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The Crystal Structure of Beta Dithiane Disulphoxide

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The crystal structure of 1·4 dithiane β disulphoxide has been determined and refined by two-dimensional Fourier series and difference syntheses using data obtained by copper X-radiation. The molecule is in the chair configuration and the oxygen atoms are *cis* to one another. The bond distances are S–C 1·78, C–C 1·47 and S–O 1·42 Å, and the C–S–O bond angle is 110°.

Introduction

In the course of examining six-membered rings containing oxygen and sulphur, the six oxides of dithiane ($C_4H_8S_2$) were prepared. In the case of the disulphoxide there is a possibility of stereoisomerism in which the oxygen atoms are *cis* of *trans* to one another. An X-ray diffraction study was undertaken to verify this point and to investigate the length and spatial arrangement of the sulphur–oxygen bond in a sulphoxide in which the sulphur is part of a ring. A secondary purpose was to settle the form of the dithiane ring. The structure of the nitrogen containing ring which corresponds to dithiane (N, N′-dimethyl-piperazine) had already been reported, and the geometric isomerism of the diquaternary salts had been demonstrated (Powell, 1945). After the preliminary calculations had been completed, an electron-diffraction study of dithiane itself was reported (Hassel & Viervoll, 1947) and later a structure based on three-dimensional diffraction data was published (Marsh, 1955).

Experimental

The dithiane disulphoxides were prepared by the method of Bell & Bennett (1927), who considered the more soluble and lower melting form (the Beta isomer) to be the *cis* form. This isomer was examined first. It crystallised from benzene–ethanol in needles, elongated in the c direction and photographs about this axis of rotation only could be obtained because all attempts to cut this type of crystal failed. A few hexagonal platelets were found and gave the intensities for the $0kl$ reflections.

No crystal suitable for the $h0l$ zone was found. Zero, first, second and third layer photographs were taken about the c axis with nickel filtered Cu radiation ($\lambda = 1{\cdot}5418$ Å) in an equi-inclination Weissenberg camera while zero and first layer line photographs were taken about the a axis. Intensities of the $hk0$ and of the $0kl$ zones were measured visually by comparison with a calibrated strip of film. In the case of the $hk0$ zone, two independent sets of measurements were made and the average relative intensities used. Corrections for Lorentz and polarization were made, but none for absorption.

The systematic extinctions were $h0l$ for $h+l=2n+1$, which indicates a space group symmetry of either $C_{2v}^7(Pmn2_1)$ or $D_{2h}^{13}(Pmmn)$. The unit cell is orthorhombic,

$$a = 6{\cdot}82 \pm 0{\cdot}01,\ b = 8{\cdot}60 \pm 0{\cdot}01,\ c = 5{\cdot}48 \pm 0{\cdot}02 \text{ Å}\,.$$

Using a density of 1·55 g.cm.$^{-3}$ the number of molecules per unit cell is 2·05. This figure suggests the space group ($Pmn2_1$). Since in addition this is also the space group of trithiane (Moerman & Wibenga, 1937) which is similar in structure to dithiane, the symmetry $Pmn2_1$ was tried first and found to be correct. The alternative space group $Pmmn$ was not considered further. At the conclusion of the intensity measurements the crystals used were ground up and powder photographs were taken to verify that no steric changes had taken place under the influence of prolonged exposure to X-rays.

Structure determination

Patterson maps for the projection on (001) and on (100) were computed and gave the approximate x and y positions for sulphur and carbon:

$$\text{S at } a/4,\ b/12,\ a/4,\ 5b/12$$
$$\text{C at } \pm a/20,\ b/12 \quad\text{or}\quad b/4\,.$$

From a knowledge of the ring structure $b/12$ can be rejected for the C atoms. It is also clear from these parameters that the molecule is symmetrically situated about $x=\frac{1}{4}$ and that is in the 'chair' form. The projection on (100) possesses no centre or plane of symmetry and the only additional information derived from the Patterson map was the difference in Z co-ordinates for the two S atoms

$$Z_2 - Z_1 = 25c/60 \quad\text{or}\quad 21c/60\,.$$

Measurement of the projection of a model of dithiane (chair form) indicated that the second value was correct. The equivalent points for the projection on (100)

$$(y, Z;\ \bar{y}, Z+\tfrac{1}{2})$$

are two fold only so that one Z parameter for sulphur may have any value: the other will then be $Z+0{\cdot}35$. For ease of calculation one sulphur was placed at $Z=0{\cdot}500$. If the dithiane ring were symmetrically placed about

