271. *The Structure of the α-Modification of* 1 : 4-*Dithian* 1 : 4-*Dioxide.*

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The crystal structure of this dioxide has been determined by *X*-ray methods. The monoclinic unit cell, $a = 6{\cdot}34 \pm 0{\cdot}01$, $b = 6{\cdot}46 \pm 0{\cdot}01$, $c = 8{\cdot}22 \pm 0{\cdot}01$ Å, $\beta = 103^\circ 57' \pm 15'$, space-group $P2_1/n$, contains two centrosymmetrical molecules. Analysis of the three principal zones leads to a model in which the dithian ring has the chair form with the oxygen atoms in the *trans*-diaxial positions. No unusual bond distances or intermolecular contacts are found.

Bell and Bennett[1] reported that oxidation of 1 : 4-dithian gave two dioxides or disulphoxides. That produced in greater yield, designated α, was described as being more soluble in water and less soluble in ethanol than the other (β). The authors suggested that it was the *trans*-compound. The present work confirms this and shows that the molecules, in crystals of the α-form, have the *trans*-diaxial configuration with the ring in the chair conformation, as in the parent compound 1 : 4-dithian[2,3] itself.

Crystal Data.—Monoclinic; $a = 6{\cdot}34 \pm 0{\cdot}01$, $b = 6{\cdot}46 \pm 0{\cdot}01$, $c = 8{\cdot}22 \pm 0{\cdot}01$ Å, $\beta = 103^\circ 57' \pm 15'$. $U = 326{\cdot}7$ Å^3, $D_m = 1{\cdot}535$ g. cm.$^{-3}$, $Z = 2$, $D_c = 1{\cdot}547$ g. cm.$^{-3}$, μ ($\lambda = 0{\cdot}7107$ Å) $= 7{\cdot}37$ cm.$^{-1}$. Space-group C_{2h}^5–$P2_1/n$ from systematic absences. Molecular symmetry, centre.

Experimental

Crystals were obtained as thin plates, with the $\{10\bar{1}\}$ and $\{101\}$ faces well developed, by evaporation from a solution in ethanol. The unit-cell dimensions were measured from precession photographs and the axial ratios (0·981 : 1 : 1·272) were found to be in good agreement with those given by Bell and Bennett[1] (0·979 : 1 : 1·267; $\beta = 104^\circ 3'$).

For intensity measurements a crystal of cross-section 0·20 × 0·23 mm. and length 0·80 mm. was used, mounted about the *b* axis. The ($h0l$) reflections were recorded on an integrating Weissenberg apparatus, and the ($hk0$) and ($0kl$) reflections on the precession camera; Zr-filtered Mo radiation was used throughout. The intensities were estimated visually, an exposure scale being used, and corrected for the usual angle factors. No corrections were applied for absorption.

Structure Determination.—The space-group is $P2_1/n$ with two molecules in the unit cell, so that the molecule possesses a centre of symmetry. It must therefore have the chair configuration with the oxygen atoms in diaxial or diequatorial positions.

The (010) projection was examined first since this was the simplest. The sharpened Patterson function was evaluated, by using as coefficients $F^2/\sum fi^2$. The Patterson map showed two large peaks of almost equal height. One was sharper and rounder than the other with an

