Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# 10,13-Bis(*p*-tolylsulfonyl)-1,4,7-trithia-10,13-diazacyclopentadecane

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Received 8 March 2004
Accepted 19 April 2004
Online 30 April 2004

**Key indicators**

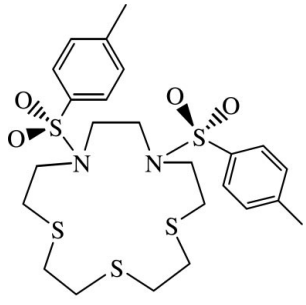
Single-crystal X-ray study
$T$ = 220 K
Mean $\sigma$(C–C) = 0.013 Å
Disorder in main residue
$R$ factor = 0.070
$wR$ factor = 0.149
Data-to-parameter ratio = 8.4

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

The title compound, $C_{24}H_{34}N_2O_4S_5$, is the ditosylated precursor to the mixed aza–thia macrocycle 1,4,7-trithia-10,13-diazacyclopentadecane ([15]ane$N_2S_3$) and is prepared by reacting bis(2-mercaptoethyl) sulfide with *O*,*O*′,*N*,*N*′-tetratosyl-*N*,*N*′-bis(2-oxyethyl)ethylendiamine in dimethylformamide in the presence of $Cs_2CO_3$. Molecules lie across crystallographic twofold axes. The macrocyclic framework adopts a [33333] conformation and the two tolylsulfonyl groups are directed away from the ring cavity. There is extensive disorder of the methylene groups of the macrocyclic backbone.

## Comment

Recently, aza–thioether macrocycles have been effectively used for the design and synthesis of selective heteroditopic receptors capable of binding both cationic and anionic moieties of a metal salt (Love *et al.*, 2001; Glenny *et al.*, 2003). The synthetic routes to aza–thioether macrocycles generally involve tosylated ring precursors, the only drawback to which is the detosylation procedure which may require long reaction times and generally gives low yields. For the synthesis of [15]ane$N_2S_3$ we prepared the title compound, (I), following a well established cyclization procedure under high dilution conditions. Unfortunately, all attempts to detosylate (I) failed to afford the deprotected macrocycle.



(I)

Molecules of (I) lie across crystallographic twofold axes (Fig. 1), with the axes passing through S7 and the mid-point of the C15—C15$^{i}$ bond [symmetry code: (i) $y$, $x$, $-z$]. The macrocyclic framework exhibits a [33333] conformation (Fig. 2) and the two tolylsulfonyl groups are directed away from the ring cavity. The C atoms of the N—C—C—S and S—C—C—S linkages are each disordered over two sites, with group occupancies of 0.705 (12) and 0.295 (12) for the major and minor components, respectively.

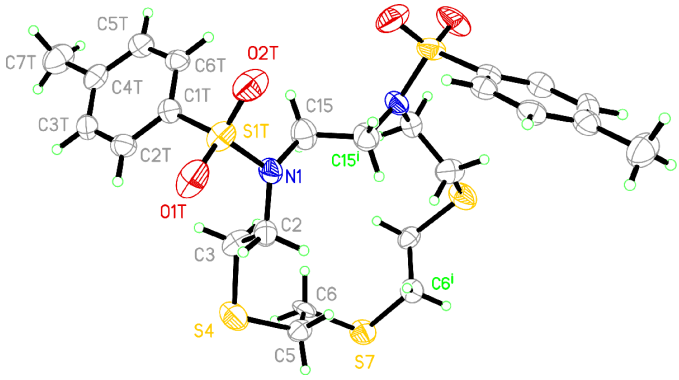



**Figure 1**
A view of the structure of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 30% probability level. The minor disorder component has been omitted for clarity. [Symmetry code: (i) $y, x, -z$.]

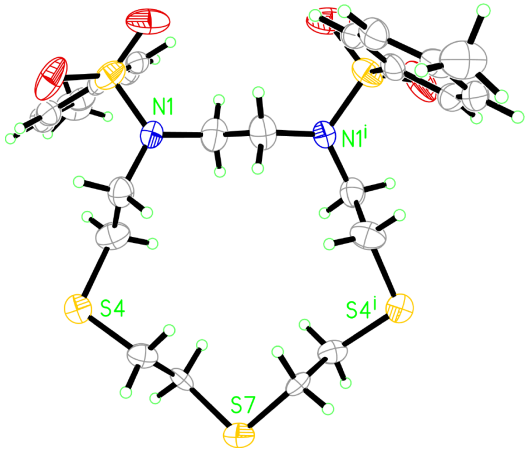



**Figure 2**
An alternative view showing the [33333] ring conformation. Ellipsoids are drawn at the 30% probability level and the minor disorder component has been omitted for clarity. [Symmetry code: (i) $y, x, -z$.]

