# The Crystal Structure of 25,27-Bis(1-propyloxy)-5,11,17,23-tetrakis(1,1-dimethylethy)calix[4]arene-26,28-[(5',6'), (14',15')-dibenzo]crown-7, $C_{70}H_{90}O_9$

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# 5,27-Bis(1-propyloxy)-5,11,17,23-tetrakis(1,1-dimethylethy) calix[4]arene-26,28-[(5',6'),(14',15')-dibenzo] crown-7, $C_{70}H_{90}O_9$의 結晶構造

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## Abstract

The title compound consisting of a calix[4]arene molecule with four phenyl rings arranged alternately in anti-orientation fashion, two propyloxy groups, and four *para-tert*-butyl group, attached on the upper rim of calix[4]arene, and polyether chain with two phenyl rings attached on the lower rim of calix[4]arene offers a big cavity inside the molecule that might possess a potential for forming host-guest complexes.

## 要 約

交叉形態로 配列된 4個의 phenyl 고리를 갖는 calix[4]arene 分子와, calix[4]arene의 위테두리에 붙은 2個의 *para-tert*-butyl 群과, calix[4]arene 의 밑테두리에 붙은 2個의 phenyl 고리를 包含한 polyether 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.

## 1. Introduction

Calix[4]arenes have been of particular interest as organic hosts and selective ionophores in inclusion complexation[1] and it is known that the calix[4]are-nes are able to exist in the following four different conformations: cone,[2-4] partial cone,[5] 1,2-alternate, and 1,3-alternate.[6,7] In order to investigate the characteristics of the calix[4]arene compounds, a series of calix[4]arene derivatives have been synthesized

and their structures have been elucidated.[8-13]

## 2. Experimental

**Synthesis.** 25,27-Bis(1-propyloxy)-5,11,17,23-tetrakis(1,1-dimethylethyl)calix[4]arene (1.46 g, 2.0 mmol) was dissolved in 50 m*l* of acetonitrile and added an excess of $Cs_2CO_3$ (1.62 g, 5.0 mmol) and 1,5-bis[2-(2-mesyloxyethyloxy)phenoxy]-3-oxapentane (1.12 g, 2.1 mmol) under nitrogen. The reaction mixture was refluxed for 24 h. Then acetonitrile was removed *in vacuo* and the residue was 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. The organic layer was separated and dried over anhydrous magnesium sulfate, and then concentrated *in vacuo* to give a brownish oil. With TLC analysis, the crude product shows an only one spot ($R_f$=0.4, ethyl acetate:hexane=1:4 as developing solvents). Crystallization from the oil residue with 5/1 diethyl ether- hexanes gave a desired product in an 82% yield. mp 278~280°C; IR (KBr pellet, cm$^{-1}$): 3068 (Ar-H), 1501, 1366, 1258, 1208. $^1$H NMR (CDCl$_3$): δ 7.00-6.81 (m, 16 H), 4.07 (t, 4 H, OPhO-C*H*$_2$C*H*$_2$-OPhO-), 3.94 (t, 4 H, OPhO-CH$_2$C*H*$_2$OC*H*$_2$CH$_2$-OPhO-), 3.87 (AB quartet, *J*=16 Hz, △=12 Hz, 8 H, ArC*H*$_2$Ar), 3.52 (t, *J*=6.0 Hz, 4 H, OC*H*$_2$CH$_2$CH$_3$), 3.36-3.13 (two triplet, *J*=8.0 Hz, 8 H, OC*H*$_2$CH$_2$O), 1.28 (s, 18 H, *t*-butyl), 1.12 (s, 18 H, *t*-butyl), 0.94 (m, *J*=6.0 Hz, 4 H, OCH$_2$C*H*$_2$CH$_3$), 0.62 (t, *J*=6.0 Hz, 6 H, OCH$_2$CH$_2$C*H*$_3$). $^{13}$C NMR (CDCl$_3$): ppm 155.5, 154.7, 150.9, 149.8, 145.3, 144.4, 134.1, 133.9, 126.69, 126.66, 123.3, 121.7, 120.3, 114.1, 72.5, 70.8, 70.6, 69.4, 68.8, 40.0, 34.6, 34.5, 32.2, 32.0, 22.6, 10.5. FAB MS m/z (M+): calcd 1075.47, found 1075.45. Anal. Calcd for $C_{70}H_{90}O_9$: C, 78.18; H, 8.44. Found: C, 78.25; H, 8.31.

