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2-Nitrophenyl 4-toluenesulfonate: supramolecular aggregation through weak C—H···O, C—H···π and π–π interactions

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.006 Å
R factor = 0.061
wR factor = 0.187
Data-to-parameter ratio = 15.3

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

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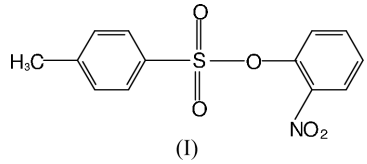
In the crystal structure of the title compound, $C_{13}H_{11}NO_5S$, the dihedral angle between the mean planes of the 4-tolyl and 2-nitrophenyl rings is 42.2 (2)°. There are weak C—H···O hydrogen bonds, which generate rings of graph-set motifs $S(5)$, $R_1^2(4)$, $R_2^1(5)$, $R_1^2(6)$, $R_1^2(6)$, $R_2^2(7)$ and $R_2^2(10)$. The supramolecular aggregation is completed by the presence of intermolecular van der Waals short contacts, and C—H···π and π–π interactions.

Comment

1-Anilino-8-naphthalenesulfonate, an aromatic sulfonate, is used in monitoring the merging of lipids in the binding of Rose bengal, a model organic anion, to sinusoidal and bile canalicular membrane fractions isolated from rat liver (Yachi *et al.*, 1989) and in many other fields (Spungin *et al.*, 1992; Tharakan *et al.*, 1992; Alford *et al.*, 1991; Jiang *et al.*, 1990; Narayanan & Krakow, 1983). The crystal structure of the title compound, (I), was determined because of 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 in that they all contain the *p*-toluenesulfonyl group. The S—C, S—O and S═O bond lengths (Table 1) are comparable to those found in related structures (Vembu, Nallu, Garrison & Youngs, 2003*a*,*b*,*c*,*d*,*e*,*f*; Vembu, Nallu, Spencer & Howard, 2003*a*,*b*,*c*,*d*,*e*,*f*,*g*; Vembu, Nallu, Garrison, Hindi & Youngs, 2003; Vembu, Nallu, Durmus *et al.*, 2004*a*,*b*,*c*).



(I)

The molecular structure of (I) is shown in Fig. 1. The dihedral angle between the mean planes of the C1–C6 and C8–C13 rings is 42.2 (2)°. This shows their non-coplanar orientation, which is similar to that reported for other aromatic sulfonates (Vembu, Nallu, Garrison & Youngs, 2003*b*,*c*,*d*,*e*; Vembu, Nallu, Spencer & Howard, 2003*a*,*b*,*c*,*d*,*f*,*g*; Vembu, Nallu, Durmus *et al.*, 2004*a*,*b*,*c*) and in contrast the near coplanar orientation observed in 2,4-dinitrophenyl 4-toluenesulfonate (Vembu, Nallu, Garrison & Youngs, 2003*a*), 4-methoxyphenyl 4-toluenesulfonate (Vembu, Nallu, Garrison, Hindi & Youngs, 2003) and 8-quinolyl 3-nitrobenzenesulfon-

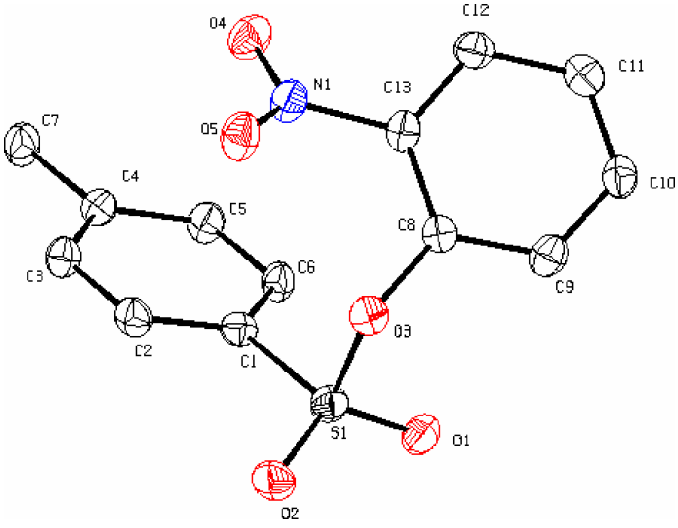


Figure 1
The molecular structure of the title molecule, showing 50% probability displacement ellipsoids. H atoms have been omitted.

