

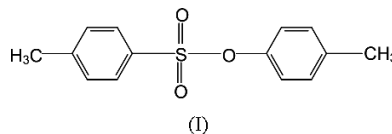
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Key indicators

Single-crystal X-ray study
 $T = 150$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.039
 wR factor = 0.083
Data-to-parameter ratio = 20.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.4-Methylphenyl 4-toluenesulfonate: supramolecular
aggregation through weak C—H···O and C—H··· π
interactionsIn the crystal structure of the title compound, $\text{C}_{14}\text{H}_{14}\text{O}_3\text{S}$, the dihedral angle between the mean planes of the two rings is $51.97(8)^\circ$. There are weak C—H···O hydrogen bonds which generate rings of graph-set motifs $S(5)$, $S(6)$, $R_1^2(4)$ and $R_2^1(9)$. The supramolecular aggregation is completed by the presence of C—H··· π interactions.

Comment

Aromatic sulfonates are used in monitoring the merging of lipids (Yachi *et al.*, 1989) and in many other fields (Spungin *et al.*, 1992; Tharakan *et al.*, 1992; Alford *et al.*, 1991; Jiang *et al.*, 1990; Narayanan & Krakow, 1983); for example, 1-anilino-8-naphthalenesulfonate, an aromatic sulfonate is used in monitoring the merging of lipids in the binding of Rose bengal, a model organic anion, to sinusoidal and bile canalicular membrane fractions isolated from rat liver. The crystal structure of the title compound, (I), was determined because of the biological importance of its analogues. A search of Version 5.23 (July 2002 updates) of the Cambridge Structural Database (Allen, 2002) revealed 16 structures (refcodes KAWDAN, FIXCAQ, NEDXUP, NEDYAW, NEDYIE, NUNCII, RASSOT, RELVUZ, SIMVUF, TCPTOS, TEBFOV, TMPDTS, TSMIPH, WOHCUR, ZZZBDA10 and MIWHIJ) that are closely related to the title compound. The S—C, S—O and S=O bond lengths (Table 1) are comparable to those found in related structures in that they all contain the *p*-toluenesulfonyl group (Vembu, Nallu, Garrison & Youngs, 2003*a,b,c,d,e,f*; Vembu, Nallu, Spencer & Howard, 2003*ab,c,d,e,f,g*; Vembu, Nallu, Garrison, Hindi & Youngs (2003); Vembu, Nallu, Durmus, Panzner, Garrison & Youngs, 2004*a,b,c*).The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. The dihedral angle between the mean planes of the two rings is $51.97(8)^\circ$. This shows their non-coplanar orientation, similar to that reported for other aromatic sulfonates (Vembu, Nallu, Garrison & Youngs, 2003*b,c,d,e*; Vembu, Nallu, Spencer & Howard, 2003*a,b,c,d,f,g*; Vembu, Nallu, Durmus, Panzner, Garrison & Youngs, 2004*a,b,c*) and in contrast to the near-coplanar orientation observed in 2,4-dinitrophenyl 4-toluenesulfonate (Vembu, Nallu, Garrison & Youngs, 2003*a*), 4-methoxyphenyl 4-toluenesulfonate (Vembu, Nallu, Garrison, Hindi & Youngs, 2003) and 8-quinolyl 3-nitrobenzenesulfonate (Vembu, Nallu, Spencer & Howard, 2003*e*).

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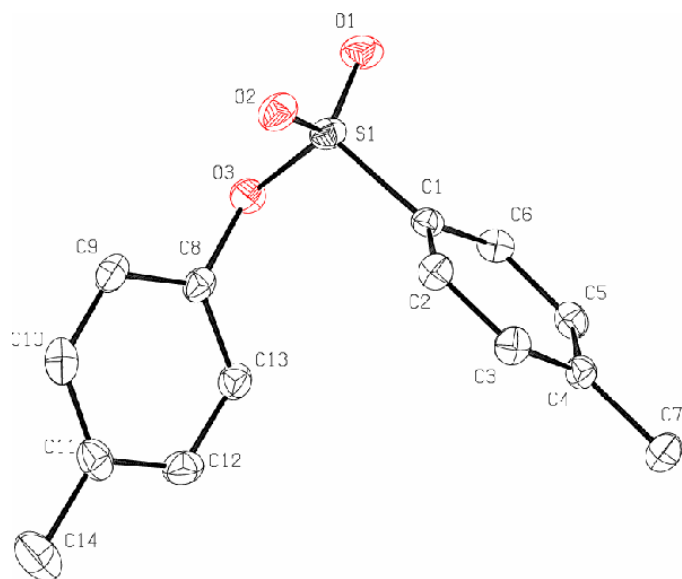


Figure 1
The molecular structure of the title molecule, showing 50% probability displacement ellipsoids. H atoms have been omitted.