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

CAD4 Express Software[14] was used for cell refinement and data collection, and XCAD4[15] for data reduction. The structure was solved by direct methods[16] and the least-squares refinement of the struc-

**Table 1. Experimental details**

| Crystal data | |
|---|---|
| $C_{70}H_{90}O_9$ | Mo $K_\alpha$ Radiation |
| $M_r$=1075.42 | λ=0.71069 Å |
| Orthorhombic | Cell parameters from 25 |
| $Pna2_1$ (# 33) | reflections |
| a=30.343(4) Å | θ=8.96-12.30° |
| b=13.176(2) Å | μ= 0.073 mm$^{-1}$ |
| c=15.815(4) Å | T=288 K |
| V=6323(3) Å$^3$ | block |
| Z=4 | 0.26×0.20×0.17 mm |
| $D_x$=1.130 Mg m$^{-3}$ | colorless |
| Dm not measured | |
| | |
| **Data collection** | |
| Enraf-Nonius CAD-4 | $R_{int}$=0.00 |
| Diffractometer | h=0→36 |
| w/2θ scans | k=0→15 |
| Reflections collected: 5773 | l=0→18 |
| 5773 independent reflections | 3 standard reflections |
| $θ_{max}$=25.0° | frequency: 300 min |
| 1058 reflections with | intensity decay: 1% |
| Fo≥4σ (Fo) | |
| Absorption correction: none | |
| | |
| **Refinement** | |
| Refinement on F | $(Δ/σ)_{max}$=0.000 |
| R(F) [Fo≥4σ (Fo)]=0.0825 | $(Δρ)_{max}$=0.311 eÅ$^{-3}$ |
| ω(F)=0.1259 | $(Δρ)_{min}$=-0.245 eÅ$^{-3}$ |
| S=0.933 | Extinction correction: |
| 357 parameters | none |
| H atoms constrained | Scattering factors from |
| $w$=1/[σ$^2$ (F$_o^2$)+(0.03$P$)$^2$+0.5$P$] | International Tables for |
| where $P$=(F$_o^2$+2F$_c^2$)/3 | Crystallography |
| | (Vol. C) |

ture was performed by the program SHELXL97.[17] During the refinement, most of the atoms had abnormally high displacement parameters, and bond lengths and angles were irregular, which might be attributed to the weak intensity data as evidenced in Table 1. Therefore a program FMODIFY[18] was employed to modify the structure, and yet only eight out of the 79 heavy atoms were refined anisotropically.

Hydrogen atoms were placed in calculated positions allowing to ride on their parent C atoms with

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**Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{A}^2 \times 10^3$) for $C_{70}H_{90}O_9$. U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O1 | 7561(4) | 5550(8) | 1758(9) | 70(4) |
| O2 | 8526(2) | 4779(5) | 3114(10) | 58(2) |
| O3 | 8169(2) | 7544(5) | 3033(10) | 59(2) |
| O4 | 7586(4) | 5628(9) | 4304(9) | 74(4) |
| O5 | 6603(5) | 4678(13) | 5030(12) | 148(6) |
| O6 | 5800(5) | 5325(11) | 4645(12) | 110(5) |
| O7 | 5392(4) | 5120(9) | 3097(17) | 152(5) |
| O8 | 5787(4) | 5206(10) | 1483(11) | 88(4) |
| O9 | 6584(4) | 4758(8) | 748(9) | 74(3) |
| C1 | 7991(7) | 5829(15) | 1486(13) | 78(6) |
| C2 | 8080(6) | 6871(14) | 1462(13) | 75(5) |
| C3 | 8522(4) | 7176(11) | 1112(10) | 41(4) |
| C4 | 8814(4) | 6453(8) | 898(9) | 13(2) |
| C5 | 8765(5) | 5477(13) | 1022(12) | 76(6) |
| C6 | 8323(6) | 5098(14) | 1329(13) | 75(5) |
| C7 | 9247(8) | 6820(18) | 539(17) | 121(8) |
| C8 | 9325(5) | 6275(12) | -324(13) | 106(6) |
| C9 | 9280(5) | 7926(11) | 386(12) | 88(5) |
| C10 | 9610(5) | 6447(12) | 1073(12) | 108(7) |
| C11 | 8223(5) | 4050(11) | 1534(11) | 53(4) |
| C12 | 8039(5) | 3688(10) | 2359(11) | 43(4) |
| C13 | 8206(3) | 4018(8) | 3094(13) | 42(3) |
| C14 | 8020(6) | 3730(13) | 3885(13) | 67(5) |
| C15 | 7717(4) | 2919(10) | 3841(11) | 32(3) |
| C16 | 7548(3) | 2583(8) | 3127(14) | 50(3) |
| C17 | 7691(6) | 3016(13) | 2388(14) | 87(6) |
| C18 | 7194(4) | 1701(10) | 3096(16) | 72(4) |
| C19 | 7083(5) | 1368(11) | 3948(12) | 89(5) |
| C20 | 6780(5) | 2194(12) | 2781(13) | 130(7) |
| C21 | 7337(5) | 885(11) | 2517(11) | 99(6) |
| C22 | 8949(3) | 4328(9) | 3147(15) | 72(4) |
| C23 | 9275(4) | 5178(9) | 3075(19) | 95(5) |
| C24 | 9739(4) | 4757(10) | 3120(20) | 132(6) |
| C25 | 8207(6) | 4030(12) | 4740(12) | 78(6) |
| C26 | 8314(4) | 5198(10) | 4754(10) | 36(4) |
| C27 | 8680(4) | 5432(11) | 5091(10) | 35(4) |
| C28 | 8781(6) | 6438(18) | 5367(13) | 107(8) |
| C29 | 8452(5) | 7138(13) | 5158(12) | 62(5) |
| C30 | 8079(4) | 6905(9) | 4856(9) | 19(3) |
| C31 | 7983(4) | 5902(10) | 4700(10) | 28(3) |
| C32 | 9247(4) | 6734(10) | 5722(10) | 33(3) |
| C33 | 9437(5) | 7546(13) | 5208(12) | 109(7) |
| C34 | 9549(5) | 5848(11) | 5690(13) | 111(7) |
| C35 | 9170(5) | 6971(12) | 6600(12) | 109(7) |

