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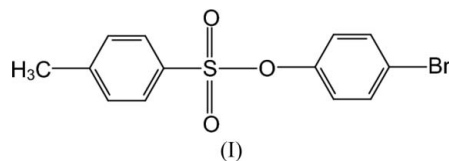
## Key indicators

Single-crystal X-ray study  
 $T = 120$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.008$  Å  
 $R$  factor = 0.035  
 $wR$  factor = 0.094  
Data-to-parameter ratio = 7.6For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.4-Bromophenyl 4-toluenesulfonate: supramolecular  
aggregation through weak C—H···O and C—H··· $\pi$   
interactions

In the crystal structure of the title compound,  $\text{C}_{13}\text{H}_{11}\text{BrO}_3\text{S}$ , the dihedral angle between the mean planes of the 4-tolyl and 4-bromophenyl rings is  $67.3(2)^\circ$ . There are weak C—H···O hydrogen bonds which generate rings of graph-set motifs  $S(5)$ ,  $S(6)$ ,  $R_1^1(4)$ ,  $R_2^1(6)$  and  $R_2^2(8)$ . The supramolecular aggregation is completed by the presence of C—H··· $\pi$  interactions. An  $R_2^2(7)$  motif formed by the combination of a C—H···O and a C—H··· $\pi$  interaction is a notable feature in the title compound.

## 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). An X-ray crystallographic study of the title compound, (I), was undertaken in order to determine its 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 (Niestroj *et al.*, 1998), FIXCAQ (Chinnakali *et al.*, 1999), NEDXUP, NEDYAW, 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 *et al.*, 2004, and references therein; Manivannan *et al.*, 2005, and references therein).



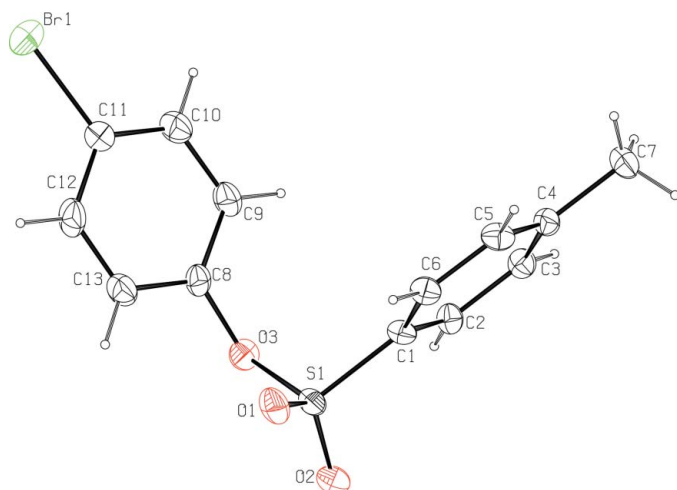
The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. The dihedral angle between the mean planes of the C1—C6 and C8—C13 rings is  $67.3(2)^\circ$ .

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

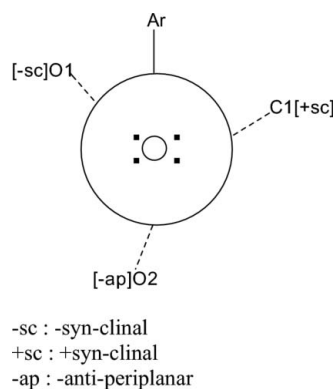
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**Figure 1**  
The molecular structure of the title compound, showing 50% probability displacement ellipsoids.

