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A new conformer of 1,4,7-tris(*p*-tolylsulfonyl)-1,4,7-triazacyclononane

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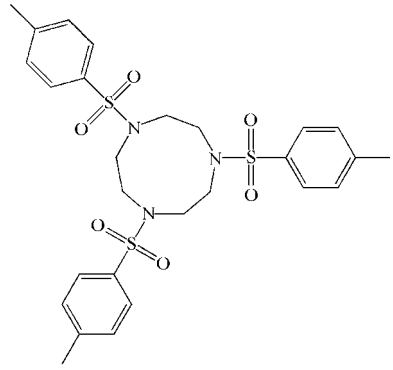
A second polymorphic form (form II) of the previously reported 1,4,7-tris(*p*-tolylsulfonyl)-1,4,7-triazacyclononane (form I), $C_{27}H_{33}N_3O_6S_3$, is presented. The molecular structures of the two forms display very different conformations, thus prompting the two forms to crystallize in two different space groups and exhibit quite diverse crystal structure assemblies. Form I crystallizes in the triclinic space group $P\overline{1}$, while form II crystallizes in the monoclinic space group $P2_1/n$. The main differences between the two molecular structures are the conformations of the *p*-tosyl groups relative to each other and to the macrocyclic ring. The resulting crystal packing displays no classical hydrogen bonds, but different supramolecular synthons give rise to different packing motifs.

Comment

1,4,7-Triazacyclononane (TACN) base ligands are used in the syntheses of high- and low-valent organometallic complexes (*e.g.* Male *et al.*, 2000; Bambirra *et al.*, 2001; Gott *et al.*, 2002; Cui *et al.*, 2003, and references therein) and also in the preparation of models for metalloprotein active sites. The *p*-tolylsulfonyl (tosyl) groups may be used to differentiate the three N atoms, as selectively tosylated TACN rings are accessible *via* the partial hydrolysis of 1,4,7-tris(*p*-tolylsulfonyl)-1,4,7-triazacyclononane (TACN-3Ts) or by statistical tosylation of the parent macrocycle (Halfen & Tolman, 1998). The utility of this compound, when used as a starting fragment, is the selective detosylation and introduction of different functional groups in any or all of the N atoms, thus generating a wide range of multidentate ligands (Wainwright, 1997).

The molecular structure of this new polymorph (form II; Fig. 1) displays a completely different overall conformation from the already known structure of TACN-3Ts [form I; Cambridge Structural Database (Allen, 2002) refcode IMIPAV (Gott & McGowan, 2003)]. The structure of the central macrocycle is a puckered ring, well expressed by the torsion angles within the ring and the distance from each N atom to the mean plane of the nine-membered ring (atom N1 is 0.326 Å and N7 is 0.650 Å away, on the same side of the mean plane, and N4 is 0.538 Å away, on the other side of the plane).



TACN-3Ts, form II

The different conformations of the two polymorphs are clearly seen in Figs. 2 and 3, where we compare the molecular structures of the two conformers and show the different positioning of the *p*-tosyl groups relative to the mean plane of the macrocycle (see also Table 1). Fig. 2 displays an overlay of the two polymorphs, showing that the central nine-membered rings are very similar but that the conformations of the *p*-tosyl groups are quite different. In form I, one tosyl ring is nearly coplanar with the mean-square plane of the nine-membered ring (making an angle of 6.54°), with the other two rings making angles of 38.44 and 62.63°, while in our structure, the three rings are arranged in a completely different orientation, with angles of 55.66, 49.22 and 63.77° (see Table 1). The largest difference is clearly in the relative configuration of the parallel ring (the tosyl group with atom S7) in form I.

