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4-Chlorophenyl 4-toluenesulfonate: supramolecular aggregation through C—H···O, C–H···Cl and C—H···π interactions

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.039
wR factor = 0.094
Data-to-parameter ratio = 15.0

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

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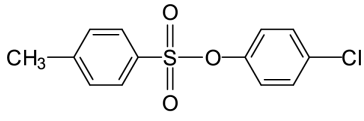
In the crystal structure of the title molecule, $C_{13}H_{11}ClO_3S$, the dihedral angle between the mean planes of the 4-tolyl and 4-chlorophenyl rings is 64.95 (6)°. There are weak C—H···O hydrogen bonds which generate rings of motifs *S*(5), *S*(6), $R_2^1(9)$, $R_1^2(4)$, $R_2^1(6)$ and $R_2^2(8)$. The supramolecular aggregation is completed by the presence of C—H···Cl and C—H···π interactions.

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 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 photosensitizer to model monoclonal antibodies (Jiang *et al.*, 1990) and 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 analogs.



(I)

The dihedral angle between the mean planes of the 4-tolyl and 4-chlorophenyl rings is 64.95 (6)°. This shows their non-coplanar orientation, similar to that found in 2-chlorophenyl 4-toluenesulfonate (Vembu, Nallu, Garrison & Youngs, 2003*b*) and 8-tosyloxyquinoline (Vembu, Nallu, Garrison & Youngs, 2003*c*), and in contrast to the near coplanar orientation observed in 2,4-dinitrophenyl 4-toluenesulfonate (Vembu, Nallu, Garrison, Hindi & Youngs, 2003*a*) and 4-methoxyphenyl 4-toluenesulfonate (Vembu, Nallu, Garrison, Hindi & Youngs, 2003).

The crystal structure of (I) is stabilized by weak C—H···O interactions. The range for the H···O distances (Table 2) agrees with those found for weak C—H···O bonds (Desiraju & Steiner, 1999). The C4—H4···O1 and C4—H4···O3 interactions constitute a pair of bifurcated donor bonds, each of them generating a *S*(5) graph set (Etter, 1990; Bernstein *et al.*, 1995) motif which are fused to each other. The C6—H6···O2 and C13—H13···O2 interactions constitute a pair of bifurcated acceptor bonds. They generate rings of graph-set motifs *S*(5) and *S*(6), respectively, which are fused to each other. The C9—H9···O2^{v} and C4—H4···O2^{v} (Table 2 and Fig. 4) inter-

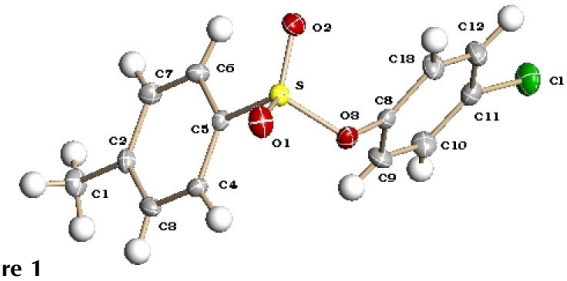


Figure 1
The molecular structure of the title molecule, with displacement ellipsoids drawn at the 50% probability level.

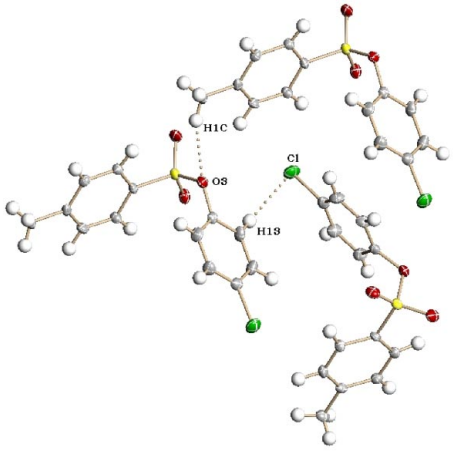


Figure 2
Diagram showing hydrogen bonds 3 and 9 (the numbering relates to the sequence of entries in Table 2).

