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Structure of 2-Iodo-2-phenylsulfonyl-1-phenylethanone

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Abstract. $C_{14}H_{11}IO_3S$, $M_r = 386{\cdot}20$, monoclinic, $P2_1/c$, $a = 15{\cdot}835\ (3)$, $b = 8{\cdot}745\ (2)$, $c = 10{\cdot}474\ (2)$ Å, $\beta = 105{\cdot}47\ (2)°$, $V = 1397{\cdot}9$ Å^3, $Z = 4$, $D_x = 1{\cdot}835$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 2{\cdot}47$ mm^{-1}, $F(000) = 752$, $T = 294$ K, final $R = 0{\cdot}046$ for 1408 unique observed reflections, material synthetic. The molecule has a folded conformation with the I atom and the benzene ring of the phenylsulfonyl group antiperiplanar with respect to the C—S bond. The I is *gauche* to both sulfonyl O atoms and the two benzene rings are tilted at 45·4 (2)° to one another. There is a short intramolecular I···O(carbonyl) interaction [3·283 (5) Å].

Introduction. In the course of a study of the chemistry of various hypervalent iodine compounds, the title compound was prepared (Hatziarapoglou & Varvoglis, 1985). Since this is an α-halosulfone with novel substituents it was deemed worthwhile to carry out its X-ray crystal-structure analysis.

Experimental. Transparent colourless crystal, 0·28 × 0·26 × 0·18 mm, m.p. 422–424 K. Computer-controlled Philips PW 1100 four-circle single-crystal diffractometer, graphite-monochromated Mo $K\alpha$, ω scan. Cell parameters and e.s.d.'s by least-squares analysis of measured θ angles of the 97 strongest reflections. Space group $P2_1/c$ from systematic absences. Three standard reflections per 90 min ($\bar{3}11$, 211, 302) without significant intensity variation. 3297 measured reflections, $\theta = 3$–$28°$ (index range $hkl = \pm17$, 11, 12), 3275 unique reflections, $R_{\text{int}} = 0{\cdot}035$, 1408 observed with $I > 2\sigma(I)$, no absorption correction. I atom located by Patterson synthesis, remaining non-H atoms by Fourier synthesis. 'Blocked cascade' full-matrix least squares using F with *SHELXTL* (Sheldrick, 1981). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). H atoms initially included at calculated positions (very close to those from a difference Fourier map) refined with isotropic temperature factors the same as those of C atoms to which they are bonded; $w = 1/[\sigma^2(F_o) + 0{\cdot}000365F_o^2]$ with $R = 0{\cdot}046$, $wR = 0{\cdot}045$, $S = 1{\cdot}259$, $(\Delta/\sigma)_{\text{max}} = 0{\cdot}325$, $(\Delta/\sigma)_{\text{mean}} = 0{\cdot}076$, $\Delta\rho = -0{\cdot}48$ to $0{\cdot}57$ e Å^{-3} in the region of the I atom.

Discussion. Final positional parameters and equivalent isotropic temperature factors are given in Table 1.† Bond lengths and angles are in Table 2. An *ORTEP*II (Johnson, 1976) view of the molecule is shown in Fig. 1. The phenylsulfonyl group adopts a conformation such that its phenyl ring (*B*) and the I atom are antiperiplanar about the C(1)—S bond [torsion angle I—C(1)—S—C(9) = 177·6 (3)°]. This is quite different from the conformation which a methylsulfonyl group adopts in 2-chloro-2-methylsulfonyl-1-phenylethanone (CMSP), where the torsion angle Me—S—C(1)—Cl is 64·5 (3)° (Grossert, Dubey, Gill, Cameron & Gardner, 1984). As a result, the I atom is *gauche* to, and nearly equidistant from, both sulfonyl O atoms. Both distances [I···O(2) = 3·471 (5), I···O(3) = 3·560 (6) Å] are slightly greater than the sum of the corresponding van der Waals radii. The same *gauche* orientation of a Br atom with respect to two sulfonyl O atoms was observed in the crystal structure of an α-bromosulfone (Bordwell & Doomes, 1974). However, this is the opposite of what has been reported so far for sulfones with a polar group (Cl or $-NMeCO_2Et$) at C(1). These sulfones adopt a conformation in the crystalline state (Grossert, Bharadwaj, Faught & Terzis, 1980; Saenger & Schwalbe, 1971; Tickle & Engberts, 1973) or in solution (Exner & Engberts, 1979) in which the polar group is *gauche* to only one of the sulfonyl O atoms. Thus, the conformation of α-substituted sulfones is dependent in part on the nature of the substituent. The phenyl ring *B* is almost orthogonal to the plane of the atoms I, C(1), S [dihedral angle 91·0 (3)°], and the distances of the *ortho* H atoms H(C10) and H(C14) from O(2) and O(3) are 2·63 (1) Å. This permits two $O(\delta^-)\cdots H(\delta^+)$ interactions between the polar sulfonyl group and ring *B*. The same conformation for a