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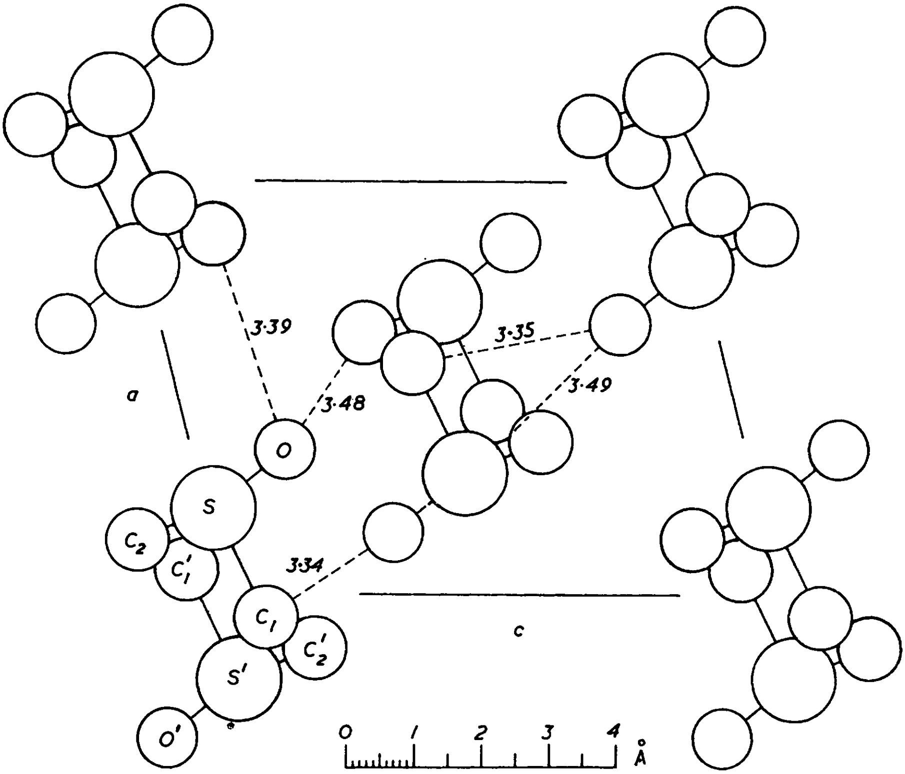
[1] Bell and Bennett, *J.*, 1927, 1798.
[2] Duthie, *Acta Cryst.*, 1953, **6**, 804.
[3] Marsh, *ibid.*, 1955, **8**, 91.

environment similar to that at the origin and so was taken as the S–S vector across the centre of symmetry. A single superposition, with the origin of the Patterson function transferred to this point, gave approximate positions for the carbon and oxygen atoms in this projection and showed the oxygen atoms to be diaxial.

Refinement was carried out by means of one F_o and two F_o-F_c syntheses, and the contributions of the hydrogen atoms (the positions of which were estimated approximately from a model) were included in the final stage. The arrangement of the atoms in this projection is shown in Fig. 1.

FIG. 1. *Arrangement of the molecules in the* (010) *projection with the shortest intermolecular distances* (*in* Å).



For the (001) projection, the determination of the approximate structure and its refinement were carried out in a similar manner. In the (100) projection, considerable overlapping of the atoms occurs and only a final structure factor calculation was made as a check of the correctness of the structure.

The structure factors were calculated by using the form factor due to Viervoll and Ogrim [4] for the sulphur atoms, those of Hoerni and Ibers [5] for the carbon and oxygen atoms, and that of McWeeny [6] for hydrogen. On the basis of the difference maps, individual temperature factors were assigned to the different atomic species and the final values of the exponent B (in Å^2) in the expression exp $(-B \sin^2\theta/\lambda^2)$ are shown below.

	S	O	C		S	O	C		S	O	C
(*h*0*l*) ...	3·1	3·4	3·3	(*hk*0) ...	3·1	4·0	3·7	(0*kl*) ...	3·1	3·8	3·5

The value of B = 3·5 Å^2 for the hydrogen atoms was adopted, somewhat arbitrarily, for all the structure factors. The reliability indices were 9·8% for the (*h*0*l*) reflections, 9·0% for the (*hk*0), and 9·1% for the (0*kl*). The structure factors are listed in Table 3.

[4] Viervoll and Ogrim, *Acta Cryst.*, 1949, **2**, 277.
[5] Hoerni and Ibers, *ibid.*, 1954, **7**, 744.
[6] McWeeny, *ibid.*, 1951, **4**, 513.

The final atomic co-ordinates are given in Table 1 and the bond lengths and angles in Table 2 with their averaged values in Fig. 2. Estimates of the standard deviations in bond lengths and angles were calculated [7] and are included in Table 3.