actions form a pair of bifurcated acceptor bonds, generating a ring of graph set $R_2^1(9)$. The C7—H7···O3^{iii} and C7—H7···O1^{iii} (Fig. 3) interactions form a pair of bifurcated donor bonds generating a ring of graph set $R_1^2(4)$. The H7···O3^{iii} and H7···O1^{iii} distances differ by 0.18 (3) Å. The resulting configuration can be regarded as a three-centered hydrogen-bonded chelate (Desiraju, 1989) and is observed in similar structures (Vembu, Nallu, Garrison & Youngs, 2003*b*,*c*; Vembu, Nallu, Garrison, Hindi & Youngs, 2003). The C7—H7···O3^{iii} (Fig. 3) and C1—H1*C*···O3^{iii} (Fig. 2) interactions constitute a pair of bifurcated acceptor bonds, generating a ring of graph set $R_2^1(6)$. The C1—H1*C*···O3^{iii} (Fig. 2) and C7—H7···O1^{iii} (Fig. 3) interactions generate a $R_2^2(8)$ motif which consists of $R_1^2(4)$ chelate and $R_2^1(6)$ ring motifs.

There are several other C—H···O interactions (Figs. 3 and 4) and a C—H···Cl (Fig. 2) interaction, which contribute to the supramolecular aggregation (Table 2). The supramolecular aggregation is completed by the presence of two C—H···π interactions (Table 2). The geometry of the C—H···π interaction was obtained from *PLATON* (Spek, 1998); *Cg*1 and *Cg*2 are the centroids of the 4-tolyl and 4-chlorophenyl rings, respectively. The molecular packing in the unit cell is shown in Fig. 5.

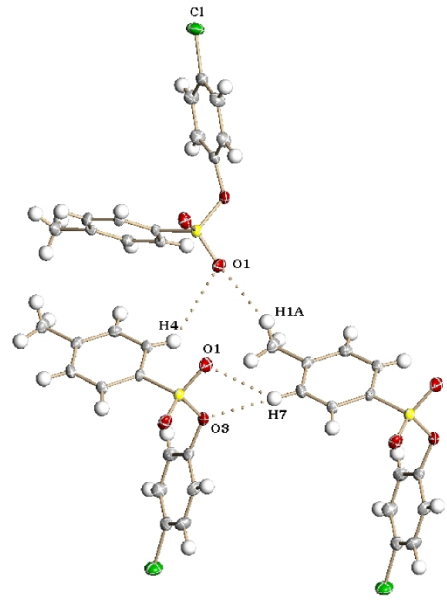


Figure 3
Diagram showing hydrogen bonds 1, 4, 6 and 7 (the numbering relates to the sequence of entries in Table 2).

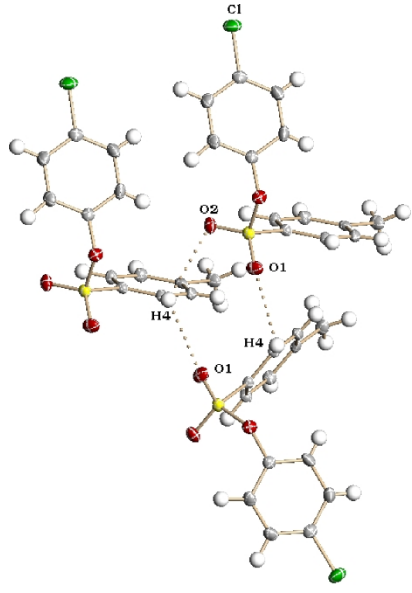


Figure 4
Diagram showing hydrogen bonds 4 and 5 (the numbering relates to the sequence of entries in Table 2).

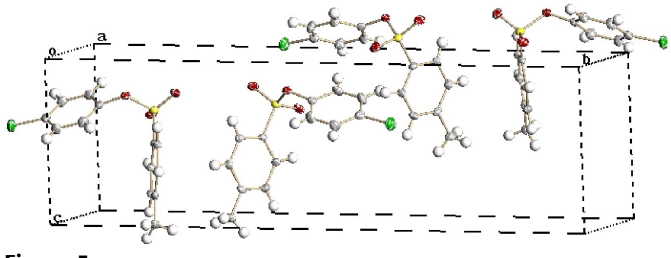


Figure 5
Packing of the molecules in the unit cell.

