

Table 3. Deviations of atoms from the least-squares plane through the TTF ring system

Atom	Deviation†
S(1), S(1')	+, -0.004 Å
S(2), S(2')	-, +0.003
C(1), C(1')	-, +0.008
C(2), C(2')	+, -0.008
C(3), C(3')	0.000
C(4), C(4')	-, +0.030*
C(5), C(5')	+, -0.157*
r.m.s. deviation	0.006

* Atoms not used in calculating the least-squares plane.

† The equation of the least-squares plane of the TTF ring system is

$$-0.5258x + 0.9032y + 0.1401z = 2.4822 \text{ \AA.}$$

The crystal structure of TCMTTF is illustrated in Fig. 2. It can be seen that the molecules pack to form a layered structure but that there is little overlap between rings of neighboring molecules in adjacent layers. There are no abnormal intermolecular contacts in the structure.

Acta Cryst. (1976). B32, 274

(2*RS*,*SRS*)-3-Methyl-3-phenylsulphinylbutan-2-ol

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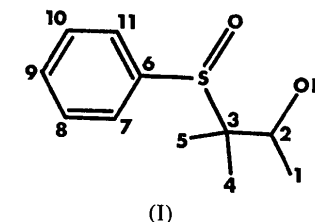
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(Received 22 August 1975; accepted 10 September 1975)

Abstract. $C_{11}H_{16}O_2S$, $M = 212.31$, monoclinic, $P2_1/c$, $a = 6.104$ (4), $b = 7.952$ (5), $c = 23.057$ (8) Å, $\beta = 92.22$ (3)°, $V = 1118.3$ Å³, $Z = 4$, $D_x = 1.261$ g cm⁻³. The structure was solved by direct methods and refined by full-matrix least-squares calculations to $R_w = 0.037$ for 1282 unique reflexions measured on a diffractometer.

Introduction. As part of a continuing study of stereo-specific rearrangements (Allen, Kennard, Nassimbeni, Shepherd & Warren, 1974) we have performed an X-ray analysis of 3-methyl-3-phenylsulphinylbutan-2-ol (I) in order to establish the relative stereochemistry of the chiral centres C(2) and S.



The data were collected with Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) and graphite crystal monochromator on a Stoe STADI-4 four-circle diffractometer (at Darmstadt). A stationary background - θ - ω scan - stationary background technique was employed, with fixed counting times which were increased for shells of increasing θ . 3114 reflexions were measured up to $2\theta = 55^\circ$, of which 1576 with $I < 2\sigma(I)$ were accepted as observed. Equivalent reflexions were averaged to give 1282 unique observations. Unit-cell parameters were

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We wish to thank Drs M. P. Cava and M. V. Lakshmintham for graciously providing the crystals of TCMTTF. This study was supported, in part, by NSF Grant No. DMR72-03025 and by a grant from the International Research and Exchanges Board.

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Table 1. Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^4$) for the non-hydrogen atoms

Estimated standard deviations are in parentheses. $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{23}b^*c^*kl + 2U_{13}a^*c^*hl + 2U_{12}a^*b^*hk)]$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
S(1)	4234 (1)	4378 (1)	1180 (1)	427 (4)	554 (5)	351 (3)	-71 (5)	74 (3)	-96 (5)
O(1)	3414 (4)	6035 (3)	940 (1)	943 (20)	453 (16)	413 (11)	40 (11)	199 (13)	-66 (15)
O(2)	5417 (4)	2792 (3)	126 (1)	460 (15)	694 (17)	381 (13)	39 (12)	98 (11)	-36 (14)
C(1)	1936 (9)	1766 (6)	-259 (2)	717 (31)	750 (33)	400 (19)	-61 (20)	11 (20)	-186 (28)
C(2)	3111 (6)	2978 (4)	159 (1)	432 (20)	431 (20)	335 (15)	22 (14)	2 (14)	-32 (18)
C(3)	2568 (5)	2707 (4)	799 (1)	378 (18)	419 (19)	326 (15)	6 (14)	22 (13)	-36 (16)
C(4)	3372 (8)	1031 (5)	1037 (2)	727 (28)	443 (24)	410 (19)	66 (16)	82 (19)	22 (21)
C(5)	140 (6)	3001 (6)	886 (2)	342 (21)	769 (31)	541 (22)	-57 (22)	30 (17)	-72 (23)
C(6)	3208 (5)	4288 (4)	1896 (1)	447 (18)	438 (18)	325 (13)	-28 (16)	15 (13)	-53 (19)
C(7)	4333 (6)	3362 (5)	2320 (1)	538 (23)	570 (24)	402 (17)	-66 (17)	-51 (17)	79 (21)
C(8)	3605 (7)	3381 (5)	2885 (1)	847 (31)	533 (24)	412 (18)	54 (18)	-121 (21)	45 (24)
C(9)	1802 (7)	4294 (6)	3019 (1)	795 (26)	662 (24)	320 (16)	-22 (19)	85 (17)	-7 (27)
C(10)	706 (7)	5240 (5)	2599 (1)	694 (27)	680 (27)	408 (18)	-39 (18)	128 (18)	117 (23)
C(11)	1419 (6)	5245 (5)	2036 (1)	582 (23)	539 (24)	377 (16)	8 (15)	38 (16)	137 (20)

