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

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In the title molecule, $C_{14}H_{14}O_4S$, the dihedral angle between the mean planes of the 4-tolyl and 4-methoxyphenyl rings is 7.2 (1)°. There are weak intermolecular C—H···O hydrogen bonds which generate rings of motifs $R_2^1(6)$, $R_2^1(9)$ and $R_1^2(4)$. There are also C—H···π interactions which stack the molecules in layers in the crystal lattice.

Comment

p-Toluenesulfonates are used in monitoring the merging of lipids (Yachi *et al.*, 1989), studying membrane fusion during acrosome reaction (Spungin *et al.*, 1992), development of immunoaffinity chromatography for the purification of human coagulation factor (Tharakan *et al.*, 1992), chemical studies on viruses (Alford *et al.*, 1991), development of technology for linking photosensitizers to model monoclonal antibodies (Jiang *et al.*, 1990) and chemical modification of sigma sub units of *E. coli* RNA polymerase (Narayanan & Krakow, 1983). An X-ray study of the title compound, (I), was undertaken in order to determine its crystal and molecular structure because of the biological importance of its analogs.

(I)
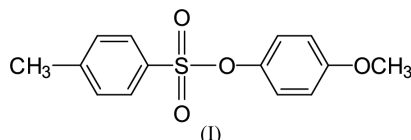
A search of Version 5.23 (July 2002 updates) of the Cambridge Structural Database (Allen, 2002) revealed 16 structures (with the following refcodes: KAWDAN, FIXCAQ, NEDXUP, NEDYAW, NEDYIE, NUNCII, RASSOT, RELVUZ, SIMVUF, TCPTOS, TEBFOV, TMPDTS, TSMIPH, WOHCUR, ZZZBDA10 and MIWHIJ) that are closely related to the title compound (I). The S—C, S—O and S=O bond lengths (Table 1) are comparable to those found in these structures. The dihedral angle between the mean planes of the 4-tolyl and the 4-methoxyphenyl rings is 7.2 (1)°. This shows their approximately coplanar orientation, similar to that found in 2,4-dinitrophenyl 4-toluenesulfonate (Vembu *et al.*, 2003*a*) and in contrast to the non-coplanar orientation in 2-chlorophenyl 4-toluenesulfonate (Vembu *et al.*, 2003*b*) and the non-coplanar orientation in 8-tosyloxyquinoline (Vembu *et al.*, 2003*c*).

The crystal structure of (I) is stabilized by weak C—H···O interactions (Table 2). The range of the H···O distances agrees with those found for weak C—H···O bonds (Desiraju & Steiner, 1999). The C3—H3···O1[iii] and C1—H1C···O1[iii]
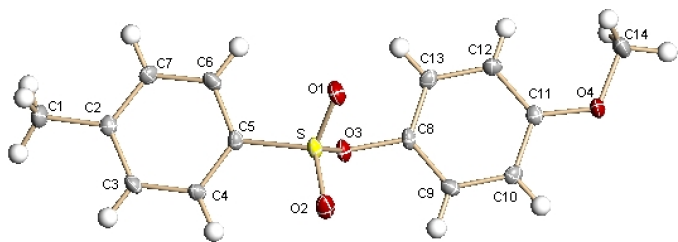
Figure 1
The molecular structure of the title compound, (I), showing displacement ellipsoids at the 50% probability level.

Figure 2
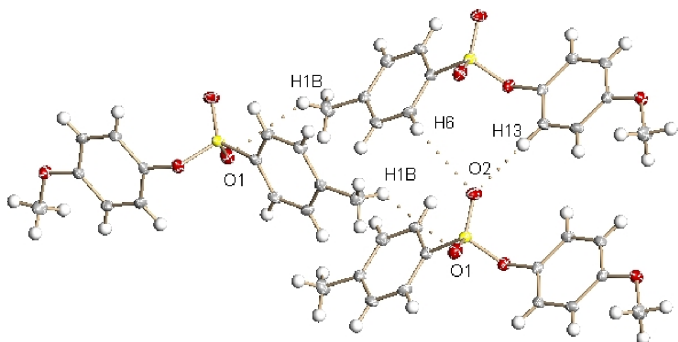Diagram showing some of the C—H···O interactions.

