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# 4-Nitrophenyl 4-toluenesulfonate: supramolecular aggregation through weak C—H···O, C—H···π and van der Waals interactions

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**Key indicators**

Single-crystal X-ray study
$T$ = 150 K
Mean $\sigma$(C–C) = 0.002 Å
$R$ factor = 0.037
$wR$ factor = 0.091
Data-to-parameter ratio = 35.0

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

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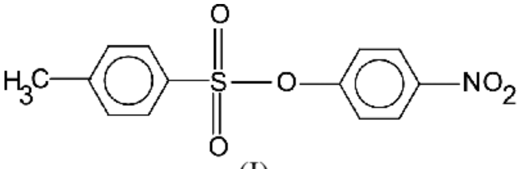
In the crystal structure of the title compound, $C_{13}H_{11}NO_5S$, the dihedral angle between the mean planes of the 4-tolyl and 4-nitrophenyl rings is 82.52 (4)°. There are weak C—H···O interactions, which generate rings of graph-set motifs $S(5)$, $S(6)$, $R_2^1(5)$, $R_2^1(6)$ and $R_2^1(9)$. The supramolecular aggregation is completed by the presence of C—H···$\pi$ and van der Waals interactions.

## Comment

Aromatic sulfonates are used in monitoring the merging of lipids (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), for example, 1-anilino-8-naphthalene 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. A crystallographic study of the title compound was undertaken in view 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 with 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, Panzner, Garrison & Youngs, 2004*a*,*b*,*c*).



(I)

The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. The methyl carbon atom C7 is almost in the same plane as the C1–C6 ring. The dihedral angle between the mean planes of the C1–C6 and C8–C13 rings is 82.52 (4)°. This angle indicates 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, Panzner, Garrison & Youngs, 2004*a*,*b*,*c*) and in contrast with the nearly

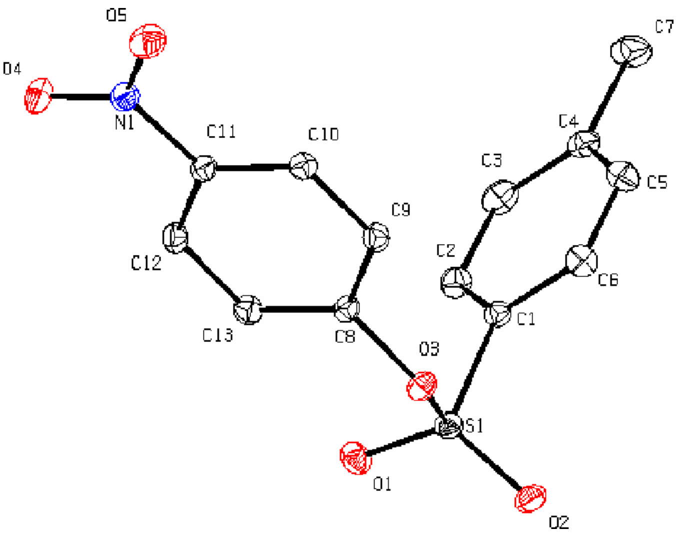


**Figure 1**
The molecular structure of the title molecule, showing 50% probability displacement ellipsoids. H atoms have been omitted.

