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2,4-Dichlorophenyl 4-toluenesulfonate: supramolecular aggregation through C—H···O, C—H···Cl, C—H···π and π···π interactions

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.028
wR factor = 0.077
Data-to-parameter ratio = 14.5

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

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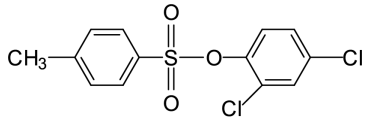
In the crystal structure of the title molecule, $C_{13}H_{10}Cl_2O_3S$, the dihedral angle between the mean planes of the 4-tolyl and 2,4-dichlorophenyl rings is 43.92 (4)°. There are weak C—H···O hydrogen bonds, which generate rings of motifs $S(5)$, $S(6)$, $R_1^2(4)$, $R_2^1(6)$ and $R_2^2(8)$. The supramolecular aggregation is completed by the presence of C—H···Cl, C—H···π and π···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 2,4-dichlorophenyl rings is 43.92 (4)°. 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 & 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 that found for weak C—H···O bonds (Desiraju & Steiner, 1999). The C4—H4···O1 interaction generates a ring of graph set $S(5)$ (Etter, 1990; Bernstein *et al.*, 1995). Another $S(5)$ motif is formed by the C6—H6···O2 interaction. The C13—H13···O2 interaction generates an $S(6)$ motif. The C6—H6···O2 and C13—H13···O2 interactions constitute a pair of bifurcated acceptor bonds. The C7—H7···O3^{iii} and C7—H7···O1^{iii} (Fig. 2) interactions constitute a pair of bifurcated

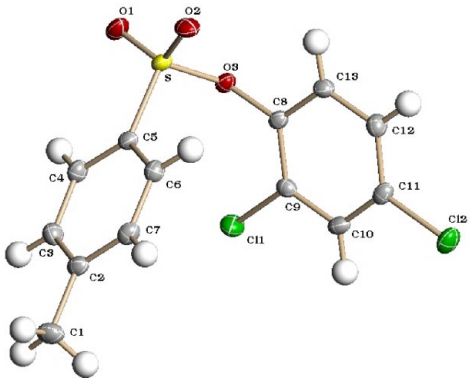


Figure 1
The molecular structure of the title molecule (I), with displacement ellipsoids drawn at the 50% probability level.

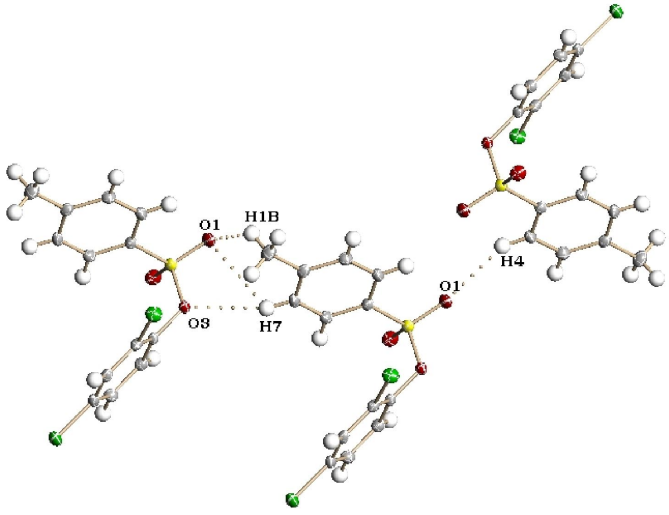


Figure 2
Diagram showing hydrogen bonds 3, 4, 6 and 8 (the numbering relates to the sequence of entries in Table 2).

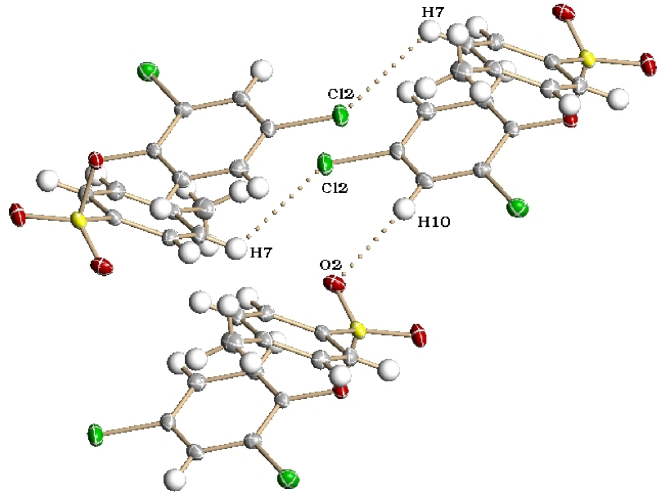


Figure 3
Diagram showing hydrogen bonds 2 and 5 (the numbering relates to the sequence of entries in Table 2).

