

## The Crystal Structure of 1,3-Alternate 25,27-Bis(1-propyloxy)calix[4]arene crown-6, $C_{44}H_{54}O_8$

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## 1,3-Alternate 25,27-Bis(1-propyloxy)calix[4]arene crown-6, $C_{44}H_{54}O_8$ 의 結晶構造

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### Abstract

The title compound consisting of a calix[4]arene molecule with four phenyl rings bridged by four methylene groups and arranged alternately in anti-orientation fashion, two 25,27-bis(1-propyloxy) groups attached on the two lower rims of calix[4]arene, and crown-6 chain attached on the other set of lower rims of calix[4]arene offers a big cavity inside a molecule which might possess a potential for forming host-guest complexes. The molecular packing is accomplished by van der Waals forces.

### 要 約

4個의 methylene群에 의하여 連結되었으며 交叉形態로 配列된 4個의 phenyl 고리를 갖는 calix[4]arene 分子와, calix[4]arene의 밀테두리에 붙은 25,27-bis(1-propyloxy)群과, calix[4]arene의 밀테두리에 붙은 또 다른 crown-6 chain을 갖는 論題의 化合物은 한 分子內에 큰 空洞을 提供하므로 host-guest complexes 를 形成할 可能性이 있다. 分子의 packing은 van der Waals 력으로 이루어져있다.

### 1. Introduction

Calix[4]arenes have received considerable attention in the field of supramolecular chemistry because they can form inclusion complexes with cations, anions or neutral molecules.<sup>1-3</sup> Especially, calix-crown ethers in which the conventional crown ether

part is incorporated into calix[4]arene framework have been attracted intense interest as a cesium selective extractant.<sup>4,5</sup> It was reported that 1,3-distal capping of calix[4]arene at the lower rim has been achieved with polyether linkage such as calixcrown ether,<sup>4</sup> calix-doubly-crowned,<sup>5</sup> double-calix-crown.<sup>6</sup> Reinhoudt and coworkers reported that 1,3-dialkox-

ycalix[4]arene crown-6 derivatives were prepared and they are exceptionally selective ionophores for cesium ion due to a complexation of cesium ion not only with the crown ether moiety but also with the two rotated aromatic nuclei (cation/ $\pi$ -interaction) when they are fixed in the 1,3-alternate conformation.<sup>4)</sup> In order to explore the factors controlling formation of inclusion complexes by calixcrowns, a series of calix[4]arene derivatives have been synthesized and their structures have been elucidated,<sup>7-17)</sup> and in this paper the crystal structure of 1,3-alternate 25,27-bis(1-propyloxy)calix[4]arene crown-6 is reported.

## 2. Experimental

### 2-1. Synthesis

25,27-bis(1-propyloxy)calix[4]arene (1.0 g, 2.0 mmol) was dissolved in 50 ml of acetonitrile and added to an excess of  $\text{Cs}_2\text{CO}_3$  (1.62 g, 5.0 mmol) and pentaerythritol di-*p*-tosylate (1.14 g, 2.1 mmol) under nitrogen. The reaction mixture was refluxed for 24 hrs. Then acetonitrile was removed *in vacuo* and the residue extracted with 100 ml of methylene chloride and 50 ml of 10% aqueous HCl solution. The organic layer was separated and washed twice with water. After the organic layer was separated and dried over anhydrous magnesium sulfate. Removal of the solvent *in vacuo* gave a brownish oil. Filtration column chromatography with ethyl acetate: hexane=1:6 as eluents provided 25,27-bis(1-propyloxy)calix[4]arene crown-6 as a white solid in over 90% yield.

### 2-2. Structure determination

The detailed information on crystal data, data collection, and structure refinement is given in Table 1.

CAD4 Express Software<sup>18)</sup> was used for cell refinement and data collection, and XCAD4<sup>19)</sup> for data reduction. The structure was solved by direct methods<sup>20)</sup> and the least-squares refinement of the structure was performed by the program SHELXL97.<sup>21)</sup> During the refinement, most of the atoms had abnormally high displacement parameters and atomic bond lengths and angles were irregular, which might be attributed to the weak intensity data as

