

Benzene 1,3,5-tris(*p*-toluenesulfonate): supramolecular aggregation through extensive C—H···O, C—H··· π and π – π interactions

Nagarajan Vembu,^{a*} Maruthai Nallu,^a Jered Garrison^b and Wiley J. Youngs^b

^aDepartment of Chemistry, Bharathidasan University, Tiruchirappalli 620 024, India, and
^bDepartment of Chemistry, University of Akron, 190 East Buchtel Commons, Akron, Ohio 44325-3601, USA

Correspondence e-mail:
mnav2003@yahoo.com

Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ (C–C) = 0.003 Å
R factor = 0.054
wR factor = 0.116
Data-to-parameter ratio = 14.5

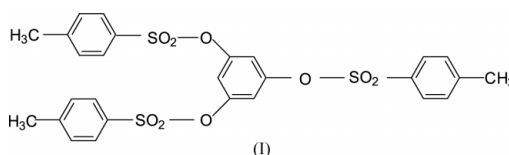
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Within and between molecules of the title compound, C₂₇H₂₄O₉S₃, there are weak C—H···O interactions which generate rings of motifs *S*(5), *S*(6), *R*₂¹(5), *R*₂²(14), *R*₂²(20), *R*₂¹(6) and *R*₁¹(4). The supramolecular aggregation is completed by the presence of C—H··· π and π – 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 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 photosensitizers to model monoclonal antibodies (Jiang *et al.*, 1990) and the 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.



The crystal structure is stabilized by weak C—H···O interactions (Table 2). The range for the H···O distances found in (I) agree with those found for weak C—H···O bonds (Desiraju & Steiner, 1999). The C2—H2···O2 and C2—H2···O6 interactions together constitute a pair of bifurcated donor bonds. Each generates a ring of graph set *S*(6) (Etter, 1990; Bernstein *et al.*, 1995). Each of the C8—H8···O3, C12—H12···O2, C15—H15···O6, C19—H19···O5, C22—H22···O8 and C26—H26···O9 interactions generates *S*(5) ring motifs. The C8—H8···O6ⁱⁱ and C9—H9···O6ⁱⁱ interactions together form a pair of bifurcated acceptor bonds, generating a ring of graph set *R*₂¹(5) (Fig. 2; see Table 2 for symmetry codes). The C11—H11···O2ⁱⁱⁱ and C13—H13C···O6ⁱⁱⁱ interactions together generate a ring of graph set *R*₂²(14). An *R*₂²(20) motif is formed by the C11—H11···O2ⁱⁱⁱ and C20—H20C···O3ⁱⁱⁱ interactions. The C23—H23···O5^{iv} and C27—H27C···O5^{iv} (Fig. 3) interactions together form a pair of bifurcated acceptor bonds, generating a ring of graph-set motif *R*₂¹(6). The C18—H18···O9^v and C19—H19···O9^v (Fig. 2) interactions constitute a pair of bifurcated acceptor bonds, generating a ring of graph set *R*₂¹(5). The C20—

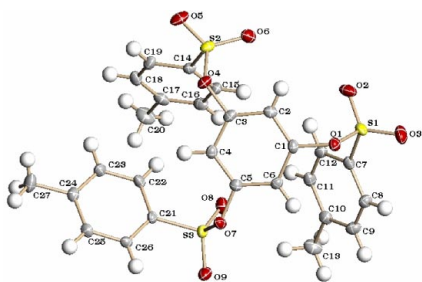


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids.