Experimental

4-Toluenesulfonyl chloride (4.7 mmol), dissolved in acetone (4 ml), was added dropwise to 4-chlorophenol (5 mmol) in aqueous NaOH (2.5 ml, 10%) with constant shaking. The precipitated title compound (3.5 mmol, yield 74%) was filtered off and recrystallized from a 1:1 mixture of petroleum ether and acetone.

Crystal data

$C_{13}H_{11}ClO_3S$
$M_r = 282.73$
Orthorhombic, $Pna2_1$
$a = 5.8937\ (6)$ Å
$b = 27.647\ (3)$ Å
$c = 7.9171\ (8)$ Å
$V = 1290.1\ (2)$ Å^3
$Z = 4$
$D_x = 1.456$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8098 reflections
$\theta = 2.6$–$28.3°$
$\mu = 0.45$ mm^{-1}
$T = 100\ (2)$ K
Plate, colorless
$0.50 \times 0.30 \times 0.10$ mm

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.805$, $T_{max} = 0.956$
10721 measured reflections
3099 independent reflections
2964 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 28.3°$
$h = -7 \rightarrow 7$
$k = -35 \rightarrow 36$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.094$
$S = 1.12$
3099 reflections
207 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0579P)^2 + 0.1095P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.77$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}
Absolute structure: Flack (1983), 1384 Friedel pairs
Flack parameter = 0.00 (7)

Table 1
Selected geometric parameters (Å, °).

S—O1	1.4216 (18)	Cl—C11	1.745 (2)
S—O2	1.4227 (17)	O3—C8	1.410 (3)
S—O3	1.6071 (16)	C1—C2	1.508 (3)
S—C5	1.743 (2)		
O1—S—O2	120.66 (11)	O2—S—C5	109.40 (10)
O1—S—O3	102.58 (10)	O3—S—C5	104.06 (9)
O2—S—O3	108.58 (9)	C8—O3—S	119.71 (13)
O1—S—C5	110.11 (10)		
C5—S—O3—C8	73.30 (17)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1A···O1^{i}	0.89 (5)	2.56 (5)	3.380 (3)	154 (4)
C1—H1B···O1^{ii}	0.96 (3)	2.83 (3)	3.471 (3)	125 (2)
C1—H1C···O3^{iii}	0.92 (4)	2.87 (4)	3.697 (3)	151 (3)
C4—H4···O1^{iv}	0.96 (3)	3.05 (3)	3.713 (3)	127.7 (19)
C4—H4···O2^{v}	0.96 (3)	2.91 (3)	3.269 (3)	103.2 (18)
C7—H7···O1^{iii}	0.98 (3)	2.75 (3)	3.537 (3)	138 (2)
C7—H7···O3^{iii}	0.98 (3)	2.57 (3)	3.500 (3)	160 (2)
C9—H9···O2^{v}	0.82 (4)	2.46 (4)	3.228 (3)	156 (4)
C13—H13···Cl^{vi}	1.00 (3)	2.77 (3)	3.709 (3)	158 (2)
C4—H4···O1	0.96 (3)	2.80 (3)	3.054 (3)	96.2 (18)
C4—H4···O3	0.96 (3)	2.98 (3)	3.210 (3)	94.8 (17)
C6—H6···O2	0.97 (5)	2.37 (5)	2.905 (3)	114 (4)
C13—H13···O2	1.00 (3)	2.79 (3)	3.108 (3)	99.0 (19)
C3—H3···$Cg1^{iv}$	0.91 (3)	2.87	3.574	135
C10—H10···$Cg2^{vii}$	0.83 (4)	3.17	3.845	141

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

All 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 0.82 (4)–1.00 (3) Å, the H—C—H angles for the methyl group are in the range 101 (3)–108 (3)° and the C—C—H angles for the aromatic rings are in the range 115 (2)–130 (3)°.

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

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