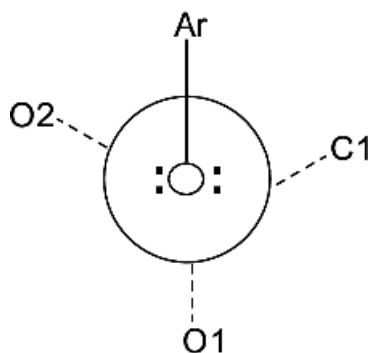


Figure 2
A Newman projection along the S—O bond.

In Fig. 2, the molecule is viewed along the S—O bond taking C8 as reference. The orientations of the two sulfonyl atoms O1 and O2 and the tolyl carbon C1, attached to sulfur, have been deduced from the corresponding torsion angles (C8—O3—S1—O1/O2/C1) and depicted in Fig. 2. Since the C1—S1—O3—C8 torsion angle is $64.0(2)^\circ$, which corresponds to a +synclinal disposition, the two aromatic planes are, as expected, not coplanar [$51.97(8)^\circ$].

The crystal structure of (I) is stabilized by weak C—H \cdots O interactions (Table 2). The H \cdots O distances in (I) agree with those found for weak C—H \cdots O bonds (Desiraju & Steiner, 1999). In (I), each of the C2—H2 \cdots O2 and C6—H6 \cdots O1 interactions generates an $S(5)$ graph-set motif (Bernstein *et al.*, 1995; Etter, 1990). The C9—H9 \cdots O2 interaction generates an $S(6)$ motif. The C2—H2 \cdots O2 and C9—H9 \cdots O2 interactions together constitute a pair of bifurcated acceptor bonds.

The C3—H3 \cdots O1ⁱ and C3—H3 \cdots O3ⁱ interactions constitute a pair of bifurcated donor bonds, generating an $R_2^1(4)$ chelate motif. The C6—H6 \cdots O2ⁱⁱ and C13—H13 \cdots O2ⁱⁱ interactions form a pair of bifurcated acceptor bonds, generating an $R_2^1(9)$ motif.

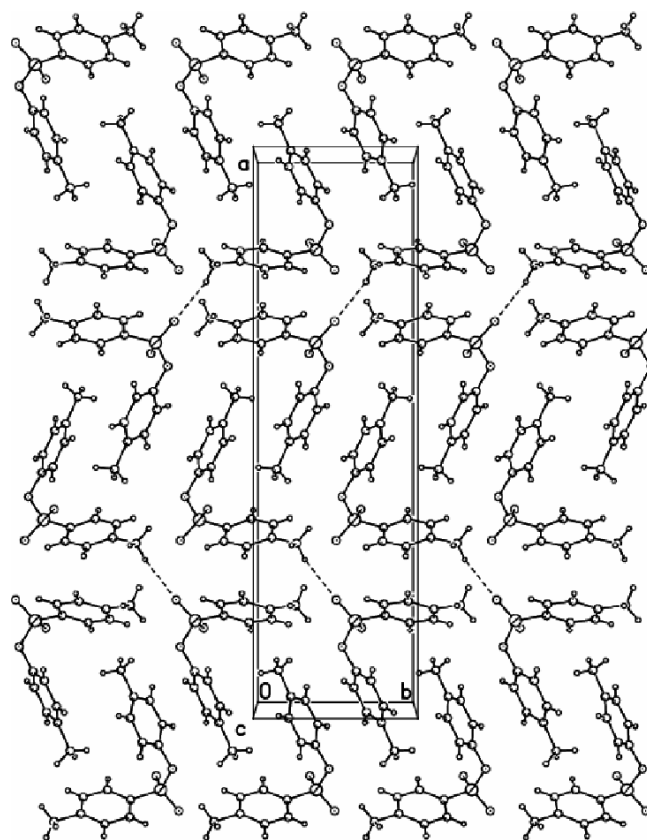


Figure 3
Packing of the title molecule, viewed down the c axis

There are a few other C—H \cdots O and C—H \cdots π and interactions which contribute to the supramolecular aggregation (Fig. 3) of the title compound.