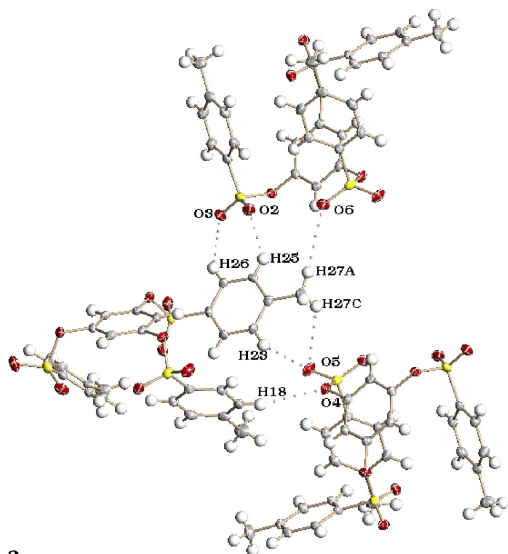


Figure 2
Diagram showing hydrogen bonds 10, 11, 12, 16 and 17 (the numbering relates to the sequence of entries in Table 2).

$\text{H20A} \cdots \text{O7}^{\text{vi}}$ and $\text{C20} - \text{H20A} \cdots \text{O9}^{\text{vi}}$ interactions constitute a pair of bifurcated donor bonds, generating a ring of graph set $R_1^2(4)$. The $\text{H20A} \cdots \text{O7}^{\text{vi}}$ and $\text{H20A} \cdots \text{O9}^{\text{vi}}$ distances differ by 0.06 (4) Å. The resulting configuration can be classified as a symmetrical three-center hydrogen-bonded chelate (Desiraju, 1989) and is also observed in related structures (Vembu, Nallu, Garrison, Hindi & Youngs, 2003; Vembu, Nallu, Garrison & Youngs, 2003*a,b,c,d,e*). The $\text{C25} - \text{H25} \cdots \text{O2}^{\text{vii}}$ and $\text{C26} - \text{H26} \cdots \text{O2}^{\text{vii}}$ interactions together constitute a pair of bifurcated acceptor bonds, generating a ring of graph set $R_2^1(5)$. There are several other $\text{C} - \text{H} \cdots \text{O}$ interactions which contribute to the supramolecular aggregation (Table 2).

The conformation of the molecule can best be described as a three-legged table stabilized by the intramolecular $\text{C} - \text{H} \cdots \text{O}$ and $\text{C} - \text{H} \cdots \pi$ interactions. The atoms H12, O2, H2, O6, H15 form a 'W'-shaped hydrogen-bonded chain, which fixes the S1 and S2 *p*-tolyl rings in almost similar disposition with respect to the central benzene ring. This is also supported by the $\text{C6} - \text{H6} \cdots \text{Cg2}$ interaction, where Cg1, Cg2, Cg3, and Cg4 are the centroids of the rings formed by C1–C6, C7–C12, C14–C19, and C21–C26 atoms, respectively. The S3 *p*-tolyl ring is not supported by a similar hydrogen-bonded network with the H atoms of the central benzene ring with special reference to H4. This may be the reason for the nearly parallel orien-

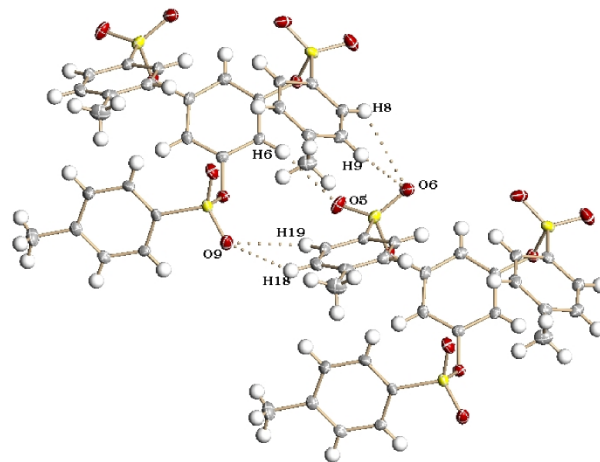


Figure 3
Diagram showing hydrogen bonds 21, 23, 24, 25 and 27 (the numbering relates to the sequence of entries in Table 2).

tation of the S3 *p*-tolyl ring with respect to the central benzene ring. In the crystal structure, the molecules are stacked in layers, held together by two $\pi - \pi$ interactions. The distance between Cg1 and $\text{Cg4}(-x, y - \frac{1}{2}, \frac{1}{2} - z)$ is 3.932 Å. The supramolecular aggregation is completed by the presence of three $\text{C} - \text{H} \cdots \pi$ interactions (Table 2), which were obtained from PLATON (Spek, 1998).

