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Structure of 2-(Methylsulphinyl)-1-phenylethanol, $C_9H_{12}O_2S$

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Abstract. $M_r = 185\cdot151$, monoclinic, $P2_1/a$, $a = 14\cdot897$ (1), $b = 5\cdot5956$ (2), $c = 12\cdot3195$ (7) Å, $\beta = 115\cdot02$ (2)°, $V = 930\cdot53$ (16) Å^3, $Z = 4$, $D_x = 1\cdot322$ Mg m^{-3}, $F(000) = 392$, Cu $K\alpha$ radiation, $\lambda = 1\cdot54184$ Å, μ(Cu $K\alpha$) = 26·84 cm^{-1}. Final $R = 0\cdot054$, $R_w = 0\cdot071$ for 1665 reflections. There is an intermolecular O—H···O hydrogen bond, in agreement with NMR spectroscopic measurements.

Introduction. The structure of the title compound has been determined and refined to reveal the relative configuration of the two chiral centres and also to compare the results with those obtained using ^{1}H NMR and ^{13}C NMR techniques.

Experimental. Samples provided by Dr Garcia-Ruano, Department of Organic Chemistry, Universidad Autónoma de Madrid, colourless crystal, 0·3 × 0·4 × 0·2 mm, mounted along **b**, room temperature, Philips PW 1100 automatic diffractometer, $\omega/2\theta$ scan, graphite-monochromated Cu $K\alpha$, 1680 reflections up to $\theta = 60°$, 1665 with $I > 2\sigma(I)$, Lp correction, absorption ignored; heavy-atom method, S atom position from a three-dimensional Patterson map, all other atoms in difference Fourier maps; anisotropic full-matrix least-squares, H isotropic, until changes $<0\cdot25\sigma$; $w = K/|f(F_o)|^2$ (Martínez-Ripoll & Cano, 1975), with $f(F_o) = 0\cdot26 + 0\cdot01|F_o|$ for $F_o \leq 7\cdot0$, $f(F_o) = -0\cdot04 + 0\cdot05|F_o|$ for $7\cdot0 < F_o \leq 13\cdot5$, $f(F_o) = -0\cdot77 + 0\cdot08|F_o|$ for $F_o > 13\cdot5$ and $K = 0\cdot55$; final $R = 0\cdot054$ and $R_w = 0\cdot071$, 12 reflections with significant secondary extinctions omitted in last cycles; scattering factors from *International Tables for X-ray Crystallography* (1974); calculations performed with the XRAY 70 system (Stewart, Kundell & Baldwin, 1970).*

Discussion. The molecular structure and atom numbering are given in Fig. 1, positional parameters in Table 1 and bond distances and angles and torsion angles in Table 2.

The phenyl ring is planar in the limit of experimental error. Averaged phenyl C—C bond lengths of 1·383 (4) Å are in close agreement with the generally accepted value of 1·39 Å. The independent C—H bonds have average values of 0·97 (4) Å which are in agreement with values determined in other compounds (Churchill, 1973; Baumgarten, McMahan, Elia, Gold, Day & Day, 1976; Cotton, Day, Hazen & Larsen, 1973).

Values of 1·423 (3) Å for the C(7)—O(2) bond as well as 0·99 (5) Å for the O(2)—H(2O) bond are typical X-ray values for single bonds from oxygen to

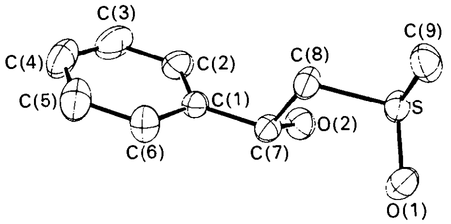

Fig. 1. *ORTEP* drawing (Johnson, 1965) of the molecule.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2 × 10^4) *for non-hydrogen atoms*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j\cos(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	$U_{\rm eq}$
S	1·10681 (3)	0·29648 (9)	0·89864 (4)	368 (3)
O(1)	1·10914 (12)	0·3441 (3)	1·01992 (13)	484 (6)
O(2)	0·95367 (11)	−0·0742 (3)	0·84245 (13)	428 (6)
C(1)	0·80727 (14)	0·1714 (4)	0·72777 (16)	331 (7)
C(2)	0·77126 (16)	−0·0032 (4)	0·64095 (19)	442 (8)
C(3)	0·67614 (20)	0·0133 (5)	0·5508 (2)	580 (10)
C(4)	0·61685 (19)	0·2049 (5)	0·5469 (2)	580 (10)
C(5)	0·65216 (18)	0·3806 (5)	0·6348 (2)	550 (10)
C(6)	0·74724 (16)	0·3636 (4)	0·7244 (2)	432 (8)
C(7)	0·91281 (14)	0·1600 (4)	0·82559 (16)	333 (7)
C(8)	0·97871 (15)	0·3196 (4)	0·79022 (18)	372 (7)
C(9)	1·14891 (17)	0·5661 (5)	0·8578 (2)	483 (9)

