Acta Chemica Scandinavica A 32 (1978)163 – 168

Crystal Structure of 1-Methylsulfonyl-2-methylsulfoxyethane, A Case of Chiral Disorder

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The structure was refined in space group $P\bar{1}$ with $a=5.511(4)$, $b=5.308(2)$, $c=7.478(6)$ Å, $\alpha=93.98(2)$, $\beta=101.72(3)$, $\gamma=116.34(2)°$ and $Z=1$. Two equivalent sets of counter data were collected to a limit in $\sin\theta/\lambda$ of 0.704 $Å^{-1}$, corrected for absorption and averaged. The final R was 0.050 after full-matrix least-squares refinement based on 993 F_o. Both chiral forms of the molecule are present in the crystal, and superimposed sulfoxide and sulfone groups give rise to an apparent centrosymmetric molecule with partial atomic disorder. Bond lengths and angles involving sulfur in this averaged structure are changed relative to the corresponding parameters of the parent di-sulfoxide, in agreement with theory. A short central C – C bond of 1.515 Å is a common feature of the two molecules.

The structure of the title compound was determined as part of our studies on oxygenated 1,2-bis(methylthio)ethanes. These small sulfur-containing molecules are interesting structurally because they allow, *a priori*, a systematic investigation of changes in electronic structure with changes in the oxidation state and hybridization of sulfur. A structure analysis of the first compound in the series, *meso*-ethane-1,2-bis(methyl sulfoxide), hereinafter called DIOX, was reported previously.[1]

EXPERIMENTAL

1-Methylsulfonyl-2-methylsulfoxyethane, hereinafter OXON, was available.[2] The molecule has one chiral centre, both enantiomers exist in solution. Thin, plateformed crystals were grown from methanol. Preliminary Weissenberg photographs showed triclinic symmetry with **c*** orthogonal to the face of the plate. The diffraction spots at low 2θ angles frequently contained short streaks in the ω direction; for some specimens the spots also were slightly blurred in certain regions of reciprocal space. These features were not of the magnitude and systematic nature typical, for instance, of disordered structures of the OD type,[3] nor were there systematically weak reflections to indicate that any of the axes should be doubled. We infer, however, that other lattice defects were present to a varying extent in all examined specimens. A crystal $0.55\times0.26\times0.065$ mm was used for the X-ray measurements.

Collection and processing of intensities. Cell dimensions were obtained from the setting angles of 19 reflections, and centring of these reflections was repeated five times during and after data collection. The cell parameters in Table 1 are averages; standard deviations reflect the spread in each set of measurements. All cell axes increased slightly during data collection. The OXON cell is very similar to that of DIOX (*cf.* Table 1). However, crystals of the former were much more stable under X-radiation. The intensities of 2305 reflections comprising the two sets $\pm h+k\pm l$ and $\pm h-k\pm l$ were measured without attenuators to a 2θ-limit of 60° with Nb-filtered Mo$K\alpha$-radiation on a Picker diffractometer controlled by the Vanderbilt disk-oriented program system.[4] The scan mode was $\omega/2\theta$ at 2° min^{-1} in 2θ, basic scan width was $2\theta(\alpha_1)-1.45°$ to $2\theta(\alpha_2)+1.5°$, and backgrounds were measured for 20 s at each limit of the scan. Intensities below $2\theta=18.5°$ were remeasured with reduced low-angle scan widths to minimize errors caused by the NbK absorption edge. Three standard reflections were monitored at intervals of 60 reflections. The data were scaled with a polynomial fit to the average standard decay and were also corrected for coincidence loss.[5,6] The experimental recovery constant with this particular

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Table 1. Crystal data of 1-methylsulfonyl-2-methylsulfoxyethane (OXON) and *meso*-ethane-1,2-bis(methyl sulfoxide)[1] (DIOX).