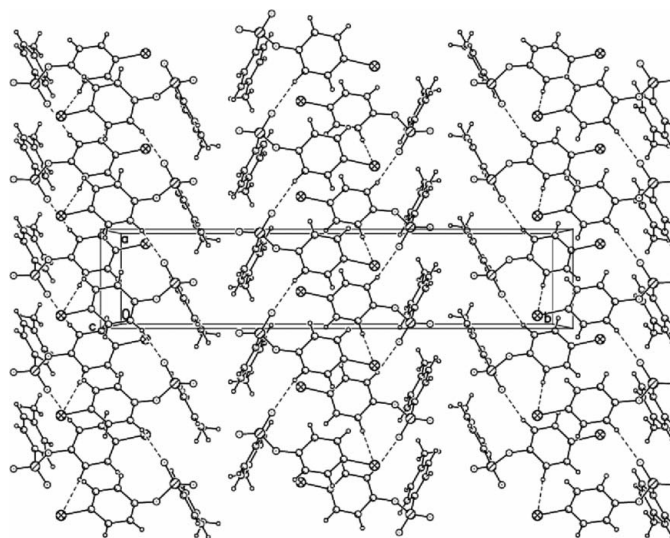


**Figure 2**  
Newman projection of the title molecule along the S—O bond.

angle is  $73.3(4)^\circ$ , which corresponds to a (+)synclinal disposition, the dihedral angle between the two aromatic planes is, as expected, large at  $67.3(2)^\circ$ .

The crystal structure of (I) is stabilized by weak C—H $\cdots$ O interactions (Table 2). The range for the H $\cdots$ O distances found 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  $S(5)$  ring generated by the C2—H2 $\cdots$ O2 interaction is non-planar, as the atom O2 deviates by  $0.94(1)$  Å from the mean plane of the other four atoms, whereas the  $S(5)$  ring generated by the C6—H6 $\cdots$ O1 interaction is planar, as the atom H6 is almost in the same plane as the other four atoms (its distance from their mean plane being  $0.024$  Å). The C13—H13 $\cdots$ O1 interaction generates an  $S(6)$  motif which is found to be non-planar, as atoms S1, O1 and H13 deviate by  $1.361(8)$ ,  $2.16(1)$  and  $0.094$  Å, respectively, from the plane of the other three atoms. The C6—H6 $\cdots$ O1 and C13—H13 $\cdots$ O1 interactions together constitute a pair of bifurcated acceptor bonds.

The C2—H2 $\cdots$ O2<sup>i</sup> and C3—H3 $\cdots$ Cg1<sup>i</sup> interactions together generate an  $R_2^2(7)$  motif (see Table 2 for symmetry codes).



**Figure 3**  
The packing in (I), viewed down the  $c$  axis. Dashed lines indicate hydrogen bonds.

This is a special kind of motif in the sense that the entire aromatic ring comprising the atoms C1—C6 (here designated as Cg1) is taken as an acceptor.

The C5—H5 $\cdots$ O2<sup>ii</sup> and C5—H5 $\cdots$ O3<sup>ii</sup> interactions together form a pair of bifurcated donor bonds generating a ring of graph set  $R_1^2(4)$ . The above motif can be considered as a symmetrical three-center hydrogen-bonded chelate (Desiraju, 1989), as the difference in distances and angles are  $0.24$  Å and  $17^\circ$ , respectively, and the bite angle and sum of the angles around the chelating H atom are  $51.7$  and  $346^\circ$ , respectively.

The C7—H7C $\cdots$ O3<sup>ii</sup> and C5—H5 $\cdots$ O3<sup>ii</sup> interactions together form a pair of bifurcated acceptor bonds generating a ring of graph set  $R_2^1(6)$ . The C5—H5 $\cdots$ O2<sup>ii</sup> and C7—H7C $\cdots$ O3<sup>ii</sup> interactions together form an  $R_2^2(8)$  motif which consists of the  $R_2^1(4)$  and the  $R_2^1(6)$  motifs.

There are a few other C—H $\cdots$ O and C—H $\cdots$  $\pi$  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-bromophenol (4.0 mmol) in aqueous NaOH (2.5 ml, 10%) with constant shaking. The precipitated title compound (2.8 mmol, yield 70%) was filtered off and recrystallized from aqueous ethanol.

