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Key indicators

Single-crystal X-ray study

T = 153 K

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

R factor = 0.043

wR factor = 0.108

Data-to-parameter ratio = 15.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.A thiophene-based azacryptand Mannich base: 18,24-bis(*p*-tolylsulfonamido)-2,5,8,11,21-pentaoxa-15,27-dithia-18,24-diazatricyclo[24.3.0.0]nonacosan-1(26),12(16),13,28-tetraene

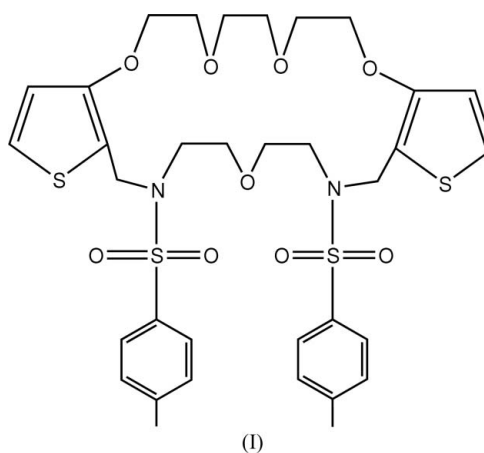
The title compound, $\text{C}_{34}\text{H}_{42}\text{N}_2\text{O}_9\text{S}_4$, is composed of two thiophene rings bridged by an $-\text{O}-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-\text{O}-$ chain and a trisubstituted diamine with pendent tosyl rings. In the crystal structure, the molecules are stabilized by several intra- and intermolecular $\text{C}-\text{H}\cdots\text{O}$ interactions, forming a two-dimensional network arranged in the *ac* plane.

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Comment

The title compound, (I), is similar to the macrocycle reported by Halfpenny & Sloman (2000), in that the bulky tosyl substituents may have a major effect on the macrocyclic ring geometry. Considering the important steric restrictions imposed in (I) by the thiophene and the tosyl rings, the flexibility must be even lower and the selectivity of this macrocycle higher than the benzyl analogue reported by Halfpenny & Sloman (2000) and Barker *et al.* (1993).



The molecule (I) can be divided into two similar parts through a local approximate C_2 axis passing through atom O5 and the mid-point of the C7–C8 bond (Fig. 1). The macrocyclic ring shows a non-planar conformation; the longest intramolecular distance between the two thiophene rings is 13.479 (4) \AA for C4 \cdots C14 and the longest between the two tosyl rings is 9.983 (3) \AA for C25 \cdots C29. The large separation of the two tosyl rings influences the geometry of the macrocyclic cavity by ensuring that the thiophene rings and therefore the O and N atoms do not lie in the same plane. The largest cross-cavity distances are N1 \cdots O1 = 7.472 (3) \AA , N2 \cdots O4 = 7.458 (3) \AA and O1 \cdots O4 = 7.798 (3) \AA . The macrocyclic cavity can be divided in two smaller distorted tetrahedral cavities, defined by the potential donor atoms O5/N1/O4/O3 and O5/N2/O1/O2. Their largest cross-cavity distances are N1 \cdots O3 = 5.085 (3) \AA , O4 \cdots O5 = 4.619 (3) \AA ,

