

25,27-(6-Tosyl-3,9-dioxa-6-azaundecane-1,11-diylodioxy)-26,28-(3,6,9-trioxaundecane-1,11-diylodioxy)-calix[4]arene

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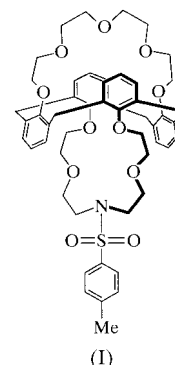
A new calix[4]-crowned azacrown ether, C₅₁H₅₉NO₁₁S, consisting of four phenyl rings in a 1,3-alternate conformation, was synthesized from the reaction of 25,27-bis(5-chloro-3-oxapentylloxy)calix[4]crown-5 and *p*-toluenesulfonamide in the presence of Cs₂CO₃. A crown-5 loop was attached on the two facing lower rims of the calix[4]arene and the *N*-tosyl azacrown group was attached on the other set of lower rims of the calix[4]arene backbone. This molecule seems to offer an inside cavity for the formation of a host-guest complex.

Comment

Calix[4]arenes have been shown to be useful three-dimensional molecular building blocks for the synthesis of receptors with specific properties (Andreotti *et al.*, 1991). They can exist in four different conformations: cone, partial cone, 1,2-alternate and 1,3-alternate (Casnati *et al.*, 1995; Kim, Suh *et al.*, 1998). Calixcrown ethers in which the conventional crown ether moiety is incorporated into the rigid 1,3-alternate calix[4]arene have also attracted intense interest as caesium-selective extractants. This selective complexation of caesium ions is attributed not only to the electrostatic interaction between the electron-donating hetero atoms of the crown ether ring and the metal ion, but also to the cation- π interaction between the two aromatic rings and the metal ion (Kim *et al.*, 1997; Kim, Lee *et al.*, 1998; Kim, Ohki *et al.*, 1999; Kim, Pang *et al.*, 1999). In addition to calixcrown ether, calixazacrown ether (Koh *et al.*, 1995) in the 1,3-alternate conformation has also received attention because of its structural peculiarities: the N atom has trivalent bonding so that the N-pendant calixazacrown ether would result in an optimized

structure for metal-ion complexation through three-dimensional encapsulation (Kim, Ko *et al.*, 2000).

As part of our work on calix[4]azacrowns, we report herein the first crystal structure of a calix-crowned azacrown ether



existing in a 1,3-alternate conformation, (I); two phenyl groups, *A* and *D*, lie above and the other two phenyl groups, *B* and *C*, below the least-squares plane defined by the four bridging methylene groups, as illustrated in Fig. 1. The upper crown-5 ring is bonded to phenyl rings *B* and *C*, and the

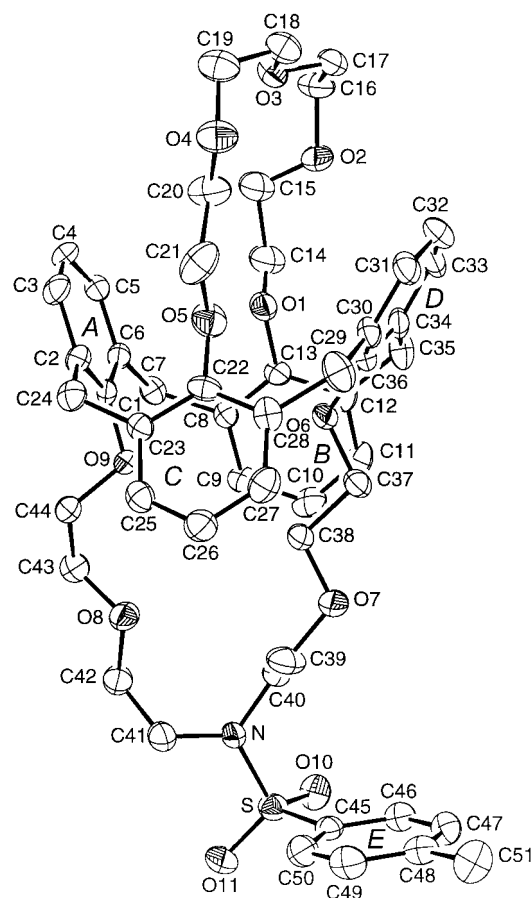


Figure 1
ORTEP (Johnson, 1976) drawing of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 25% probability level. Phenyl rings *A* and *D* are played out upwards, and phenyl rings *B* and *C* downwards. H atoms and hydrogen bonds have been omitted for clarity.

azacrown ether group is bonded to phenyl rings *A* and *D*, where the azacrown ether group consists of an azacrown ring and an *N*-*para*-toluenesulfonyl group. All bond lengths and angles in this compound are similar to those in 25,27:26,28-bis(3,9-dioxa-6-azaundecane-1,11-diyldioxy)calix[4]arene tetrahydrate (Kim, Jensen *et al.*, 2000) and in 1,3-alternate calix[4]arenebis-crown-7 (Khrifi *et al.*, 1997).