Forms I and II crystallize in two completely different space groups, *viz*. triclinic $P\overline{1}$ and monoclinic $P2_1/n$, respectively. As

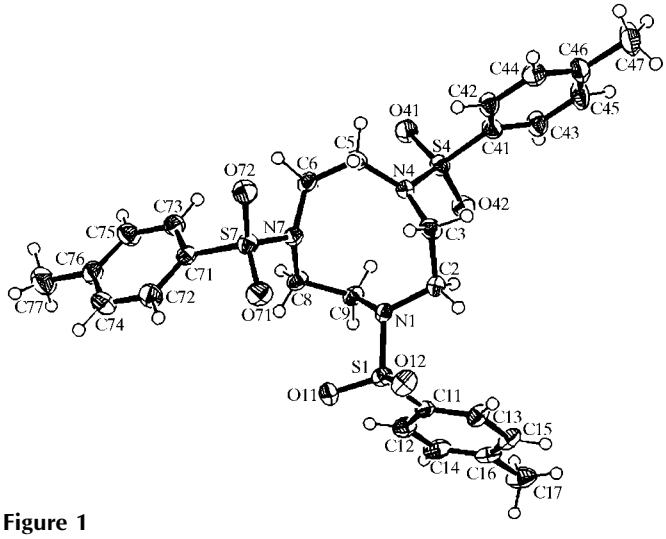


Figure 1
The molecular structure of a new TACN-3Ts polymorph, form II. Displacement ellipsoids are drawn at the 50% probability level. Only the H atoms of the major component (~70%) of the disordered C77 *p*-methyl group are shown.

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well as the differences in conformation, the two different crystal forms pack with quite different supramolecular arrangements. No classical hydrogen bond based synthons are found in either of the structures, but in both forms there are weak intermolecular C—H···O and C—H···π interactions that explain the supramolecular arrangement found.

In the view along *c*, the crystal packing of form I shows a layer of alternating 'pseudo-dimers' of *p*-tosyl rings (connected to S4) that spread along *b*, connected by C—H···O interactions (Fig. 4*a* and Table 2). There are also some weak C—H···O and C—H···π interactions with molecules above and below the *ab* plane. The numbering scheme for form II was adapted from that of form I (Gott & MacGowan, 2003).

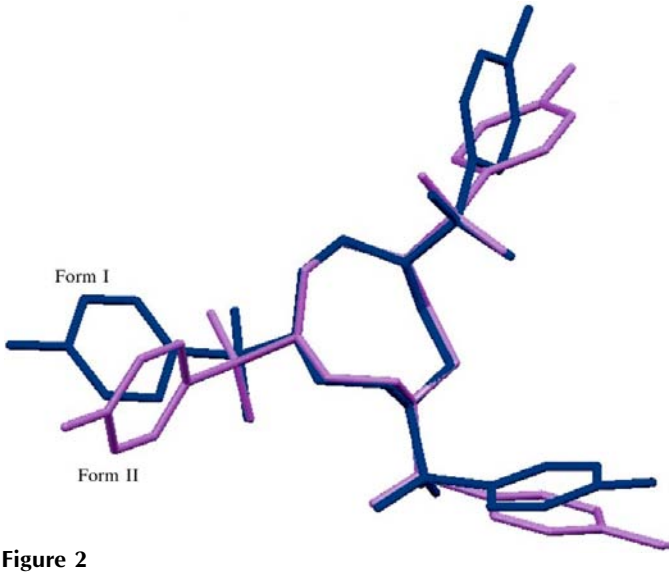

Figure 2
An overlay of the two polymorphs of TACN-3Ts; form I is shown in a darker colour.

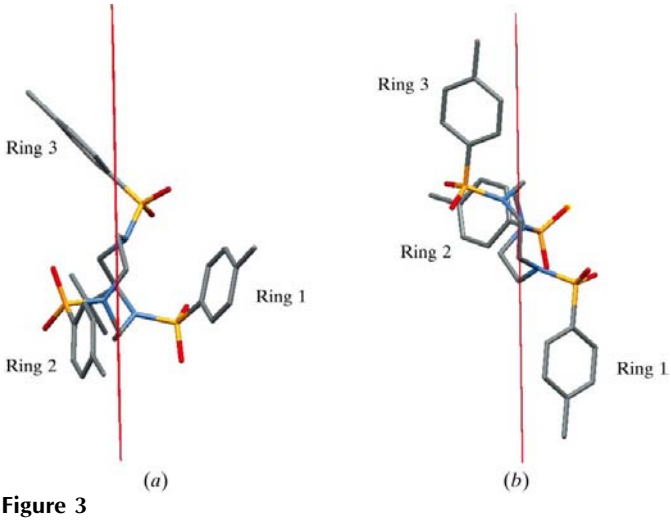

Figure 3
TACN-3Ts structures, with the mean plane of the macrocycle represented by the near vertical lines through the structures: (*a*) form I and (*b*) form II. In both cases, ring 1 corresponds to the benzene ring connected to atom S7, ring 2 corresponds to the benzene ring connected to atom S1, and ring 3 corresponds to the benzene ring connected to atom S4.

