

2-Naphthyl 4-toluenesulfonate: supra-molecular aggregation through C—H···O and C—H··· π interactions

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Key indicators

Single-crystal X-ray study

$T = 120$ K

Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å

R factor = 0.047

wR factor = 0.112

Data-to-parameter ratio = 17.0

For details of how these key indicators were automatically derived from the article, see

<http://journals.iucr.org/e>.

In the title compound, $\text{C}_{17}\text{H}_{14}\text{O}_3\text{S}$, there are two independent molecules and the intramolecular dihedral angles between the mean planes of the 4-tolyl and the 2-naphthyl rings are $55.11(7)^\circ$ and $65.10(7)^\circ$. C—H···O interactions generate rings of graph-set motif $S(5)$, $S(6)$, $R_1^2(4)$, $R_2^2(6)$, $R_2^1(8)$ and $R_2^1(9)$. The supramolecular aggregation is completed by the presence of several C—H··· π interactions.

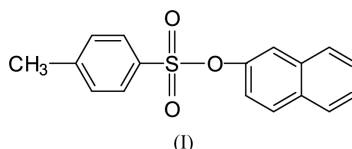
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Comment

p-Toluenesulfonates are used in monitoring the merging of lipids (Yachi *et al.*, 1989), studying membrane fusion during acrosome reactions (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 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 because of the biological importance of its analogs.



The dihedral angle between the mean planes of the 4-tolyl and 2-naphthyl rings is $65.10(7)^\circ$ for the molecule involving S1, and $55.11(7)^\circ$ for the molecule involving S2 (Fig. 1 and Table 1). 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, 2003b) and the 4-tolyl and quinoline rings in 8-tosyloxyquinoline (Vembu, Nallu, Garrison & Youngs, 2003c) 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, 2003a) and 4-tolyl and 4-methoxyphenyl rings in 4-methoxyphenyl 4-toluenesulfonate (Vembu, Nallu, Garrison & Youngs, 2003).

The crystal structure of (I) is stabilized by weak C—H···O interactions. The range of H···O distances (Table 2) agrees with that found for weak C—H···O bonds (Desiraju & Steiner, 1999). The C4—H4···O2, C6—H6···O1, C15—H15···O2 (Fig. 2), C21—H21···O4, C23—H23···O5 and

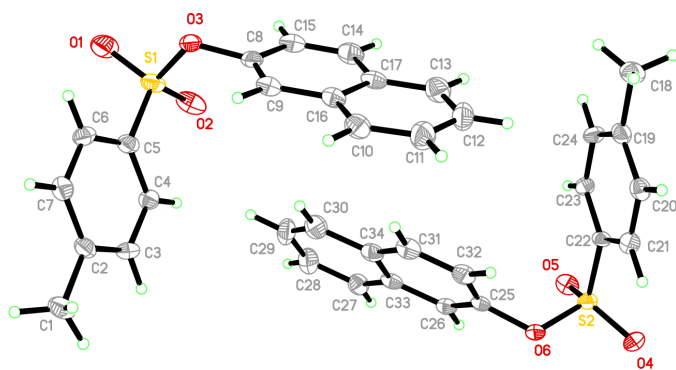


Figure 1
The structure of the two independent molecules of (I), showing 50% probability displacement ellipsoids.

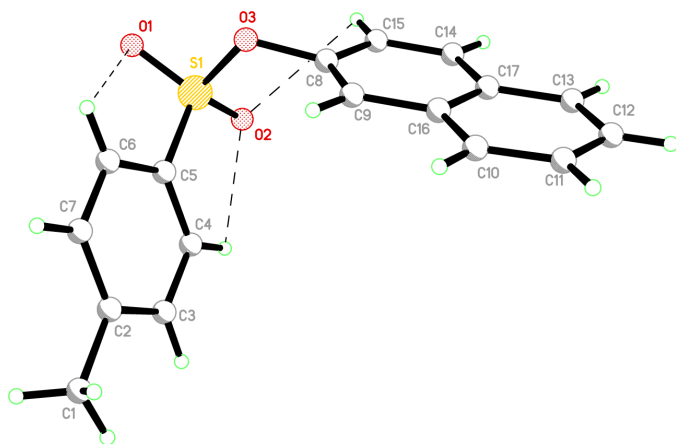


Figure 2
Diagram showing the intramolecular hydrogen bonds in (I).