ate (Vembu, Nallu, Spencer & Howard, 2003*e*). The aromatic carbon, C8, attached to an O atom is taken as fiducial and the molecule is viewed along the S—O bond (Fig. 2). The orientations of the sulfonyl atoms O1 and O2 and the tolyl atom C1 attached to the S atom have been deduced from the corresponding torsion angles (C8—O3—S1—O1, C8—O3—S1—O2 and C8—O3—S1—C1) and are depicted in Fig. 2. Since the C8—O3—S1—C1 torsion angle is 72.7 (3)°, which corresponds to a synclinal conformation, the two aromatic planes are, as expected, not coplanar [dihedral angle 42.2 (2)°].

The crystal structure of (I) is stabilized by weak C—H···O interactions (Table 2). The range for the H···O distances in (I) agrees with those found for weak C—H···O bonds (Desiraju & Steiner, 1999). In (I), each of the C2—H2···O2 and C6—H6···O1 interactions generates an $S(5)$ graph-set motif (Bernstein *et al.*, 1995; Etter, 1990). The $S(5)$ rings were found to be non-planar. The C2—H2···O4^{i} and C2—H2···O5^{i} interactions together constitute a pair of bifurcated donor bonds generating a chelate ring of graph set $R_1^2(4)$ (symmetry codes are as in Table 2). The C2—H2···O4^{i} and C3—H3···O4^{i} interactions together form a pair of bifurcated acceptor bonds generating an $R_2^1(5)$ motif. The above $R_1^2(4)$ and $R_2^1(5)$ motifs together form an $R_2^2(7)$ motif, which is formed by the interactions C2—H2···O5^{i} and C3—H3···O4^{i}. The C7—H7*B*···O3^{ii} and C5—H5···O3^{ii} interactions constitute a pair of bifurcated acceptor bonds generating an $R_2^1(6)$ motif. The C7—H7*B*···O5^{ii} and C7—H7*B*···O3^{ii} interactions form a pair of bifurcated donor bonds generating an $R_1^2(6)$ motif. The above $R_2^1(6)$ and $R_1^2(6)$ motifs together form an $R_2^2(10)$ motif, which is formed by the interactions, C5—H5···O3^{ii} and C7—H7*B*···O5^{ii}. The two symmetry-related 2-nitrophenyl rings ($3-x$, $1-y$, $1-z$) are stacked over each other, with a centroid–centroid distance of 3.621 Å. There are several other C—H···O, C—H···π and van der Waals interactions, which contribute to the supramolecular aggregation (Fig. 3 and Table 2) of the title compound.

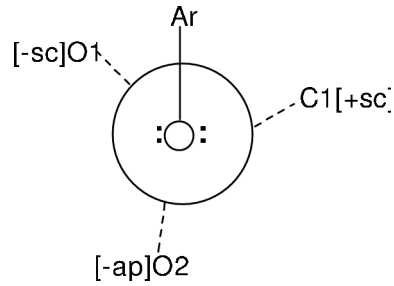


Figure 2
Newman projection of the title molecule along the S—O bond.

Experimental

4-Toluenesulfonyl chloride (4.7 mmol), dissolved in acetone, was added dropwise to 2-nitrophenol (4.3 mmol) in aqueous NaOH (2.5 ml, 10%) with constant shaking. The precipitated title compound (3.1 mmol, yield 72%) was filtered off and recrystallized from aqueous ethanol.