Fig. 4(*b*), where the packing of form II is shown along *a*, reveals that repeat units, each formed by two pairs of *p*-tosyl rings (those connected to atoms S4 and S7, with centroids *Cg*2 and *Cg*3, respectively) antiparallel to each other, interact *via* C—H···π interactions. These two antiparallel pairs do not interact with each other and the motif is terminated by a different *p*-tosyl ring (connected to atom S1) on each end. These units repeat themselves along the [0$\overline{1}$1] direction and the tosyl group ending this sequence belongs to the next chain (along *b*). It can be seen that the *p*-tosyl ring connected to atom S1 forms a chain along the [010] direction, the tosyl groups interacting *via* a C—H···O contact. This arrangement is reinforced by further C—H···O interactions above and below the chain (see Fig. 4*b* and Table 2).

Even though there are no classical intermolecular hydrogen bonds, it can be seen that the packing is influenced by an energetic interplay between longer contacts and close packing considerations, such as the Kitaigorodskii–Aufbau principle (Kitaigorodskii, 1961) and the achievement of a maximum packing efficiency (Fagan *et al.*, 1989; Braga & Grepioni,

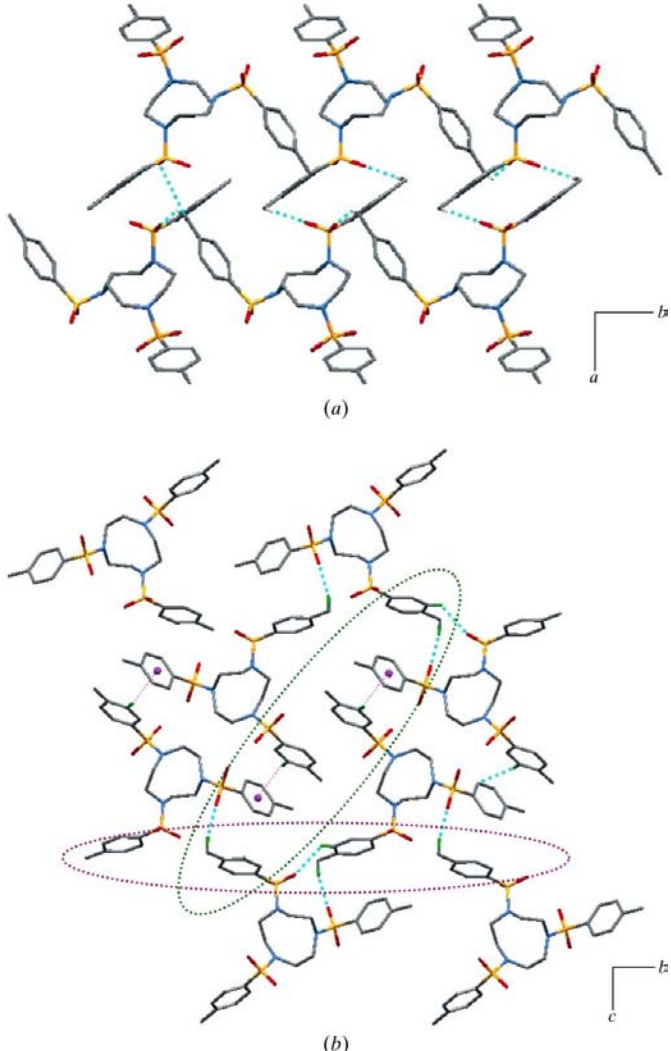

Figure 4
The packing of the TACN-3Ts structures, showing (*a*) form I, viewed down *c*, and (*b*) form II, viewed down *a*.

1996). This is confirmed by comparison of the similar packing efficiencies obtained in the two polymorphic forms (68.6 and 68.0% in forms I and II, respectively).