C26—H26···O5 intramolecular interactions generate rings of graph-set motif (Etter, 1990; Bernstein *et al.*, 1995) $S(5)$, $S(5)$, $S(6)$, $S(5)$, $S(5)$ and $S(6)$, respectively. The C3—H3···O1^{vii} and C3—H3···O3^{vii} interactions constitute a pair of bifurcated donor bonds, generating a ring of graph set $R_1^2(4)$ (symmetry codes are in Table 2). The H3···O1^{vii} and H3···O3^{vii} distances differ by only 0.04 Å. The resulting configuration is best regarded as a three-centered symmetrical hydrogen-bonded chelate motif (Desiraju, 1989) and is also observed in similar structures (Vembu, Nallu, Garrison & Youngs, 2003*b,c,d,e,f,g*; Vembu, Nallu, Garrison, Hindi & Youngs, 2003). The C3—H3···O3^{vii} and C1—H1A···O3^{vii} interactions constitute a pair of bifurcated acceptor bonds, generating a ring of graph set $R_2^1(6)$. The C3—H3···O1^{vii} and C1—H1A···O3^{vii} interactions together generate a ring of graph set $R_2^1(8)$. The $R_1^2(4)$ chelate motif and the $R_2^1(6)$ ring motif are present within the $R_2^1(8)$ ring motif. The C21—H21···O5^{iv} and C32—H32···O5^{iv} interactions constitute a pair of bifurcated acceptor bonds, generating a ring of graph set $R_1^2(9)$. The C24—H24···O4ⁱ and C24—H24···O6ⁱ (Fig. 3) interactions constitute a pair of bifurcated donor bonds, forming another symmetrical three-centered hydrogen-bonded chelate motif of graph set $R_1^2(4)$. The H24···O4ⁱ and

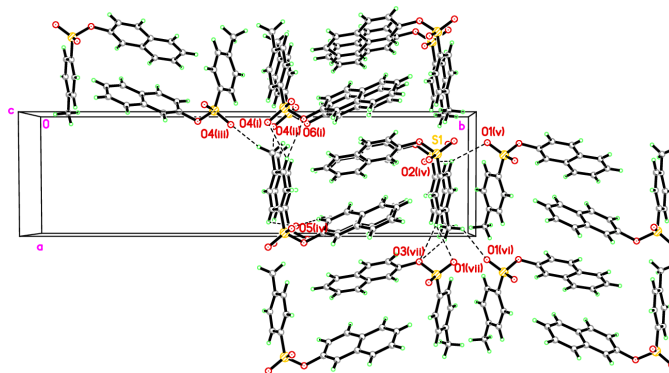


Figure 3
View of the crystal structure along the *c* axis, showing the intermolecular hydrogen bonds.

H24···O6ⁱ distances differ by 0.07 Å. There are several other weak C—H···O bonds (Table 2, Fig. 3), which contribute to the aggregation of the title compound in the crystal structure. The supramolecular aggregation is completed by the presence of ten C—H··· π interactions (Table 2), where Cg1—Cg6 are the centroids of the rings C2—C7, C8—C9/C14—C17, C10—C13/C16—C17, C19—C24, C25—C26/C31—C34 and C27—C30/C33—C34, respectively. The details of these C—H··· π interactions were calculated using *PLATON* (Spek, 1998).

Experimental

4-Toluenesulfonyl chloride (4.7 mmol) dissolved in acetone (4 ml) was added dropwise to 2-naphthol (5.5 mmol) in aqueous NaOH (2.5 ml, 10%) with constant shaking. The precipitated compound, (I), (3.3 mmol, yield 70%) was filtered off and recrystallized from ethyl acetate.