	OXON	DIOX
Composition	$C_4H_{10}S_2O_3$	$C_4H_{10}(SO)_2$
F.W.	170.25	154.25
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	5.511(4)	5.305(4)
b	5.308(2)	5.261(3)
c	7.478(6)	7.280(8)
α (°)	93.98(2)	94.79(4)
β	101.72(3)	98.87(7)
γ	116.34(2)	116.22(2)
Z	1	1
D_x (g cm^{-3})	1.50	1.44
λ (Å)	0.71069	1.5418
μ (cm^{-1})	6.17	59.0
M.p. (°C)	136–137	174–175

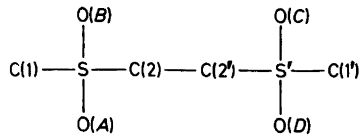
crystal was 1.9×10^{-8} counts^{-1}. Absorption coefficients were in the range 1.162 to 1.041, and corrections were applied to the intensities with a modified version of the program ABSOR[7] which is based on the analytical method.[8]

Weighted averages of F^2 and $\sigma(F^2)$ were calculated from pairs of equivalents, averages of four measurements were used for the $h0l$ reflections. For an F_i^2: $\sigma(F_i^2)=\sigma(I_i)(\mathrm{Lp})^{-1}(\mathrm{scale})$ and $\sigma^2(I_i)=\sigma^2_{i\,\mathrm{count}}+(SI_{i\,\mathrm{net}})^2$; $i=1, 2$. The agreement index $D=\Sigma|F_1^2-F_2^2|/\Sigma F^2_{\mathrm{ave}}$, was 0.035. The parameter S was adjusted to 0.015 to make the weighted mean of the differences $\Delta_i=|F_i^2-F^2_{\mathrm{ave}}|$ follow a normal distribution. Of the 1100 averaged intensities, 13 at low 2θ were deleted because the NbK edge interfered with the peak itself. Another 94 reflections with $F^2<\sigma(F^2)$ were given zero weight.

Programs used for analyses and corrections of the data are described elsewhere.[9] Other crystallographic programs were from the X-RAY 76 system.[10] Molecular drawings were made with ORTEP.[11]

STRUCTURE DETERMINATION AND REFINEMENT

Since the OXON molecule has no inherent centrosymmetry and $Z=1$, space group $P1$ was assumed. The two S atoms were placed according to the S–S vector peak in the Patterson map. A ΔF map showed the positions of all C atoms with densities of about 6 e Å^{-3} and maxima corresponding to O(A) and O(C) (see Formula 1) of densities about



8 e Å^{-3}. In addition, there were two weaker maxima, approximately 4 e Å^{-3}, for a fourth atom bonded in a tetrahedral arrangement about each S. These peaks were less well-defined, a ridge of density extending from each (assigned O(B) and O(D), respectively) towards the nearest S position. Isotropic refinement of all non-H atoms excluding O(B) and O(D) gave a crystallographic R index $(=\Sigma\|F_o|-K|F_c\|/\Sigma|F_o|)$ of 0.24. Refinements without O(B) but with unit weight for O(D), and *vice versa*, gave $R=0.19$, and the densest maximum in subsequent ΔF maps appeared in the position of the absent O(B), respectively O(D) atom. A model with half weight assigned to both O(B) and O(D) refined to $R=0.18$, and anisotropic refinement of this model reduced R to 0.06. We ascribe these results to the presence of both chiral forms of OXON in the crystal. In the averaged X-ray structure, sulfoxide and sulfone groups superimpose, but not exactly, because their common structural features are not identical, and partial disorder arises. The drastic drop in R following anisotropic refinement lends support to this interpretation. Non-centrosymmetric refinement including isotropic H atoms did not converge properly. At an R of 0.043 there were several physically untenable bond lengths, thermal parameters and, for O(B) and O(D), population parameters. Correlation coefficients between parameters related by a pseudo-centre of symmetry were in the range 0.60–0.95, average 0.83.

The strong correlation clearly favours refinement of a structure with a centre of symmetry in the C–C bond. A starting model including all non-H atoms was shifted accordingly. Anisotropic refinement in $P\bar{1}$ also gave $R=0.06$. Symmetry restricts the population parameter of O(2) to 0.5; see Fig. 1 for final atomic numbering. Further full-matrix least-squares refinement of 66 parameters which include isotropic H atoms was based on 993 F_o with weights $w=1/\sigma^2(F_o)$. The final maximum parameter shift was less than 5×10^{-3} of the corresponding e.s.d., $R=0.050$ and $R_w\{=[\Sigma w(|F_o|-K|F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}}\}=0.041$.

