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2-Chlorophenyl 4-toluenesulfonate: molecular aggregration through weak C—H···O interactions

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.038
wR factor = 0.096
Data-to-parameter ratio = 10.8

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

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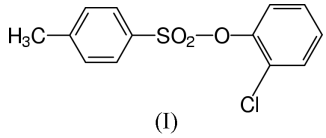
The title molecule, $C_{13}H_{11}ClO_3S$, is stabilized by weak C—H···O interactions. The dihedral angle between the mean planes of the 4-tolyl and the 2-chlorophenyl rings is 51.47 (9)°. Both the sulfonyl O atoms form a three-centred symmetrical hydrogen-bonded chelate motif with an H atom of the neighbouring 2-chlorophenyl ring. In addition, two of the sulfonyl O atoms form two other weak hydrogen bonds with the H atoms of the 4-tolyl rings of two different neighbouring molecules.

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 the 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 σ subunits 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 of the Cambridge Structural Database (Allen, 2002) revealed 16 structures (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. The Cl atom lies almost in the plane of the phenyl ring to which it is bonded. The dihedral angle between the 2-chlorophenyl and the 4-tolyl rings is found to be 51.47 (9)°, thereby confirming their non-coplanar orientation. This is in contrast to the near coplanar orientation of the 4-tolyl and 2,4-dinitrophenyl rings in 2,4-dinitrophenyl 4-toluenesulfonate (Vembu *et al.*, 2003).



(I)

The crystal structure of (I) is stabilized by weak C—H···O interactions. The range of H···O distances (Table 2) found in (I) agrees with those found for weak C—H···O bonds (Desiraju & Steiner, 1999). Both O1 and O2 of the sulfonyl

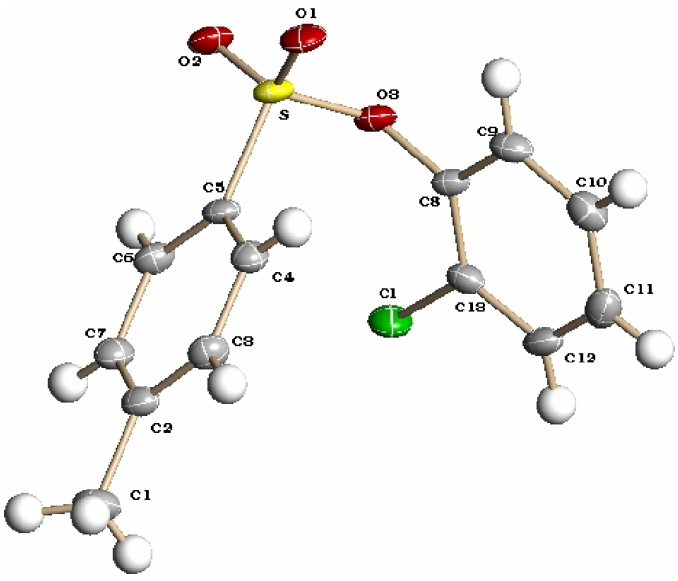


Figure 1
The molecular structure of the title molecule, showing 50% probability displacement ellipsoids.

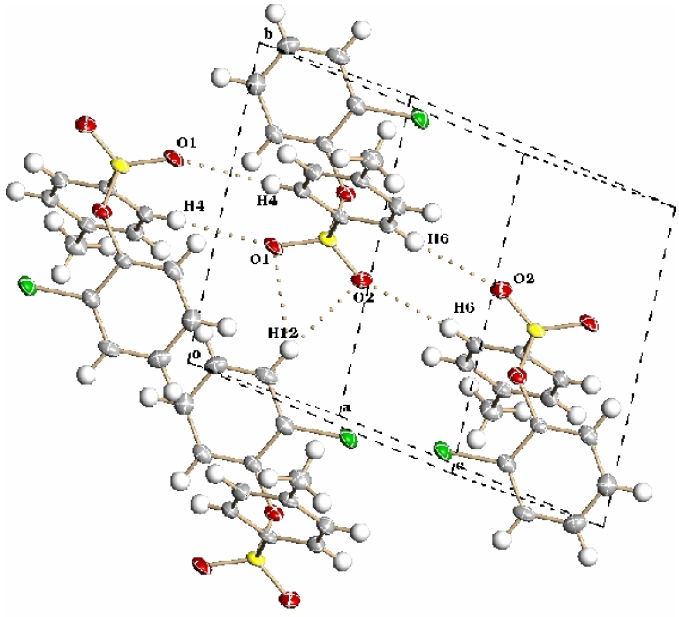


Figure 2
Diagram showing the C—H···O interactions as dotted lines.