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† Lists of structure factors, anisotropic thermal parameters, H-atom parameters, selected torsion angles, intermolecular contact distances and least-squares-planes' calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42865 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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tolylsulfonylmethyl group was observed in ethyl *N*-methyl-*N*-(*p*-tolylsulfonylmethyl)carbamate (MTSC) by Tickle & Engberts (1973). They also considered possible orbital overlap, which in systems like $R^1R^2SO_2$ may affect the R^2—S π-bond order according to the electronegativity of R^2 (Cruickshank, 1961). The S—C(9) bond distance in the present compound [1·760 (8) Å] differs slightly from the corresponding one in MTSC [1·751 (1) Å].

The geometry of the sulfone group, with the two S—O bond distances equivalent and the angles O–S–O and C–S–C significantly different from the tetrahedral value, is not unusual (Harlow, Simonsen, Pfluger & Sames, 1974, and literature cited therein). The S—O bond lengths, the O–S–O angle and the distance O(2)···O(3) = 2·468 (8) Å all agree well with the mean values 1·439 Å, 118·3°, 2·470 Å reported for sulfonyl groups by Hargittai (1978). The angle C(1)—S—C(9) = 99·7 (4)°, though, is somewhat smaller than the corresponding angles not only in CMSP [104·1 (2)°], 1-chloro-1-phenylsulfonyl-2,3-dimethylcyclopropane (103·7°) (Saenger & Schwalbe, 1971) and MTSC [104·85 (6)°], but also in 2,4-dinitrobenzyl *p*-tolyl sulfone (101·8°) (Harlow *et al.*, 1974). This, however, may be attributed to intermolecular interactions resulting from the particular packing mode in the present compound (Table 2).

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2 × 10^3)

U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
I	0·19010 (4)	0·97959 (6)	−0·00007 (6)	0·0655 (2)
S	0·3447 (1)	0·7561 (2)	−0·0312 (2)	0·0444 (6)
O(1)	0·1492 (4)	0·6845 (7)	−0·2010 (5)	0·074 (1)
O(2)	0·4036 (3)	0·8444 (5)	0·0687 (5)	0·057 (1)
O(3)	0·3311 (4)	0·7983 (6)	−0·1676 (5)	0·065 (1)
C(1)	0·2419 (4)	0·7523 (7)	0·0081 (6)	0·037 (1)
C(2)	0·1736 (5)	0·6505 (8)	−0·0858 (6)	0·044 (1)
C(3)	0·1385 (4)	0·5147 (7)	−0·0326 (6)	0·044 (1)
C(4)	0·0691 (5)	0·4375 (8)	−0·1150 (7)	0·054 (1)
C(5)	0·0325 (5)	0·3159 (9)	−0·0727 (7)	0·065 (1)
C(6)	0·0641 (5)	0·2650 (8)	0·0551 (7)	0·060 (1)
C(7)	0·1322 (5)	0·3354 (8)	0·1404 (7)	0·058 (1)
C(8)	0·1706 (4)	0·4614 (8)	0·0969 (7)	0·049 (1)
C(9)	0·3728 (4)	0·5613 (7)	−0·0101 (6)	0·041 (1)
C(10)	0·4190 (4)	0·5100 (7)	0·1119 (6)	0·044 (1)
C(11)	0·4384 (5)	0·3584 (8)	0·1318 (7)	0·061 (1)
C(12)	0·4099 (6)	0·2586 (8)	0·0278 (8)	0·069 (1)
C(13)	0·3637 (5)	0·3091 (9)	−0·0937 (8)	0·068 (1)
C(14)	0·3456 (5)	0·4614 (8)	−0·1147 (7)	0·058 (1)

