Methyl 4-tosyloxybenzoate: supramolecular aggregation through C—H⋯O, C—H⋯π and π–π interactions

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In the title molecule, $C_{15}H_{14}O_5S$, the dihedral angle between the mean planes of the 4-tolyl and the 4-benzoate rings is 58.63 (6)°. There are weak intermolecular C—H⋯O interactions, which generate rings of motifs $S(5)$, $S(6)$, $R_2^1(5)$, $R_2^1(6)$ and $R_1^2(4)$. The supramolecular aggregation is completed by C—H⋯π and π–π interactions.

Comment

p-Toluene sulfonates are used in monitoring the merging of lipids (Yachi *et al.*, 1989), studying membrane fusion during acrosome reaction (Spungin *et al.*, 1992), development of immuno-affinity 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 the chemical modification of sigma sub-units of the *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 owing to the biological importance of its analogues.
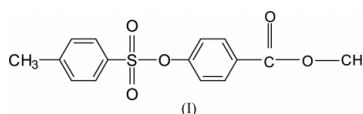

A search of version 5.23 (July 2002 updates) of the Cambridge Structural Database (Allen, 2002) revealed 16 structures (with the following refcodes: KAWDAN, FIXCAQ, NEDXUP, NEDYAW, NEDYIE, NUNCII, RASSOT, RELVUZ, SIMVUF, TCPTOS, TEBFOV, TMPDTS, TSMIPH, WOHCUR, ZZZBDA10 and MIWHIJ) that are closely related to the title compound. The S—C, S—O and S═O bond lengths (Table 1) are comparable to those found in these structures. Atoms C14, O4, O5 and C15 deviate from the mean plane through the central aromatic ring (C8–C13) by −0.078 (3), 0.113 (3), −0.410 (3) and −0.591 (4) Å, respectively. The dihedral angle between the above plane and that formed by the 4-tolyl ring is 58.74 (8)°. This shows their non-coplanar orientation, similar to that found between the 4-tolyl and

2-chlorophenyl rings in 2-chlorophenyl 4-toluenesulfonate (Vembu, Nallu, Garrison & Youngs, 2003*b*) and the 4-tolyl and quinoline rings in 8-tosyloxyquinoline (Vembu, Nallu, Garrison & Youngs, 2003*c*) and in contrast to the near coplanar orientation of the 4-tolyl and 2,4-dinitrophenyl rings in 2,4-dinitrophenyl 4-toluenesulfonate (Vembu, Nallu, Garrison & Youngs, 2003*a*) and 4-tolyl and 4-methoxyphenyl rings in 4-methoxyphenyl 4-toluenesulfonate (Vembu, Nallu, Garrison, Hindi & Youngs, 2003).
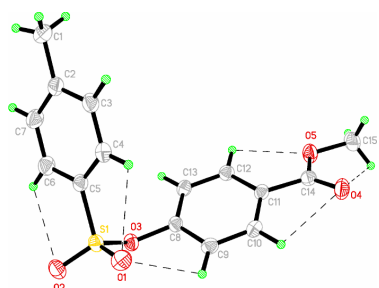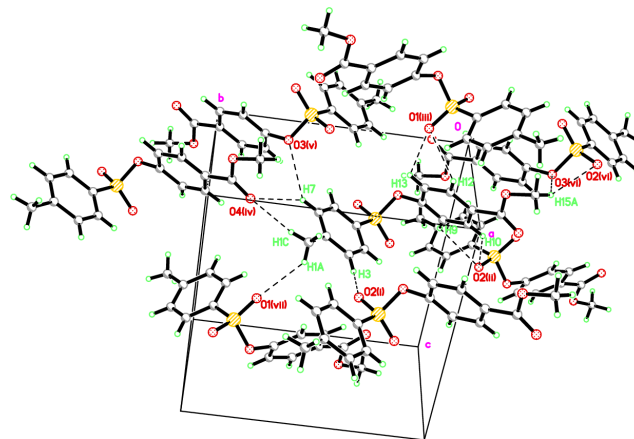
Figure 1
The structure of (I), showing 50% probability displacement ellipsoids and intramolecular C—H···O interactions.