**Table 2. Continued**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C36 | 7716(6) | 7752(15) | 4667(12) | 91(7) |
| C37 | 7484(4) | 7680(10) | 3822(11) | 32(3) |
| C38 | 7030(5) | 7804(11) | 3788(11) | 54(4) |
| C39 | 6823(3) | 7997(8) | 2998(12) | 44(3) |
| C40 | 7074(5) | 7958(11) | 2292(12) | 57(5) |
| C41 | 7529(6) | 7722(14) | 2305(13) | 71(5) |
| C42 | 7711(3) | 7755(8) | 3122(13) | 46(3) |
| C43 | 6310(4) | 8159(9) | 3000(13) | 53(3) |
| C44 | 6201(5) | 9039(11) | 3553(11) | 104(6) |
| C45 | 6107(4) | 7218(11) | 3382(12) | 117(7) |
| C46 | 6142(5) | 8243(12) | 2178(11) | 94(6) |
| C47 | 8402(4) | 8426(9) | 3122(17) | 88(5) |
| C48 | 8921(4) | 8122(10) | 3194(17) | 104(6) |
| C49 | 9144(5) | 8996(12) | 3372(15) | 148(8) |
| C50 | 7749(4) | 7670(10) | 1502(10) | 32(3) |
| C51 | 7325(6) | 5454(15) | 4961(13) | 75(6) |
| C52 | 6856(8) | 5114(16) | 4409(14) | 119(8) |
| C53 | 6392(9) | 5390(20) | 5607(18) | 124(9) |
| C54 | 6577(7) | 5678(15) | 6287(15) | 115(8) |
| C55 | 6358(6) | 6245(14) | 6813(14) | 98(7) |
| C56 | 5960(7) | 6663(16) | 6677(15) | 118(8) |
| C57 | 5693(8) | 6417(17) | 5905(15) | 111(8) |
| C58 | 5936(8) | 5680(18) | 5416(17) | 114(8) |
| C59 | 5309(7) | 5360(18) | 4561(10) | 142(10) |
| C60 | 5171(9) | 4830(20) | 3785(10) | 151(11) |
| C61 | 5224(9) | 4760(20) | 2422(14) | 147(11) |
| C62 | 5372(6) | 5409(15) | 1676(11) | 86(6) |
| C63 | 5941(5) | 5710(12) | 831(12) | 49(4) |
| C64 | 5693(7) | 6307(15) | 367(14) | 85(6) |
| C65 | 5789(7) | 6772(16) | -347(15) | 125(8) |
| C66 | 6164(6) | 6529(14) | -794(14) | 109(8) |
| C67 | 6458(6) | 5948(13) | -327(14) | 87(6) |
| C68 | 6343(7) | 5494(17) | 442(15) | 95(7) |
| C69 | 6840(7) | 5040(15) | 1480(13) | 88(6) |
| C70 | 7285(7) | 5336(16) | 1176(14) | 97(7) |

$U_{iso}(H) = 1.2\ U_{eq}(C)$, while the methyl groups were treated as rotating rigid groups with $U_{iso}(H) = 1.5\ U_{eq}(C)$.