Table 2. *Bond lengths* (Å) *and angles* (°)

I—C(1)	2·143 (8)	S—O(2)	1·429 (6)
S—O(3)	1·435 (6)	S—C(1)	1·783 (9)
S—C(9)	1·760 (8)	O(1)—C(2)	1·201 (8)
C(1)—C(2)	1·537 (9)	C(2)—C(3)	1·482 (11)
C(3)—C(4)	1·379 (10)	C(3)—C(8)	1·395 (10)
C(4)—C(5)	1·343 (12)	C(5)—C(6)	1·372 (11)
C(6)—C(7)	1·351 (11)	C(7)—C(8)	1·393 (11)
C(9)—C(10)	1·368 (9)	C(9)—C(14)	1·377 (10)
C(10)—C(11)	1·364 (10)	C(11)—C(12)	1·375 (11)
C(12)—C(13)	1·361 (11)	C(13)—C(14)	1·368 (11)

O(2)—S—O(3)	119·0 (4)	O(2)—S—C(1)	107·4 (4)
O(3)—S—C(1)	109·4 (3)	O(2)—S—C(9)	109·7 (3)
O(3)—S—C(9)	109·8 (4)	C(1)—S—C(9)	99·7 (4)
I—C(1)—S	109·7 (3)	I—C(1)—C(2)	108·4 (4)
S—C(1)—C(2)	113·1 (5)	O(1)—C(2)—C(1)	118·8 (6)
O(1)—C(2)—C(3)	121·6 (6)	C(1)—C(2)—C(3)	119·6 (5)
C(2)—C(3)—C(4)	118·2 (6)	C(2)—C(3)—C(8)	123·9 (6)
C(4)—C(3)—C(8)	117·9 (7)	C(3)—C(4)—C(5)	121·5 (6)
C(4)—C(5)—C(6)	120·1 (7)	C(5)—C(6)—C(7)	121·1 (8)
C(6)—C(7)—C(8)	119·0 (7)	C(3)—C(8)—C(7)	120·3 (6)
S—C(9)—C(10)	119·3 (5)	S—C(9)—C(14)	120·0 (5)
C(10)—C(9)—C(14)	120·7 (6)	C(9)—C(10)—C(11)	120·3 (6)
C(10)—C(11)—C(12)	118·9 (6)	C(11)—C(12)—C(13)	121·0 (7)
C(12)—C(13)—C(14)	120·2 (7)	C(9)—C(14)—C(13)	118·8 (6)

The phenylethanone group is rotated about the C(1)—C(2) bond [torsion angle I—C(1)—C(2)—O(1) = 58·1 (8)°] by 31·2° more than in the case of CMSP, where the torsion angle Cl—C$_\alpha$—C$_\beta$—O is only 26·9°. In this position the phenyl ring *P* forms a dihedral angle of 45·4 (2)° with the plane of *B* and H(C8) approaches C(9) and C(10) at distances 3·47 (2) and 3·42 (3) Å. This kind of tilted mutual disposition of aromatic rings, with mean dihedral angle 46°, was found in a recent study to be one of the preferred geometries of interaction between aromatic rings in phenylalanine structures which allow access of the H(δ^+) atoms of one ring to the π cloud of the other (Gould, Gray, Taylor & Walkinshaw, 1985). Two additional interactions are also observed. The first is intermolecular, O(1)···H(C5) (at $-x, \frac{1}{2}+y, -\frac{1}{2}-z$) = 2·47 (2) Å. The second is intramolecular, I···O(1) = 3·283 (5) Å, which is less than 3·46 Å, the sum of the van der Waals radii (Bondi, 1964). This kind of intra- or intermolecular interaction between a monovalent I and an adjacent carbonyl O is not unusual, and occurs in the structures of some benzoxiodole compounds (Gougoutas & Clardy, 1972; Gougoutas & Lessinger, 1973), or in the structure of phenacyl iodide (Lere-Porte, Petrissans, Petrissans & Brianso, 1982).