obtained by least squares from diffractometer measurements for 20 strong reflexions. The structure was solved by a multiresolution sign expansion technique (Sheldrick, 1975). The 14 non-hydrogen atoms were located from the highest 15 peaks of the *E* map corresponding to the best sign set. Anisotropic refinement of all C, O and S atoms converged to $R=0.083$. All 16 H atoms were located in a subsequent difference map, and were refined successfully without any constraints. The refinement converged to $R_w=0.037$ where $R_w = \sum w^{1/2}|F_o - F_c| / \sum w^{1/2}|F_o|$ and $w = 1/\sigma^2(F)$; the corresponding *R* was 0.043. Final positional and thermal parameters are presented in Tables 1 and 2.* These results were preferred to those obtained employing an $I > 3\sigma(I)$ acceptance criterion, where, although the *R* indices were lower ($R=0.037$, $R_w=0.034$), the standard deviations were slightly higher.

* A list of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31352 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Fractional atomic coordinates ($\times 10^3$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for the hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
H(11)	243 (5)	198 (4)	-63 (1)	54 (10)
H(12)	236 (6)	52 (5)	-17 (1)	63 (11)
H(13)	457 (7)	188 (5)	-29 (2)	82 (15)
H(21)	271 (5)	420 (4)	38 (1)	43 (8)
H(41)	312 (5)	93 (4)	145 (1)	59 (10)
H(42)	491 (7)	89 (5)	100 (2)	82 (14)
H(43)	272 (7)	3 (5)	83 (2)	85 (14)
H(51)	-25 (5)	276 (4)	129 (1)	58 (10)
H(52)	-25 (6)	409 (5)	75 (2)	76 (14)
H(53)	-69 (6)	205 (4)	65 (1)	66 (11)
H(71)	566 (6)	281 (5)	222 (2)	61 (11)
H(81)	430 (6)	275 (5)	317 (2)	75 (12)
H(91)	133 (6)	437 (5)	344 (1)	72 (10)
H(101)	-60 (6)	588 (5)	271 (2)	79 (13)
H(111)	70 (6)	591 (4)	175 (1)	61 (10)
H(O2)	580 (7)	310 (5)	-23 (2)	93 (15)

Discussion. Fig. 1 shows a view of the molecule and indicates that the relative stereochemistry may be described as (2*RS*, *SRS*). Final bond lengths and angles are shown in Tables 3 and 4. The S atom is pyramidal; the S=O and S-C_{ar} distances and the C-S-O angles are comparable with values found in 2-ethylsulphinyl-L-tryptophan (Hoppe, Gieren, Narayanan & Sturm, 1973) and (-)-*o*-carboxyphenyl methyl sulphoxide (Dahlén, 1974). S(1)-C(3) at 1.871 (3) Å and C(3)-S(1)-C(6) at 101.6 (1)° are, however, significantly larger than comparable values in either structure; the C-S-C angle in methyl sulphoxides, for example, is usually in the range 96-98° (Tranqui, Richard, Vicat & Fillion, 1974). These distortions are almost certainly due to the presence of the larger methylbutan-2-ol moiety instead of a methyl or ethyl group, as exemplified by the geometry found for the 2,3-dimethyl-2-butenyl-1,1,2-trimethylpropyl methylsulphonium ion (Barnes & Sundaralingam, 1973). Here the C-S distances increase with increasing size of the alkyl group, and the C-S-C angles follow the order of increasing steric interactions between neighbouring groups. It should be noted that the geometry in the present structure results in all S-C_β intramolecular non-bonded interactions lying in the narrow range 2.67-2.78 Å. Other geometric characteristics of the molecule are close to normal values.