Figure 3
Projection of the crystal structure of (I) approximately along the *b* axis.

interactions constitute a pair of bifurcated acceptor bonds involving H atoms of the neighboring 4-tolyl moiety (see Table 2 for symmetry code). They generate a ring of graph-set (Etter, 1990; Bernstein *et al.*, 1995) motif $R_2^1(6)$. The C1—H1C···O1^{iii} and C1—H1C···O2^{iii} interactions form a pair of bifurcated donor bonds involving the sulfonyl O atoms. They generate a ring of graph set motif $R_1^2(4)$. The H1C···O1^{iii} and H1C···O2^{iii} distances differ by 0.10 Å. The resulting configuration is best regarded as a three-center symmetrical hydrogen-bonded chelate (Desiraju, 1989) and is also observed in 2-chlorophenyl 4-toluenesulfonate (Vembu *et al.*, 2003b) and 8-tosyloxyquinoline (Vembu *et al.*, 2003c). The inter-fusion of $R_2^1(6)$ and $R_1^2(4)$ motifs generates a ring of graph set motif $R_2^2(8)$. The C6—H6···O2^{iv} and C13—H13···O2^{iv} interactions constitute a pair of bifurcated acceptor bonds involving the H atoms of the neighboring 4-tolyl and 4-methoxyphenyl moieties (see Table 2 for symmetry code). They generate a ring of graph-set motif $R_2^1(9)$ (Fig. 2).

The supramolecular aggregation is completed by the presence of four C—H···π interactions which pack the molecules in a slipped stack along the *b* axis (Fig. 3). The geometry of the C—H···π interactions obtained from *PLATON* (Spek, 1998) is given in Table 2, where *Cg*1 and *Cg*2 are the centroids of the 4-tolyl and 4-methoxyphenyl rings, respectively.

Experimental

4–Toluenesulfonyl chloride (4.7 mmol) dissolved in acetone (4 ml) was added dropwise to 4-methoxyphenol (4 mmol) in aqueous NaOH (2.5 ml, 10%) with vigoro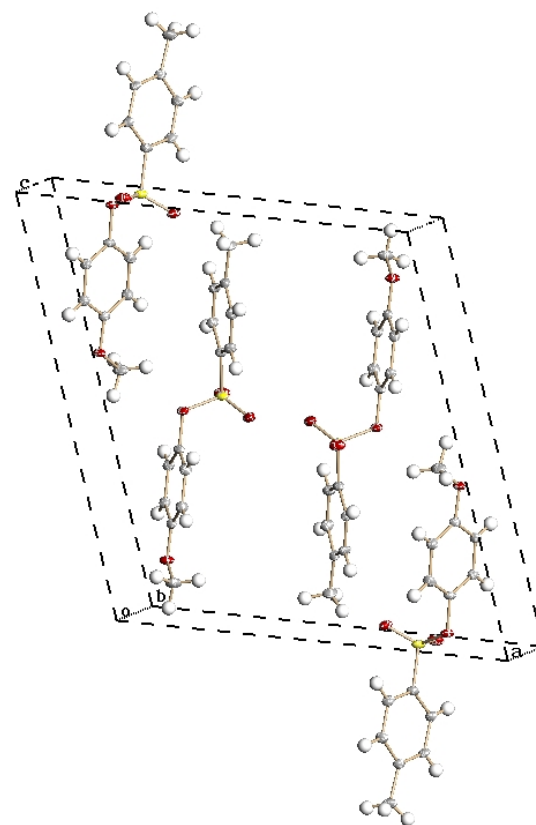us shaking. The precipitated 4-methoxy- phenyl 4-toluenesulfonate (2.7 mmol, yield 67%) was filtered off and recrystallized from diethyl ether.

