

References

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Acta Cryst. (1977). B **33**, 2972–2974

(1SR,SRS)-1-(1-Phenylsulphinylcyclohexyl)ethanol

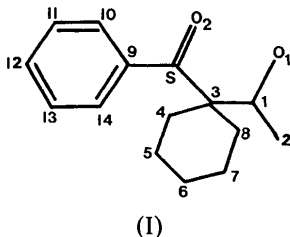
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Abstract. C₁₄H₂₀O₂S, *M_r* = 252.39, monoclinic, *P*2₁/*c*, *a* = 13.300 (1), *b* = 9.760 (2), *c* = 10.802 (3) Å, β = 101.51 (2)°, *V* = 1373.6 (5) Å³, *Z* = 4, *D_x* = 1.220 g cm⁻³, μ = 19.35 cm⁻¹ for Cu *K*α radiation (λ = 1.54178 Å). The structure was refined to *R* = 0.043 for 1638 counter reflexions. The relative stereochemistry of the molecule is (1*SR*, *SRS*).

Introduction. As part of a continuing study of stereo-specific rearrangements (Allen, Kennard, Nassimbeni, Shepherd & Warren, 1974) we have carried out an X-ray analysis of the title compound (I) (Brownbridge, Hodgson, Shepherd & Warren, 1976) to establish the relative stereochemistry at the chiral centres C(1) and S.



Intensities were collected with Cu *K*α radiation on a Syntex *P*2₁ diffractometer equipped with a graphite-crystal monochromator. 2358 reflexions were measured up to 2θ = 120°; 1994 with *F* > 4σ(*F*) were classified

as observed. Equivalent reflexions were averaged to yield 1638 unique observations. Cell parameters were obtained by least squares from diffractometer measurements for 15 strong high-order reflexions. The structure was solved by a multisolution sign expansion technique (Sheldrick, 1977). The highest 17 peaks from the *E* map corresponding to the best sign set yielded the positions of the 17 non-hydrogen atoms. Anisotropic refinement of all C, O and S atoms converged to *R* = 0.082. All 20 H atoms were located in a subsequent difference map and were refined without constraints.

Table 1. Fractional atomic coordinates (× 10⁴)

	<i>x</i>	<i>y</i>	<i>z</i>
S(1)	1774 (1)	71 (1)	900 (1)
O(1)	3811 (2)	-1659 (4)	1382 (3)
O(2)	2152 (2)	-583 (2)	2174 (2)
C(1)	3517 (2)	-1039 (4)	195 (3)
C(2)	4074 (3)	-1780 (6)	-689 (5)
C(3)	2336 (2)	-996 (3)	-247 (2)
C(4)	1842 (2)	-2408 (3)	-194 (3)
C(5)	687 (3)	-2425 (4)	-683 (4)
C(6)	414 (3)	-1848 (4)	-2001 (4)
C(7)	842 (3)	-423 (4)	-2067 (4)
C(8)	2003 (3)	-396 (4)	-1574 (3)
C(9)	2447 (2)	1663 (3)	909 (3)
C(10)	3289 (2)	1948 (4)	1838 (3)
C(11)	3767 (3)	3205 (4)	1853 (4)
C(12)	3397 (4)	4161 (4)	927 (4)
C(13)	2544 (4)	3883 (4)	17 (4)
C(14)	2064 (3)	2640 (3)	8 (3)

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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(O1)	348 (4)	-137 (5)	182 (4)	90 (16)
H(11)	372 (3)	-5 (3)	11 (3)	51 (9)
H(21)	477 (3)	-185 (4)	-26 (3)	64 (10)
H(22)	405 (4)	-129 (5)	-141 (5)	99 (17)
H(23)	382 (4)	-265 (6)	-86 (5)	102 (16)
H(41)	202 (3)	-273 (5)	64 (4)	81 (11)
H(42)	217 (2)	-301 (3)	-69 (3)	51 (8)
H(51)	43 (3)	-334 (4)	-74 (3)	60 (9)
H(52)	36 (3)	-183 (4)	-7 (4)	86 (12)
H(61)	70 (3)	-241 (5)	-252 (4)	87 (12)
H(62)	-36 (4)	-188 (5)	-226 (4)	115 (15)
H(71)	69 (3)	-14 (4)	-290 (4)	75 (12)
H(72)	51 (2)	10 (3)	-164 (3)	36 (8)
H(81)	228 (2)	50 (3)	-156 (3)	48 (8)
H(82)	232 (2)	-104 (3)	-213 (3)	53 (8)
H(101)	350 (2)	128 (3)	240 (3)	46 (8)
H(111)	432 (3)	340 (4)	243 (4)	93 (13)
H(121)	377 (4)	502 (5)	103 (5)	100 (14)
H(131)	237 (4)	460 (6)	-66 (5)	118 (16)
H(151)	148 (3)	249 (5)	-65 (4)	93 (12)