Experimental

TACN-3Ts was synthesized according to a previously published procedure (Searle & Geue, 1984). All the other starting materials were obtained from Sigma–Aldrich and were used as received. Attempted cocrystallization of paracetamol using TACN-3Ts as a co-former led to the serendipitous discovery of a novel polymorphic form of the latter. Paracetamol (0.1170 g, 0.774 mmol) and TACN-3Ts (0.0893 g, 0.1509 mmol) were dissolved in ethanol (4 ml) and chloroform (1 ml); the mixture was heated at 353 K for 15 min and allowed to cool. Colourless crystals of form II were obtained after two days on maintaining the solution at room temperature.

Crystal data

$C_{27}H_{33}N_3O_6S_3$
M_r = 591.74
Monoclinic, $P2_1/n$
a = 5.877 (4) Å
b = 14.939 (3) Å
c = 32.128 (5) Å
β = 95.04 (2)°
V = 2810 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 150 (2) K
0.14 × 0.08 × 0.03 mm

Data collection

Bruker SMART CCD area-detector diffractometer
27803 measured reflections
5053 independent reflections
3112 reflections with $I > 2\sigma(I)$
R_{int} = 0.124

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.141
S = 1.01
5053 reflections
356 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.86 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Comparative geometric parameters (°) for both polymorphs.

Torsion angles and angles between planes	Form I[a]	Form II[b]
C2—N1—S1—C11	83.08	−64.5 (3)
C3—N4—S4—C41	66.05	−63.4 (3)
C5—N4—S4—C41	−73.72	95.9 (3)
C6—N7—S7—C71	76.52	95.0 (3)
C8—N7—S7—C71	−73.59	−56.7 (3)
C9—N1—S1—C11	72.56	79.0 (3)
N1—C2—C3—N4	73.35	−67.6 (4)
N4—C5—C6—N7	−62.41	67.3 (4)
N7—C8—C9—N1	−62.5	58.6 (4)
Mean plane[c]–ring 1[d] plane	6.54	55.7 (2)
Mean plane[c]–ring 2[e] plane	38.44	49.2 (1)
Mean plane[c]–ring 3[f] plane	62.63	63.8 (2)
Ring 1[d] plane–ring 2[e] plane	40.05	77.7 (2)
Ring 1[d] plane–ring 3[f] plane	57.75	61.5 (2)
Ring 2[e] plane–ring 3[f] plane	31.00	31.1 (2)
Mean plane[c]–mean N plane[g]	24.20	23.4 (2)

Notes: (*a*) IMIPAV; (*b*) polymorph presented in this work; (*c*) mean plane of the nine-membered ring; (*d*) ring 1 is connected to S7; (*e*) ring 2 is connected to S1; (*f*) ring 3 is connected to S4; (*g*) mean plane through the three N atoms in the nine-membered ring.

H atoms were placed in calculated positions and allowed to ride on their parent C atoms, with C—H distances of 0.93 Å for aromatic H atoms, 0.97 Å for methylene H atoms and 0.96 Å for methyl H atoms. The disorder of the C77 *p*-methyl group was modelled using AFIX127 (*SHELXL97*; Sheldrick, 1997); the occupancies of the two components refined to about 70 and 30%.

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

*Cg*1 is the centroid of the *p*-tosyl ring connected to atom S4 in form I, while *Cg*2 and *Cg*3 are the centroids of the *p*-tosyl rings connected to atoms S4 and S7, respectively, in form II.

D—H···A	D—H	H···A	D···A	D—H···A
Form I				
C17—H17*B*···O11^{i}	0.98	2.51	3.406 (1)	153
C47—H47*B*···O12^{ii}	0.98	2.44	3.282 (2)	144
C75—H75···O12^{iii}	0.95	2.63	3.544 (1)	161
C77—H77*B*···*Cg*1^{iii}	0.98	2.88	3.813 (2)	160
Form II				
C15—H15···O11^{iv}	0.93	2.58	3.278 (5)	132
C17—H17*B*···O71^{iv}	0.96	2.48	3.298 (5)	143
C44—H44···*Cg*3^{v}	0.93	2.88	3.620 (5)	137
C75—H75···*Cg*2^{i}	0.93	2.89	3.648 (5)	140

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-32* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3048). Services for accessing these data are described at the back of the journal.

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