**Table 1. Experimental details**

Crystal data	
$\text{C}_{44}\text{H}_{54}\text{O}_8$	Mo $K_\alpha$ Radiation
$M_r=710.87$	$\lambda=0.71069 \text{ \AA}$
Orthorhombic	Cell parameters from 25 reflections
$Pc2_1n$ (# 33)	$\theta=11.428\text{--}13.438^\circ$
$a=12.204(4) \text{ \AA}$	$\mu=0.080 \text{ mm}^{-1}$
$b=12.965(3) \text{ \AA}$	$T=288 \text{ K}$
$c=25.428(4) \text{ \AA}$	block
$V=4023(2) \text{ \AA}^3$	$0.56 \times 0.53 \times 0.53 \text{ mm}$
$Z=4$	colorless
$D_x=1.174 \text{ Mg m}^{-3}$	
$D_m$ not measured	
Data collection	
Enraf-Nonius CAD-4 Diffractometer	$R_{\text{int}}=0.00$
$w/2\theta$ scans	$h=0 \rightarrow 14$
3785 independent reflections	$k=0 \rightarrow 15$
$\theta_{\text{max}}=25.17^\circ$	$l=0 \rightarrow 30$
1427 reflections with $\text{Fo} \geq 4\sigma(\text{Fo})$	3 standard reflections
Absorption correction: none	frequency: 300 min intensity decay: 0.8%
Refinement	
Refinement on $F$	$(\Delta/\sigma)_{\text{max}}=0.001$
$R(F)[\text{Fo} \geq 4\sigma(\text{Fo})]=0.090$	$(\Delta\rho)_{\text{max}}=0.538 \text{ e\AA}^{-3}$
$wR(F)=0.1612$	$(\Delta\rho)_{\text{min}}=-0.753 \text{ e\AA}^{-3}$
$S=1.434$	Extinction correction: none
397 parameters	Scattering factors from International Tables for Crystallography (Vol. C)
H atoms constrained	
$w=1/[\sigma^2(F_o^2)+(0.03P)^2+0.5P]$ where $P=(F_o^2+2F_c^2)/3$	

evidenced in Table 1. Therefore a program FMODIFY<sup>22)</sup> was employed to modify the structure, and yet only thirty one atoms out of fifty two heavy atoms were refined anisotropically and twelve atoms out of the thirty one atoms were refined with a fixed displacement parameter.

Hydrogen atoms were placed in calculated positions allowing to ride on their parent C atoms with  $U_{\text{iso}}(\text{H})=1.2 U_{\text{eq}}(\text{C})$ , while the methyl groups were treated as rotating rigid groups with  $U_{\text{iso}}(\text{H})=1.5 U_{\text{eq}}(\text{C})$ . R-factor for symmetry-equivalent intensities  $R_{\text{int}}$  in Table 1 is 0.000 because only an asymmet-

**Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{C}_{44}\text{H}_{54}\text{O}_8$ . U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor**

	x	y	z	U(eq)
O1	7300(3)	2700(3)	840(13)	50(11)
O2	4300(2)	4900(4)	1370(11)	60(9)
O3	8640(17)	4900(3)	2200(9)	40(6)
O4	7200(3)	7100(3)	870(13)	50(10)
O5	7600(3)	8100(2)	-140(11)	70
O6	9000(2)	6100(2)	-870(11)	70
O7	9200(3)	3700(3)	-1230(12)	70
O8	7800(3)	2600(2)	-130(13)	70
C1	6900(4)	2800(3)	1340(18)	40(13)
C2	7600(5)	2900(4)	1800(2)	50(15)
C3	7200(4)	2900(4)	2300(2)	50(16)
C4	6000(4)	2900(5)	2350(19)	60(17)
C5	5400(4)	2900(4)	1920(15)	50(16)
C6	5800(4)	2900(4)	1410(16)	30(12)
C7	5000(5)	2900(4)	960(19)	50(16)
C8	5100(4)	4000(4)	680(18)	50(15)
C9	5600(4)	4000(5)	200(17)	60(19)
C10	5900(3)	4900(5)	-40(15)	60(13)
C11	5600(4)	5800(4)	200(18)	50(17)
C12	5100(4)	5800(4)	690(17)	40(14)
C13	4800(3)	4900(4)	910(14)	40(11)
C14	3200(4)	4800(5)	1290(15)	70(15)
C15	2500(4)	4300(4)	1710(13)	70
C16	2800(3)	4700(4)	2260(14)	70
C17	4900(4)	6800(4)	1000(2)	50(15)
C18	6800(4)	7000(4)	1370(14)	40(14)
C19	5700(4)	6900(4)	1500(2)	50(15)
C20	5300(5)	6800(4)	2000(2)	60(17)
C21	6000(4)	6800(5)	2400(2)	50(15)
C22	7100(4)	6800(4)	2280(19)	50(15)
C23	7500(3)	6900(4)	1800(2)	40(12)
C24	8800(3)	6800(4)	1700(2)	50(16)
C25	9100(3)	5800(4)	1400(2)	40(15)
C26	9400(4)	5800(4)	900(2)	50(16)
C27	9600(3)	4900(5)	660(15)	60(13)
C28	9400(4)	4000(5)	900(2)	50(16)
C29	9100(4)	4000(3)	1420(18)	40(13)
C30	9000(3)	4900(4)	1680(14)	40(10)
C31	9600(3)	4900(6)	2520(12)	50(12)
C32	9300(3)	4800(7)	3100(12)	70(14)
C33	10200(3)	5000(5)	3460(14)	60(16)
C34	8800(4)	3000(3)	1680(18)	40(15)
C35	7000(4)	8100(3)	700(2)	100(2)
C36	7900(4)	8600(4)	350(12)	70