$$x=\tfrac{1}{4},\ y=\tfrac{1}{4}$$

as the preliminary parameters would suggest, then the reflections for $h+k$ odd planes would be missing. This pattern of intensities is noticeable in the $hk0$ zone for $h>3$. Now if the dithiane ring is rotated slightly about $y=\frac{1}{4}$, then the oxygen would be unsymmetrically placed in the projection on (001) and would then be the sole contributors to the $h+k$ odd reflections. However, as $\sin\theta$ increases, the oxygen contribution decreases to such an extent that the intensities were not recorded by film. Measurements with a scale model

(S–C 1·81, C–C 1·54, S–O 1·44 Å)

confirmed this arrangement. It also indicated that the molecule was in the *cis* form, because only this form could have unsymmetrically placed oxygen atoms in the projection.

Table 1. *Atomic parameters*

	x/a	y/b	z/c
S_1	0·250	0·087	0·133
S_2	0·250	0·411	0·500
C_1	0·0545	0·220	0·192
C_2	0·4455	0·220	0·192
C_3	0·0545	0·280	0·444
C_4	0·4455	0·280	0·444
O_1	0·250	0·9615	0·304
O_2	0·250	0·453	0·706

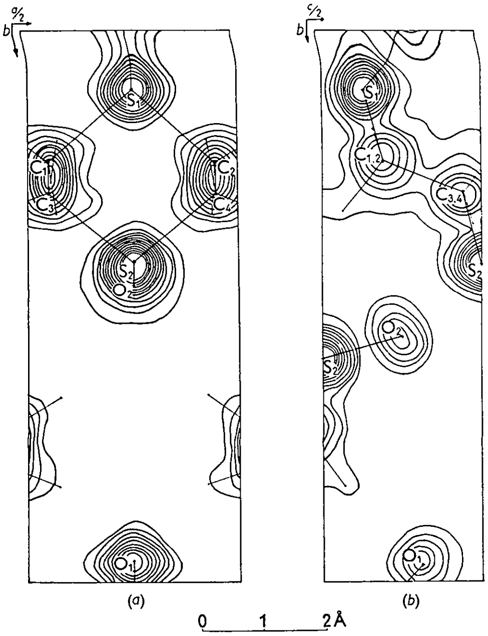

Fig. 1. (*a*) Electron-density projection down (001). The contours are at intervals of 1 e.Å^{-2}, for C, O, and at 2 e.Å^{-2} for sulphur, the lowest contour being the two electron line. (*b*) Electron-density projection down (100). The contours are at intervals of 2 e.Å^{-2} starting at the two electron line.

The normal process of calculation and refinement was applied using James & Brindley's atomic scattering factors (*Internationale Tabellen zur Bestimmung von Kristallstrukturen*) and an isotropic temperature factor of 2·9 Å^{-2} for the $hk0$ reflections and 2·5 Å^{-2} for the $0kl$ reflections until the correlation factor R was reduced to 0·20. At this stage calculations were changed to use Berghuis & MacGillavry (1955) scattering factors, hydrogen positions were calculated and the strongest reflections in the $hk0$ zone (110, 200, 220, 330) which showed F_c much greater than F_o were considered as suffering from extinction, that is the F_c values were used in the calculation of Fourier maps. The difference maps (ΔF) showed a degree of anisotropy the in $hk0$ zone (coefficient along the b axis 2·2 Å^{-2} and along the a axis 3·6 Å^{-2}) but it was felt that because of the small number of measured intensities in both zones (47 and 46) there was little point in continuing with the anisotropic temperature factor refinement although R was thereby reduced to 0·113 for the $hk0$ zone. The best fit for the y co-ordinates from each projection and a common temperature factor were chosen (3·0 Å^{-2}) and the final parameters taken from the two derived Fourier projections. These co-ordinates are listed in Table 1 and the two Fourier summations in Fig. 1(*a*) and (*b*). The correlation factor R

$$R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$$

and R^* (which includes unobserved reflections, giving them an average value of one half that of the smallest observed intensity) were 0·149 and 0·168 respectively for the $hk0$ zone and 0·145 and 0·170 respectively for the $0kl$ zone. Bond lengths and angles are recorded in Table 2, and observed and calculated structure factors in Table 3. The uncertainties in bond lengths were calculated by the method of Cruickshank (1949*a*, *b*) and from the ΔF maps. The figures in parenthesis are the standard deviations of bond lengths if a weighting factor of 2 is given to the uncertainties of the $0kl$ projection. However, from a consideration of the ΔF maps during the refinement process it seemed more probable that the uncertainties in the positions of the atoms is of the same order in each projection, and the standard deviations given were calculated on this basis.

