)	107.8(1)	S(1)–C(1)–S(2)	113.0(1)
O(1)–S(1)–C(2)	109.3(1)	S(1)–C(1)–C(5)	109.2(2)
O(2)–S(1)–C(1)	106.4(1)	S(1)–C(1)–H(1)	107(1)
O(2)–S(1)–C(2)	108.0(1)	S(2)–C(1)–C(5)	110.2(2)
C(1)–S(1)–C(2)	105.7(1)	S(2)–C(1)–H(1)	107(1)
O(3)–S(2)–O(4)	118.3(1)	C(5)–C(1)–H(1)	111(1)
O(3)–S(2)–C(1)	108.5(1)	S(1)–C(2)–C(3)	111.7(2)
O(2)–S(2)–C(4)	109.4(1)	C(2)–C(3)–C(4)	110.8(2)
O(4)–S(2)–C(1)	106.6(1)	S(2)–C(4)–C(3)	111.8(2)
O(4)–S(2)–C(4)	108.5(1)	C(8)–O(5)–C(9)	109.9(2)

[a] Values marked * are abnormal as a result of disorder. [b] Angles associated with disordered sites are not included.

Table 4. Geometry of close contacts about H(1)

(*a*) Compound (1), molecule A, intramolecular			
H(1) ···· N	2.41(3) Å	C(7)–N ···· H(1)	93.5(7)°
C(1) ···· N	3.042(4) Å	C(8)–N ···· H(1)	109.9(7)°
C(1)–H(1) ···· N	129(2)°	C(9)–N ···· H(1)	122.4(7)°
(*b*) Compound (1), intermolecular [a]			
H(1′) ···· O(3)	2.39(3) Å	C(1′)–H(1′) ···· O(3)	155(2)°
C(1′) ···· O(3)	3.215(4) Å	S(2)–O(3) ···· H(1′)	132.2(7)°
(*c*) Compound (2), intramolecular			
H(1) ···· N	2.57(2) Å	C(6A)–N ···· H(1)	77(1)°
C(1) ···· N	2.977(4) Å	C(7)–N ···· H(1)	118(1)°
C(1)–H(1) ···· N	104(2)°	C(10)–N ···· H(1)	127(1)°
C(6)–N ···· H(1)	74(1)°		

[a] Primed atoms are from molecule B.

Molecule B exists in a more extended conformation which prohibits an intramolecular C–H ···· N interaction. However, there is a short (2.39 Å) *inter*molecular contact between H(1) of this molecule and the axial O(3) of molecule A (Table 4), the distance being substantially less than the sum of the van-der-Waals radii (2.70 Å).[4] Intermolecular C–H ···· O close contacts have recently received considerable attention, in many cases being recognised both as hydrogen bonds, and as playing an important role in determining molecular packing and conformation.[4,7] The C(1′) ···· O(3) distance and C(1′)–H(1′) ···· O(3) angle (Table 4) lie well within the ranges for such hydrogen bonds. The spatial relationship between molecules A and B is shown in the unit cell packing diagram (Figure 3).

Compound (2).—The side chain in this compound is badly disordered, C(6) existing in two distinct sites: C(6) and C(6A)