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38093 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 2. *Molecular geometry*

(*a*) Intramolecular distances (Å)

C(1)–C(2)	1·379 (3)	C(2)–H(2)	1·02 (3)
C(2)–C(3)	1·385 (3)	C(3)–H(3)	0·95 (4)
C(3)–C(4)	1·377 (4)	C(4)–H(4)	0·95 (4)
C(4)–C(5)	1·385 (4)	C(5)–H(5)	0·97 (3)
C(5)–C(6)	1·386 (3)	C(6)–H(6)	1·02 (3)
C(6)–C(1)	1·388 (3)	C(7)–H(7)	0·96 (3)
C(1)–C(7)	1·525 (2)	C(8)–H(81)	1·01 (4)
C(7)–C(8)	1·521 (3)	C(8)–H(82)	1·00 (3)
C(7)–O(2)	1·423 (3)	C(9)–H(91)	0·97 (4)
C(8)–S	1·813 (2)	C(9)–H(92)	0·89 (4)
C(9)–S	1·786 (3)	C(9)–H(93)	0·94 (4)
O(1)–S	1·504 (2)	O(2)–H(2O)	0·99 (5)

(*b*) Intramolecular angles (°)

C(1)–C(2)–C(3)	120·3 (2)	H(7)–C(7)–C(1)	111 (1)
C(2)–C(3)–C(4)	120·2 (3)	H(7)–C(7)–C(8)	108 (1)
C(3)–C(4)–C(5)	119·8 (3)	H(7)–C(7)–O(2)	108 (1)
C(4)–C(5)–C(6)	119·9 (3)	H(2O)–O(2)–C(7)	108 (2)
C(5)–C(6)–C(1)	120·2 (2)	H(81)–C(8)–C(7)	112 (2)
C(6)–C(1)–C(2)	119·4 (2)	H(81)–C(8)–S	106 (2)
C(2)–C(1)–C(7)	121·1 (2)	H(81)–C(8)–H(82)	109 (2)
C(6)–C(1)–C(7)	119·5 (2)	H(82)–C(8)–C(7)	110 (2)
C(1)–C(7)–O(2)	112·9 (2)	H(82)–C(8)–S	109 (2)
C(1)–C(7)–C(8)	108·9 (2)	H(91)–C(9)–S	105 (2)
O(2)–C(7)–C(8)	107·1 (2)	H(92)–C(9)–S	107 (2)
C(7)–C(8)–S	110·7 (2)	H(93)–C(9)–S	104 (2)
C(8)–S–C(9)	96·8 (1)	H(91)–C(9)–H(92)	103 (3)
C(8)–S–O(1)	107·1 (1)	H(91)–C(9)–H(93)	119 (3)
C(9)–S–O(1)	105·5 (1)	H(92)–C(9)–H(93)	117 (3)

(*c*) Phenyl ring angles involving H (°)

H(2)–C(2)–C(1)	121 (2)	H(4)–C(4)–C(5)	120 (2)
H(2)–C(2)–C(3)	118 (2)	H(5)–C(5)–C(4)	120 (2)
H(3)–C(3)–C(2)	113 (2)	H(5)–C(5)–C(6)	120 (2)
H(3)–C(3)–C(4)	126 (2)	H(6)–C(6)–C(5)	121 (2)
H(4)–C(4)–C(3)	120 (2)	H(6)–C(6)–C(1)	118 (2)

Averaged value 119 (1)

(*d*) Torsion angles (°)