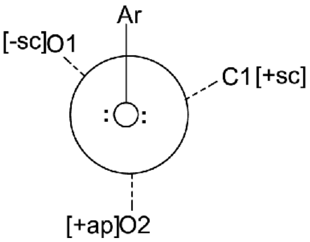


**Figure 2**
Newman projection of the title molecule along the S—O bond

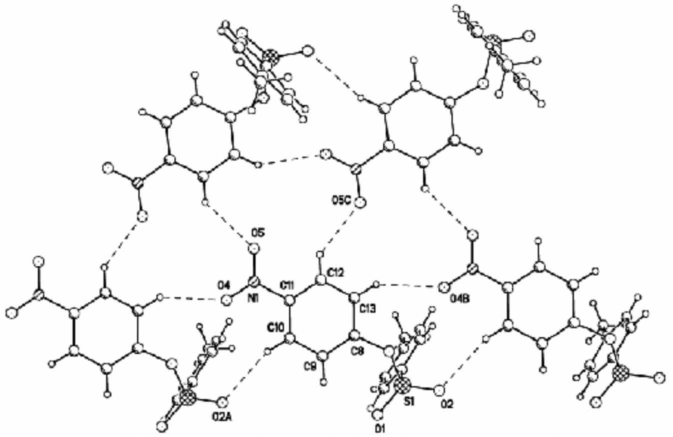


**Figure 3**
Diagram showing some of the C—H⋯O interactions (dashed lines) in the title compound.

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-nitrobenzenesulfonate (Vembu, Nallu, Spencer & Howard, 2003*e*). The aromatic C atom 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 two sulfonyl O atoms and the tolyl C atom attached to the S atom have been deduced from the corresponding torsion angles; these are depicted in Fig. 2. Helical nomenclature (Nasipuri, 1994) is followed in assigning + or − synclinal and + antiperiplanar conformations. The synclinal disposition of the two aromatic rings accounts for their non-coplanar orientations. A distorted tetrahedral geometry around sulfur is observed. The O═S═O bond angle deviates from the normal tetrahedral bond angle, which can be attributed to the repulsive interaction between the lone pairs of O atoms and $p_\pi$–$d_\pi$ bonding.

The crystal structure of (I) is stabilized by weak C—H⋯O interactions (Fig. 3 and Table 2). The range for the H⋯O distances found in (I) agrees with those found for weak C—H⋯O bonds (Desiraju & Steiner, 1999). In (I), each of the C2—H2⋯O1, C6—H6⋯O2, C6—H6⋯O3, C10—H10⋯O5 and C12—H12⋯O4 interactions generates an *S*(5) graph-set motif, and the C13—H13⋯O1 interaction generates an *S*(6) graph-set motif (Bernstein *et al.*, 1995; Etter, 1990). The *S*(5) ring generated by the C10—H10⋯O5 interaction is found to be planar, whereas all other *S*(5) rings mentioned above are found to be non-planar. The C6—H6⋯O2 and C6—H6⋯O3 interactions together form a pair of bifurcated donor bonds. The C3—H3⋯O2$^{i}$ and C7—H7*B*⋯O2$^{i}$ interactions together constitute a pair of bifurcated acceptor bonds, generating a ring of graph-set $R_2^1(6)$. The C6—H6⋯O1$^{ii}$ and C5—H5⋯O1$^{ii}$ interactions form a pair of bifurcated acceptor bonds generating an $R_2^1(5)$ motif. The C6—H6⋯O4$^{iii}$ and C9—H9⋯O4$^{iii}$ interactions constitute a pair of bifurcated acceptor bonds generating an $R_2^1(9)$ ring motif. There are a few other C—H⋯O, C—H⋯π and intermolecular van der Waals interactions, which contribute to the supramolecular aggregation (Fig. 4) of the title compound. There is a short intermolecular van der Waals contact involving the atoms O4 and C11($-x + 1, -y - 1, -z$) at 3.203 (2) Å.

## Experimental

4-Toluenesulfonyl chloride (4.7 mmol), dissolved in acetone (4 ml), was added to 4-nitrophenol (4.3 mmol) in aqueous NaOH (2.5 ml, 10%) with constant shaking. The precipitated title compound (3.2 mmol, yield 74%) was filtered and recrystallized from aqueous ethanol.

*Crystal data*

$C_{13}H_{11}NO_5S$
$M_r = 293.29$
Monoclinic, $P2_1/c$
$a = 13.3450\ (4)$ Å
$b = 8.0160\ (4)$ Å
$c = 12.3780\ (7)$ Å
$\beta = 104.391\ (3)^\circ$
$V = 1282.57\ (10)$ Å$^3$
$Z = 4$
$D_x = 1.519$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 7340 reflections
$\theta = 2.5$–$37.0^\circ$
$\mu = 0.27$ mm$^{-1}$
$T = 150\ (2)$ K
Prism, colorless
0.37 × 0.27 × 0.10 mm

*Data collection*

Nonius KappaCCD diffractometer
$\omega$ scans with $\kappa$ offsets
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min} = 0.887$, $T_{\max} = 0.973$
10 707 measured reflections
6437 independent reflections
3045 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.043$
$\theta_{\max} = 37.1^\circ$
$h = -22 \rightarrow 22$
$k = -13 \rightarrow 13$
$l = -19 \rightarrow 20$

### Refinement

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.092$
$S = 0.88$
6437 reflections
184 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.29$ e Å$^{-3}$
$\Delta\rho_{min} = -0.52$ e Å$^{-3}$
Extinction correction: none

