

## N-Tosyl Calix[4]arene Azacrown Ether, C<sub>45</sub>H<sub>49</sub>NO<sub>6</sub>S

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### Abstract

The calix[4]arene molecule adopting the 1,3-alternate conformation forms a square cavity, and two pair phenyl rings lying above and below a least-square plane defined by the four bridging methylene groups in the calix[4]arene are widened upwards and downwards, respectively, from central axis, which leads to O1-O4=4.064 Å and O2-O3=3.864 Å. Two propyloxy groups are stabilized with all trans conformations, but the rather short azacrown ether chain with two oxygen atoms includes cis/trans conformations with O1-C35=2.906 Å. Therefore the cavity does not seem to be big enough to form a host-guest complex.

### 要 約

1,3-交叉形態를 갖는 calix[4]arene 분자는 矩形의 空洞을 形成하고 있으며, 4개의 bridging methylene群으로 된 最小平面的 위 및 아래로 配置된 2쌍의 phenyl 고리들은 中心軸에 對하여 위 쪽과 아래쪽으로 벌어져서 O1-O4=4.064 Å과 O2-O3=3.864 Å이다. 두 個의 propyloxy群은 모두 trans configuration으로 安定化되어있고 2個의 酸素原子를 갖는 짧은 azacrown ether 고리는 cis와 trans가 섞여있으며 O1-C35=2.906 Å이다. 따라서 그 空洞의 크기는 host-guest 複合體를 形成하기에 充分히 크지 못한것같다.

### 1. Introduction

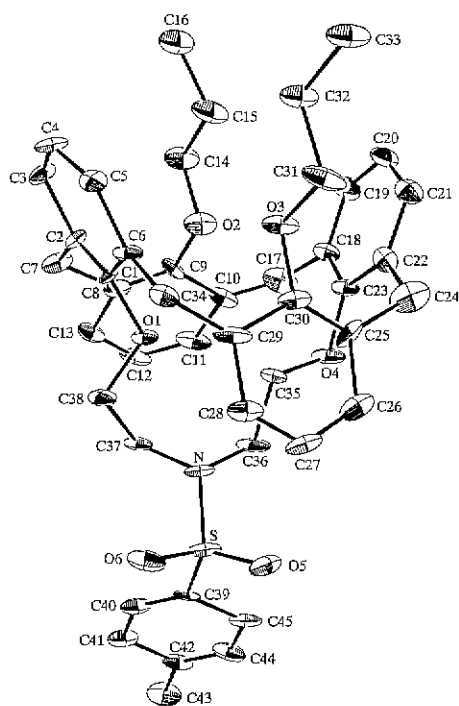
The design and synthesis of macrocyclic molecules directed to the selective binding of metal cations has been a field of continuous interest since the discovery of crown ethers and cryptands. The extensively investigated family of calixarenes provides a wider range of derivatives available for such a pur-

pose.<sup>1,2)</sup>

As a part of a series of structure investigation on calix[4]arene derivatives,<sup>3-8)</sup> we now report the conformation of the title compound.

### 2. Experimental

The C<sub>45</sub>H<sub>49</sub>NO<sub>6</sub>S represented in Fig. 1 was pre-



**Fig. 1. Molecular structure with atomic numbering scheme showing 7% probability displacement ellipsoids. H atoms are omitted for clarity. The nitrogen, oxygen and sulphur atoms are expressed with ellipsoids with octant shading. The upper two phenyl rings 1 and 3 widened upwards.**

pared as described below.

Under nitrogen, potassium carbonate (0.96 g, 6.95 mmol) with 30 ml of dry DMF was placed in three neck round bottom flask. 25,27-Bis(2-chloroethoxy)-26,28-bis(1-propyloxy)calix[4]arene (0.85 g, 1.38 mmol) in 10 ml of dry DMF was poured into dropping funnel. *p*-Toluenesulfonamide (0.23 g, 1.38 mmol) in 10 ml of DMF was prepared with another dropping funnel. To potassium carbonate solution were simultaneously added dropwise the starting material and *p*-toluenesulfonamide during a period of 2 hours at 60°C. Upon complete addition, the reaction mixture refluxed for 24 hours. Removal of DMF by simple distillation gave a brown oil. NaHCO<sub>3</sub> (100 ml) and methylene chloride (100 ml) were added and the organic layer was separated, washed with water and dried over anhydrous MgSO<sub>4</sub> provided yellowish oil. Column chromatography from ethyl acetate and hexanes (1:10) on sil-

