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2-[1-(Phenylsulfonyl)ethyl]benzoic acid and 2-[1-(phenylsulfonyl)propyl]-benzoic acid

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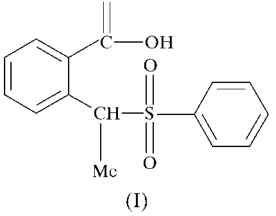
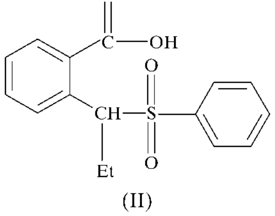
In the title acids, $C_{15}H_{14}O_4S$, (I), and $C_{16}H_{16}O_4S$, (II), respectively, the angle between the planes of the benzene ring and the carboxyl group is 13.7 (1)° for (I) and 21.3 (1)° for (II). The molecular structures are stabilized by intramolecular C—H···O hydrogen bonds. The crystal packing is stabilized by a single O—H···O hydrogen bond in both compounds, in which the O and H atoms are ordered; H···O 1.87 Å for (I) and 1.83 Å for (II), O···O 2.680 (2) Å for (I) and 2.652 (3) Å for (II), and O—H···O 172° for (I) and 175° for (II). The hydrogen bond forms a cyclic dimer, with graph-set descriptor $R_2^2(8)$, about a centre of symmetry.

Comment

The title compounds, (I) and (II), are potential intermediates for the synthesis of 2-alkylbenzoic acid starting from *o*-toluic acid. Sulfates, sulfones, thiols, sulfonamides and sulfoxides are some of the compounds that belong to this class, and many of these exhibit insecticidal, germicidal or antimicrobial activities (Krishnaiah *et al.*, 1995; De Benedetti *et al.*, 1985; Dupont *et al.*, 1978). Sulfur-containing compounds, for the most part, act as simple narcotics (Schultz *et al.*, 2001). A series of acyclic sulfones have been identified as high-affinity selective 5-HT(2A) receptor antagonists (Fletcher *et al.*, 2002). *para*-Amino,*para*-phenyl sulfones are well known as antibacterial and antileprotic agents (McCullough & Maren, 1973; De Benedetti, 1992). The conformation about the S atom determines whether the pharmacological activity of the compound is mild or strong (McKenna *et al.*, 1989). In order to obtain detailed information on their molecular conformation in the solid state, the present X-ray study on the title sulfones has been carried out and the results are presented here.



(I)



(II)

Figs. 1 and 2 show the molecular structures of (I) and (II), respectively, with the atom-numbering schemes. In both compounds, the C—O distances are as expected. The S—C_{Ph} distances [1.766 (2) Å in (I) and 1.767 (2) Å in (II)] compare well with the literature value of 1.763 (9) Å for $C_{ar}—SO_2—C$ (Allen *et al.*, 1987). The S1—C8 distances [1.806 (2) Å for (I) and 1.813 (2) Å for (II)] are longer than the literature value of 1.786 (18) Å for $Csp^3—SO_2—C$ (Allen *et al.*, 1987). The mean S═O distance of 1.436 (2) Å agrees well with the reported value of 1.436 (2) Å (Bocelli & Rizzoli, 1990; Jeyakanthan & Velmurugan, 1998).

The angular disposition of the bonds about atom S1 in (I) and (II) shows significant deviation from that of a regular tetrahedron, with the largest deviation being in the O—S—O angle for both (I) and (II). In both compounds, the widening of the O4—S1—O2 angle [to 118.6 (1)° in (I) and 118.4 (1)° in (II)], and the resulting narrowing of C—S—C from the ideal tetrahedral value [C10—S1—C8 to 102.6 (1)° in (I) and C11—

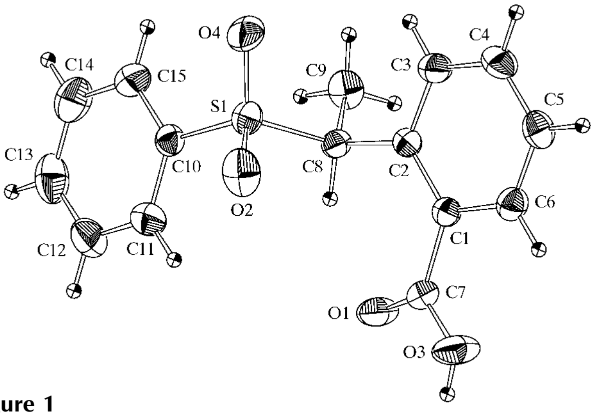


Figure 1
A view of the molecular structure of (I) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