Table 2. *Bond lengths and bond angles*

S_1–O_1	$1{\cdot}43\ \pm 0{\cdot}02$ Å	(0·05 Å)	C_1–S_1–O_1	111·4° ± 1°
S_2–O_2	$1{\cdot}40\ \pm 0{\cdot}02$	(0·05)	C_1–S_1–C_2	96·6 ± 1
S_1–C_1	$1{\cdot}78_6 \pm 0{\cdot}03$	(0·08)	C_3–S_2–C_4	97·6 ± 1
S_2–C_3	$1{\cdot}77_2 \pm 0{\cdot}03$	(0·08)	C_3–S_2–O_2	109·4 ± 1
C_1–C_3	$1{\cdot}47_4 \pm 0{\cdot}04$	(0·09)	S_1–C_2–C_4	113·2 ± 1
			S_2–C_3–C_1	112·6 ± 1

Discussion

The stereochemistry of sulphur in the sulphoxide grouping is fairly well established, and the average

Table 3. *Observed and calculated structure factors* (×10)

*hk*0	F_o	F_c
010	<11	4
020	78	49
030	<19	21
040	30	11
050	50	20
060	296	−271
070	34	7
080	81	−71
090	<31	0
0,10,0	67	55
110	291	−428
120	163	132
130	298	−333
140	154	138
150	179	−141
160	101	84
170	144	122
180	51	40
190	148	122
1,10,0	<26	16
200	256	−402
210	<18	−3
220	358	−586
230	<22	−17
240	217	206
250	<29	−17
260	198	185
270	<33	−6
280	62	65
290	<30	0
2,10,0	34	−27
310	<22	4
320	82	−83
330	329	435
340	93	−95
350	<30	24
360	49	−62
370	81	−90
380	34	−32
390	109	−92
400	328	437
410	<27	2
420	163	195
430	<29	11
440	47	−70
450	<33	11
460	160	−166
470	<33	4
480	44	−47
490	<24	0
510	208	−228
520	<31	43
530	91	−113
540	<33	52
550	101	−100
560	<33	38
570	84	85
580	<25	21
600	226	−276
610	<34	−1
620	72	−81
630	<34	−6
640	35	38
650	<31	−6
660	89	107
710	<32	23
720	<31	−20
730	124	141
740	<29	−27
750	<25	16
800	37	74
810	<25	0
820	96	97
830	<22	3
840	47	−57
0*kl*	F_o	$\lvert F_c \rvert$
011	387	346
021	460	495
031	137	135
041	211	180
051	29	28
061	46	48
071	124	124
081	163	171
091	95	73
0,10,1	54	25
002	206	191
012	233	263
022	80	89
032	180	179
042	156	171
052	78	63
062	70	125
072	163	156
082	<34	21
092	63	79
0,10,2	66	58
*hk*0	F_o	$\lvert F_c \rvert$
013	260	307
023	<28	17
033	216	213
043	104	96
053	157	154
063	103	88
073	81	74
083	<31	16
093	80	71
004	99	118
014	259	223
024	103	120
034	50	31
044	36	39
054	116	138
064	<33	43
074	96	87
084	<26	8
094	<15	13
015	<34	20
025	63	87
035	125	156
045	<33	25
055	<31	23
065	<28	27
075	51	46
006	90	89
016	71	51
026	<29	38
036	<28	30
046	<25	38
056	<21	72

angle for C–S–O derived from this investigation (110°) is very close to the tetrahedral angle and to the average (107°) of the angles measured for other sulphoxides (Abrahams, 1956). The length of the S–O bond is of some interest. The accepted value of this bond is 1·44 Å (Jeffrey & Stadler, 1951) and a molecular orbital analysis of the sulphur–oxygen bond was carried out by Moffitt (1950). The average value from this determination (1·415 Å) is close to that predicted from the bond orders as calculated by Moffitt (1·425 Å).