Table 3. Bond lengths (\AA)

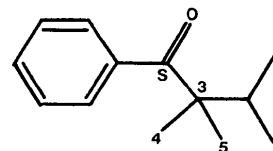
C(1)—O(1)	1.401 (6)	O(1)—H(O1)	0.76 (7)
C(1)—C(2)	1.506 (7)	C(1)—H(11)	1.01 (4)
C(1)—C(3)	1.548 (5)	C(2)—H(21)	0.95 (5)
C(3)—S(1)	1.883 (4)	C(2)—H(22)	0.91 (7)
C(3)—C(4)	1.532 (6)	C(2)—H(23)	0.92 (7)
C(3)—C(8)	1.530 (5)	C(4)—H(41)	0.94 (6)
C(4)—C(5)	1.522 (6)	C(4)—H(42)	0.95 (5)
C(5)—C(6)	1.507 (8)	C(5)—H(51)	0.95 (5)
C(6)—C(7)	1.509 (8)	C(5)—H(52)	1.04 (6)
C(7)—C(8)	1.530 (7)	C(6)—H(61)	0.92 (6)
S(1)—O(2)	1.509 (3)	C(6)—H(62)	1.01 (7)
S(1)—C(9)	1.792 (4)	C(7)—H(71)	0.92 (6)
C(9)—C(10)	1.375 (6)	C(7)—H(72)	0.87 (5)
C(9)—C(14)	1.385 (6)	C(8)—H(81)	0.95 (4)
C(10)—C(11)	1.380 (7)	C(8)—H(82)	1.02 (5)
C(11)—C(12)	1.385 (8)	C(10)—H(101)	0.90 (5)
C(12)—C(13)	1.371 (8)	C(11)—H(111)	0.88 (6)
C(13)—C(14)	1.370 (7)	C(12)—H(121)	0.97 (6)
		C(13)—H(131)	1.00 (7)
		C(14)—H(141)	0.95 (5)

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

C(2)—C(1)—O(1)	106.9 (5)	C(3)—S(1)—O(2)	105.2 (2)
C(2)—C(1)—C(3)	114.5 (4)	C(3)—S(1)—C(9)	102.7 (2)
O(1)—C(1)—C(3)	112.0 (4)	O(2)—S(1)—C(9)	106.7 (2)
C(1)—C(3)—S(1)	108.9 (3)	S(1)—C(9)—C(10)	120.8 (3)
C(1)—C(3)—C(4)	112.4 (3)	S(1)—C(9)—C(14)	118.7 (3)
C(1)—C(3)—C(8)	112.6 (3)	C(10)—C(9)—C(14)	120.4 (4)
S(1)—C(3)—C(4)	104.1 (3)	C(9)—C(10)—C(11)	119.6 (5)
S(1)—C(3)—C(8)	109.0 (3)	C(10)—C(11)—C(12)	119.6 (5)
C(4)—C(3)—C(8)	109.5 (3)	C(11)—C(12)—C(13)	120.6 (5)
C(3)—C(4)—C(5)	114.1 (4)	C(12)—C(13)—C(14)	119.8 (5)
C(4)—C(5)—C(6)	111.1 (4)	C(13)—C(14)—C(9)	119.9 (5)
C(5)—C(6)—C(7)	111.5 (4)		
C(6)—C(7)—C(8)	111.3 (4)		
C(7)—C(8)—C(3)	113.7 (4)		

The refinement converged to $R = 0.043$ with weights given by $w = 1/[\sigma^2(F) + aF^2]$, where a refined to 0.0034. Final positional and thermal parameters are presented in Tables 1 and 2,* bond lengths and angles in Tables 3 and 4.