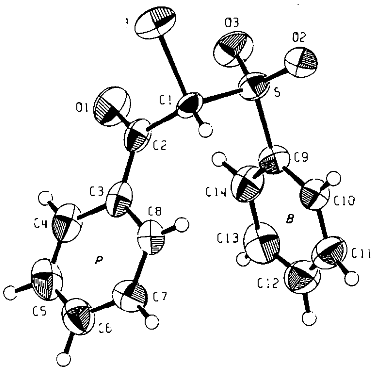

Fig. 1. *ORTEP* drawing of the molecule. Thermal ellipsoids are drawn at 50% probability level; isotropic hydrogen thermal parameters are represented by spheres of arbitrary size.

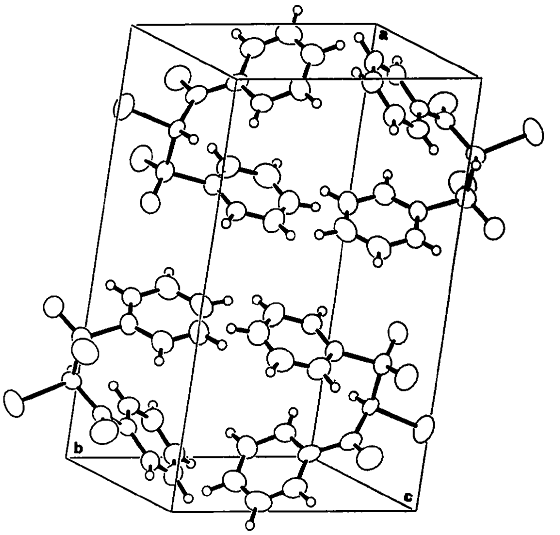

Fig. 2. Perspective view of the unit cell showing the molecular packing.

Fig. 2 shows the molecular packing in the unit cell. Most of the shortest intermolecular O···H and H···H distances correspond to peaks (at 2·45–2·55 Å) in frequency distributions of O···H and H···H interactions described for a considerable number of phenylalanine structures by Gould *et al.* (1985).

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Room-Temperature Phase of *n*-Decylammonium Chloride

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Abstract. $[NH_3(C_{10}H_{21})]Cl$, $M_r = 193{\cdot}76$, monoclinic, $P2_1$, $a = 5{\cdot}6996\,(4)$, $b = 7{\cdot}1638\,(5)$, $c = 15{\cdot}490\,(1)$ Å, $\beta = 91{\cdot}297\,(5)°$, $V = 632{\cdot}29\,(7)$ Å^3, $Z = 2$, $D_m = 1{\cdot}04$, $D_x = 1{\cdot}02$ g cm^{-3}, Cu $K\bar{\alpha}$, $\lambda = 1{\cdot}54184$ Å, $\mu = 23{\cdot}3$ cm^{-1}, $F(000) = 216$, $T = 296$ K, $R = 0{\cdot}032$ for 426 $[I > 3\sigma(I)]$ reflections. The amphiphilic character of the alkylammonium ion causes crystallization in layers. The polar layers consist of NH_3 groups and Cl atoms; they alternate with the neutral layers consisting of aliphatic chains. These are held together by van der Waals bonds whereas N and Cl atoms are linked by hydrogen bonds to form a two-dimensional honeycomb net.

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