## Experimental

A 5 l three-necked flask fitted with a precision dropping funnel and a mechanical stirrer was purged with nitrogen. Freshly distilled dimethylformamide (DMF; 1.8 l) and dry $Cs_2CO_3$ (11.0 g, 0.0338 mol) were added and the solution was heated to 333 K. A solution of bis(2-mercaptoethyl) sulfide (2.61 g, 0.0169 mol) and *O,O′,N,N′*-tetratosyl-*N,N′*-bis(2-oxyethyl)ethylendiamine (12.93 g, 0.0169 mol) in DMF (250 ml) was then added dropwise over a period of 12 h. After the addition was complete, a second portion of $Cs_2CO_3$ (11.0 g, 0.0338 mol) was added and an identical solution as before was added over a further 12 h period. Once all the reagents had been added, the reaction mixture was stirred for 6 h at 333 K. The DMF was then removed *in vacuo* and the residue was dissolved in $CH_2Cl_2$, washed with water and concentrated *in vacuo*. The residue was crystallized from hot ethanol to give a white solid of the desired product (9.45 g, 48.6% yield). Crystals suitable for X-ray diffraction analysis were grown by diffusion of $Et_2O$ vapour into a $CH_2Cl_2$ solution of the product. Elemental analysis, found (calculated for $C_{24}H_{34}N_2O_4S_5$): C 49.95 (50.15), H 5.88 (5.96), N 4.77 (4.87)%.

### *Crystal data*

$C_{24}H_{34}N_2O_4S_5$
$M_r$ = 574.83
Tetragonal, $P4_12_12$
$a$ = 12.377 (3) Å
$c$ = 18.296 (1) Å
$V$ = 2802.8 (10) Å$^3$
$Z$ = 4
$D_x$ = 1.362 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 35 reflections
$\theta$ = 10.1–14.9°
$\mu$ = 0.45 mm$^{-1}$
$T$ = 220 (2) K
Column, colourless
0.50 × 0.39 × 0.20 mm

### *Data collection*

Stoe STADI-4 four-circle diffractometer
$\omega$ scans
Absorption correction: none
3449 measured reflections
1491 independent reflections
911 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.115
$\theta_{max}$ = 25.1°
$h = -9 \rightarrow 14$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 21$
3 standard reflections
frequency: 60 min
intensity variation: ±3.7%

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.070
$wR(F^2)$ = 0.149
$S$ = 1.11
1491 reflections
178 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.017P)^2 + 7.15P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.018
$\Delta\rho_{max}$ = 0.26 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.20 e Å$^{-3}$
Absolute structure: Flack (1983), 997 Friedel pairs
Flack parameter = 0.0 (3)

The C atoms of the N—C—C—S and S—C—C—S linkages are each disordered over two sites. This was modelled in terms of two orientations for each linkage and restraints were applied to the relevant C—C, C—N and C—S distances. The occupancies of the two components (C2/C3/C5/C6 and C2′/C3′/C5′/C6′) converged at 0.705 (12) and 0.295 (12), respectively. Our decision to refine a single parameter to describe the disorder of C2/C3 and C5/C6 was based on two observations. The first was that independent refinement of the occupancies of the two dimethylene links gave very similar values. The second is that the angles at the central S atom are both more consistent and typical (104.0 and 104.8°) when the major and minor components are not mixed, but less so (87.7 and 99.0°) with major/minor and minor/major combinations. For these reasons, we believe that the disorder of the two $-CH_2-CH_2-$ units is a concerted phenomenon.

Methyl H atoms were located in $\Delta F$ syntheses and refined as part of rigid rotating groups, with $U_{iso}(H) = 1.5U_{eq}(C)$. Other H atoms were positioned geometrically and refined using a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$. C—H distances of 0.94, 0.97 and 0.98 Å were used for aryl, methyl and methylene H atoms, respectively. Rigid-bond restraints were applied to the anisotropic displacement parameters. With a value of 0.0 (3), the Flack (1983) parameter was not reliably determined.

Data collection: *STADI*4 (Stoe & Cie, 1997); cell refinement: *STADI*4; data reduction: *X-RED* (Stoe & Cie, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004) and *PLATON* (Spek, 2003).

We thank the EPSRC (UK) for the provision of a diffractometer.

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