donor bonds, generating a ring of graph set $R_1^2(4)$. The H7···O3^{iii} and H7···O1^{iii} distances differ by 0.42 (2) Å. The resulting configuration is classed as an unsymmetrical three-

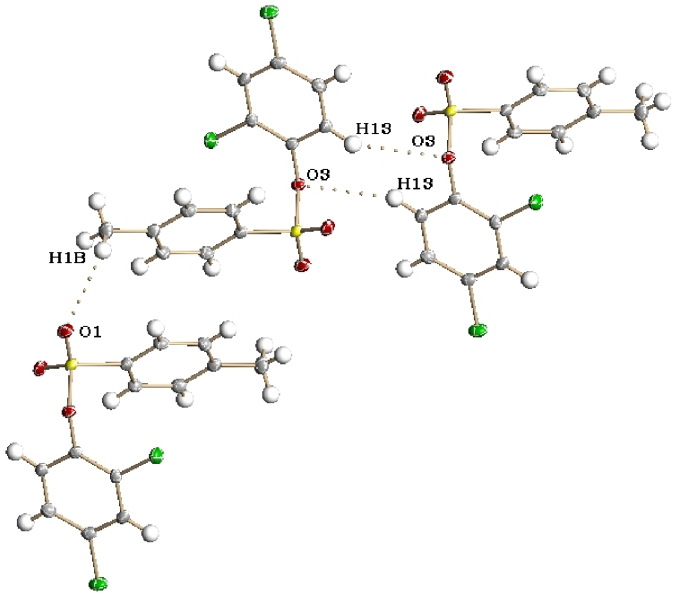


Figure 4
Diagram showing hydrogen bonds 1 and 7 (the numbering relates to the sequence of entries in Table 2).

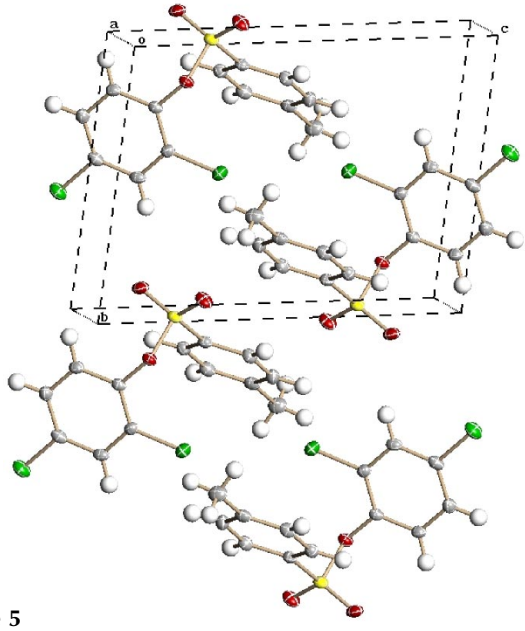


Figure 5
Packing of the molecules in the unit cell.

centered H-bonded chelate (Desiraju, 1989), which is different from the symmetrical three-centered hydrogen-bonded chelate observed in similar structures (Vembu, Nallu, Garrison & Youngs, 2003*b*,*c*; Vembu, Nallu, Garrison, Hindi & Youngs, 2003). The C1—H1*B*···O1^{iii} and C7—H7···O1^{iii} (Fig. 2) interactions constitute a pair of bifurcated acceptor bonds, generating a ring of graph set $R_2^1(6)$. The C7—H7···O3^{iii} and C1—H1*B*···O1^{iii} (Fig. 2) interactions generate a $R_2^2(8)$ motif which consists of the $R_1^2(4)$ chelate and $R_2^1(6)$ ring motifs. There are several other C—H···O interactions (Fig. 2–4, Table 2) and a C—H···Cl interaction (Fig. 3) which contribute to the supramolecular aggregation. The supramolecular