Experimental

4-Toluenesulfonyl chloride (4.7 mmol) dissolved in acetone (4 ml) was added dropwise to 4-cresol (4.3 mmol) in aqueous NaOH (2.5 ml, 10%) with constant shaking. The precipitated title compound (2.9 mmol, yield 67%) was filtered off and recrystallized from aqueous ethanol.

Crystal data

$C_{14}H_{14}O_3S$
 $M_r = 262.31$
Orthorhombic, $Pca2_1$
 $a = 27.6120(2) \text{ \AA}$
 $b = 7.9470(3) \text{ \AA}$
 $c = 5.9770(10) \text{ \AA}$
 $V = 1311.5(2) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.328 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
Cell parameters from 11 929 reflections
 $\theta = 2.5\text{--}30.0^\circ$
 $\mu = 0.24 \text{ mm}^{-1}$
 $T = 150(2) \text{ K}$
Plate, colorless
 $0.37 \times 0.20 \times 0.02 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
with an Oxford Cryosystems
Cryostream cooler
 ω scans with κ offsets
Absorption correction: multi-scan
(SCALEPACK; Otwinowski & Minor, 1997)
 $T_{\min} = 0.926$, $T_{\max} = 0.995$

19 182 measured reflections
3402 independent reflections
1991 reflections with $I > 2\sigma(I)$
 $\theta_{\max} = 30.0^\circ$
 $h = 0 \rightarrow 37$
 $k = 0 \rightarrow 11$
 $l = -8 \rightarrow 8$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.083$
 $S = 0.85$
 3402 reflections
 167 parameters
 H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.17 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.29 \text{ e } \text{Å}^{-3}$
 Absolute structure: Flack (1983),
 2093 Friedel pairs
 Flack parameter = 0.36 (8)

Table 1
 Selected geometric parameters (Å, °).

S1–O1	1.4153 (14)	S1–C1	1.749 (2)
S1–O2	1.4199 (16)	O3–C8	1.415 (2)
S1–O3	1.6023 (15)		
O1–S1–O2	120.89 (12)	O2–S1–C1	109.12 (10)
O1–S1–O3	102.99 (9)	O3–S1–C1	103.59 (9)
O2–S1–O3	108.15 (9)	C8–O3–S1	117.81 (12)
O1–S1–C1	110.54 (10)		
O1–S1–O3–C8	179.25 (15)	C1–S1–O3–C8	64.02 (17)
O2–S1–O3–C8	−51.70 (16)		

Table 2
 Hydrogen-bonding geometry (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A
C2–H2...O2	0.93	2.54	2.912 (2)	104
C6–H6...O1	0.93	2.75	3.036 (3)	99
C9–H9...O2	0.93	2.80	3.091 (3)	99
C3–H3...O1 ⁱ	0.93	2.70	3.442 (2)	137
C3–H3...O3 ⁱ	0.93	2.85	3.727 (2)	158
C6–H6...O2 ⁱⁱ	0.93	2.86	3.144 (3)	99
C13–H13...O2 ⁱⁱ	0.93	2.60	3.506 (3)	166
C7–H7A...O1 ⁱⁱⁱ	0.96	2.54	3.428 (2)	154
C7–H7B...O1 ^{iv}	0.96	3.00	3.566 (3)	119
C5–H5...Cg1 ⁱⁱⁱ	0.93	2.84	3.58	137
C9–H9...Cg2 ^v	0.93	3.18	3.70	117
C10–H10...Cg2 ^v	0.93	3.36	3.80	111

Symmetry codes: (i) $x, y - 1, z$; (ii) $x, y, z - 1$; (iii) $\frac{1}{2} - x, y - 1, z - \frac{1}{2}$; (iv) $x, y - 1, z - 1$; (v) $-x, 1 - y, \frac{1}{2} + z$. Cg1 and Cg2 are the centroids of the C1–C6 and C8–C13 rings, respectively.

All H atoms were included in calculated positions, with aromatic C–H distances of 0.93 Å and methyl C–H distances of 0.96 Å, and refined as riding. Displacement parameters were refined for the aromatic and methyl groups. The Flack (1983) parameter, with low precision, indicates partial inversion twinning.

Data collection: COLLECT (Nonius, 1997); cell refinement: DENZO and SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO and SCALEPACK; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97.

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