Bond angles involving the bridging methylenes, *i.e.* C6—C7—C8 117.0 (4), C2—C24—C23 118.0 (4), C28—C29—C30 122.2 (5) and C12—C35—C34 119.9 (5)°, are significantly larger than the tetrahedral angle due to repulsions among the four phenyl groups. Similar trends were found in other calix[4]arene derivatives (Kim, Jensen *et al.*, 2000).

The dihedral angles of two pairs of facing rings, namely *A* and *D*, to which the crown-5 ring is bonded, and *B* and *C*, to which the azacrown-5 ring is bonded, are 49.0 (2) and 42.2 (2)°, respectively, so that rings *A* and *D* are splayed out upwards, and *C* and *B* are splayed out downwards from the central axis. This particular conformation leads to the distances O6···O9 4.026 (4), C1···C36 5.139 (6), C4···C32 7.361 (8), and O1···O5 4.053 (6), C13···C22 5.139 (7) and C10···C26 7.078 (8) Å. Dihedral angles of adjacent phenyl rings in the calix[4]arene range from 72.9 (2) to 89.3 (2)°.

The somewhat flexible cavities lined with five O atoms in the crown-5 ring [O1···O4 5.897 (6), O2···O3 3.000 (6), O2···O4 5.419 (6) and O2···O5 5.504 (6) Å] and with four O atoms and an N atom in the azacrown-5 ring [O7···O8 4.219 (5), N···O7 3.728 (6), N···O8 3.145 (6), N···O6 6.689 (5) and N···O9 5.722 (5) Å] might enable the molecule to accept a guest atom.

As is evident from Table 1, the S—O10 and S—O11 distances in the *N*-*para*-toluenesulfonyl group clearly show double-bond character and the S—N and S—C45 single bonds are comparable with those found in *N*-tosyl calix[4]arene azacrown ether (Kim, Kim *et al.*, 1999). The valence angles around the S atom in *N*-*para*-toluenesulfonyl are very close to the tetrahedral angle, with the exception of 118.9 (3)° for O10—S—O11. The benzene ring in this group is planar within 0.012 (4) Å and the methyl C51 atom is also in the plane, but the S atom is −0.150 (7) Å out of the plane.

As shown in Table 2, the four potential intramolecular C—H···O hydrogen bonds seem to help stabilize the structure, and pairs of molecules related by crystallographic inversion centers form dimers held together by bonds of type C51—H51A···O7ⁱ; the C···O separation is 3.413 (8) Å and the C—H···O angle is 154.1° [symmetry code: (i) $-x, 2 - y, -z$]. Similar intramolecular C—H···N hydrogen bonds were found in 25,27:26,28-bis(3,9-dioxa-6-azaundecane-1,11-dioxy)calix[4]arene tetrahydrate (Kim, Pang *et al.*, 2000).

Experimental

p-Toluenesulfonamide (0.90 g, 5.26 mmol), Cs₂CO₃ (6.54 g, 20.1 mmol) and *N,N'*-dimethylformamide (DMF) (100 ml) were heated to 353 K for 30 min. Then, 25,27-bis(5-chloro-3-oxapentyl-oxo)calix[4]crown-5 (4.04 g, 5.04 mmol) dissolved in DMF (20 ml)