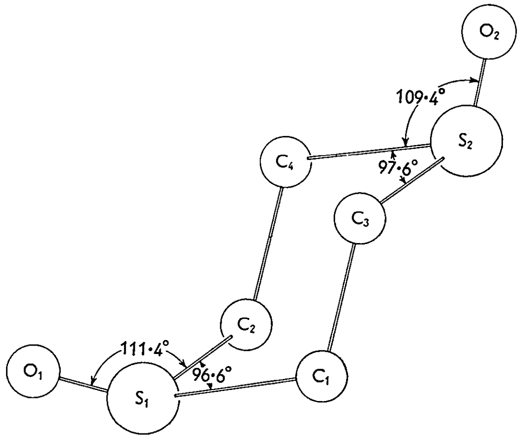

Fig. 2. Molecule of β dithiane disulphoxide.

The bond lengths and angles of the dithiane ring agree well with those already published by Marsh (1955). The S–C bond is equal to the sum of the covalent radii of sulphur and carbon. The shorter C–C bond (1·47 Å) also agrees with Marsh's value (1·49 Å) but is somewhat shorter than that given by Hassel & Viervoll (1·54 Å).

Table 4. *Intermolecular distances*

S–S	4·45 Å	C–C	4·13 Å
S–C	3·94	C–O	3·51
S–O	3·86	O–O	4·45

The shortest intermolecular distances between various types of atoms are listed in Table 4.

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The Crystal Structure of Eosphorite

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The crystal structure of eosphorite, $AlPO_4.(Mn, Fe)(OH)_2.H_2O$, is described with reference to the pseudo-orthorhombic space group *Bbam* with

$$a=10\cdot52,\ b=13\cdot60,\ c=6\cdot97\ \text{Å},\ Z=8\ .$$

The structure was determined by inspection of some Patterson sections, and refined with the aid of three-dimensional differential syntheses. In the structure described there are two parallel sets of infinite chains, one composed of $(Mn, Fe)O_4(OH)_2$ octahedra sharing opposite O–O edges, and the other of $AlO_2(OH)_2(H_2O)_2$ octahedra sharing opposite H_2O corners. These chains alternate, sharing OH corners to form a set of parallel sheets held together by phosphorus ions in tetrahedral coordination of oxygen ions.

Introduction

Crystallographic studies of the childrenite–eosphorite series of minerals ($AlPO_4.(Mn, Fe)(OH)_2.H_2O$) have revealed a contradiction between optical and X-ray diffraction data. Barnes (1949), on the evidence of X-ray diffraction photographs and the report of a small but measurable piezoelectric effect, concluded that childrenite was orthorhombic *Bba*2. However, Hurlbut (1950), on consideration of optical properties, has concluded that these minerals should be classified as monoclinic (pseudo-orthorhombic) with $\beta=90°\ 00'$. Barnes & Shore (1951) have critically re-examined the X-ray diffraction evidence for eosphorite, employing very long X-ray exposures in order to record weak reflections. They have found no evidence of any departure from the space group *Bba*2 (or *Bbam*).

In the present paper a structure will be described which is consistent with the space group *Bbam*. However, certain anomalies of electron density suggest that the structure is only approximate.

Experimental details

The specimen of eosphorite examined was from Newry, Maine. In this specimen the ratio of manganese to iron is about 2 to 1 (Hurlbut, 1950). From single-crystal photographs the crystal appears to be orthorhombic *Bba*2 or *Bbam*, with

$$a=10\cdot52\pm0\cdot04,\ b=13\cdot60\pm0\cdot05,\ c=6\cdot97\pm0\cdot03\ \text{Å}.$$

Also,

D_x (calculated density) $=3\cdot04$ g.cm.$^{-3}$ ($Z=8$)
D_o (measured density) $=3\cdot07$ g.cm.$^{-3}$ (Hurlbut, 1950)
$\mu=33\cdot5$ cm.$^{-1}$ (Mo $K\alpha$) .

The crystal selected for data collection was a rectangular solid $0\cdot17\times0\cdot17\times0\cdot85$ mm., with the long axis parallel to **c**.

Three-dimensional intensity data were recorded on *z*-axis Weissenberg photographs, with molybdenum radiation, for values of *l* up to 12. The equi-inclination setting was used for upper levels, and the correlation of the data was accomplished by means of a double-slit technique. A few reflections on and near the *z**-axis were not recorded by this procedure, and some of these were obtained from precession photographs of the same crystal.

Intensities were estimated visually by comparison with a standard wedge. Corrections were made, where necessary, for distortion of spots on upper-level photo-