Several more elaborate models were tried in order to describe the disorder more completely. The

Table 2. Final atomic parameters. Thermal parameters, U_{ij}(Å$^2 \times 10^4$) for C, O and S, and U(Å$^2 \times 10^4$) for H, are defined by: $\exp[-2\pi^2(U_{11}a^{*2}h^2+\cdots+2U_{12}a^*b^*hk+\cdots)]$ and $\exp[-8\pi^2U(\sin^2\theta/\lambda^2)]$, respectively. E.s.d.'s appear in parentheses.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.6442(5)	0.3475(5)	0.3068(4)	459(12)	373(12)	600(15)	77(9)	−74(11)	90(11)
C(2)	0.1471(4)	0.1217(4)	0.0398(3)	428(10)	256(9)	498(12)	170(8)	26(9)	67(9)
O(1)	0.3360(3)	−0.2060(3)	0.1937(2)	617(9)	316(8)	825(11)	256(7)	−69(8)	75(8)
O(2)	0.1583(6)	0.0418(7)	0.3712(4)	562(17)	585(20)	453(16)	187(15)	152(14)	137(15)
S	0.3079(1)	0.0488(1)	0.2481(1)	451(3)	291(3)	521(3)	140(2)	−32(2)	59(2)

Atom	x	y	z	U	Atom	x	y	y	U
H(11)	0.733(5)	0.358(5)	0.199(4)	595(70)	H(21)	0.263(4)	0.152(4)	−0.044(3)	388(55)
H(12)	0.612(6)	0.519(7)	0.327(4)	865(90)	H(22)	0.133(5)	0.267(6)	0.071(3)	545(68)
H(13)	0.742(6)	0.318(6)	0.399(4)	761(86)					

best of them involved two anisotropic S atoms with population parameters fixed at 0.5. The number of variables increased from 66 to 75, corresponding final values of R and R_w were 0.040 and 0.031, respectively. Straightforward application of Hamilton's R-test[12] classifies this as a significant improvement; however, parameters of the two S atoms were strongly correlated and there were obvious inconsistencies in their U_{ij} values. We believe, therefore, that this model is not a better description physically; it is mainly useful in showing that the S positions of the disordered end groups are too close to be resolved in a meaningful way by the least-squares technique. Rae[13] has described a modified least-squares method by which a pseudo-centrosymmetric structure may be refined in a non-centrosymmetric space group. While this scheme might have made refinement in $P1$ possible, the problem of partial atomic disorder still remains.

Only results from the normal refinement in $P\bar{1}$ will be discussed in the following. Final coordinates and thermal parameters from this refinement are in Table 2. A list of structure factors is available from the authors. Scattering factors were those of Doyle and Turner[14] except for H.[15] Anomalous dispersion corrections[16] were applied for S.

RESULTS AND DISCUSSION

The averaged structure of OXON is shown in Fig. 1. Table 3 gives bond lengths and angles together with some corresponding values of DIOX. The fact that H parameters can be refined to give reasonable X-ray values of C−H bond lengths and angles seems to justify a more detailed discussion of the structure. The apparent shortening of the S−O(2) bond can be attributed largely to the elongated density between these atoms in the first ΔF map. Valency angles and the bond involving O(2) will not be considered in comparing parameters of OXON and DIOX.

A short C−C bond in DIOX, also found in a number of related structures, was explained[1] as a secondary effect of rehybridization of the S atom. A set of general rules relating properties of chemical bonds and the degree of hybridization were for-

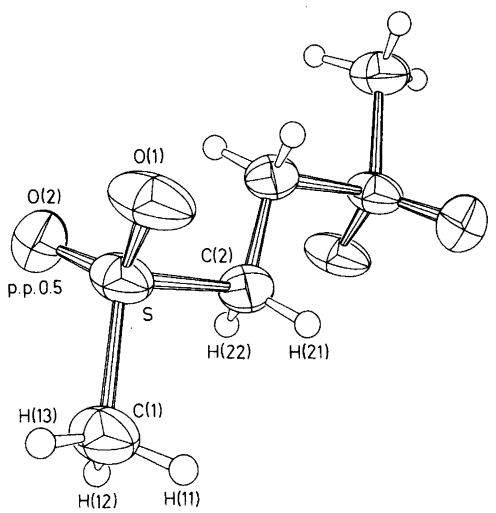


Fig. 1. Averaged centrosymmetric conformation and atomic numbering of OXON. Thermal ellipsoids correspond to a 50 % probability.