The crystal structure of (I) is stabilized by weak C—H···O interactions. The range for the H···O distances (Table 2) found in (I) agree with those found for weak C—H···O bonds (Desiraju & Steiner, 1999). The C9—H9···O1 (Fig. 1) interaction forms a ring of graph-set motif $S(6)$ (Etter, 1990; Bernstein *et al.*, 1995) and the C4—H4···O1 (Fig. 1) interaction forms a ring of graph set $S(5)$. The above two interactions together constitute a pair of bifurcated acceptor bonds, and these two ring motifs are fused to each other. The C10—H10···O4 and C15—H15A···O4 interactions (Fig. 1) constitute a pair of bifurcated acceptor bonds, each of them generating an $S(5)$ ring motif, which are fused to each other. Two other $S(5)$ rings are formed by C12—H12···O5 and C6—H6···O2 interactions.

The C10—H10···O2[ii] and C9—H9···O2[ii] interactions constitute a pair of bifurcated acceptor bonds, generating a ring of graph set $R^1_2(5)$ (see Table 2 for symmetry codes). The C12—H12···O1[iii] and C13—H13···O1[iii] (Fig. 2) interactions form a pair of bifurcated acceptor bonds, generating another $R^1_2(5)$ motif. The C1—H1C···O4[iv] and C7—H7···O4[iv] interactions constitute a pair of bifurcated acceptor bonds, generating a ring of graph-set $R^1_2(6)$. The C15—H15A···O3[vi] and C15—H15A···O2[vi] interactions constitute a pair of bifurcated donor bonds, generating a ring of graph set $R^2_1(4)$. The H15A···O2[vi] and H15A···O3[vi] distances differ only by 0.14 Å. The resulting configuration is best regarded as a three-centre symmetrical hydrogen-bonded chelate (Desiraju, 1989) and is also observed in similar structures (Vembu, Nallu, Garrison, Hindi & Youngs, 2003; Vembu, Nallu, Garrison & Youngs, 2003b,c). There are several other weak C—H···O interactions (Fig. 2) and C—H···π interactions (Table 2) which contribute to the supramolecular aggregation. In Table 2, Cg1 and Cg2 denote the centroids of the aromatic rings comprising atoms C2–C7 and C8–C13, respectively. In the crystal structure, the inversion-related benzoate phenyl rings (symmetry code: $1 - x$, $-y$, $-z$) are stacked with a centroid···centroid separation of 3.659 (1) Å, indicating weak π–π interactions.

Experimental

Methyl 4-hydroxybenzoate (4.9 mmol) and triethylamine (4.9 mmol) were dissolved separately in acetone (10 ml) and mixed. To this solution, 4-toluenesulfonyl chloride (3.9 mmol) dissolved in acetone (10 ml) was added. The solution was left overnight and evaporated.

Figure 2
Part of the molecular network, showing intermolecular C—H···O interactions. Symmetry codes are as in Table 2.

The residue obtained was washed several times with 2% aqueous triethylamine solution to obtain the crude product. Diffraction quality crystals were obtained by recrystallizing the crude product (2.5 mmol, 64% yield) from ethanol.

Crystal data

$C_{15}H_{14}O_5S$	$D_x = 1.427$ Mg m^{-3}
$M_r = 306.32$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 889
$a = 8.2921$ (10) Å	reflections
$b = 12.2799$ (16) Å	$\theta = 3.1–27.3°$
$c = 14.2746$ (18) Å	$\mu = 0.25$ mm^{-1}
$\beta = 101.229$ (3)°	$T = 120$ (2) K
$V = 1425.7$ (3) Å^3	Block, colourless
$Z = 4$	$0.28 \times 0.24 \times 0.15$ mm

Data collection

Bruker SMART 6K CCD area-detector diffractometer	3289 independent reflections
	2588 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.037$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1998)	$\theta_{max} = 27.6°$
	$h = -10 \rightarrow 10$
$T_{min} = 0.933$, $T_{max} = 0.964$	$k = -15 \rightarrow 15$
15405 measured reflections	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0671P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$+ 0.4296P]$
$wR(F^2) = 0.116$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
3289 reflections	$\Delta\rho_{max} = 0.41$ e Å^{-3}
246 parameters	$\Delta\rho_{min} = -0.41$ e Å^{-3}
All H-atom parameters refined	

Table 1
Selected geometric parameters (Å, °).

