

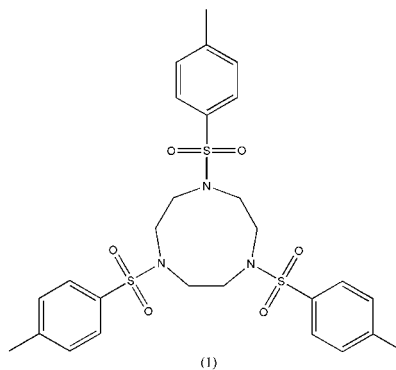
# 1,4,7-Tris(*p*-toluenesulfonyl)-1,4,7-triazacyclononane

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patrickm@chem.leeds.ac.uk**Key indicators**Single-crystal X-ray study  
 $T = 150\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$   
 $R$  factor = 0.041  
 $wR$  factor = 0.133  
Data-to-parameter ratio = 18.0For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The X-ray crystal structure of the title compound,  $\text{C}_{27}\text{H}_{33}\text{N}_3\text{O}_6\text{S}_3$ , a key intermediate in the synthesis of 1,4,7-triazacyclononane and its functionalized derivatives, is presented. Two of the *p*-tosyl groups are coplanar with the macrocyclic ring, with the third pointing away from it.

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The first reported synthesis of the title compound, (I), was published in 1937 (Peacock & Gwan, 1937). Following the publication of bulk-scale syntheses which avoided the high-dilution conditions (Koyama & Yoshino, 1972; Richman & Atkins, 1974) traditionally associated with the synthesis of macrocycles, the title compound thus became an important precursor to a wide range of compounds based on the nine-membered macrocyclic core. The importance of (I) is shown in the wide use of the parent macrocycle, 1,4,7-triazacyclononane, and derived ligands in both coordination chemistry (Chaudhuri & Wieghardt, 1987) and organometallic chemistry (*e.g.* Male *et al.*, 2000; Bambirra *et al.*, 2001; Gott *et al.*, 2002; Cui *et al.*, 2003). Part of the widespread synthetic utility of (I) is the ability to introduce, by selective detosylation, further functional groups at one, two, or all three N atoms, thus giving a wide and varied range of multidentate ligands (Wainwright, 1997). We obtained crystals of (I) suitable for X-ray crystallographic analysis. The structure had not been previously reported and it is to this end that we report the structure here.



Molecules of (I) crystallized in the space group  $P\bar{1}$ . There is one molecule in the asymmetric unit of the structure, which can be seen in Fig. 1. The structure of the central macrocyclic core is a puckered nine-membered ring in which the three symmetrically placed N atoms (N1, N4 and N7) are all approximately located in the mean plane of the ring.

Two of the *p*-tosyl groups are also approximately coplanar with the macrocyclic ring, whereas the third is oriented outwards from it. The bond lengths N1—S1 [1.6277 (14)], S1—C11 [1.7664 (17)] and S1—O11 [1.4353 (13)], and bond angles (which can be seen in Table 1) are unremarkable when

compared with other similar *p*-tosylamides found in the literature. The same is also true for the C—H and C—N bonds of the macrocyclic ring. The two most directly related complexes, *viz.* 1-(*p*-toluenesulfonyl)-4,7-mercaptobenzoyl-1,4,7-triazacyclononane (Evans *et al.*, 1993) and 2-(C<sub>5</sub>H<sub>4</sub>N)CH<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>NHTs)<sub>2</sub> (Skinner *et al.*, 2002), show almost identical values. The latter compound can be considered as a 1,4,7-triazacyclononane ligand with one of the ethylene bridging units removed.

## Experimental

1,4,7-Tris(*p*-toluenesulfonyl)-1,4,7-triazacyclononane was prepared according to published procedures (McAuley *et al.*, 1984). Single crystals suitable for X-ray crystallographic analysis were obtained from a solution of 4:1 ethanol/chloroform by slow evaporation.