**Table 2. Continued**

	x	y	z	U(eq)
C37	8400(3)	7300(3)	-210(11)	100(2)
C38	8100(3)	6800(3)	-750(13)	70
C39	8700(4)	5500(3)	-1290(15)	70
C40	9600(4)	4700(3)	-1320(16)	70
C41	8500(4)	3700(3)	-770(15)	70
C42	8400(4)	2500(3)	-590(15)	70
C43	7800(4)	1600(3)	120(12)	100(2)
C44	7400(5)	1700(4)	690(15)	80(19)

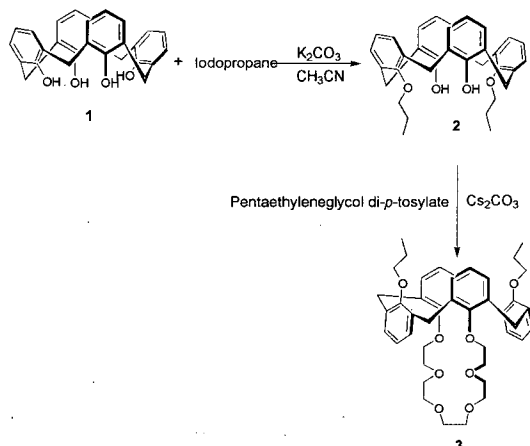
ric intensity data were collected.<sup>23)</sup>

ORTEP<sup>24)</sup> was for molecular graphics and WinGX<sup>25)</sup> for preparation of publication material.

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 one of the authors (Suh).

### 3. Discussion

The reaction of calix[4]arene with alkylating agents in acetonitrile in the presence of  $\text{K}_2\text{CO}_3$  is a well established synthetic method to obtain 1,3-dialkoxy-calix[4]arene in the cone form.<sup>4)</sup> The synthetic route for the preparation of corresponding dibenzodimesylate as precursors is described in Scheme 1. For 2, AB quartet splitting patterns ( $J=13$  Hz,  $\Delta=378$  Hz, chemical shift difference value) in  $^1\text{H}$  NMR

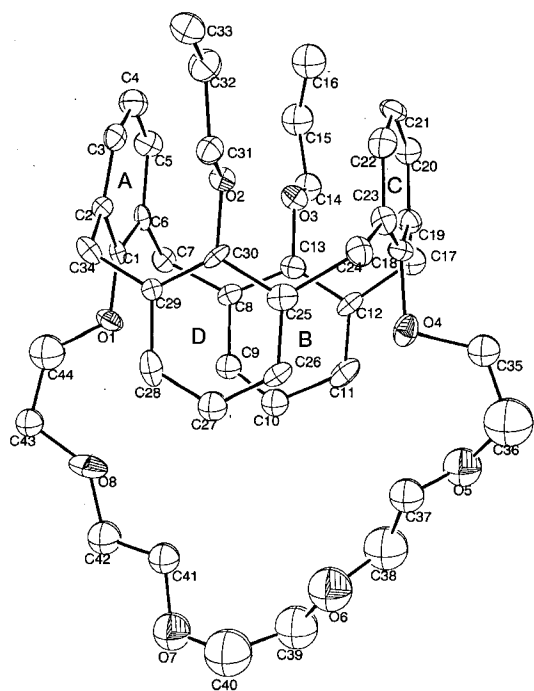


**Scheme 1. Synthetic route for the preparation of title compound.**

spectra were observed, indicating a characteristic cone conformation. As a key reaction, cyclization of 1,3-dipropyloxy calix[4]arene with pentaethylene glycol ditosylates in the presence of  $\text{Cs}_2\text{CO}_3$  provided the 1,3-alternate conformer calixcrown ether 3 as a target molecule within 80% yield.