group act as acceptors, forming weak hydrogen bonds with a CH group of the 2-chlorophenyl ring of a neighbouring molecule (Fig. 2). The H12···O1 and H12···O2 distances differ by only 0.12 Å. The resulting configuration is best regarded as a three-centre symmetrical hydrogen-bonded chelate (Desiraju, 1989) and is observed in molecules containing fewer functional H atoms and several acceptors. The O1···H12···O2 bite angle is 55.2 (3)° and the sum of angles around H12, 352.4 (2)°, indicates the configuration around it to be almost planar, as observed for many molecules with such hydrogen bonds (Jeffrey & Mitra, 1984). One of the sulfonyl O atoms, O1, acts as an acceptor, forming a weak hydrogen bond with H4 of the 4-tolyl ring of a neighbouring molecule. The other sulfonyl O atom, O2, acts as an acceptor to form another weak hydrogen bond with H6 of the 4-tolyl ring of another neighbouring molecule (Fig. 2). The above intermolecular C—H···O interactions contribute to the molecular aggregation of the title molecule.

Experimental

p-Toluenesulfonyl chloride (0.9 g, 4.7 mmol), dissolved in acetone (4 ml), was added dropwise to 2-chlorophenol (0.5 g, 3.9 mmol) in aqueous NaOH (2.5 ml, 10%) with constant shaking. The precipitated 2-chlorophenyl 4-toluenesulfonate (0.9 g, 3.2 mmol, yield: 82%) was filtered off and recrystallized from aqueous ethanol.

Crystal data

$C_{13}H_{11}ClO_3S$
M_r = 282.73
Triclinic, $P\overline{1}$
a = 7.487 (3) Å
b = 8.675 (4) Å
c = 10.277 (4) Å
α = 95.378 (6)°
β = 97.886 (6)°
γ = 96.404 (6)°
V = 653.0 (5) Å^3
Z = 2
D_x = 1.438 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1959 reflections
θ = 2.4–26.7°
μ = 0.45 mm^{-1}
T = 100 (2) K
Needle, colourless
0.40 × 0.10 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.841, T_{max} = 0.957
4385 measured reflections
2227 independent reflections
1762 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 25.0°
$h = -8 \rightarrow 8$
$k = -10 \rightarrow 10$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.096
S = 1.02
2227 reflections
207 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0594P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S—O2	1.4439 (16)	Cl—C13	1.758 (2)
S—O1	1.4460 (16)	O3—C8	1.433 (3)
S—O3	1.6276 (16)	C1—C2	1.524 (3)
S—C5	1.777 (2)		
O2—S—O1	119.82 (9)	O1—S—C5	109.25 (10)
O2—S—O3	102.91 (9)	O3—S—C5	104.10 (9)
O1—S—O3	108.77 (9)	C8—O3—S	118.70 (13)
O2—S—C5	110.68 (10)		
C5—S—O3—C8	−55.94 (16)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···O1^{i}	0.89 (2)	2.70 (2)	3.571 (3)	164.1 (19)
C6—H6···O2^{ii}	0.95 (2)	2.76 (2)	3.477 (3)	132.9 (16)
C12—H12···O1^{iii}	0.96 (3)	2.77 (2)	3.466 (3)	130.2 (17)
C12—H12···O2^{iii}	0.96 (3)	2.65 (3)	3.592 (3)	167.2 (19)

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

All the H atoms were located in a difference Fourier map and their positional and isotropic displacement parameters were refined. The C—H bond lengths are in the range 0.88 (3)–1.02 (3) Å. The H—C—H angles for the methyl group are in the range 102 (3)–111 (3)°. The C—C—H angles for the phenyl groups are in the range 119 (1)–124 (1)°.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (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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