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Key indicators

Single-crystal X-ray study
 $T = 150$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.041
 wR factor = 0.117
Data-to-parameter ratio = 25.2

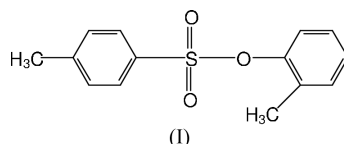
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

2-Methylphenyl 4-toluenesulfonate: supramolecular aggregation through weak C—H···O, C—H··· π and π — π interactions

In the crystal structure of the title compound, $\text{C}_{14}\text{H}_{14}\text{O}_3\text{S}$, the dihedral angle between the planes of the two benzene rings is $45.51(5)^\circ$. There are weak C—H···O hydrogen bonds which generate rings of graph-set motifs $S(5)$, $S(6)$ and $R_2^1(6)$. The supramolecular aggregation is completed by the presence of C—H··· π and π — 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-naphthalene sulfonate, 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. An X-ray study of the title compound, (I), was undertaken in order to determine its crystal and molecular structure owing to 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, NUNCHI, RASSOT, RELVUZ, SIMVUF, TCPTOS, TEBFOV, TMPDTS, TSMIPH, WOHCUR, ZZZBDA10 and MIWHIJ) that are closely related to the title compound in that they all contain the *p*-toluenesulfonyl group. The S—C, S—O and S=O bond lengths (Table 1) are comparable to those found in related structures (Vembu, Nallu, Garrison & Youngs, 2003*a,b,c,d,e,f*; Vembu, Nallu, Spencer & Howard, 2003*a,b,c,d,e,f,g*; Vembu *et al.*, 2003; Vembu *et al.*, 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 planes of the two benzene rings is $45.51(5)^\circ$. 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 *et al.*, 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 *et al.*, 2003) and 8-quinolyl 3-nitrobenzenesulfonate (Vembu, Nallu, Spencer & Howard, 2003*e*).

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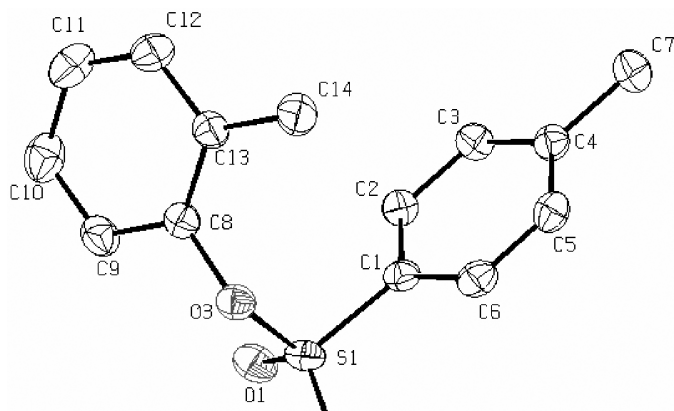


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted.

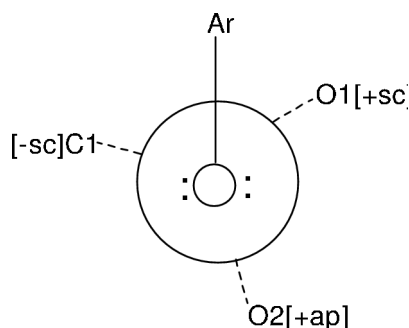


Figure 2
A Newman projection of the title molecule along the S1—O3 bond.

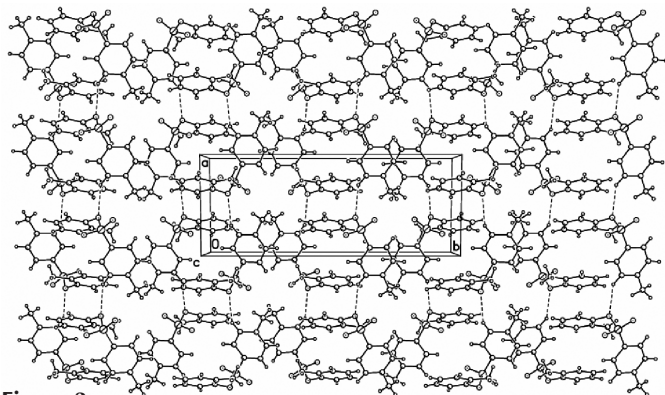


Figure 3
The molecular packing, viewed down the *c* axis. Dashed lines indicate hydrogen bonds.

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 atom C1, attached to sulfur, have been deduced from the corresponding torsion angles (C8—O3—S1—O1/O2/C1) and depicted in Fig. 2. The C1—S1—O3—C8 torsion angle is $-73.44(8)^\circ$, which corresponds to a $-$ synclinal conformation.