Table 3. Bond lengths and angles of OXON, some relevant values of DIOX[1] are also given. E.s.d.'s of the parameters are in parentheses.

Bond lengths (Å)

	OXON	DIOX		OXON
S–C(1)	1.762(2)	1.788(2)[a]	C(1)–H(11)	1.02(3)
S–C(2)	1.786(3)	1.802(2)	C(1)–H(12)	1.01(4)
S–O(1)	1.468(2)	1.501(2)[a]	C(1)–H(13)	0.85(3)
S–O(2)	1.347(4)		C(2)–H(21)	0.95(3)
C(2)–C(2′)	1.515(3)	1.516(2)	C(2)–H(22)	0.83(3)

Bond angles (°)

	OXON	DIOX
C(1)–S–C(2)	100.7(1)	97.0(1)
C(1)–S–O(1)	108.2(1)	106.8(1)
C(1)–S–O(2)	113.5(2)	
C(2)–S–O(1)	106.5(1)	106.3(1)
C(2)–S–O(2)	107.3(2)	
O(1)–S–O(2)	118.9(2)	
S–C(2)–C(2′)	109.2(2)	109.4(1)

	OXON		OXON
S–C(1)–H(11)	110(1)	S–C(2)–H(21)	109(1)
S–C(1)–H(12)	105(2)	S–C(2)–H(22)	106(2)
S–C(1)–H(13)	107(2)	C(2′)–C(2)–H(21)	113(1)
H(11)–C(1)–H(12)	110(3)	C(2′)–C(2)–H(22)	108(2)
H(11)–C(1)–H(13)	108(3)	H(21)–C(2)–H(22)	112(2)
H(12)–C(1)–H(13)	117(3)		

[a] 'Minimum' corrections[22] applied to these bonds are in the range 0.001 to 0.002 Å.

mulated by Walsh[17] and further extended and substantiated by Bent.[18,19] According to the theory, substitution of the lone pair (formally an atom of zero electronegativity) at S in sulfoxide with the strongly electronegative O in sulfone will effect less *p* character in all σ-bonds from S. Decreasing *p* character implies shorter bonds and larger valency angles. Table 3 shows that all bonds involving S are shorter and all valency angles at S, except one, are larger in the averaged structure of OXON, in agreement with the theory. The C(2)–S–O(1) angles are equal. Theory also predicts that the primary rehybridization is relayed in an attenuated manner throughout the bonded system.[19] Thus, if these molecules were purely σ-bonded systems, one would expect shortening of the C–C bond next to S, the magnitude increasing from DIOX to OXON. Both angles S–C(2)–C(2′) and bonds C(2)–C(2′) are equal in the two compounds, however. Interestingly, this bond length is unchanged, 1.515 Å, in the fully oxygenated di-sulfone.[20]

The final ΔF map calculated in the S–C(2)–C(2′) plane (Fig. 2) shows surprisingly well-defined deformation density in the C(2)–C(2′) bond. There are similar features in both S–C bonds. Excess density of about 0.4 e Å^{-3} in the S position is evidence of residual disorder not accounted for by the refinement. In the ΔF map through O(1)–S–O(2) (not shown) both O positions are on zero density level.

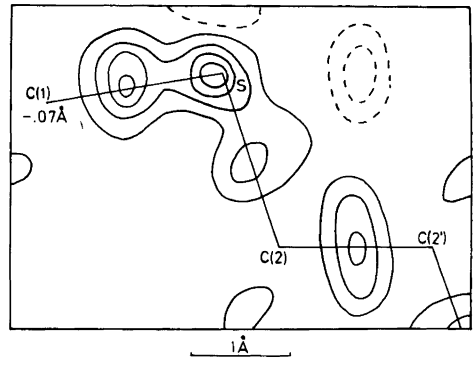


Fig. 2. Residual electron density calculated in the plane S–C(2)–C(2′). Atom C(1) is 0.07 Å below this plane. Contours are at intervals of 0.10 e Å^{-3}; solid lines are positive, broken lines negative. Zero contour is not shown.