### Crystal data

$C_{13}H_{11}BrO_3S$   
 $M_r = 327.19$   
Orthorhombic,  $Pna2_1$   
 $a = 5.9422(2)$  Å  
 $b = 28.3304(10)$  Å  
 $c = 7.9071(3)$  Å  
 $V = 1331.12(8)$  Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.633$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
Cell parameters from 1207 reflections  
 $\theta = 2.5$ – $25.0^\circ$   
 $\mu = 3.24$  mm<sup>-1</sup>  
 $T = 120$  K  
Prism, colorless  
 $0.27 \times 0.22 \times 0.10$  mm

Data collection

KappaCCD diffractometer (with an Oxford Cryosystems Cryostream cooler)	4173 measured reflections 1253 independent reflections 1199 reflections with $I > 2\sigma(I)$
$\omega$ scans with $\kappa$ offsets	$R_{\text{int}} = 0.030$
Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997)	$\theta_{\text{max}} = 25.0^\circ$ $h = -7 \rightarrow 7$ $k = -33 \rightarrow 33$ $l = -9 \rightarrow 9$
$T_{\text{min}} = 0.543$ , $T_{\text{max}} = 0.738$	

Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.054P)^2 + 1.694P]$
$R[F^2 > 2\sigma(F^2)] = 0.035$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.094$	$(\Delta/\sigma)_{\text{max}} = 0.013$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.39 \text{ e } \text{Å}^{-3}$
1253 reflections	$\Delta\rho_{\text{min}} = -0.51 \text{ e } \text{Å}^{-3}$
164 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Br1—C11	1.893 (5)	S1—O3	1.600 (4)
S1—O2	1.418 (4)	S1—C1	1.748 (5)
S1—O1	1.423 (4)	O3—C8	1.402 (6)
O2—S1—O1	120.5 (3)	O1—S1—C1	109.2 (3)
O2—S1—O3	103.4 (2)	O3—S1—C1	103.9 (2)
O1—S1—O3	108.3 (2)	C8—O3—S1	121.3 (3)
O2—S1—C1	110.1 (3)		
O2—S1—O3—C8	−171.7 (4)	C1—S1—O3—C8	73.3 (4)
O1—S1—O3—C8	−42.7 (5)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H2 $\cdots$ O2	0.93	2.85	3.082 (7)	95
C6—H6 $\cdots$ O1	0.93	2.53	2.903 (8)	105
C13—H13 $\cdots$ O1	0.93	2.88	3.145 (7)	98
C2—H2 $\cdots$ O2 <sup>ii</sup>	0.93	2.94	3.664 (7)	136
C5—H5 $\cdots$ O2 <sup>ii</sup>	0.93	2.84	3.593 (7)	139
C7—H7C $\cdots$ O3 <sup>iii</sup>	0.96	2.84	3.724 (8)	154
C5—H5 $\cdots$ O3 <sup>iii</sup>	0.93	2.60	3.470 (6)	156
C7—H7A $\cdots$ O2 <sup>iii</sup>	0.96	2.53	3.398 (8)	150
C7—H7B $\cdots$ O2 <sup>iv</sup>	0.96	2.90	3.454 (7)	118
C9—H9 $\cdots$ O1 <sup>v</sup>	0.93	2.37	3.230 (6)	153
C3—H3 $\cdots$ Cg1 <sup>i</sup>	0.93	2.84	3.595	139
C10—H10 $\cdots$ Cg2 <sup>vi</sup>	0.93	3.23	3.980	139

Symmetry codes: (i)  $x - \frac{1}{2}, -y + \frac{1}{2}, z$ ; (ii)  $x, y, z + 1$ ; (iii)  $x - \frac{1}{2}, -y + \frac{1}{2}, z + 1$ ; (iv)  $x - 1, y, z + 1$ ; (v)  $x - 1, y, z$ ; (vi)  $-x, -y, z + \frac{1}{2}$ .

With Friedel pairs present, the Flack (1983) parameter refined to 0.55 (2). The crystal was judged therefore to be an inversion twin with essentially equal twin components, and the final refinement was carried out with Friedel pairs merged. 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 were refined with a riding model. The displacement parameters of the H atoms were assigned as 1.2 $U_{\text{eq}}$  for aromatic and 1.5 $U_{\text{eq}}$  for methyl H atoms.

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) and SHELXTL (Sheldrick, 1998); software used to prepare material for publication: SHELXL97.

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