**Table 1. Experimental details**

Crystal data	
C <sub>45</sub> H <sub>49</sub> NO <sub>6</sub> S	Mo K <sub>α</sub> Radiation
M <sub>r</sub> =731.91	λ=0.71069 Å
Monoclinic	Cell parameters from 25 reflections
P2 <sub>1</sub> /c	θ=11.121-12.537°
a=14.254(2) Å	μ=0.134 mm <sup>-1</sup>
b=17.019(3) Å	T=291 K
c=16.273(9) Å	Cube
β=102.26(2)°	0.56×0.56×0.53 mm
V=3857.3(2.2) Å <sup>3</sup>	colorless
Z=4	
D <sub>x</sub> =1.260 Mg m <sup>-3</sup>	
D <sub>m</sub> not measured	
Data collection	
Enraf-Nomus	R <sub>m</sub> =0.0000
CAD-4 Diffractometer	
ω/2θ scans	h=-16→16
Absorption correction:	k=0→20
none	
6766 independent reflections	l=0→19
3615 reflections with I <sub>o</sub> ≥2σ(I <sub>o</sub> )	3 standard reflections
θ <sub>max</sub> =25.0°	frequency: 300 min
	intensity decay: 5.1%
Refinement	
Refinement on F	(Δ/σ) <sub>max</sub> =0.000
R(F)=0.0749	(Δρ) <sub>max</sub> =0.524 e Å <sup>-3</sup>
ωR(F)=0.2137	(Δρ) <sub>min</sub> =-0.665 e Å <sup>-3</sup>
S=1.145	Extinction correction: none
3615 reflections	Scattering factors from International Tables for Crystallography (Vol. C)
478 parameters	
H atoms constrained	
w=1/[σ <sup>2</sup> (F <sub>o</sub> <sup>2</sup> )+(0.1P) <sup>2</sup> +0.0P]	
where P=(F <sub>o</sub> <sup>2</sup> +2F <sub>c</sub> <sup>2</sup> )/3	

ica gel provided 33% of desire product as a white solid. IR (deposit. cm<sup>-1</sup>): 1325 (SO<sub>2</sub>), 1120 (SO<sub>2</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.52 (d, 2 H), 7.18 (m, 4 H), 6.88 (m, 4 H), 6.78 (d, 2 H), 6.59-6.50 (m, 4 H), 4.00 (d, J=13.1 Hz, 2H), 3.88-3.69 (m, 8 H), 3.45 (q, 2 H), 3.14 (d, J=13.1 Hz, 2 H), 3.00 (t, 2 H), 2.35 (s, 3 H), 1.74-1.52 (m, 4 H), 0.85 (t, 6 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): ppm 155.9, 155.2, 154.1, 143.3, 136.7, 134.6, 134.1, 131.6, 130.4, 130.2, 129.3, 129.0, 128.8, 127.6, 127.3, 124.4, 123.8, 119.3, 69.0, 66.5, 43.7, 38.6, 31.9, 31.6, 30.3, 23.8, 22.1, 15.9, 11.2; FAB MS m/z (M<sup>+</sup>) calcd 731.0, found

**Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^{-3}$ ) for N-tosyl calix[4]arene azacrown ether,  $\text{C}_{45}\text{H}_{49}\text{NO}_6\text{S}$ . U(eq) is defined as one third of the trace of the orthogonalized Uij tensor**