The crystal structure of (I) is stabilized by weak C—H \cdots O interactions (Table 2). The H \cdots O distances found in (I) agree with those found for weak C—H \cdots O bonds (Desiraju & Steiner, 1999). In (I), the C2—H2 \cdots O2, C6—H6 \cdots O2 and C14—H14B \cdots O3 interactions each generate an $S(5)$ graph-

set motif (Bernstein *et al.*, 1995; Etter, 1990). All the $S(5)$ rings were found to be non-planar. The C9—H9 \cdots O1 interaction generates an $S(6)$ motif. The C2—H2 \cdots O1 and C9—H9 \cdots O1 interactions together constitute a pair of bifurcated acceptor bonds.

The C3—H3 \cdots O3ⁱⁱ and C7—H7A \cdots O3ⁱⁱ interactions constitute a pair of bifurcated acceptor bonds generating an $R_2^1(6)$ motif. Another $R_2^1(6)$ is generated by C12—H12 \cdots O1ⁱⁱⁱ and C14—H14C \cdots O1ⁱⁱⁱ interactions (symmetry codes as in Table 2). The two symmetry-related (by $1-x, -y, 2-z$) 2-methylphenyl rings are stacked with a distance of 3.775 \AA between them.

Fig. 3 shows the complete range of intermolecular interactions which contribute to the supramolecular aggregation of the title compound.

Experimental

4-Toluenesulfonyl chloride (4.7 mmol), dissolved in acetone (4 ml) was added dropwise to 2-cresol (4.3 mmol) in aqueous NaOH (2.5 ml, 10%) with constant shaking. The precipitated title compound (2.7 mmol, yield 63%) was filtered and recrystallized from aqueous ethanol.

Crystal data

$C_{14}H_{14}O_3S$
 $M_r = 262.31$
Monoclinic, $P2_1/c$
 $a = 7.8660(4) \text{ \AA}$
 $b = 20.0760(9) \text{ \AA}$
 $c = 8.1060(3) \text{ \AA}$
 $\beta = 97.794(2)^\circ$
 $V = 1268.26(10) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.374 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 9865 reflections
 $\theta = 2.5\text{--}35.0^\circ$
 $\mu = 0.25 \text{ mm}^{-1}$
 $T = 150(2) \text{ K}$
Fragment, colorless
 $0.50 \times 0.35 \times 0.35 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
with an Oxford Cryosystems
Cryostream cooler
 ω scans with κ offsets
Absorption correction: multi-scan
(SCALEPACK; Otwinowski &
Minor, 1997)
 $T_{\min} = 0.858, T_{\max} = 0.917$

21 364 measured reflections
5524 independent reflections
3367 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$
 $\theta_{\max} = 34.9^\circ$
 $h = 0 \rightarrow 12$
 $k = -26 \rightarrow 32$
 $l = -13 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.117$
 $S = 0.92$
5524 reflections
219 parameters

All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0644P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.41 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.59 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

S1—O2	1.4261 (9)	S1—C1	1.7482 (12)
S1—O1	1.4268 (9)	O3—C8	1.4210 (13)
S1—O3	1.6070 (8)		
O2—S1—O1	120.20 (5)	O1—S1—C1	109.40 (6)
O2—S1—O3	103.35 (5)	O3—S1—C1	103.26 (5)
O1—S1—O3	108.89 (5)	C8—O3—S1	119.06 (7)
O2—S1—C1	110.26 (6)		
O2—S1—O3—C8	171.63 (8)	C1—S1—O3—C8	$-73.44(8)$
O1—S1—O3—C8	42.75 (9)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H2···O1	0.922 (14)	2.591 (13)	2.9441 (14)	103.4 (10)
C6—H6···O2	0.874 (19)	2.631 (18)	2.9859 (16)	105.5 (13)
C9—H9···O1	0.988 (17)	2.647 (16)	3.0043 (16)	101.5 (11)
C14—H14A···Cg1	0.96 (2)	2.780	3.597	143
C14—H14B···O3	0.905 (18)	2.575 (18)	2.8873 (16)	101.0 (13)
C2—H2···O1 ⁱ	0.922 (14)	2.785 (15)	3.5757 (15)	144.5 (10)
C3—H3···O3 ⁱⁱ	0.982 (16)	2.579 (16)	3.4333 (14)	145.5 (12)
C7—H7A···O3 ⁱⁱ	0.96 (2)	2.77 (2)	3.4705 (17)	130.6 (14)
C12—H12···O1 ⁱⁱⁱ	1.004 (14)	2.701 (15)	3.6097 (15)	150.6 (11)
C14—H14C···O1 ⁱⁱⁱ	0.82 (2)	2.94 (2)	3.7115 (16)	156.5 (16)
C7—H7B···Cg1 ^{iv}	0.97 (2)	3.100	3.977	151

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $x-1, y, z$; (iii) $x, y, 1+z$; (iv) $x, -\frac{1}{2}-y, z-\frac{1}{2}$.
Note: Cg1 is the centroid of the of the C1–C6 aromatic ring.

All H atoms were located in a difference Fourier map and their positions and isotropic displacement parameters were refined.

Data collection: *COLLECT* (Nonius, 2000); 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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