### Crystal data

C <sub>27</sub> H <sub>33</sub> N <sub>3</sub> O <sub>6</sub> S <sub>3</sub>	<i>Z</i> = 2
<i>M<sub>r</sub></i> = 591.74	<i>D<sub>x</sub></i> = 1.399 Mg m <sup>-3</sup>
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> $\alpha$ radiation
<i>a</i> = 10.3019 (2) Å	Cell parameters from 29674 reflections
<i>b</i> = 12.3216 (2) Å	$\theta$ = 2.8–27.5°
<i>c</i> = 12.6131 (2) Å	$\mu$ = 0.31 mm <sup>-1</sup>
$\alpha$ = 101.5528 (8)°	<i>T</i> = 150 (2) K
$\beta$ = 113.5558 (8)°	Prism, colourless
$\gamma$ = 96.3429 (6)°	0.23 × 0.17 × 0.11 mm
<i>V</i> = 1405.22 (4) Å <sup>3</sup>	

### Data collection

Nonius KappaCCD area-detector diffractometer	6402 independent reflections
$\omega$ and $\varphi$ scans	5459 reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	<i>R</i> <sub>int</sub> = 0.127
<i>T</i> <sub>min</sub> = 0.932, <i>T</i> <sub>max</sub> = 0.967	$\theta$ <sub>max</sub> = 27.5°
29674 measured reflections	<i>h</i> = −13 → 13
	<i>k</i> = −15 → 15
	<i>l</i> = −16 → 16

### Refinement

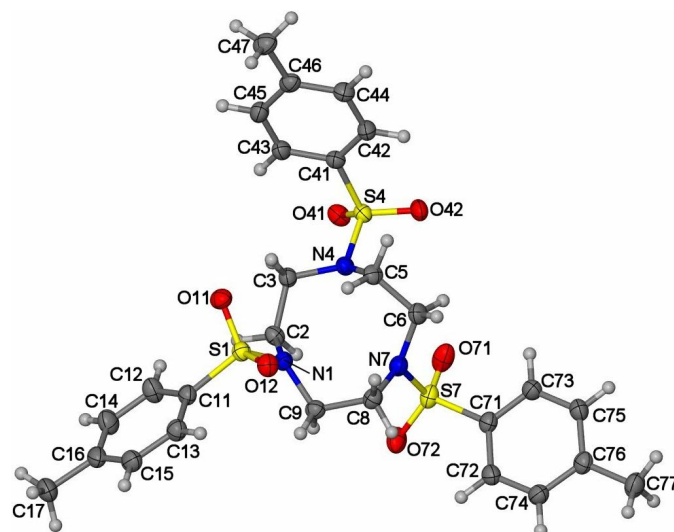
Refinement on <i>F</i> <sup>2</sup>	$w = 1/[\sigma^2(F_o^2) + (0.0762P)^2 + 0.4075P]$
$R[F^2 > 2\sigma(F^2)] = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.134$	( $\Delta/\sigma$ ) <sub>max</sub> = 0.001
<i>S</i> = 1.09	$\Delta\rho$ <sub>max</sub> = 0.95 e Å <sup>-3</sup>
6402 reflections	$\Delta\rho$ <sub>min</sub> = −1.27 e Å <sup>-3</sup>
356 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	Extinction coefficient: 0.047 (7)

**Table 1**

Selected geometric parameters (Å, °).

S1—O11	1.4353 (13)	N1—C2	1.483 (2)
S1—N1	1.6277 (14)	C2—C3	1.519 (2)
S1—C11	1.7664 (17)		
O12—S1—O11	119.47 (8)	C3—N4—C5	116.22 (13)
O11—S1—N1	106.81 (7)	N1—C2—C3	115.41 (13)
N1—S1—C11	110.24 (8)	N4—C3—C2	113.94 (14)
C2—N1—S1	119.59 (11)		

No crystallographic disorder was observed in the structure. All H atoms were placed in calculated positions and refined using a riding model. The fixed distances were C—H(aryl) = 0.95 Å, C—H(methyl) = 0.98 Å and C—H(ethylene bridge) = 0.99 Å. For all H atoms,



**Figure 1**

Plot (*XSeed*; Barbour, 1999) of the molecular structure of (I). Displacement ellipsoids are at the 50% probability level. All H atoms have arbitrary radii.

*U*<sub>iso</sub>(H) values were set at 1.2*U*<sub>eq</sub>(C). The deepest difference density holes were located within 1 Å of atom S1.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XSeed* (Barbour, 1999); software used to prepare material for publication: local program.

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