	x	y	z	U(eq)
S	9181(1)	1681(1)	8202(1)	60(1)
N	8369(2)	2311(2)	8373(2)	51(1)
O(1)	8228(2)	3922(1)	9051(2)	40(1)
C(1)	8311(2)	4672(2)	9457(2)	33(1)
C(2)	7800(3)	4850(2)	9990(2)	39(1)
C(3)	7874(3)	5624(2)	10351(3)	58(1)
C(4)	8378(3)	6176(2)	10063(3)	69(1)
C(5)	8852(3)	6002(2)	9443(3)	57(1)
C(6)	8871(2)	5229(2)	9061(3)	47(1)
C(7)	7228(3)	4263(2)	10422(3)	66(1)
C(8)	6467(3)	3709(2)	9786(3)	48(1)
C(9)	5994(2)	3887(2)	9073(2)	43(1)
C(10)	5346(3)	3317(2)	8489(3)	56(1)
C(11)	5281(3)	2598(2)	8963(4)	73(2)
C(12)	5745(3)	2436(2)	9748(4)	71(1)
C(13)	6376(3)	2983(2)	10231(3)	56(1)
O(2)	6093(2)	4581(2)	8647(2)	65(1)
C(14)	5638(4)	5214(2)	8956(4)	77(2)
C(15)	5975(4)	5959(3)	8485(4)	90(2)
C(16)	5747(4)	6680(3)	8940(4)	87(2)
C(17)	4858(3)	3471(3)	7747(4)	79(2)
C(18)	5109(2)	4054(2)	7069(3)	49(1)
C(19)	4563(3)	4723(3)	6853(3)	64(1)
C(20)	4799(4)	5264(3)	6345(3)	77(2)
C(21)	5605(3)	5168(2)	5962(3)	68(1)
C(22)	6196(3)	4508(2)	6195(3)	54(1)
C(23)	5897(3)	3952(2)	6730(3)	49(1)
C(24)	7043(4)	4439(3)	5818(4)	95(2)
C(25)	8045(3)	4310(2)	6464(2)	55(1)
C(26)	8618(4)	3676(3)	6307(3)	73(2)
C(27)	9445(4)	3506(3)	6855(4)	74(2)
C(28)	9723(3)	3932(2)	7525(3)	63(1)
C(29)	9198(3)	4580(2)	7739(3)	59(1)
C(30)	8365(3)	4756(2)	7097(3)	50(1)
O(3)	7830(2)	5405(1)	7332(2)	56(1)
C(31)	8010(3)	6079(2)	6785(4)	85(2)
C(32)	7478(3)	6766(2)	7137(3)	72(1)
C(33)	7567(2)	7505(2)	6559(2)	86(2)
C(34)	9516(2)	5065(2)	8503(2)	49(1)
O(4)	6417(2)	3228(1)	6895(2)	67(1)
C(35)	7145(2)	3177(2)	7537(3)	42(1)
C(36)	7480(3)	2342(2)	7781(3)	72(1)
C(37)	8367(3)	2529(2)	9197(3)	49(1)
C(38)	8839(3)	3320(2)	9531(3)	65(1)
O(5)	9224(2)	1667(2)	7390(2)	76(1)
O(6)	10036(2)	1883(2)	8807(2)	76(1)
C(39)	8813(3)	742(2)	8538(3)	44(1)
C(40)	8947(3)	498(2)	9238(3)	60(1)
C(41)	8681(3)	-229(2)	9523(3)	68(1)
C(42)	8200(3)	-742(2)	8842(3)	63(1)
C(43)	7889(4)	-1544(3)	9140(4)	92(2)
C(44)	8044(3)	-494(2)	8106(4)	74(2)
C(45)	8343(3)	253(2)	7811(3)	66(1)

732.3 (M+1).

The detailed information on crystal data, data collection and structure refinement is given in Table 1. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. H atoms were placed in calculated positions; those on the phenyl rings were allowed to ride on their parent C atoms with  $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$ , while the methyl groups were treated as rotating rigid groups with  $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{C})$ .

Data collection: CAD4 Express Software.<sup>9)</sup> Data reduction: WinGX.<sup>10)</sup> Program(s) used to solve structure: SHELX86<sup>11)</sup> Program used to refine structure: SHELXL97<sup>12)</sup> Molecular graphics: ORTEP3.<sup>13)</sup>

The final atomic coordinates are listed in Table 2, and the data for atomic bond distances and bond angles, least-squares planes, torsion angles and anisotropic displacement parameters for the atoms can be obtained from authors.

### 3 Discussion

The title compound consists of the calix[4]arene molecule adopting the 1,3-alternate conformation: two phenyl groups 1(C1,C2,C3,C4,C5,C6) and 3(C18,C19,C20,C21,C22,C23) are lying above and the other two phenyl groups 2(C8,C9,C10,C11,C12,C13) and 4(C25,C26,C27,C28,C29,C30) below the least-squares plane defined by the four bridging methylene groups as clearly illustrated in Fig. 1, two propyloxy groups bonded to phenyl rings 2 and 4, and a shorter azacrown ether (two O atoms) linked to the ortho carbon atoms of the aromatic phenyl rings 1 and 3. An N-tosyl group is bonded to the N atom of the azacrown ether chain.