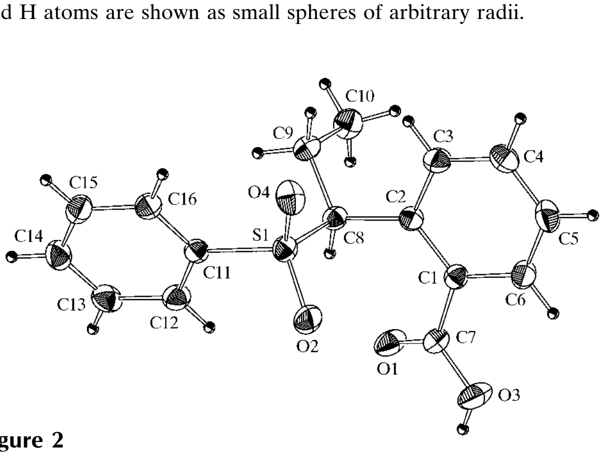


Figure 2
A view of the molecular structure of (II) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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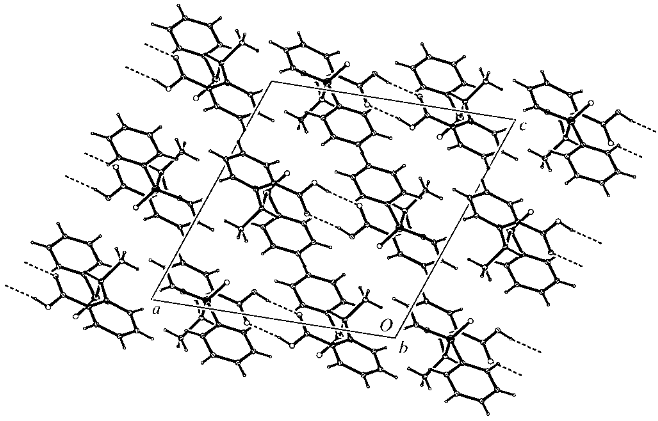

Figure 3
The crystal structure of (I) viewed along **b**, with the hydrogen bonds shown as dashed lines.

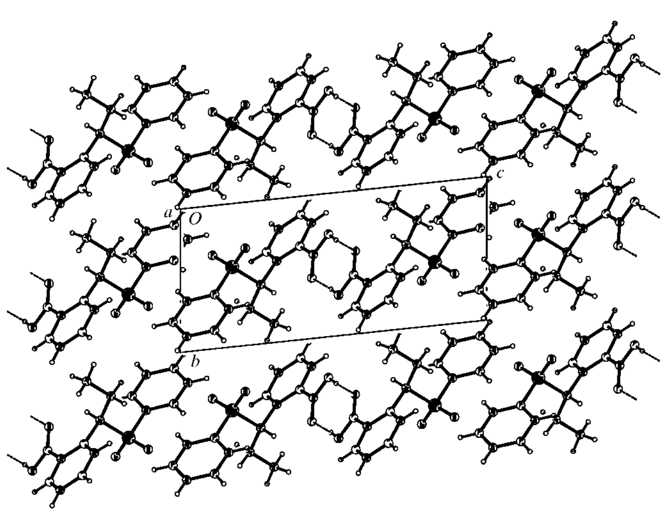

Figure 4
The crystal structure of (II) viewed along **a**, with the hydrogen bonds shown as dashed lines.

S1—C8 to 105.2 (1)° in (II)], are attributed to the Thorpe–Ingold effect (Bassindale, 1984). The dihedral angles between the carboxyl group and the C1–C6 phenyl ring are 13.7 (1) and 21.3 (1)° in (I) and (II), respectively. In both compounds, the orientation of the carboxyl group with respect to the phenyl ring is influenced by C6—H6···O3 and C8—H8···O1 interactions (Tables 2 and 4). The interplanar angle between the phenyl rings in (I) is 9.2 (1)°. In the case of (II), this angle increases to 22.5 (1)°, due to the bulkier nature of the propyl group compared with the ethyl group. By changing the ethyl substituent for propyl, the space group is changed and the volume per molecule increases by 26.9 Å^3, corresponding to an increase of 7.98%.

The slight increases in the C7—C1—C2 [123.4 (2)° in (I) and 123.5 (2)° in (II)] and C1—C2—C8 [123.7 (2)° in (I) and 123.1 (2)° in (II)] angles in both compounds, from the ideal value of 120°, can be attributed to the steric interaction of the C7 and C8 substituents. The slight difference in the C2—C8—C9 bond angle between (I) and (II) is due to the slightly bulkier nature of the propyl group in (II) compared with the ethyl group in (I).

In addition to van der Waals interactions, there is one O—H···O intermolecular hydrogen bond in both compounds. Each of the hydrogen bonds in (I) and (II) participates in an eight-membered cyclic dimer arrangement, as shown in the packing diagrams (Figs. 3 and 4), with an $R_2^2(8)$ ring descriptor (Bernstein *et al.*, 1995). A similar pattern is observed for 2-(isopropylthio)benzoic acid (Gerkin, 1999). The molecular structures of (I) and (II) are stabilized by intramolecular C—H···O hydrogen bonds.

Experimental

The title compounds were prepared by the alkylation of methyl 2-phenylsulfonyl methylbenzoate with the corresponding alkyl iodides in the presence of sodium hydride in dry dimethyl sulfoxide at room temperature. The ester group suffered hydrolysis under the reaction conditions. Compounds (I) and (II) were recrystallized from ethyl acetate and hexane by slow evaporation.