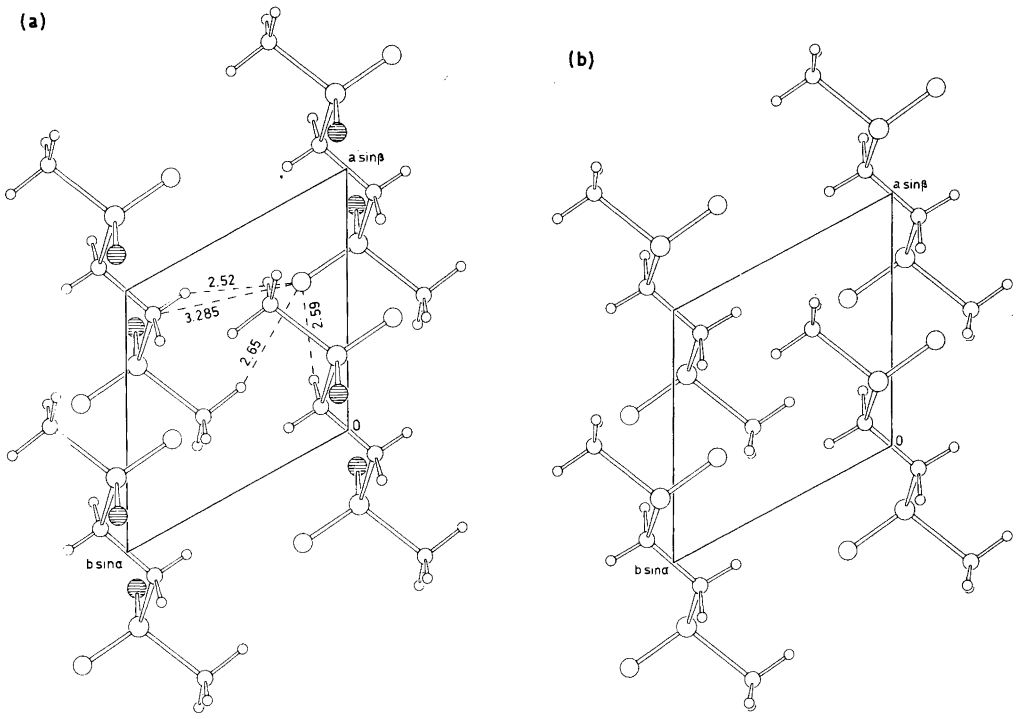


Fig. 3. Molecular packing of OXON (a) and DIOX (b) as seen down c. In the packing diagram of OXON, the oxygen site of 50 % occupancy is hatched and some short intermolecular contacts are given.

Fig. 3(a) shows the molecular packing of OXON. O(1) participates in three intermolecular van der Waals contacts with atoms of the methyl and methylene groups, the shortest distance being O(1)···H(22) at $x,y-1,z$, 2.52 Å. There are two normal contacts between O(2) and C(1) in symmetry-related molecules. In addition, O(2) makes one short contact with its centrosymmetrically related partner in the half-molecule at $-x,-y,1-z$. The distance, 2.783 Å, is significantly less than a normal O···O van der Waals contact, 3.05 Å,[21] and it is further shortened if a normal S–O(2) bond length is assumed. In view of this, a random distribution of both chiral forms throughout the crystal appears to be energetically unfavourable. A more plausible model of the disorder involves a block structure, each block containing ideally only one or the other enantiomer. The short O···O contact then would occur only at the boundaries between blocks in the c* direction. The weak attractive forces along c* are reflected in the mechanical strength and shape of the crystals.

Both the conformation and packing of the molecules are very similar in the OXON and DIOX structures, *cf.* Figs. 3(a) and 3(b). Crystals of DIOX were unstable under X-radiation, the *a* and *c* axes increasing almost linearly with exposure, the angle α contracting and β expanding.[1] The signed shifts suggest (*cf.* Table 1) that the proposed autoxidation of sulfoxide groups may involve a transformation of DIOX into OXON in the solid state.

"Norges Tekniske Høgskoles Fond" is thanked for a grant to F.M.

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Received September 5, 1977.