Table 3. Bond lengths (Å)

S(1)-O(1)	1.507 (2)	C(1)-H(11)	0.94 (3)
S(1)-C(3)	1.871 (3)	C(1)-H(12)	1.04 (4)
S(1)-C(6)	1.790 (5)	C(1)-H(13)	0.91 (4)
C(1)-C(2)	1.524 (5)	C(2)-H(21)	1.03 (3)
C(2)-O(2)	1.421 (4)	C(4)-H(41)	0.96 (3)
C(2)-C(3)	1.539 (4)	C(4)-H(42)	0.95 (4)
C(3)-C(4)	1.515 (5)	C(4)-H(43)	1.00 (4)
C(3)-C(5)	1.521 (5)	C(5)-H(51)	0.98 (3)
C(6)-C(7)	1.384 (4)	C(5)-H(52)	0.95 (4)
C(7)-C(8)	1.394 (5)	C(5)-H(53)	1.06 (3)
C(8)-C(9)	1.364 (5)	C(7)-H(71)	0.95 (4)
C(9)-C(10)	1.379 (5)	C(8)-H(81)	0.92 (4)
C(10)-C(11)	1.386 (4)	C(9)-H(91)	1.02 (3)
C(11)-C(6)	1.380 (5)	C(10)-H(101)	0.99 (4)
		C(11)-H(111)	0.94 (3)
		O(2)-H(O2)	0.89 (4)

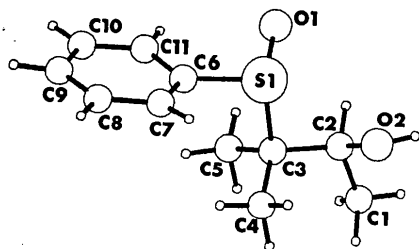


Fig. 1. Perspective view of the molecule indicating the relative stereochemistry.

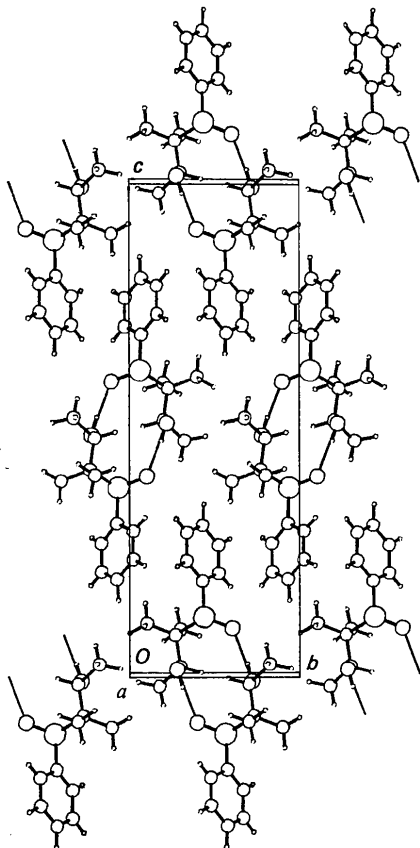


Fig. 2. Molecular packing viewed down *a*. Hydrogen bonds are indicated by weaker lines.

Table 4. Bond angles ($^{\circ}$)

O(1)—S(1)—C(3)	106.3 (1)	S(1)—C(3)—C(5)	110.1 (2)
O(1)—S(1)—C(6)	104.5 (2)	C(4)—C(3)—C(5)	113.0 (3)
C(3)—S(1)—C(6)	101.6 (1)	S(1)—C(6)—C(7)	119.4 (3)
C(1)—C(2)—O(2)	110.0 (3)	S(1)—C(6)—C(11)	120.1 (2)
C(1)—C(2)—C(3)	113.9 (3)	C(7)—C(6)—C(11)	120.3 (3)
C(3)—C(2)—O(2)	106.8 (3)	C(6)—C(7)—C(8)	119.1 (4)
C(2)—C(3)—S(1)	102.5 (2)	C(7)—C(8)—C(9)	120.5 (3)
C(2)—C(3)—C(4)	113.1 (3)	C(8)—C(9)—C(10)	120.3 (3)
C(2)—C(3)—C(5)	110.6 (3)	C(9)—C(10)—C(11)	119.9 (4)
S(1)—C(3)—C(4)	107.0 (2)	C(10)—C(11)—C(6)	119.8 (3)

The molecular packing is illustrated in Fig. 2. The molecules form centrosymmetric hydrogen-bonded dimers through O(2)—H(O2) \cdots O(1)' interactions. The O—H distances refined to 0.89 and 1.86 Å with an O \cdots O separation of 2.747 Å. The angle O(2)—H(O2)—O(1)' is therefore 174°. These figures are quite normal for this type of hydrogen bonding (Donohue, 1968; Hamilton & Ibers, 1968). Other intermolecular contacts correspond to van der Waals interactions.

We thank Dr S. Warren for suggesting the problem and for the crystals. All calculations were carried out on the University of Cambridge IBM 370/165 computer with programs written by Dr W. D. S. Motherwell and G.M.S.

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