aggregation is completed by the presence of an intramolecular C—H···π interaction (Table 2). The geometry of the C—H···π interaction was obtained from *PLATON* (Spek, 1998); *Cg*2 is the centroid of the 2,4-dichlorophenyl ring. In the crystal structure, the molecules are stacked in layers (Fig. 5), held together by $\pi\cdots\pi$ interactions, with distances of 4.059 Å and 3.672 Å between the centroids of adjacent 4-tolyl rings (symmetry code: $-x, -y, 1-z$) and 2,4-dichlorophenyl rings (symmetry code: $1-x, 1-y, -z$), respectively.

Experimental

4-Toluenesulfonyl chloride (4.7 mmol), dissolved in acetone (4 ml), was added dropwise to 2,4-dichlorophenol (5.5 mol) in aqueous NaOH (2.5 ml, 10%) with constant shaking. The precipitated title compound (3.3 mmol, yield 70%) was filtered off and recrystallized from a 1:1 mixture of petroleum ether and acetone.

Crystal data

$C_{13}H_{10}Cl_2O_3S$
M_r = 317.17
Triclinic, $P\overline{1}$
a = 7.7314 (11) Å
b = 8.3724 (11) Å
c = 10.7055 (15) Å
α = 99.079 (2)°
β = 96.119 (2)°
γ = 103.134 (2)°
V = 659.04 (16) Å^3
Z = 2
D_x = 1.598 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7298 reflections
θ = 2.5–28.4°
μ = 0.65 mm^{-1}
T = 100 (2) K
Block, colorless
0.55 × 0.50 × 0.40 mm

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.716, T_{max} = 0.781
8295 measured reflections
3074 independent reflections
2954 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 28.4°
$h = -10 \rightarrow 9$
$k = -11 \rightarrow 10$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.077
S = 1.08
3074 reflections
212 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0378P)^2 + 0.4025P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S—O1	1.4242 (11)	Cl1—C9	1.7239 (14)
S—O2	1.4262 (11)	Cl2—C11	1.7350 (15)
S—O3	1.6174 (10)	O3—C8	1.4021 (16)
S—C5	1.7458 (14)	C1—C2	1.504 (2)
O1—S—O2	120.41 (7)	O2—S—C5	109.13 (7)
O1—S—O3	102.48 (6)	O3—S—C5	103.91 (6)
O2—S—O3	108.04 (6)	C8—O3—S	117.63 (8)
O1—S—C5	111.35 (7)		
C5—S—O3—C8	−61.64 (11)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C13—H13···O3^{i}	0.959 (19)	2.871 (19)	3.7361 (18)	150.5 (14)
C10—H10···O2^{ii}	0.95 (2)	2.47 (2)	3.3876 (18)	162.0 (16)
C7—H7···O3^{iii}	0.93 (2)	2.62 (2)	3.5211 (18)	163.8 (18)
C7—H7···O1^{iii}	0.93 (2)	3.04 (2)	3.5505 (19)	116.3 (16)
C7—H7···Cl2^{iv}	0.93 (2)	2.97 (2)	3.4404 (15)	112.9 (16)
C4—H4···O1^{v}	0.95 (2)	2.52 (2)	3.3907 (18)	153.6 (17)
C1—H1*B*···O1^{vi}	0.94 (3)	2.81 (3)	3.644 (2)	147.7 (19)
C1—H1*B*···O1^{iii}	0.94 (3)	2.97 (3)	3.668 (2)	131.7 (18)
C4—H4···O1	0.95 (2)	2.66 (2)	2.9874 (19)	100.7 (14)
C6—H6···O2	0.965 (18)	2.605 (18)	2.9436 (18)	100.9 (12)
C13—H13···O2	0.959 (19)	2.583 (19)	3.0093 (18)	107.2 (13)
C6—H6···*Cg*2	0.97 (2)	3.388	3.778	106.6

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

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 0.91 (3)–0.97 (2) Å, the H—C—H angles for the methyl group are in the range 103 (2)–110 (2)° and the C—C—H angles for the aromatic rings are in the range 117.4 (1)–122.2 (1)°.

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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