was added dropwise over a period of 3 h. After refluxing for 24 h, the crude mixture was dissolved in CH₂Cl₂ and treated with 10% aqueous NaHCO₃ solution. The organic layer was dried over anhydrous MgSO₄. Column chromatography on silica with 1:2 EtOAc—hexane as eluent gave the desired product as a solid in 50% yield (m.p. 398–400 K). ¹H NMR (400 MHz, CDCl₃, p.p.m.): δ 7.74 (*d*, *J* = 8.1 Hz, 2H, ArH-tosyl), 7.34 (*d*, *J* = 8.1 Hz, 2H, ArH-tosyl), 7.12 (*d*, *J* = 7.5 Hz, 4H, ArH_{*m*}-calix), 7.05 (*d*, *J* = 7.5 Hz, 4H, ArH_{*m*}-calix), 6.91 (*t*, *J* = 8.7 Hz, 2H, ArH_{*p*}-calix), 6.82 (*t*, *J* = 8.7 Hz, 2H, ArH_{*p*}-calix), 3.87 (*s*, 8H, Ar—CH₂—Ar), 3.63 (*s*, 4H, OCH₂CH₂O), 3.57 (*s*, 4H, OCH₂CH₂NH), 3.49–3.46 (*m*, 8H, ArOCH₂CH₂O), 3.34–3.28 (*m*, 8H, ArOCH₂CH₂O), 3.16–3.07 (*m*, 8H, OCH₂CH₂O), 2.46 (*s*, 3H, ArCH₃-tosyl). Analysis calculated for C₅₁H₅₉NO₁₁S: C 68.53, H 6.60%; found: C 68.50, H 6.63%.

Crystal data

C ₅₁ H ₅₉ NO ₁₁ S	<i>D</i> _x = 1.291 Mg m ^{−3}
<i>M</i> _r = 894.05	Mo Kα radiation
Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>	Cell parameters from 25 reflections
<i>a</i> = 23.547 (2) Å	<i>θ</i> = 11.45–13.44°
<i>b</i> = 10.922 (3) Å	<i>μ</i> = 0.133 mm ^{−1}
<i>c</i> = 19.4876 (18) Å	<i>T</i> = 289 (2) K
<i>β</i> = 113.340 (7)°	Plate, colorless
<i>V</i> = 4601.6 (14) Å ³	0.53 × 0.46 × 0.15 mm
<i>Z</i> = 4	

Data collection

Enraf–Nonius CAD-4 diffractometer	<i>R</i> _{int} = 0.047
Non-profiled ω/2θ scans	<i>θ</i> _{max} = 24.98°
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	<i>h</i> = 0 → 27
<i>T</i> _{min} = 0.933, <i>T</i> _{max} = 0.981	<i>k</i> = 0 → 12
8225 measured reflections	<i>l</i> = −23 → 21
8018 independent reflections	3 standard reflections
3475 reflections with <i>I</i> > 2σ(<i>I</i>)	frequency: 300 min
	intensity decay: 3%

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0680P)^2 + 2.5027P]$
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.081	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>wR</i> (<i>F</i> ²) = 0.206	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.011	Δρ _{max} = 0.57 e Å ^{−3}
8018 reflections	Δρ _{min} = −0.30 e Å ^{−3}
571 parameters	
H atoms constrained	

Table 1

Selected geometric parameters (Å, °).

S—O11	1.432 (4)	S—C45	1.751 (6)
S—O10	1.434 (4)	N—C40	1.459 (6)
S—N	1.632 (4)	N—C41	1.459 (6)
O11—S—O10	118.9 (3)	N—S—C45	105.5 (3)
O11—S—N	107.2 (2)	C40—N—C41	118.6 (4)
O10—S—N	108.0 (2)	C40—N—S	118.0 (4)
O11—S—C45	109.3 (3)	C41—N—S	120.3 (4)
O10—S—C45	107.2 (3)		

The largest residual electron-density peaks were located around the O1, O2, O4 and O5 atoms, and equal anisotropic displacement parameter restraints (*SHELXL97*; Sheldrick, 1997) were imposed on the C15 atom in order to avoid unusual values, which are probably the reason for the *R* factor being somewhat high. All H atoms were located in calculated positions and allowed to ride on their attached C atoms.

Table 2

Hydrogen-bonding and short contact geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C20—H20A \cdots O3	0.97	2.57	3.033 (7)	110
C40—H40B \cdots O10	0.97	2.60	3.032 (7)	107
C41—H41B \cdots O11	0.97	2.29	2.814 (7)	113
C46—H46 \cdots O10	0.93	2.51	2.894 (7)	105
C51—H51A \cdots O7 ⁱ	0.96	2.52	3.413 (8)	154

Symmetry code: (i) $-x, 2-y, -z$.

Data collection: *CAD-4 EXPRESS Software* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *WinGX* (Farrugia, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1002). Services for accessing these data are described at the back of the journal.

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