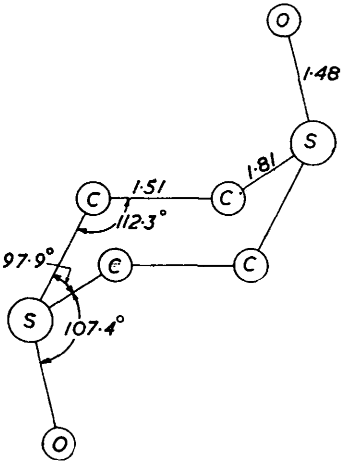


FIG. 2. *Averaged molecular dimensions (in Å).*

TABLE 1. *Atomic co-ordinates.*

	x/a	y/b	z/c		x/a	y/b	z/c
S	0·207	0·181	0·016	H_1	−0·141	0·224	−0·050
O	0·350	0·095	0·170	H_2	−0·070	0·340	0·163
C_1	−0·058	0·219	0·061	H_3	0·281	−0·065	−0·190
C_2	0·133	−0·025	−0·134	H_4	0·027	0·031	−0·237

TABLE 2. *Bond lengths* (Å) *and angles.*

S–O	1·48 ± 0·014	$S–C_2$	1·80 ± 0·018	$C_1–S–O$	106·4° ± 0·8°	$C_2'–C_1–S$	111·2° ± 1·25°
$S–C_1$	1·82 ± 0·018	$C_1–C_2'$	1·51 ± 0·025	$C_2–S–O$	108·3° ± 0·8°	$C_1'–C_2–S$	113·3° ± 1·25°
				$C_1–S–C_2$	97·9° ± 0·8°		

TABLE 3. *Structure factors.*

hk	F_o	F_o
200	36·0	−32·3
400	1·8	−2·2
600	4·0	+3·1
800	3·3	−3·2
020	20·2	−18·6
040	1·9	−1·4
060	9·7	+9·4
080	7·1	−6·3
002	42·1	+38·8
004	13·7	+13·7
006	21·4	+23·0
008	5·4	+5·8
$10\bar{9}$	5·1	+7·3
$10\bar{7}$	14·9	+16·9
$10\bar{5}$	5·6	+5·6
$10\bar{3}$	18·2	+20·9
$10\bar{1}$	42·3	+45·2
101	27·0	+25·4
103	16·5	+19·2
105	8·0	−8·4
107	10·8	−12·1
109	2·9	−3·4
1,0,11	3·9	−4·4
$20\bar{8}$	8·5	−9·4
$20\bar{6}$	10·2	−12·4
$20\bar{4}$	5·2	−3·9
$20\bar{2}$	58·4	−56·8
202	4·9	+6·0
204	30·4	−28·2
206	21·4	−21·2
208	6·2	−7·4
2,0,10	4·9	−5·8
$30\bar{9}$	12·8	−14·8

hk	F_o	F_c
$30\bar{7}$	14·0	−17·3
$30\bar{5}$	17·9	−18·8
$30\bar{3}$	38·8	−42·6
$30\bar{1}$	23·3	−23·3
301	12·9	−11·0
303	11·4	−8·5
305	2·3	+1·8
307	3·9	−3·4
$40\bar{8}$	3·1	−3·0
$40\bar{6}$	9·9	−12·2
$40\bar{4}$	<1·7	+1·3
$40\bar{2}$	13·3	+12·9
402	18·3	+16·8
404	26·9	+23·3
406	7·3	+7·6
408	4·1	+4·4
4,0,10	3·6	+3·3
$5,0,\overline{11}$	4·3	+5·3
$50\bar{9}$	7·4	+8·2
$50\bar{7}$	3·1	+4·0
$50\bar{5}$	13·1	+14·3
$50\bar{3}$	18·0	+18·6
$50\bar{1}$	11·7	+11·0
501	21·6	+18·8
503	14·8	+13·6
505	9·7	+9·3
507	6·6	+5·5
$6,0,\overline{10}$	4·3	+4·9
$60\bar{8}$	7·8	+7·7
$60\bar{6}$	4·7	+6·1
$60\bar{4}$	2·6	−2·3
$60\bar{2}$	4·8	+4·1
602	7·1	−6·8
604	<2·3	−0·6