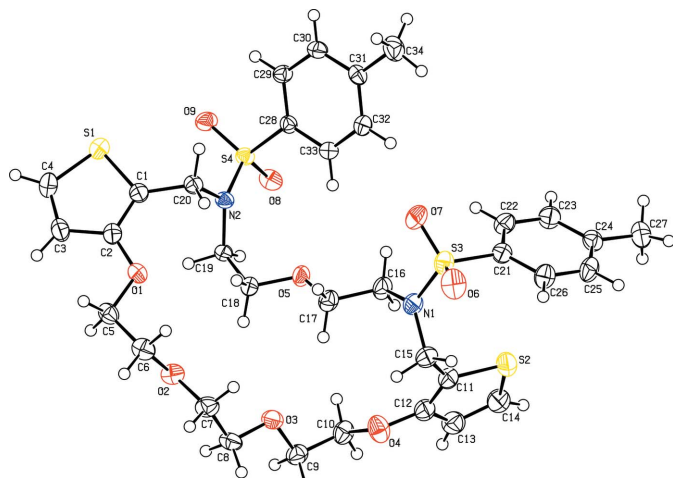


Figure 1
A view of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

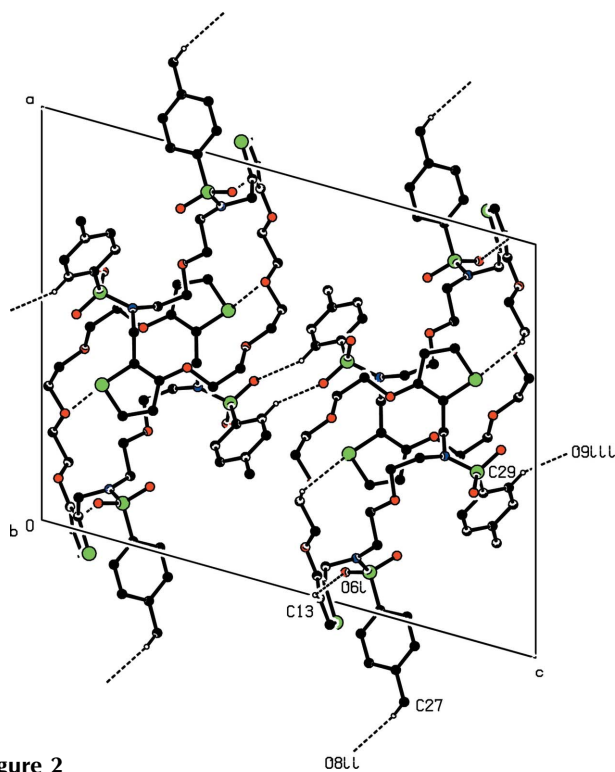


Figure 2
The molecular packing of (I), viewed down the *b* axis. H atoms have been omitted unless these are involved in C—H...O interactions (dashed lines). [Symmetry codes: (i) $x, 1 + y, z$; (ii) $-x, y - \frac{1}{2}, \frac{3}{2} - z$; (iii) $1 - x, -y, 2 - z$]

$N2 \cdots O2 = 5.304(3) \text{ \AA}$ and $O1 \cdots O5 = 4.597(2) \text{ \AA}$. The macrocycle conformation of (I) is stabilized by intramolecular C—H...O interactions (Table 2). The molecules are linked by C—H...O interactions, forming a two-dimensional network in the *ac* plane (Fig. 2).

Experimental

Compound (I) was synthesized according to the procedure described by Chaffin *et al.* (2002). Crystals suitable for X-ray analysis were

grown from a cyclohexane/methanol solution (1:1 *v/v*) by slow evaporation at 278 K.

Crystal data

$C_{34}H_{42}N_2O_9S_4$
 $M_r = 750.94$
Monoclinic, $P2_1/c$
 $a = 18.2875(13) \text{ \AA}$
 $b = 9.0910(5) \text{ \AA}$
 $c = 22.6813(17) \text{ \AA}$
 $\beta = 105.619(9)^\circ$
 $V = 3631.6(4) \text{ \AA}^3$

$Z = 4$
 $D_x = 1.373 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
 $\mu = 0.32 \text{ mm}^{-1}$
 $T = 153(2) \text{ K}$
Block, colourless
 $0.50 \times 0.50 \times 0.30 \text{ mm}$

Data collection

Stoe IPDS diffractometer
 φ scans
Absorption correction: none
27910 measured reflections

7077 independent reflections
4692 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.116$
 $\theta_{\text{max}} = 26.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.108$
 $S = 0.88$
7077 reflections
444 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0522P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.44 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.43 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

S1—C4	1.708 (3)	S3—N1	1.620 (2)
S1—C1	1.722 (2)	S3—C21	1.762 (2)
S2—C11	1.712 (3)	S4—N2	1.6200 (19)
S2—C14	1.719 (3)	S4—C28	1.768 (2)
C4—S1—C1	92.06 (12)	C20—C1—S1	123.41 (17)
C11—S2—C14	92.06 (14)	C12—C11—C15	125.9 (2)
C2—C1—C20	126.3 (2)	C15—C11—S2	123.7 (2)
O1—C5—C6—O2	71.3 (3)	N1—C16—C17—O5	-168.6 (2)
O2—C7—C8—O3	-84.8 (3)	O5—C18—C19—N2	68.5 (2)
O3—C9—C10—O4	-72.1 (3)	S1—C1—C20—N2	92.0 (2)
S2—C11—C15—N1	-72.0 (3)		

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C15—H15A...O4	0.99	2.54	2.941 (3)	104
C15—H15B...O6	0.99	2.45	2.914 (4)	108
C16—H16A...O7	0.99	2.36	2.828 (4)	108
C19—H19B...O8	0.99	2.34	2.859 (3)	112
C26—H26A...O6	0.95	2.56	2.923 (3)	103
C29—H29A...O9	0.95	2.50	2.885 (3)	104
C32—H32A...O7	0.95	2.57	3.386 (3)	145
C33—H33A...O5	0.95	2.59	3.450 (3)	151
C13—H13A...O6 ⁱ	0.95	2.53	3.245 (4)	132
C27—H27B...O8 ⁱⁱ	0.98	2.58	3.463 (3)	149
C29—H29A...O9 ⁱⁱⁱ	0.95	2.48	3.221 (3)	135

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

H atoms were included in calculated positions and treated as riding atoms, with C—H = 0.95–0.99 \AA and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, or $1.5U_{\text{eq}}(\text{C})$ for methyl groups.

Data collection: *IPDS-I* (Stoe & Cie, 2000); cell refinement: *IPDS-I*; data reduction: *IPDS-I*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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