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| S1—O2 | 1.4232 (8) | O3—C8 | 1.4119 (12) |
| S1—O1 | 1.4288 (8) | O4—N1 | 1.2304 (12) |
| S1—O3 | 1.5935 (8) | O5—N1 | 1.2282 (11) |
| S1—C1 | 1.7556 (11) | N1—C11 | 1.4660 (13) |
| | | | |
| O2—S1—O1 | 119.64 (5) | O3—S1—C1 | 103.66 (4) |
| O2—S1—O3 | 102.82 (5) | C8—O3—S1 | 123.29 (7) |
| O1—S1—O3 | 110.36 (4) | O5—N1—O4 | 123.53 (10) |
| O2—S1—C1 | 110.05 (5) | O5—N1—C11 | 118.45 (9) |
| O1—S1—C1 | 109.03 (5) | O4—N1—C11 | 118.02 (9) |
| | | | |
| O2—S1—O3—C8 | 177.66 (7) | C1—S1—O3—C8 | 63.01 (8) |
| O1—S1—O3—C8 | −53.62 (9) | | |

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

| | $D$—H | H$\cdots$$A$ | $D\cdots A$ | $D$—H$\cdots$$A$ |
|---|---|---|---|---|
| C2—H2$\cdots$O1 | 0.93 | 2.54 | 2.9161 (14) | 105 |
| C6—H6$\cdots$O2 | 0.93 | 2.97 | 3.1474 (13) | 92 |
| C6—H6$\cdots$O3 | 0.93 | 2.87 | 3.1002 (14) | 95 |
| C10—H10$\cdots$O5 | 0.93 | 2.43 | 2.7187 (14) | 98 |
| C12—H12$\cdots$O4 | 0.93 | 2.42 | 2.7098 (14) | 98 |
| C13—H13$\cdots$O1 | 0.93 | 2.37 | 2.9907 (13) | 124 |
| C3—H3$\cdots$O2$^{i}$ | 0.93 | 2.64 | 3.5305 (15) | 162 |
| C7—H7$B\cdots$O2$^{i}$ | 0.96 | 3.00 | 3.8851 (17) | 155 |
| C6—H6$\cdots$O1$^{ii}$ | 0.93 | 2.86 | 3.3893 (13) | 117 |
| C5—H5$\cdots$O1$^{ii}$ | 0.93 | 2.63 | 3.2848 (14) | 128 |
| C6—H6$\cdots$O4$^{iii}$ | 0.93 | 2.69 | 3.5770 (15) | 159 |
| C9—H9$\cdots$O4$^{iii}$ | 0.93 | 2.53 | 3.3362 (14) | 146 |
| C7—H7$C\cdots$O1$^{iv}$ | 0.96 | 2.59 | 3.4696 (16) | 153 |
| C10—H10$\cdots$O5$^{v}$ | 0.93 | 2.50 | 3.2389 (13) | 137 |
| C12—H12$\cdots$O2$^{vi}$ | 0.93 | 2.59 | 3.4828 (13) | 161 |
| C13—H13$\cdots$O5$^{vii}$ | 0.93 | 2.90 | 3.2512 (14) | 104 |
| C2—H2$\cdots$$Cg^{viii}$ | 0.93 | 3.066 | 3.772 | 134 |

Symmetry codes: (i) $-x+2, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $x, y+1, z$; (iv) $-x+2, y+\frac{1}{2}, -z+\frac{1}{2}$; (v) $-x+1, y+\frac{1}{2}, -z-\frac{1}{2}$; (vi) $x, y-1, z$; (vii) $x, -y-\frac{1}{2}, z+\frac{1}{2}$; (viii) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$. $Cg$ 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 a riding model. A group displacement parameter was refined for each type of H atom.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