Experimental

4-Toluenesulfonyl chloride (4.9 mmol) dissolved in acetone (15 ml) was added to a mixture of phloroglucinol (4.9 mmol) and triethylamine (4.9 mmol) in 30 ml acetone. The solution was kept overnight and evaporated. The residue was washed several times with water and the crude title compound (0.8 mmol, yield: 50%) was recrystallized from a 1:1 mixture of ethanol and acetone.

Crystal data

$\text{C}_{27}\text{H}_{24}\text{O}_9\text{S}_3$
 $M_r = 588.64$
 Monoclinic, $P2_1/c$
 $a = 9.8953$ (14) Å
 $b = 11.6682$ (17) Å
 $c = 23.626$ (3) Å
 $\beta = 99.719$ (3)°
 $V = 2688.8$ (7) Å³
 $Z = 4$

$D_x = 1.454$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 8345 reflections
 $\theta = 2.5 - 28.3^\circ$
 $\theta_{\text{max}} = 28.3^\circ$
 $\mu = 0.33$ mm⁻¹
 $T = 100$ (2) K
 Block, colorless
 0.30 × 0.20 × 0.10 mm

Data collection

Bruker CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.908$, $T_{\text{max}} = 0.968$
 33621 measured reflections

6509 independent reflections
 5840 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$
 $\theta_{\text{max}} = 28.3^\circ$
 $h = -12 \rightarrow 12$
 $k = -15 \rightarrow 15$
 $l = -31 \rightarrow 31$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.054$
 $wR(F^2) = 0.116$
 $S = 1.18$
 6509 reflections
 448 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 2.7273P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.55$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.37$ e Å⁻³

Table 1
Selected geometric parameters (Å, °).

S1—O2	1.4199 (19)	S3—O8	1.4209 (17)
S1—O3	1.4211 (18)	S3—O9	1.4216 (17)
S1—O1	1.6077 (16)	S3—O7	1.6177 (16)
S1—C7	1.744 (2)	S3—C21	1.752 (2)
S2—O5	1.4212 (17)	O1—C1	1.410 (2)
S2—O6	1.4286 (18)	O4—C3	1.412 (3)
S2—O4	1.6126 (16)	O7—C5	1.408 (3)
S2—C14	1.750 (2)		
O2—S1—O3	120.02 (11)	O4—S2—C14	104.58 (9)
O2—S1—O1	109.00 (10)	O8—S3—O9	121.26 (11)
O3—S1—O1	103.28 (10)	O8—S3—O7	108.56 (9)
O2—S1—C7	108.25 (11)	O9—S3—O7	102.92 (9)
O3—S1—C7	111.79 (11)	O8—S3—C21	110.11 (10)
O1—S1—C7	103.05 (9)	O9—S3—C21	109.62 (10)
O5—S2—O6	120.55 (11)	O7—S3—C21	102.52 (9)
O5—S2—O4	102.78 (10)	C1—O1—S1	116.77 (13)
O6—S2—O4	108.92 (9)	C3—O4—S2	118.57 (13)
O5—S2—C14	109.67 (11)	C5—O7—S3	118.84 (13)
O6—S2—C14	109.07 (11)		
C7—S1—O1—C1	−57.22 (17)	C21—S3—O7—C5	−90.20 (16)
C14—S2—O4—C3	67.62 (17)		