O4—C14	1.202 (2)	S1—O2	1.4213 (14)
C11—C14	1.489 (2)	S1—O1	1.4242 (13)
C14—O5	1.339 (2)	S1—O3	1.5983 (12)
C5—S1	1.7461 (18)	O5—C15	1.445 (2)
C1—C2	1.505 (3)		
O2—S1—O1	120.51 (8)	O1—S1—C5	109.63 (8)
O2—S1—O3	102.52 (7)	O3—S1—C5	104.13 (7)
O1—S1—O3	108.83 (7)	C8—O3—S1	120.17 (10)
O2—S1—C5	109.80 (8)	C14—O5—C15	115.82 (15)
C5—S1—O3—C8	72.20 (13)		

Table 2
Geometry of C—H...O and C—H...\p interactions (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9···O1	0.964 (18)	2.495 (19)	2.948 (2)	108.6 (14)
C12—H12···O5	0.98 (2)	2.43 (2)	2.735 (2)	97.3 (13)
C10—H10···O4	0.97 (2)	2.54 (2)	2.834 (2)	97.3 (13)
C6—H6···O2	0.97 (3)	2.62 (3)	2.971 (2)	101.6 (18)
C4—H4···O1	0.94 (2)	2.60 (2)	2.942 (2)	102.2 (14)
C15—H15A···O4	0.96 (3)	2.55 (3)	2.656 (3)	85.5 (17)
C3—H3···O2^{i}	0.94 (2)	2.54 (2)	3.392 (2)	150.3 (19)
C10—H10···O2^{ii}	0.97 (2)	2.64 (2)	3.314 (2)	126.6 (16)
C9—H9···O2^{ii}	0.964 (18)	2.807 (19)	3.371 (2)	118.2 (14)
C13—H13···O1^{iii}	0.95 (2)	2.652 (19)	3.174 (2)	115.0 (14)
C12—H12···O1^{iii}	0.98 (2)	2.61 (2)	3.166 (2)	115.7 (14)
C1—H1C···O4^{iv}	0.90 (3)	2.58 (4)	3.403 (3)	153 (3)
C7—H7···O4^{iv}	0.95 (2)	2.52 (2)	3.355 (2)	145.7 (18)
C7—H7···O3^{v}	0.95 (2)	2.84 (2)	3.585 (2)	135.6 (18)
C15—H15A···O3^{vi}	0.96 (3)	2.82 (3)	3.540 (3)	132 (2)
C15—H15A···O2^{vi}	0.96 (3)	2.96 (3)	3.824 (3)	151 (2)
C1—H1A···O1^{vii}	0.91 (4)	2.83 (4)	3.560 (3)	139 (3)
C1—H1B···Cg1^{viii}	0.94 (4)	3.09 (4)	3.982 (3)	160 (3)
C15—H15B···Cg2^{ix}	0.91 (3)	2.84 (3)	3.693 (3)	156 (2)
C15—H15C···Cg1^{iii}	0.95 (3)	3.09 (3)	3.844 (2)	138 (2)

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

All H atoms were located from a difference Fourier map and both positional and isotropic displacement parameters were refined. The C—H bond lengths are in the range 0.90 (3)–0.98 (2) Å, the H—C—H angles for the methyl group are in the range 102 (3)–113 (2)° and the C—C—H angles for the aromatic rings are in the range 118 (1)–123 (1)°. The U_{iso} values range from 0.021 (5)–0.097 (12) Å^2

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

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