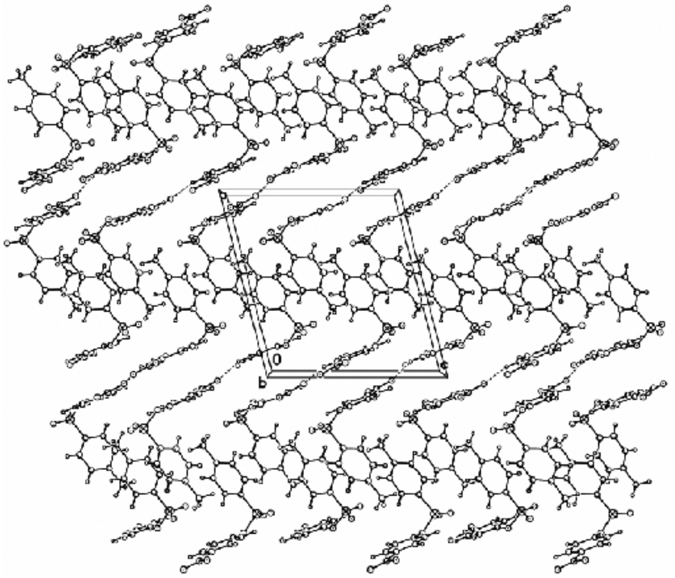


**Figure 4**
Packing of the molecules, viewed down the *b* axis.

## References

Alford, R. L., Honda, S., Lawrence, C. B. & Belmont, J. W. (1991). *Virology*, **183**, 611–619.
Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology.* New York: Oxford University Press.
Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
Jiang, F. N., Jiang, S., Liu, D., Richter, A. & Levy, J. G. (1990). *J. Immunol. Methods*, **134**, 139–149.
Narayanan, C. S. & Krakow, J. S. (1983). *Nucleic Acids Res.* **11**, 2701–2716.
Nasipuri, D. (1994). *Stereochemistry of Organic Compounds: Principles and Applications*, 2nd ed., p. 94. New Delhi: New Age International (P) Ltd.
Nonius (2000). *COLLECT.* Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Spungin, B., Levinshal, T., Rubenstein, S. & Breitbart, H. (1992). *FEBS Lett.* **311**, 155–160.
Tharakan, J., Highsmith, F., Clark, D. & Drohsn, W. (1992). *J. Chromatogr.* **595**, 103–111.
Vembu, N., Nallu, M., Durmus, S., Panzner, M., Garrison, J. & Youngs, W. J. (2004*a*). *Acta Cryst.* E**60**, o1–o3.
Vembu, N., Nallu, M., Durmus, S., Panzner, M., Garrison, J. & Youngs, W. J. (2004*b*). *Acta Cryst.* C**60**, o65–o68.
Vembu, N., Nallu, M., Durmus, S., Panzner, M., Garrison, J. & Youngs, W. J. (2004*c*). *Acta Cryst.* C**60**, o248–o251.
Vembu, N., Nallu, M., Garrison, J., Hindi, K. & Youngs, W. J. (2003). *Acta Cryst.* E**59**, o830–o832.
Vembu, N., Nallu, M., Garrison, J. & Youngs, W. J. (2003*a*). *Acta Cryst.* E**59**, o378–o380.
Vembu, N., Nallu, M., Garrison, J. & Youngs, W. J. (2003*b*). *Acta Cryst.* E**59**, o503–o505.
Vembu, N., Nallu, M., Garrison, J. & Youngs, W. J. (2003*c*). *Acta Cryst.* E**59**, o776–o779.
Vembu, N., Nallu, M., Garrison, J. & Youngs, W. J. (2003*d*). *Acta Cryst.* E**59**, o936–o938.
Vembu, N., Nallu, M., Garrison, J. & Youngs, W. J. (2003*e*). *Acta Cryst.* E**59**, o939–o941.
Vembu, N., Nallu, M., Garrison, J. & Youngs, W. J. (2003*f*). *Acta Cryst.* E**59**, o1019–o1021.
Vembu, N., Nallu, M., Spencer, E. C. & Howard, J. A. K. (2003*a*). *Acta Cryst.* E**59**, o1009–o1011.
Vembu, N., Nallu, M., Spencer, E. C. & Howard, J. A. K. (2003*b*). *Acta Cryst.* E**59**, o1033–o1035.

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Vembu, N., Nallu, M., Spencer, E. C. & Howard, J. A. K. (2003*c*). *Acta Cryst.* E**59**, o1213–o1215.

Vembu, N., Nallu, M., Spencer, E. C. & Howard, J. A. K. (2003*d*). *Acta Cryst.* E**59**, o1216–o1219.

Vembu, N., Nallu, M., Spencer, E. C. & Howard, J. A. K. (2003*e*). *Acta Cryst.* E**59**, o1379–o1382.

Vembu, N., Nallu, M., Spencer, E. C. & Howard, J. A. K. (2003*f*). *Acta Cryst.* E**59**, o1387–o1389.

Vembu, N., Nallu, M., Spencer, E. C. & Howard, J. A. K. (2003*g*). *Acta Cryst.* E**59**, o1390–o1392.

Yachi, K., Sugiyama, Y., Sawada, Y., Iga, T., Ikeda, Y., Toda, G. & Hanano, M. (1989). *Biochim. Biophys. Acta*, **978**, 1–7.