Crystal data

$C_{14}H_{14}O_4S$	$D_x = 1.439$ Mg m^{-3}
$M_r = 278.31$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 5896
$a = 14.778$ (5) Å	reflections
$b = 5.6665$ (18) Å	$\theta = 2.6–27.6°$
$c = 16.133$ (5) Å	$\mu = 0.26$ mm^{-1}
$\beta = 108.049$ (5)°	$T = 100$ (2) K
$V = 1284.6$ (7) Å^3	Plate, colorless
$Z = 4$	$0.40 \times 0.20 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	2956 independent reflections
	2687 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.042$
Absorption correction: multi-scan	$\theta_{max} = 27.7°$
(*SADABS*; Sheldrick, 1996)	$h = -19 \rightarrow 19$
$T_{min} = 0.736$, $T_{max} = 0.974$	$k = -7 \rightarrow 7$
10615 measured reflections	$l = -20 \rightarrow 21$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.058$	$+ 1.3915P]$
$wR(F^2) = 0.128$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.24$	$(\Delta/\sigma)_{max} = 0.002$
2956 reflections	$\Delta\rho_{max} = 0.58$ e Å^{-3}
228 parameters	$\Delta\rho_{min} = -0.45$ e Å^{-3}
All H-atom parameters refined	

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Table 1
Selected geometric parameters (Å, °).

S—O2	1.4200 (19)	O3—C8	1.417 (3)
S—O1	1.4223 (18)	O4—C11	1.359 (3)
S—O3	1.5936 (17)	O4—C14	1.432 (3)
S—C5	1.745 (2)	C1—C2	1.495 (3)
O2—S—O1	118.77 (11)	O1—S—C5	109.97 (11)
O2—S—O3	108.41 (11)	O3—S—C5	100.21 (10)
O1—S—O3	108.13 (10)	C8—O3—S	114.78 (13)
O2—S—C5	109.71 (11)	C11—O4—C14	117.35 (18)
C5—S—O3—C8	162.5 (2)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C1—H1$A\cdots$O1^{i}	0.92 (5)	2.67 (4)	3.424 (3)	141 (3)
C1—H1$B\cdots$O1^{ii}	0.95 (4)	2.96 (4)	3.551 (3)	122 (3)
C1—H1$C\cdots$O1^{iii}	0.94 (4)	2.73 (4)	3.534 (4)	143 (3)
C1—H1$C\cdots$O2^{iii}	0.94 (4)	2.83 (4)	3.728 (3)	160 (3)
C3—H3$\cdots$O1^{iii}	0.90 (3)	2.61 (3)	3.454 (3)	155 (2)
C6—H6$\cdots$O2^{iv}	0.93 (3)	2.75 (3)	3.383 (3)	126 (3)
C9—H9$\cdots$O4^{v}	0.94 (3)	2.69 (3)	3.414 (3)	135 (2)
C13—H13$\cdots$O2^{iv}	0.93 (3)	2.58 (3)	3.426 (3)	152 (2)
C14—H14$A\cdots$O2^{vi}	0.96 (3)	2.84 (3)	3.486 (4)	125 (2)
C14—H14$A\cdots$O3^{vii}	0.96 (3)	2.71 (3)	3.131 (3)	107 (2)
C14—H14$B\cdots$O4^{viii}	0.99 (3)	2.53 (3)	3.425 (3)	152 (2)
C3—H3$\cdots$$Cg2^{ix}$	0.90 (3)	3.17	3.742	124
C7—H7$\cdots$$Cg1^{x}$	0.95 (3)	2.88	3.644	138
C10—H10$\cdots$$Cg2^{xi}$	0.89 (3)	2.85	3.527	134
C12—H12$\cdots$$Cg1^{vii}$	0.90 (3)	3.09	3.781	135

Symmetry codes: (i) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (ii) $1 - x, \frac{1}{2} + y, \frac{5}{2} - z$; (iii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $x, 1 + y, z$; (v) $-x, y - \frac{1}{2}, \frac{3}{2} - z$; (vi) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (vii) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (viii) $-x, 1 - y, 1 - z$; (ix) $x, \frac{5}{2} - y, \frac{1}{2} + z$; (x) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (xi) $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

All the H atoms were located in a difference Fourier map and their positional coordinates and isotropic displacement parameters were refined. The C—H bond lengths are in the range 0.89 (3)–0.99 (3) Å, the H—C—H angles for the methyl group are in the range 98 (3)–112 (2)° and the C—C—H angles for the aromatic rings are in the range 118.1 (2)–121.9 (2)°.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *SHELXTL*.

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