Discussion. Fig. 1 shows a perspective view of the molecule and indicates that the relative stereochemistry is (1*SR*,*SRS*). The molecular geometry and conformation, except for that around S, is as expected: the planar phenyl ring has a mean C—C distance of 1.378 \AA while the cyclohexane ring is a chair with a mean intra-annular torsion angle of 53.6°. This latter ring is slightly flattened at the disubstituted C(3) where the intra-annular valence angle is almost exactly tetrahedral (109.5°) while other angles range from 111.1–114.1°; this gives rise to torsion angles of 50.7 and -51.2° about C(3)—C(8) and C(3)—C(4), values significantly lower than those about other ring bonds (54.0–55.7°) which are in agreement with minimum-energy predictions for unsubstituted cyclohexane (Bucourt & Hainaut, 1965).



(II)

The S atom is pyramidal, 0.68 \AA above the C(3)—C(9)—O(2) plane, with S=O at 1.509 and S—C_{ar} at 1.792 \AA ; these values are almost identical to those

* Lists of structure factors and the anisotropic thermal parameters for C, O, S have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32733 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

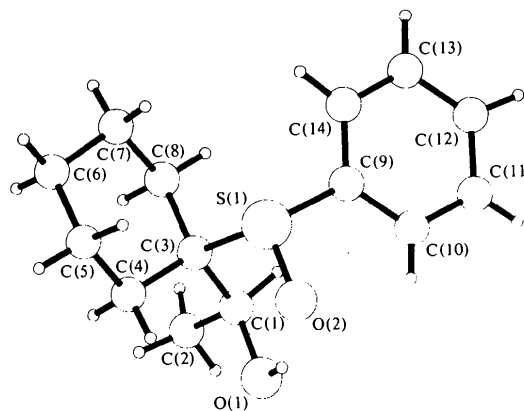


Fig. 1. Perspective view of the molecule showing the relative stereochemistry.

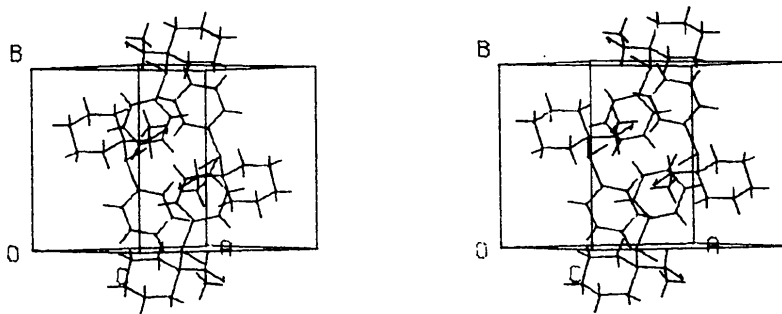


Fig. 2. Stereoview of the molecular packing.

found in 3-methyl-3-phenylsulphinylbutan-2-ol (II) (Allen, Kennard, Sheldrick & Oeser, 1976). The S—C(3) distance [1.883 (4) Å] and the C—S—C angle [102.7 (1)°] in the present structure (I) are, however, slightly increased over the corresponding figures for (II) [1.871 (3) Å, 101.6 (1)°]. In both cases these values are significantly greater than for simpler sulphoxides; the C—S—C angle in methyl sulphoxides, for example, is invariably in the range 96–98° (Tranqui, Richard, Vicat & Fillion, 1974). While the differences between S—C(3) and the C—S—C angles in (I) and (II) are small [0.012 Å, or 4σ , 1.1° , or 8σ] they appear to be real and result from the replacement of the *gem*-dimethyl groups [C(4), C(5)] in (II) by the more bulky cyclohexyl moiety. These results then follow the trend best exemplified by the 2,3-dimethyl-2-butenyl-1,1,2-trimethylpropylmethylsulphonium ion (Barnes & Sundaralingam, 1973) where 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 was noted (Allen *et al.*, 1976) that the configuration adopted in (II) resulted in the five S—C _{β} intramolecular non-bonded interactions lying in the narrow range 2.67–2.78 Å. In the present study (I) all five S—C _{β} interactions lie between 2.70 and 2.79 Å and the configuration is stabilized by an intramolecular hydrogen bond O(1)—H···O(2) where O···O is 2.729 Å and the angle at H is 153°. The packing of (I), shown in

Fig. 2, results in no intermolecular contacts shorter than van der Waals sums, in contrast to (II) where the O—H···O hydrogen bond (2.747 Å) is intermolecular and links the molecules into centrosymmetric dimers.

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