hkl	F_o	F_c
606	<2·7	+0·8
608	3·6	−2·3
$70\bar{5}$	9·9	−10·4
$70\bar{3}$	8·9	−8·7
$70\bar{1}$	10·0	−10·0
701	11·5	−10·4
703	5·3	−5·8
705	4·3	−3·8
$80\bar{8}$	2·8	−3·4
$80\bar{6}$	2·6	−3·3
$80\bar{4}$	7·5	−6·1
$80\bar{2}$	9·7	−9·1
802	<2·7	−1·2
804	2·9	−2·2
$10,0,\bar{4}$	4·6	+4·0
110	8·4	+9·5
120	40·6	−39·5
130	3·4	−3·8
140	20·0	+19·3
150	14·0	+13·8
160	3·1	−2·6
170	1·7	−0·9
210	4·5	+6·8
220	8·5	+9·0
230	14·5	+15·7
240	7·8	+7·7
250	9·4	+10·2
260	10·7	−10·0
270	4·7	−5·2
280	5·1	+5·4
310	2·9	−3·3

hkl	F_o	F_c
320	13·2	+13·6
330	10·2	+9·6
340	15·8	−15·9
350	15·5	−14·4
360	7·4	+7·6
410	19·7	+22·0
420	12·0	−13·3
430	11·6	−12·2
440	2·1	−1·2
450	4·7	−5·4
460	4·4	+4·4
470	6·7	+6·2
480	1·7	−2·3
510	4·6	+5·1
520	2·1	+2·3
530	13·5	−15·2
540	<1·8	+2·0
550	7·3	+6·9
610	11·6	−11·4
620	1·8	+2·9
630	1·8	−1·2
640	<1·8	−1·7
650	3·1	+3·5
710	4·1	−3·7
720	1·8	−2·5
730	10·2	+8·9
740	<1·7	+1·1
750	3·2	−3·4
810	6·6	+5·4
820	5·8	+3·7
011	49·3	+50·4

hkl	F_o	F_c
012	34·4	−33·7
013	13·0	−10·8
014	9·1	−9·6
015	9·4	+11·1
016	10·0	−13·3
017	8·0	+9·1
018	8·0	−10·1
021	26·0	−25·9
022	43·7	−40·5
023	13·0	−11·3
024	26·1	−24·5
025	2·1	−2·0
026	2·7	−3·6
027	9·7	−11·3
028	<2·2	−1·3
029	4·0	−5·1
0,2,10	2·0	−2·1
031	30·7	−29·5
032	9·7	−10·2
033	30·9	−29·8
034	15·4	+16·2
035	15·9	−18·1
036	6·1	+5·3
037	4·6	−6·0
038	<2·2	−0·5
039	2·8	−2·9
0,3,10	1·7	+1·5
041	5·9	−5·8
042	2·6	+2·6
043	9·1	+8·1
044	3·6	−2·7
045	15·7	+15·4
046	4·6	−5·4

hkl	F_o	F_o
047	4·9	+6·1
048	<2·1	+0·1
049	2·9	+4·1
0,4,10	1·4	−1·2
051	20·3	+18·8
052	4·4	−3·4
053	16·9	+18·2
054	3·0	+2·7
055	5·7	+5·5
056	2·9	+3·9
057	4·3	+4·4
058	<2·0	+2·0
059	2·3	+3·2
061	3·2	−2·1
062	12·3	+12·4
063	6·4	−5·8
064	7·9	+8·6
065	4·3	−3·4
066	4·4	+4·7
067	2·3	−1·7
068	3·9	+5·0
071	5·0	−3·4
072	2·3	−1·8
073	2·3	−1·3
074	2·9	−4·1
075	<2·0	−1·0
076	1·7	−1·7
077	1·2	+0·8
081	<1·9	+0·9
082	6·7	−6·4
083	<1·8	−0·2
084	4·6	−5·3

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[7] Cruickshank and Robertson, *Acta Cryst.*, 1953, **6**, 698.

Application of statistical tests shows that the differences between the chemically equivalent bonds S–C_1, S–C_2 and the equivalent angles C_1–S–O, C_2–S–O and C_1'–C_2–S, C_2'–C_1–S are not significant; nor do the dimensions of the dithian ring differ significantly from these obtained for dithian itself.[3] The dimensions of the sulphoxide group are similar to those found in other compounds.[8]

The shortest van der Waals contacts are of 3·34, 3·35, and 3·39 Å between the oxygen atom of one molecule and carbon atoms of adjacent molecules. All the intermolecular distances of less than 3·75 Å are shown in Fig. 1.

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[8] Abrahams, *Quart. Rev.*, 1956, **10**, 407.