

25,27-Bis(1-propyloxy)calix[4]arene-26,28-[(5',6')(14',15')- dibenzo]crown-7, $C_{54}H_{58}O_9$

Jong Seung Kim, Moon-Jib Kim^a, Jin-Ho Lee^b, Jin-Gyu Kim^c and Il-Hwan Suh^c

Department of Chemistry, Konyang University, Nonsan, Chungnam, 320-711 Korea

^a*Department of Physics, Soonchunghyang University, Onyang 336-600 Korea*

^b*Neutron Physics Department, Korea Atomic Energy Research Institute,
P.O. Box 105, Taejon, 305-600 Korea*

^c*Department of Physics, Chungnam National University,
Taejon, 305-764 Korea*

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金鍾昇 · 金文執^a · 李珍昊^b · 金珍圭^c · 徐日煥^c

建陽大學校 化學科, ^a順天鄉大學校 物理學科

^b韓國原子力研究所 中性子物理室,

^c忠南大學校 物理學科

Abstract

The title compound consisting of a calix[4]arene molecule with four phenyl rings arranged alternately in anti-orientation fashion. two propyloxy groups 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 a molecule which might possess a potential for forming host-guest complexes.

要 約

交叉形態로 配列된 4개의 phenyl 고리를 갖는 calix[4]arene 분자와, calix[4]arene 의 위테두리에 붙은 2개의 propyloxy 群과, calix[4]arene 의 밑테두리에 붙은 2개의 phenyl 고리를 포함한 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 complexation¹⁾ and it is known that the calix[4]arenes are able to exist in the following four different conformations: cone,²⁻³⁾ partial cone,⁴⁾ 1,2-alternate, and 1,3-alternate.⁵⁻⁶⁾ 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.⁷⁻¹⁰⁾

2. Experimental

25,27-Dipropyloxy-calix[4]arene (1.01 g, 2.0 mmole) was dissolved in 50 mL of acetonitrile and added to an excess of Cs_2CO_3 (1.62 g, 5.0 mmole) and dibenzodimesylate (1.12 g, 2.1 mmole) 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. After the organic layer was separated and dried over anhydrous magnesium sulfate followed by removing the solvent in vacuo to give a brownish oil. Filtration column chromatography with ethyl acetate:hexane=1:6 as eluents provided pure 1.3-alternate calix[4]arene dibenzocrown ethers as a white solid which is recrystallized from diethyl ether-hexanes to give a desired product with 90% yield. Mp 451-454 K; IR(KBr pallet, cm^{-1}); 3068 (Ar-H), 1501, 1451, 1254, 1196; ^1H NMR (CDCl_3) δ 7.02-6.87 (m, 16 H), 6.78-6.70 (m, 4 H), 4.22 (t,

$J=5.1$ Hz, 4 H), 4.08 (t, $J=5.1$ Hz, 4 H), 3.89 (t, $J=5.1$ Hz, 4 H), 3.76 (t, $J=5.1$ Hz, 4 H), 3.70 (s, 8 H, ArCH_2Ar), 3.41 (t, $J=7.4$ Hz, 4 H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 1.47-1.38 (m, $J=7.4$ Hz, 4 H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 0.77 (t, $J=7.4$ Hz, 6 H, $\text{OCH}_2\text{CH}_2\text{CH}_3$); ^{13}C NMR(CDCl_3): δ 157.4, 156.8, 150.7, 149.8, 134.4, 134.3, 130.6, 130.5, 123.1, 122.8, 122.6, 122.3, 118.3, 116.1, 73.4, 71.1, 70.6, 69.8, 38.1, 23.7, 10.8; FAB MS $m/z(\text{M}^+)$ calcd 850.31, found 850.30. Anal. Calcd for $\text{C}_{54}\text{H}_{58}\text{O}_9$: C, 76.20; H, 6.82. Found: C, 76.18; H, 6.87.

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

Hydrogen atoms were placed in calculated positions allowing 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 $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{C})$.

Intensity data are not corrected for absorption and decay effects. Software; data collection: CAD4 Express Software⁽¹⁾; data reduction: WinGX⁽²⁾; program(s) used to solve structure: SHELX86⁽³⁾; program used to refine structure: SHELXL9⁽⁴⁾; Molecular graphics: ORTEP3⁽⁵⁾.