Compound (I)

Crystal data

$C_{15}H_{14}O_4S$
$M_r = 290.32$
Monoclinic, $P2_1/c$
$a = 12.8969$ (3) Å
$b = 8.5064$ (1) Å
$c = 13.0472$ (3) Å
$\beta = 109.803$ (1)°
$V = 1346.71$ (5) Å^3
$Z = 4$

$D_x = 1.432$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7690 reflections
$\theta = 2.9$–28.4°
$\mu = 0.25$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.38 × 0.28 × 0.24 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
9552 measured reflections
3352 independent reflections
2293 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.050$
$\theta_{\rm max} = 28.3°$
$h = -17 \rightarrow 16$
$k = -9 \rightarrow 11$
$l = -13 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.124$
$S = 0.94$
3352 reflections
183 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0693P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.30$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.57$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

S1—O4	1.434 (2)	O1—C7	1.218 (2)
S1—O2	1.434 (2)	C7—O3	1.309 (2)
O4—S1—C10	108.48 (9)	O1—C7—C1	125.3 (2)
O2—S1—C10	108.3 (1)	O3—C7—C1	113.2 (2)
O4—S1—C8	110.14 (9)	C2—C8—S1	108.5 (1)
O2—S1—C8	107.45 (9)	C9—C8—S1	110.8 (1)
O1—C7—O3	121.5 (2)		
O4—S1—C8—C2	75.2 (1)	O2—S1—C8—C9	178.6 (1)
O2—S1—C8—C2	−55.3 (1)	O4—S1—C10—C15	15.3 (2)
O4—S1—C8—C9	−51.0 (2)	O2—S1—C10—C15	145.2 (2)

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Table 2
Hydrogen-bonding and short-contact geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···O3	0.93	2.32	2.665 (2)	102
C8—H8···O1	0.98	2.10	2.895 (2)	138
O3—H3···O1^{i}	0.82	1.87	2.680 (2)	172

Symmetry code: (i) $1 - x, -y, -z$.

Compound (II)

Crystal data

$C_{16}H_{16}O_4S$
$M_r = 304.35$
Triclinic, $P\overline{1}$
$a = 7.4805$ (10) Å
$b = 7.5125$ (9) Å
$c = 14.4853$ (18) Å
$\alpha = 94.634$ (9)°
$\beta = 91.807$ (1)°
$\gamma = 116.020$ (8)°
$V = 727.09$ (16) Å^3
$Z = 2$
$D_x = 1.390$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 2.8$–25.0°
$\mu = 0.24$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.40 × 0.30 × 0.26 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$w/2\theta$ scans
2625 measured reflections
2518 independent reflections
2004 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$
$\theta_{\rm max} = 25°$
$h = -8 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 300 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.107$
$S = 1.01$
2518 reflections
192 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2 + 0.1743P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.28$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}

All H atoms were fixed geometrically, with C—H = 0.93–0.98 Å and O—H = 0.82 Å, and allowed to ride on the corresponding parent atoms, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ or $1.5U_{\rm eq}({\rm O})$.

Table 3
Selected geometric parameters (Å, °) for (II).

S1—O2	1.437 (2)	O1—C7	1.220 (3)
S1—O4	1.438 (2)	O3—C7	1.311 (2)
S1—C11	1.767 (2)		
O4—S1—C11	108.1 (1)	O1—C7—C1	124.5 (2)
O2—S1—C8	106.8 (1)	O3—C7—C1	113.7 (2)
O4—S1—C8	108.8 (1)	C2—C8—S1	105.6 (1)
O1—C7—O3	121.8 (2)	C9—C8—S1	111.9 (1)
O2—S1—C8—C2	−62.6 (2)	O4—S1—C11—C12	−178.7 (2)
O4—S1—C8—C2	66.3 (2)	C8—S1—C11—C12	65.2 (2)
C11—S1—C8—C2	−178.1 (1)	O2—S1—C11—C16	131.2 (2)
O2—S1—C8—C9	170.6 (2)	O4—S1—C11—C16	1.4 (2)
O4—S1—C8—C9	−60.5 (2)	C8—S1—C11—C16	−114.7 (2)
C11—S1—C8—C9	55.1 (2)	S1—C11—C12—C13	179.6 (2)
O2—S1—C11—C12	−48.9 (2)	S1—C11—C16—C15	−178.3 (2)

Table 4
Hydrogen-bonding and short-contact geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···O3	0.93	2.36	2.695 (3)	101
C8—H8···O1	0.98	2.15	2.917 (3)	134
C16—H16···O4	0.93	2.50	2.887 (3)	105
O3—H3···O1^{i}	0.82	1.83	2.652 (3)	175

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

For compound (I), data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*. For compound (II), data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *SDP* (Frenz, 1989). For both compounds, program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997); software used to prepare material for publication: *SHELX*97 and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1557). Services for accessing these data are described at the back of the journal.

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