The valence angles around N-atom range from 117.4(3) to 118.7(3)<sup>o</sup> with an average value of 118.0(2)<sup>o</sup>, which are regarded as resulting from the steric hinderance due to the N-tosyl group, and those around S-atom are close to the tetrahedral angle. In the azacrown ethereal linkage, the torsion angle of O4-C35-C36-N=169.2(4)<sup>o</sup> while N-C37-C38-O1=67.1(4)<sup>o</sup>, and all the five phenyl rings are planar within 0.050(5) Å.

The structure illustrates a vivid conformational difference from 25,27-bis(1-propyloxy) calix[4]arene-

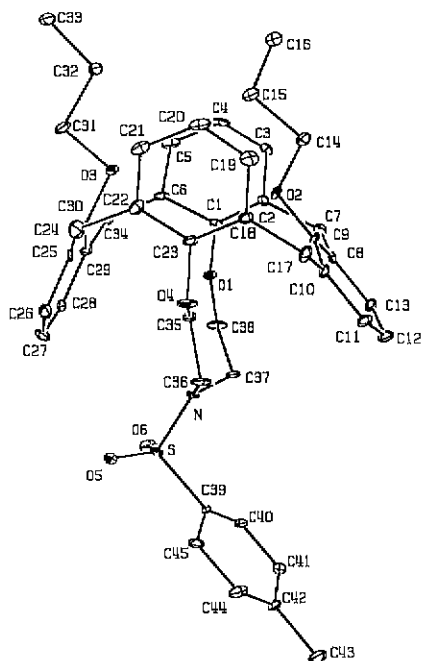


Fig. 2. Molecular structure with atomic numbering scheme showing 7% probability displacement ellipsoids. H atoms are omitted for clarity. The nitrogen, oxygen and sulphur atoms are expressed with ellipsoids with octant shading. The viewing direction is about 90 degrees different from Fig. 1. The lower two phenyl rings 2 and 4 widened downwards.

26,28-[(5',6')(14',15')-dibenzo]crown-7 (PCC).<sup>8)</sup> The upper two benzene rings 1 and 3 are splayed out upwards from the central axis with dihedral angle  $45.7(2)^\circ$  leading to O1-O4=4.064 Å, C1-C23=5.152 Å, C4-C20=7.206 Å (ref. Fig. 1) and another pair rings 2 and 4 are widely splayed out downwards from the central axis with dihedral angle  $120.54(12)^\circ$  leading to O2-O3=3.864 Å in the propyloxy groups, C9-C30=5.344 Å, C12-C27=7.989 Å (ref. Fig. 2). This peculiar structural conformation brings about O1-C35=2.906 Å in the azacrown ethereal linkage and therefore, as shown in Fig. 3 viewed along the central axis, the whole azacrown ether together with N-tosyl group sits inside the square cavity unlike PCC.<sup>8,14)</sup> This rather cramped cavity reflects that the title molecule would not be able to form host-guest complexes. This conformation might be attributable to the short azacrown ethereal linkage (two O atoms) bonded to the ortho carbon

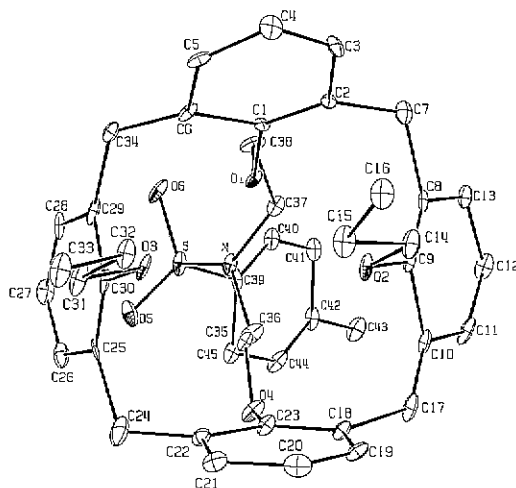


Fig. 3. Molecular structure viewed along central axis. The calix[4]arene in the title compound offers a square cavity and the azacrown ether including N-tosyl group sits inside the square cavity. The nitrogen, oxygen and sulphur atoms are expressed with ellipsoids with octant shading.

atoms of the aromatic phenyl rings 2 and 4.

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