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

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
C2—H2···O2	0.89 (3)	2.86 (2)	3.122 (3)	98.9 (18)
C2—H2···O6	0.89 (3)	2.58 (3)	2.959 (3)	106.9 (19)
C8—H8···O3	0.94 (3)	2.73 (3)	3.049 (3)	100.7 (18)
C12—H12···O2	0.95 (3)	2.51 (3)	2.885 (3)	104.0 (19)
C15—H15···O6	0.96 (3)	2.67 (3)	2.976 (3)	99.1 (17)
C19—H19···O5	0.91 (3)	2.53 (3)	2.919 (3)	106 (2)
C22—H22···O8	0.90 (3)	2.59 (3)	2.934 (3)	103.6 (18)
C26—H26···O9	0.94 (3)	2.70 (2)	3.008 (3)	100.4 (17)
C2—H2···O3 ⁱ	0.89 (3)	2.88 (3)	3.529 (3)	131 (2)
C6—H6···O5 ⁱⁱ	0.92 (3)	2.60 (3)	3.494 (3)	164 (2)
C8—H8···O6 ⁱⁱ	0.94 (3)	3.02 (3)	3.540 (3)	116.8 (19)
C9—H9···O6 ⁱⁱ	0.94 (3)	2.89 (3)	3.488 (3)	122.9 (19)
C11—H11···O2 ⁱⁱⁱ	0.92 (3)	2.96 (3)	3.725 (3)	142 (2)
C13—H13C···O6 ⁱⁱⁱ	0.94 (3)	2.98 (3)	3.835 (3)	151 (2)
C18—H18···O4 ^{iv}	0.91 (3)	2.94 (3)	3.788 (3)	156 (2)
C18—H18···O9 ^v	0.91 (3)	2.99 (3)	3.531 (3)	120 (2)
C19—H19···O9 ^v	0.91 (3)	2.67 (3)	3.343 (3)	131 (2)
C20—H20A···O7 ^{vi}	0.90 (4)	2.88 (4)	3.701 (4)	152 (3)
C20—H20A···O9 ^{vi}	0.90 (4)	2.82 (4)	3.311 (3)	116 (3)
C20—H20C···O3 ⁱⁱⁱ	0.95 (4)	2.77 (4)	3.670 (4)	159 (3)
C20—H20A···O9 ^{vi}	0.90 (4)	2.82 (4)	3.311 (3)	116 (3)
C23—H23···O5 ^{iv}	0.97 (3)	2.70 (3)	3.102 (3)	105.4 (18)
C25—H25···O1 ^{vi}	0.92 (3)	2.94 (3)	3.118 (3)	92.5 (17)
C25—H25···O2 ^{vii}	0.92 (3)	2.42 (3)	3.154 (3)	136 (2)
C26—H26···O2 ^{vii}	0.94 (3)	2.92 (3)	3.382 (3)	112.1 (18)
C27—H27A···O6 ^{viii}	0.99 (4)	2.97 (4)	3.958 (3)	175 (3)
C27—H27B···O3 ^{viii}	0.84 (4)	2.71 (4)	3.431 (4)	145 (3)
C27—H27C···O5 ^{iv}	0.98 (4)	2.80 (4)	3.455 (3)	125 (3)
C6—H6···Cg2	0.92 (3)	3.26	3.576	103
C22—H22···Cg3	0.90 (3)	2.86	3.638	145
C13—H13B···Cg3 ^v	0.97 (3)	2.98	3.728	142

Symmetry codes: (i) $2-x, 1-y, 1-z$; (ii) $1+x, y, z$; (iii) $2-x, 2-y, 1-z$; (iv) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (v) $x-1, y, z$; (vi) $2-x, \frac{1}{2}+y, \frac{1}{2}-z$; (vii) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (viii) $x-1, \frac{1}{2}-y, z-\frac{1}{2}$.

All the H atoms were located from a difference Fourier map and refined isotropically. The C—H bond lengths are in the range 0.84 (4)–0.99 (4) Å, the H—C—H angles for the methyl group are in the range 103 (3)–112 (3)° and the C—C—H angles for the aromatic rings are in the range 118.4 (2)–122.2 (2)°.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINTE* (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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