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).

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{54}\text{H}_{58}\text{O}_9$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

| | x | y | z | $U(\text{eq})$ |
|------|---------|----------|----------|----------------|
| O(1) | 1094(1) | -1342(2) | -9(2) | 41(1) |
| O(2) | 2088(1) | 260(2) | 2438(2) | 46(1) |
| O(3) | 3234(2) | -107(2) | -433(2) | 51(1) |
| O(4) | 3711(1) | -2320(2) | 1875(2) | 48(1) |
| O(5) | 4451(3) | -4020(4) | 1472(3) | 157(3) |
| O(6) | 3526(3) | -5477(4) | 1151(3) | 142(2) |
| O(7) | 1918(2) | -5589(3) | -425(2) | 70(1) |
| O(8) | 783(2) | -4628(3) | -613(2) | 59(1) |
| O(9) | 505(2) | -2733(2) | -1274(2) | 54(1) |
| C(1) | 1346(2) | -330(3) | 115(3) | 40(1) |
| C(2) | 1721(2) | 67(3) | -403(3) | 39(1) |
| C(3) | 1941(2) | 1093(4) | -299(3) | 52(1) |

Table 1. Experimental details

| Crystal data | |
|--|---|
| $\text{C}_{54}\text{H}_{58}\text{O}_9$ | Mo K_{α} Radiation |
| $M_r=851.00$ | $\lambda=0.71069$ \AA |
| Monoclinic | Cell parameters from 25 reflections |
| $P2_1/c$ | $\theta=11.29-14.21^\circ$ |
| $a=20.979(5)$ \AA | $\mu=0.082$ mm^{-1} |
| $b=12.722(1)$ \AA | $T=293$ K |
| $c=17.618(6)$ \AA | Block |
| $\beta=98.88^\circ$ | $V=4645.9(18)$ \AA^3 |
| $Z=4$ | $0.46 \times 0.40 \times 0.36$ mm |
| $D_x=1.217$ Mg m^{-3} | Colorless |
| D_m not measured | |
| Data collection | |
| Enraf-Nonius CAD-4 Diffractometer | $R_{\text{int}}=0.0590$ |
| $\omega/2\theta$ scans | $h=0 \rightarrow 24$ |
| Absorption correction: none | $k=0 \rightarrow 15$ |
| 8140 independent reflections | $l=-20 \rightarrow 20$ |
| 3599 reflections with $I_o \geq 2\sigma(I_o)$ | 3 standard reflections |
| $\theta_{\text{max}}=25.0^\circ$ | frequency: 300 min intensity decay: 2 % |
| Refinement | |
| Refinement on I | $(\Delta/\sigma)_{\text{max}}=0.000$ |
| $R(I)=0.0893$ | $(\Delta \rho)_{\text{max}}=0.750$ e \AA^{-3} |
| $\omega R(I)=0.1397$ | $(\Delta \rho)_{\text{min}}=-0.775$ e \AA^{-3} |
| $S=1.320$ | Extinction correction: none |
| 3599 reflections | Scattering factors from International Tables for Crystallography (Vol. C) |
| 568 parameters | |
| H atoms constrained | |
| $w=1/[\sigma^2(F_o^2)+(0.03P)^2+0.5P]$ where $P=(F_o^2+2F_c^2)/3$ | |