Crystal data

$C_{17}H_{14}O_3S$	$D_x = 1.405 \text{ Mg m}^{-3}$
$M_r = 298.34$	Mo $K\alpha$ radiation
Monoclinic, Pc	Cell parameters from 942 reflections
$a = 7.9315(6) \text{ \AA}$	$\theta = 2.9\text{--}27.4^\circ$
$b = 29.130(2) \text{ \AA}$	$\mu = 0.24 \text{ mm}^{-1}$
$c = 6.1111(5) \text{ \AA}$	$T = 120(2) \text{ K}$
$\beta = 92.383(3)^\circ$	Block, colorless
$V = 1410.73(19) \text{ \AA}^3$	$0.51 \times 0.45 \times 0.26 \text{ mm}$
$Z = 4$	

Data collection

Bruker SMART 6K CCD area-detector diffractometer	6450 independent reflections
ω scans	5907 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1998)	$R_{\text{int}} = 0.045$
$T_{\text{min}} = 0.699$, $T_{\text{max}} = 0.930$	$\theta_{\text{max}} = 27.5^\circ$
20999 measured reflections	$h = -10 \rightarrow 10$
	$k = -37 \rightarrow 37$
	$l = -7 \rightarrow 7$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 0.7718P]$
$R[F^2 > 2\sigma(F^2)] = 0.047$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.112$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.34 \text{ e \AA}^{-3}$
6450 reflections	$\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$
379 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	3197 Friedel pairs
	Flack parameter = 0.03 (7)

Table 1
Selected geometric parameters (Å, °).

S1—O1	1.421 (2)	S1—C5	1.755 (3)
S1—O2	1.426 (2)	O3—C8	1.421 (3)
S1—O3	1.608 (2)	C1—C2	1.504 (4)
O1—S1—O2	120.88 (16)	O4—S2—O5	120.52 (14)
O1—S1—O3	102.82 (13)	O4—S2—O6	102.75 (12)
O2—S1—O3	108.90 (12)	O5—S2—O6	108.85 (11)
O1—S1—C5	109.55 (14)	O4—S2—C22	110.52 (13)
O2—S1—C5	109.36 (15)	O5—S2—C22	109.39 (12)
O3—S1—C5	103.87 (12)	O6—S2—C22	103.24 (11)
C8—O3—S1	118.41 (17)	C25—O6—S2	118.53 (15)
C5—S1—O3—C8	82.6 (2)	C22—S2—O6—C25	65.6 (2)

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

D—H...A	D—H	H...A	D...A	D—H...A
C24—H24...O6 ⁱ	0.95	2.77	3.663 (3)	157
C24—H24...O4 ⁱ	0.95	2.70	3.458 (4)	138
C18—H18A...O4 ⁱⁱ	0.98	2.86	3.495 (4)	124
C18—H18C...O4 ⁱⁱⁱ	0.98	2.38	3.298 (4)	156
C32—H32...O5 ^{iv}	0.95	2.63	3.549 (4)	163
C21—H21...O5 ^{iv}	0.95	2.90	3.273 (3)	105
C6—H6...O2 ^{iv}	0.95	2.88	3.138 (3)	97
C6—H6...O1 ^v	0.95	2.82	3.555 (4)	135
C1—H1B...O1 ^{vi}	0.98	2.66	3.386 (4)	131
C1—H1A...O3 ^{vii}	0.98	2.85	3.753 (4)	153
C3—H3...O3 ^{vii}	0.95	2.69	3.554 (3)	152
C3—H3...O1 ^{vii}	0.95	2.73	3.521 (4)	142
C26—H26...O5	0.95	2.80	3.111 (3)	100
C23—H23...O5	0.95	2.51	2.900 (3)	104
C21—H21...O4	0.95	2.77	3.054 (4)	98
C15—H15...O2	0.95	2.78	3.012 (4)	95
C6—H6...O1	0.95	2.81	3.061 (4)	96
C4—H4...O2	0.95	2.51	2.895 (4)	104
C7—H7...Cg1 ^{viii}	0.95	2.84	3.578	133
C10—H10...Cg6	0.95	2.74	3.383	121
C11—H11...Cg5	0.95	3.14	3.835	121
C14—H14...Cg5 ^{ix}	0.95	2.74	3.430	128
C15—H15...Cg6 ^{ix}	0.95	3.05	3.744	123
C20—H20...Cg4 ^x	0.95	2.82	3.574	138
C26—H26...Cg3 ^{vii}	0.95	3.15	3.806	128
C27—H27...Cg2 ^{vii}	0.95	2.63	3.415	132
C30—H30...Cg2 ^{iv}	0.95	3.23	3.956	138
C31—H31...Cg3 ^{iv}	0.95	2.84	3.582	132

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

H atoms were located from a difference Fourier map and refined isotropically. The C—H bond lengths are in the range, with isotropic

displacement parameters 1.2 to 1.5 times U_{eq} of the parent atom 0.95–0.98 Å².

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