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

Vadivelu Manivannan,[a] Nagarajan Vembu,[b]*‡ Maruthai Nallu,[b] Kandasamy Sivakumar[c] and Anthony Linden[d]

[a]Department of Physics, Presidency College, Chennai 600 005, India, [b]Department of Chemistry, Bharathidasan University, Tiruchirappalli 620 024, India, [c]Department of Physics, Anna University, Chennai 600 025, India, and [d]Institute of Organic Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland

‡ Correspondence address: Department of Chemistry, Urumu Dhanalakshmi College, Tiruchirappalli 620 019, Tamil Nadu, India.

Correspondence e-mail: vembu57@yahoo.com

In the crystal structure of the title compound, $C_{13}H_{12}O_3S$, the dihedral angle between the mean planes of the 4-tolyl and phenyl rings is 52.6 (1)°. There are weak C—H···O hydrogen bonds, which generate rings of graph-set motifs $R_1^2(4)$ and $R_2^1(9)$. The supramolecular aggregation is completed by the presence of van der Waals short contacts and C—H···π interactions.

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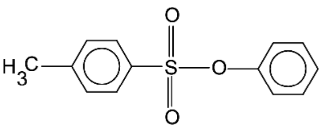
Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.005 Å
R factor = 0.067
wR factor = 0.177
Data-to-parameter ratio = 20.9

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

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). The crystal structure of the title compound 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 (Niestroj *et al.*, 1998), FIXCAQ (Chinnakali *et al.*, 1999), NEDXUP, NEDYAW and NEDYIE (Gallucci *et al.*, 1998), NUNCII (Goswami *et al.*, 1998), RASSOT (Işik *et al.*, 1997), RELVUZ (Bott *et al.*, 1996), SIMVUF (Bindal *et al.*, 1990), TCPTOS (Wieczorek & Galdecki, 1978), TEBFOV (Prince *et al.*, 1991), TMPDTS (Wieczorek *et al.*, 1975), TSMIPH (Sarkar & Gupta, 1980), WOHCUR (Meents *et al.*, 2000), ZZZBDA10 (Wieczorek, 1980) and MIWHIJ (Lee *et al.*, 2001)] that are closely related to the title compound in having benzene rings attached to the sulfonate 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, Nallu, Durmus *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 mean planes of the C1–C6 and C8–C13 rings is 52.6 (1)°.



(I)

Fig. 2 shows a Newman projection along the S1—O3 bond, with atom C8 at the top for reference. Helical nomenclature is followed in assigning + or −synclinal and +antiperiplanar conformations. Since the C1—S1—O3—C8 torsion angle is −72.1 (2)°, which corresponds to a −synclinal conformation, the dihedral angle between the two aromatic planes is, as expected, large [52.6 (1)°].

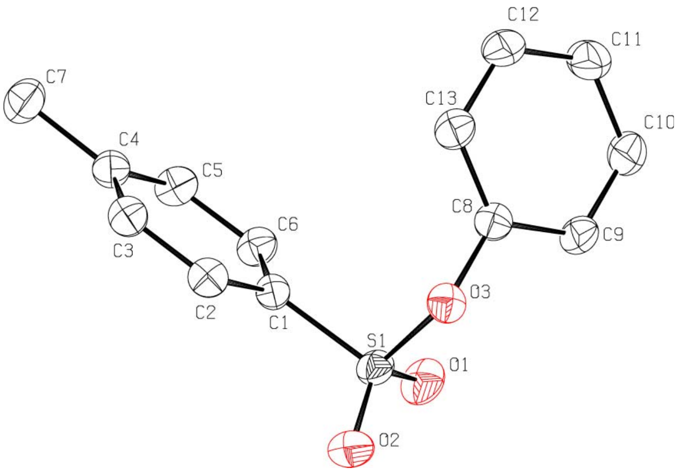


Figure 1
The molecular structure of the title molecule, showing 50% probability displacement ellipsoids. H atoms have been omitted.

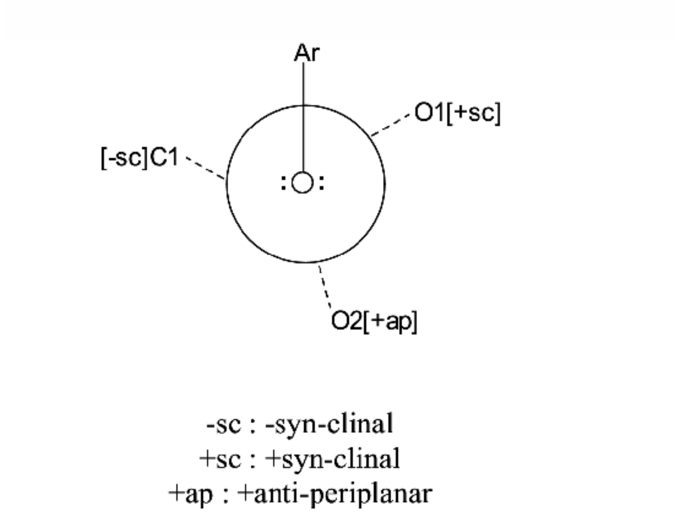


Figure 2
Newman projection of the title molecule, along the S—O bond.

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). The C2—H2$\cdots$O1^{i} and C13—H13$\cdots$O1^{i} interactions (see Table 2 for symmetry codes) together constitute a pair of bifurcated acceptor bonds generating a ring of graph set $R_2^1(9)$. The C5—H5$\cdots$O3^{iii} and C5—H5$\cdots$O2^{iii} interactions together form a pair of bifurcated donor bonds generating a ring of graph set $R_1^2(4)$. This motif can be considered as a symmetrical three-center hydrogen-bonded chelate, as the difference in H$\cdots$*A* distances and *D*—H$\cdots$*A* angles are 0.02 Å and 19.7°, respectively, and the sum of the angles around the chelating H atom is 341°. There are a few other C—H$\cdots$O, C—H$\cdots\pi$ and van der Waals interactions, which contribute to the supramolecular aggregation (Fig. 3) of the title compound.