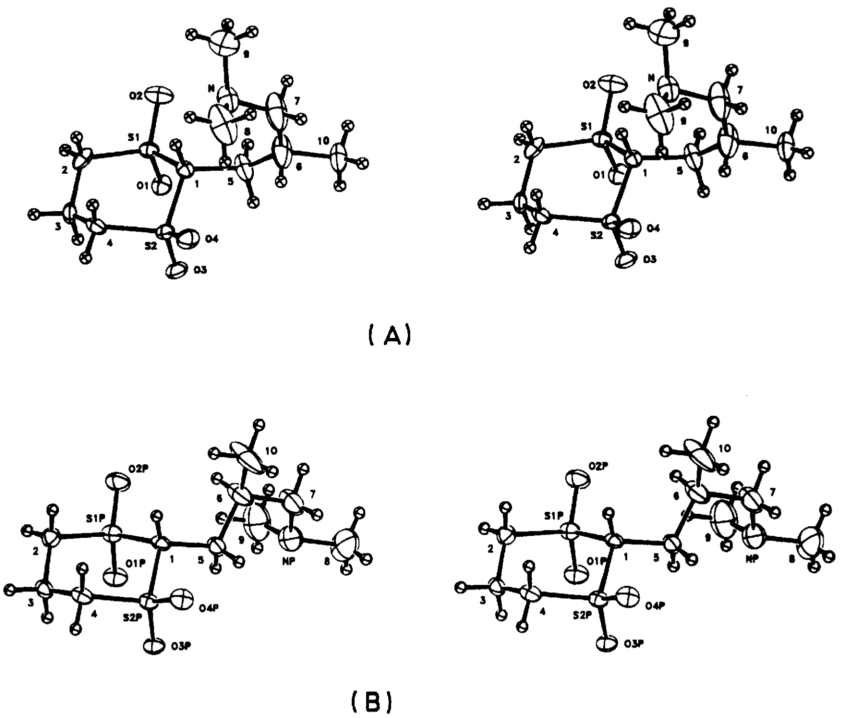

Figure 1. ORTEP drawing for compound (1), showing the two molecular conformations, (A) and (B), and the atom numbering scheme

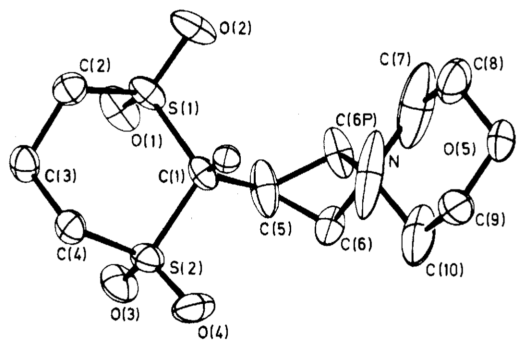

Figure 2. ORTEP drawing for compound (2), showing the disorder and the atom numbering scheme

have occupancies of 0.6 and 0.4 respectively. Further, atoms C(5), C(7), C(10), and N have very large thermal ellipsoids rendering the associated bond distances and angles highly inaccurate. Thus, only selected data are included in Table 3. Nevertheless, the conformation of the molecule is suggestive of an intramolecular hydrogen bond, and the N • • • • H(1) distance (2.57 Å; Table 3) is sufficiently short to qualify for such a classification.

The Disulphone Ring.—These are the second and third structures we have reported which include the 1,3-dithiane 1,1,3,3-tetraoxide ring. Bond distances and angles found for this moiety agree closely with those determined for the first structure.[3] We also observed with the first structure a slight twist to the ring, such that S(1) and C(4) lay *ca.* 0.03 Å above,

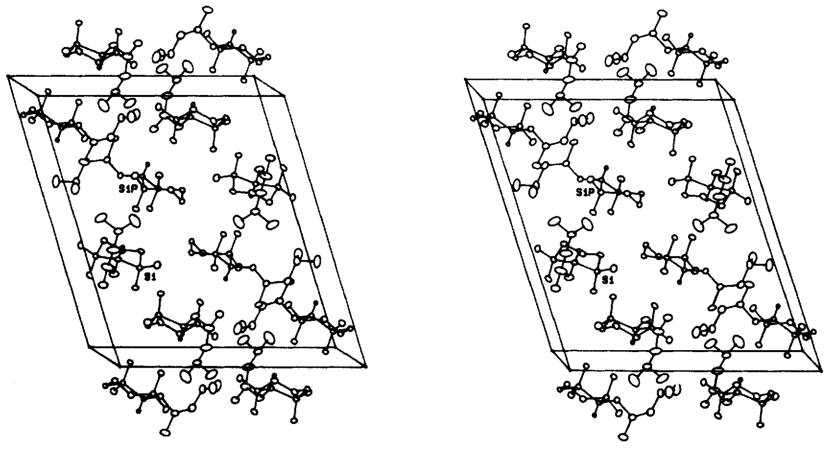

Figure 3. Unit cell packing diagram for compound (1)

and S(2) and C(2) *ca.* 0.03 Å below, a plane defined by these four atoms.[3] In compound (1), a similar but smaller twist is observed in molecule A, the same atoms deviating from the plane in the same sense by *ca.* 0.015 Å.

Currently, structures are being determined for amino-disulphones showing even larger downfield shifts for their corresponding H(1) n.m.r. signals, in the hope of finding non-disordered examples which have intramolecular C–H · · · N hydrogen bonds.

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