Crystal data

$C_{13}H_{11}NO_5S$
M_r = 293.29
Monoclinic, $P2_1/a$
a = 7.953 (1) Å
b = 20.468 (3) Å
c = 7.9450 (9) Å
β = 99.516 (8)°
V = 1275.5 (3) Å^3
Z = 4
D_x = 1.527 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 23 615 reflections
θ = 2.5–27.4°
μ = 0.27 mm^{-1}
T = 150 (2) K
Irregular fragment, colorless
0.35 × 0.25 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
ω scans with κ offsets
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.902, T_{max} = 0.973
3173 measured reflections
2839 independent reflections
1446 reflections with $I > 2\sigma(I)$
R_{int} = 0.055
θ_{max} = 27.4°
$h = -10 \rightarrow 10$
$k = -26 \rightarrow 25$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.187
S = 0.98
2839 reflections
185 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0948P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—O2	1.423 (3)	O3—C8	1.401 (4)
S1—O1	1.427 (3)	O4—N1	1.224 (4)
S1—O3	1.626 (3)	O5—N1	1.236 (4)
S1—C1	1.754 (3)	N1—C13	1.475 (5)
O2—S1—O1	121.17 (17)	O3—S1—C1	102.62 (16)
O2—S1—O3	102.07 (16)	C8—O3—S1	117.7 (2)
O1—S1—O3	107.75 (16)	O4—N1—O5	124.3 (3)
O2—S1—C1	111.42 (18)	O4—N1—C13	117.3 (3)
O1—S1—C1	109.82 (17)	O5—N1—C13	118.2 (3)
O2—S1—O3—C8	−171.8 (3)	C1—S1—O3—C8	72.7 (3)
O1—S1—O3—C8	−43.1 (3)		

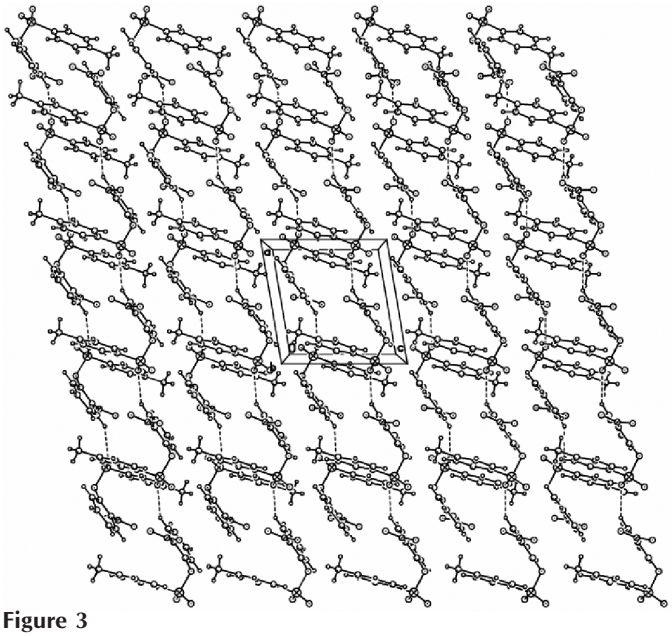


Figure 3
Packing of the molecules, viewed down the *b* axis. Dashed lines indicate hydrogen bonds.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O2	0.93	2.68	3.009 (5)	102
C6—H6···O1	0.93	2.57	2.929 (4)	103
C2—H2···O4^{i}	0.93	2.95	3.430 (5)	114
C2—H2···O5^{i}	0.93	2.84	3.688 (5)	153
C3—H3···O4^{i}	0.93	2.70	3.313 (5)	124
C7—H7*B*···O5^{ii}	0.96	2.72	3.570 (5)	149
C5—H5···O3^{ii}	0.93	2.64	3.504 (4)	156
C7—H7*B*···O3^{ii}	0.96	2.74	3.590 (5)	148
C6—H6···O1^{iii}	0.93	2.69	3.463 (5)	141
C7—H7*C*···O5^{iv}	0.96	2.87	3.793 (5)	163
C9—H9···O1^{v}	0.93	2.89	3.566 (4)	130
C12—H12···O1^{vi}	0.93	2.57	3.392 (5)	148
C7—H7*A*···*Cg*1^{vii}	0.96	3.08	3.99	158

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, z$; (ii) $x, y, z-1$; (iii) $-x+2, -y+1, -z$; (iv) $x-\frac{1}{2}, -y+\frac{1}{2}, z-1$; (v) $-x+2, -y+1, -z+1$; (vi) $x+1, y, z$; (vii) $x-\frac{1}{2}, -y-\frac{1}{2}, z$. *Cg*1 is the centroid of the C1–C6 ring.

All H atoms were included in calculated position with aromatic C—H distances of 0.93 Å and methyl C—H distances of 0.96 Å and refined with riding model. A group displacement parameter was refined for each type of H atom.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO* and *SCALEPAK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPAK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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