ORTEP3[19] was used for molecular graphics and WinGX[20] for preparation of publication material.

The final atomic coordinates are listed in Table 2, and the data for 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 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 propyloxy groups bonded to phenyl rings B and D, four para-tert-butyl groups bonded to four phenyl rings in the calix[4]arene molecule and a dibenzo crown-7 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.[12] Two adjacent phenyl rings in the calix[4]arene are almost perpendicular to each other with dihedral angles of A-B=78.5(6)°, B-C=82.0(5)°, C-D=81.0(5)°, A-D= 82.0(6)° so that the calix[4]arene has a fairly perfect square cavity (see Fig. 2). However, two facing rings A and C are considerably splayed out down-

wards from the central axis with a dihedral angle of 42.7(3)° leading to O1...O4=4.03(1) Å and C1...C31= 5.08(2) Å, C4-C28=7.07(2) Å because of the ethereal linkage 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 quite a lot from the central axis with a dihedral angle of 51.6(3)° leading to O2..O3=3.80(1) Å and C13...C42=5.15(2) Å that might be attributed to the repulsion among two phenyl rings 1 and 3 and the two propyloxy groups bonded to the ortho carbon atoms of the aromatic phenyl groups in the calix[4]arene molecule. The torsion angles of O2-C22-C23-C24=179(2)° and O3-C47-C48-C49=-174(2)° in two propyloxy groups are *trans*. Both torsion angles of O1-C70-C69-O9= -176(2)° and O4-C51-C52-O5=166(2)° in the side ethereal linkage are *trans* and those of O6-C59-C60-O7=-49.0(3)° and O7-C61-C62-O8=75.0(2)° in the bottom ethereal linkage are *gauche*, and the dihedral angle of two pairs of benzo groups E and F in the dibenzocrown-7 unit is 69.4(2)°.

Oxygen-oxygen distances in the ethereal linkages are O1-O4=4.03(1)°, O1-O8=5.42(2)° and O4-O6= 5.46(2)°. Therefore the title macrocyclic molecule
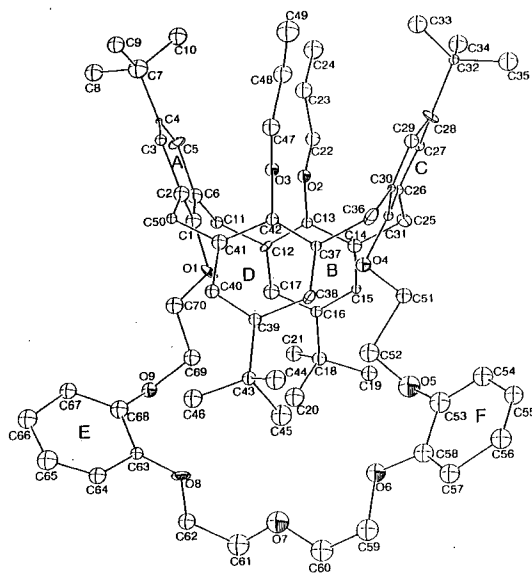
**Fig. 1. Molecular structure with atomic numbering scheme showing 50% probability displacement ellipsoids. H atoms are omitted for clarity. The oxygen atoms are expressed with ellipsoids with octant shading.**
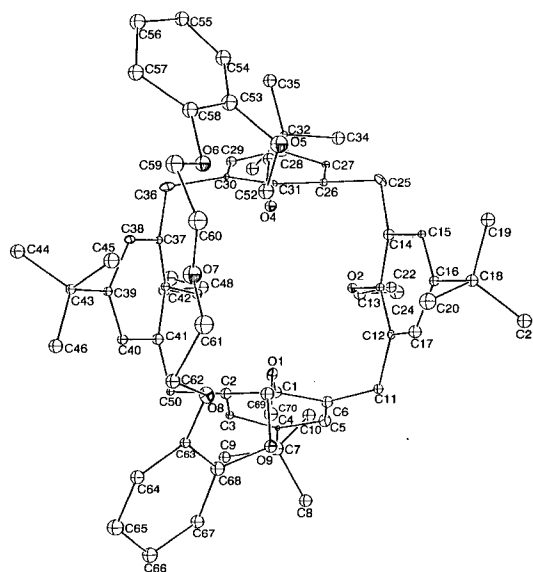
**Fig. 2. The calix[4]arene in the title compound offers a square cavity. The oxygen atoms are expressed with ellipsoids with octant shading.**

contains a somewhat flexible cavity lined with nine O atoms.

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