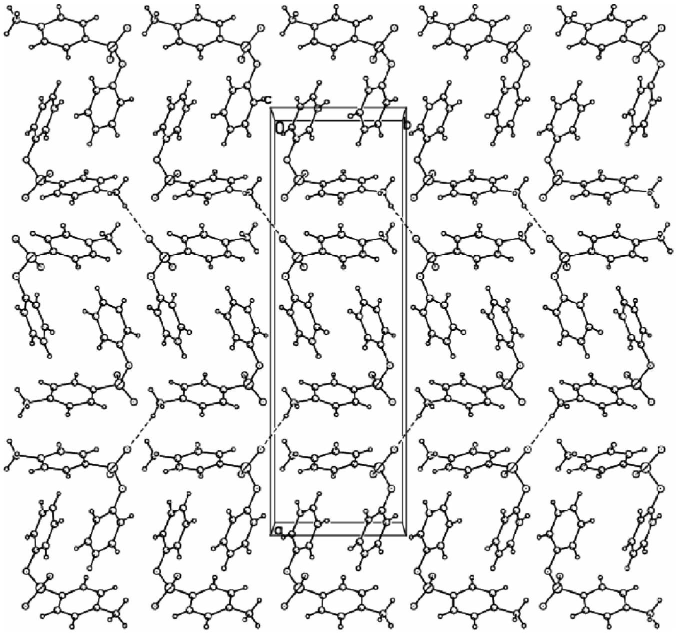


Figure 3
Packing of the title molecule, viewed down the *c* axis. Dashed lines indicate hydrogen bonds.

Experimental

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

Crystal data

$C_{13}H_{12}O_3S$
$M_r = 248.29$
Orthorhombic, $Pca2_1$
$a = 25.149\ (4)$ Å
$b = 7.976\ (5)$ Å
$c = 5.916\ (4)$ Å
$V = 1186.7\ (10)$ Å^3
$Z = 4$

$D_x = 1.390$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 15$–$19°$
$\mu = 0.27$ mm^{-1}
$T = 173\ (2)$ K
Thick plate, colorless
0.50 × 0.33 × 0.15 mm

Data collection

Rigaku AFC-5*R* diffractometer
ω scans
Absorption correction: ψ scan
(North *et al.*, 1968)
$T_{\min} = 0.946$, $T_{\max} = 0.963$
3909 measured reflections
3277 independent reflections
2819 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.052$
$\theta_{\max} = 30.0°$
$h = -35 \rightarrow 35$
$k = -11 \rightarrow 10$
$l = -8 \rightarrow 8$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.177$
$S = 1.09$
3277 reflections
157 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1163P)^2 + 0.1087P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.60$ e Å^{-3}
$\Delta\rho_{\min} = -1.40$ e Å^{-3}
Absolute structure: (Flack, 1983), 1386 Friedel pairs
Flack parameter: −0.07 (12)

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Table 1
Selected geometric parameters (Å, °).

S1—O2	1.427 (2)	S1—C1	1.754 (3)
S1—O1	1.431 (3)	O3—C8	1.410 (3)
S1—O3	1.611 (2)		
O2—S1—O1	120.98 (17)	O1—S1—C1	108.99 (14)
O2—S1—O3	103.05 (13)	O3—S1—C1	103.50 (13)
O1—S1—O3	108.36 (14)	C8—O3—S1	117.68 (18)
O2—S1—C1	110.40 (14)		
O2—S1—O3—C8	172.8 (2)	C1—S1—O3—C8	−72.1 (2)
O1—S1—O3—C8	43.5 (3)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C13—H13···O1$^{\rm i}$	0.93	2.76	3.643 (4)	158
C2—H2···O2$^{\rm ii}$	0.93	2.99	3.761 (4)	141
C5—H5···O3$^{\rm iii}$	0.93	2.78	3.649 (4)	155
C5—H5···O2$^{\rm iii}$	0.93	2.76	3.484 (4)	135
C7—H7*B*···O2$^{\rm iv}$	0.96	2.98	3.543 (5)	119
C7—H7*C*···O2$^{\rm v}$	0.96	2.53	3.406 (4)	152
C10—H10···O3$^{\rm vi}$	0.93	2.89	3.644 (4)	140
C3—H3···Cg1$^{\rm ii}$	0.93	2.83	3.58	138
C9—H9···Cg2$^{\rm vii}$	0.93	2.92	3.64	135
C11—H11···Cg1$^{\rm viii}$	0.93	3.33	4.09	141
C12—H12···Cg2$^{\rm ix}$	0.93	3.08	3.84	141

Symmetry codes: (i) $x, y, z+1$; (ii) $-x+\frac{1}{2}, y, z+\frac{1}{2}$; (iii) $x, y+1, z$; (iv) $x, y+1, z+1$; (v) $-x+\frac{1}{2}, y+1, z+\frac{1}{2}$; (vi) $-x+1, -y+1, z-\frac{1}{2}$; (vii) $-x, -y+1, z-\frac{1}{2}$; (viii) $-x, -y+2, z-\frac{1}{2}$; (ix) $-x, -y+2, z+\frac{1}{2}$. Notes: *Cg*1 and *Cg*2 are the ceentroids 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 with a riding model. Their displacement parameters were tied to common free varibles which were refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); 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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