The title compound consists of the calix[4]arene molecule adopting the 1,3-alternate conformation: two phenyl groups A and C lie above and the other two phenyl groups B and D below the least-squares plane defined by the four bridging methylene groups as clearly illustrated in Fig. 1, two 1-propyloxy groups bonded to phenyl rings B and D and a crown-6 unit bonded to phenyl rings A and C.

All bond lengths and angles are roughly similar to those found in 25,27-bis(1-propyloxy)calix[4]arene-26,28-[(5',6')(14',15')-dibenzo]crown-7<sup>11)</sup>, 25,27-bis(1-propyloxy)-5,11,17,23-tetrakis(1,1-dimethylethyl)calix[4]arene-26,28-[(5',6')(14',15')-dibenzo]crown-7<sup>13)</sup> and 1,3-alternate calix[4]arenebis-crown-7.<sup>14)</sup> Four

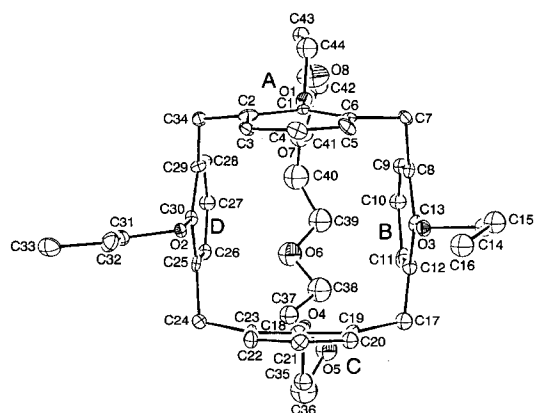


**Fig. 1.** Molecular structure with atomic numbering scheme showing 50% probability displacement ellipsoids. H atoms are omitted for clarity. The oxygen atoms are expressed with ellipsoids with octant shading.

phenyl rings in the calix[4]arene are planar within 0.05 Å and two adjacent phenyl rings are almost perpendicular to each other with dihedral angles of A-B=90(19), B-C=88(19), C-D=89(19), A-D=90(18)<sup>o</sup> so that the calix[4]arene has a fairly perfect square cavity (see Fig. 2). However, two facing rings A and C are slightly splayed out downwards from the central axis with a dihedral angle of 8(4)<sup>o</sup> leading to O1...O4=5.7(4) Å and C1...C18=5.5(5) Å, C4-C21=5.00(5) Å because of the crown-6 chain bonded to the ortho carbon atoms of the aromatic phenyl groups in the calix[4]arene molecule, while another pair rings B and D are splayed out upwards a little from the central axis with a dihedral angle of 11(13)<sup>o</sup> leading to O2...O3=5.8(3) Å, C13...C30=5.4(5) Å and C10...C27=4.9(5) Å that might be attributed to the repulsion between the two 1-propyloxy groups bonded to the ortho carbon atoms of the aromatic phenyl groups in the calix[4]arene molecule.

Other oxygen...oxygen distances in the crown-6 chain linkage having torsion angles of O4-C35-C36-O5=74.06<sup>o</sup>, O5--C37-C38-O6=168.86<sup>o</sup>, O6-C39-C40-O7=118.79<sup>o</sup>, O7-C41-C42-O8=-179.91<sup>o</sup>, and O8-C43-C44-O1=-6.10<sup>o</sup> are O5...O8=7.2(4) Å and O6...O8=5.2(5) Å. Therefore the title macrocyclic molecule contains a somewhat flexible cavity lined with six O atoms.

The closest intermolecular contact O5-HC14A (1-x, 0.5+y, -z)=2.863 Å confirms that the molecules



**Fig. 2.** The calix[4]arene in the title compound offers a square cavity. The oxygen atoms are expressed with ellipsoids with octant shading.

are held together by normal van der Waals interactions.

### Acknowledgement

This project has been carried out under the Nuclear R&D Program by MOST.

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