C(3)–C(2)–C(1)–C(7)	−178·2 (2)	H(7)–C(7)–O(2)–H(2O)	38 (3)
C(2)–C(1)–C(7)–C(8)	98·1 (2)	H(2)–C(2)–C(1)–C(7)	7 (2)
C(2)–C(1)–C(7)–O(2)	−20·8 (3)	C(1)–C(7)–O(2)–H(2O)	−85 (2)
C(1)–C(7)–C(8)–S	−176·0 (1)	H(7)–C(7)–C(8)–H(81)	−179 (2)
C(7)–C(8)–S–C(9)	−161·5 (2)		
C(7)–C(8)–S–O(1)	−53·0 (2)		
O(2)–C(7)–C(8)–S	−53·7 (2)		

(*e*) Hydrogen bond

O(2)–H(2O)···O(1)	171 (3)°	O(1)–O(2)	2·715 (3)
		O(1)–H(2O)	1·74 (4)

carbon and hydrogen, respectively (*International Tables for X-ray Crystallography*, 1974).

The value of 1·525 (2) Å for C(1)–C(7) is very nearly the 1·515 Å which one obtains by summing the appropriate single-bond radii for sp^2 and sp^3-hybridized carbon atoms.

The value of 1·521 (3) Å for C(7)–C(8) is slightly shorter than the ideal value of 1·544 Å for sp^3–sp^3 C–C bonds; this appears to be sterically induced.

The elongations of the S–O(1), S–C(8) and S–C(9) bonds as well as the contraction of the C(8)–S–C(9) angle are all presumably the results of the tendency for the sulphur atom to keep an unshared electron pair in the more stable *s* (relative to *p*) orbital, thereby reducing the amount of *s* character in the sulphur bond orbitals and producing weaker (and longer) S–*X* (where *X* = C or O) bonds and smaller *X*–S–*X'* bond angles (Day, Kingsbury & Day, 1981). The 1·504 (2) Å value of the S–O(1) bond is presumably due to participation of O(1) in a solid-state intermolecular hydrogen bond with the hydroxylic proton of a symmetry-related molecule. Fig. 2 shows the crystal structure as viewed down the *b* axis. There exists a pair of symmetry-related intermolecular O–H···O hydrogen bonds spanning a centre of symmetry, involving sulphinyl and ethanol groups, leading to hydrogen-bonded dimers.

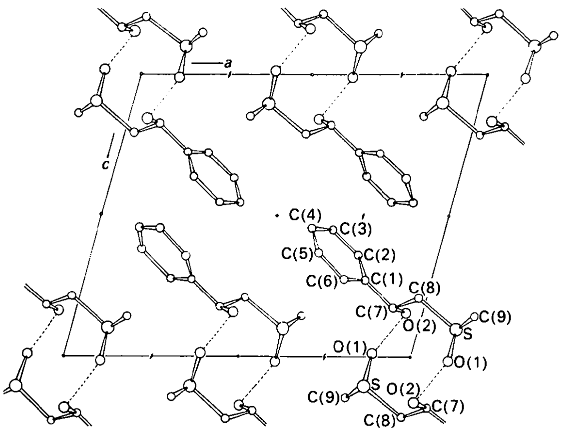

Fig. 2. Molecular configuration and packing showing the hydrogen bonding.

The diastereoisomer (α) studied has the same relative configuration in the two chiral centres (*RR,SS*) and the conformation around C(7)–C(8) is antiperiplanar between phenyl and methylsulphinyl groups. These results are in agreement with ^{1}H NMR measurements in solution, based upon relative values of the vicinal coupling constants in each diastereoisomer.

The melting point of this compound is higher than the diastereoisomer (*RS,SR*) (Garcia Ruano, 1982) and it is predicted that in this the hydrogen bond will be intramolecular. An X-ray diffraction study of the diastereoisomer (*RS,SR*) is therefore planned in order to decide whether the hydrogen bond is asymmetric or symmetric.

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References

Baumgarten, H. E., McMahan, D. G., Elia, V. I., Gold, B. I., Day, V. W. & Day, R. O. (1976) *J. Org. Chem.* **41**, 3798–3805.

Churchill, M. R. (1973). *Inorg. Chem.* **12**, 1213.

Cotton, F. A., Day, V. W., Hazen, E. E. & Larsen, S. (1973). *J. Am. Chem. Soc.* **95**, 4834–4840.

Day, R. O., Kingsbury, C. A. & Day, V. W. (1981). *J. Org. Chem.* **46**, 1004–1009.

Garcia Ruano, J. L. (1982). Private communication.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Martínez-Ripoll, M. & Cano, F. H. (1975). *PESOS* program. Instituto Rocasolano, CSIC, Serrano 119, Madrid-6, Spain.

Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.