Table 2. Continued

| | x | y | z | U(eq) |
|-------|---------|----------|----------|--------|
| C(4) | 1799(3) | 1680(4) | 306(3) | 61(2) |
| C(5) | 1467(2) | 1239(4) | 844(3) | 54(1) |
| C(6) | 1241(2) | 213(4) | 769(3) | 42(1) |
| C(7) | 954(2) | -310(4) | 1412(3) | 52(1) |
| C(8) | 1415(2) | -1114(4) | 1819(3) | 44(1) |
| C(9) | 1981(2) | -800(4) | 2281(2) | 40(1) |
| C(10) | 2462(2) | -1522(4) | 2566(2) | 43(1) |
| C(11) | 2333(2) | -2578(4) | 2434(3) | 52(1) |
| C(12) | 1757(3) | -2907(4) | 2024(3) | 60(2) |
| C(13) | 1311(2) | -2179(4) | 1708(3) | 54(1) |
| C(14) | 1867(3) | 589(4) | 3130(3) | 71(2) |
| C(15) | 2078(5) | 1634(6) | 3338(4) | 174(5) |
| C(16) | 2114(4) | 2456(5) | 2810(4) | 112(3) |
| C(17) | 3114(2) | -1135(4) | 2966(2) | 48(1) |
| C(18) | 3490(2) | -630(4) | 2395(3) | 44(1) |
| C(19) | 3552(2) | 450(4) | 2364(3) | 55(1) |
| C(20) | 3839(2) | 921(4) | 1795(3) | 59(2) |
| C(21) | 4020(2) | 319(4) | 1213(3) | 54(1) |
| C(22) | 3962(2) | -772(4) | 1224(3) | 45(1) |
| C(23) | 3724(2) | -1230(4) | 1831(3) | 41(1) |
| C(24) | 4091(2) | -1429(4) | 542(3) | 50(1) |
| C(25) | 3459(2) | -1826(4) | 84(2) | 42(1) |
| C(26) | 3265(2) | -2847(4) | 151(3) | 48(1) |
| C(27) | 2661(2) | -3189(4) | -201(3) | 48(1) |
| C(28) | 2239(2) | -2464(4) | -595(2) | 44(1) |
| C(29) | 2417(2) | -1430(4) | -673(2) | 37(1) |
| C(30) | 1924(2) | -624(3) | -1023(2) | 45(1) |
| C(31) | 3036(2) | -1132(4) | -354(2) | 41(1) |
| C(32) | 3542(3) | 68(4) | -1085(3) | 68(2) |
| C(33) | 3804(3) | 1176(5) | -1052(3) | 97(2) |
| C(34) | 4091(4) | 1497(5) | -1714(4) | 132(3) |
| C(35) | 4242(3) | -2766(4) | 2375(3) | 79(2) |
| C(36) | 4373(3) | -3827(5) | 2153(3) | 90(2) |
| C(37) | 4592(4) | -5000(5) | 1209(3) | 81(2) |
| C(38) | 5202(4) | -5216(6) | 1067(4) | 109(3) |
| C(39) | 5323(4) | -6136(7) | 732(4) | 94(2) |
| C(40) | 4855(4) | -6845(6) | 526(4) | 99(2) |
| C(41) | 4247(4) | -6638(5) | 657(4) | 108(3) |
| C(42) | 4105(4) | -5715(5) | 996(4) | 87(2) |
| C(43) | 3029(3) | -5869(5) | 817(5) | 136(4) |
| C(44) | 2411(3) | -5424(5) | 1070(3) | 91(2) |
| C(45) | 1294(2) | -5353(4) | 559(3) | 70(2) |
| C(46) | 832(2) | -5555(4) | -167(3) | 61(2) |
| C(47) | 353(2) | -4614(4) | -1285(3) | 46(1) |
| C(48) | 52(2) | -5496(4) | -1640(3) | 54(1) |
| C(49) | -364(2) | -5396(5) | -2319(3) | 60(2) |
| C(50) | -490(2) | -4434(5) | -2646(3) | 64(2) |
| C(51) | -201(2) | -3542(4) | -2293(3) | 62(2) |
| C(52) | 213(2) | -3638(4) | -1612(3) | 46(1) |
| C(53) | 234(2) | -2408(4) | -621(3) | 56(1) |
| C(54) | 444(2) | -1314(4) | -400(3) | 57(2) |

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) lie above and the other two phenyl groups 2 (C8, C9, C10, C11, C12, C13) and 4 (C25, C26, C27, C28, C29, C31) 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 an ethereal linkage with two benzo groups bonded to phenyl rings 1 and 3.

The aromatic Csp²-Csp² distances in the molecule vary from 1.342(8) to 1.400(6) Å with an average value of 1.380(1) Å,¹⁵⁾ Osp³-Csp² distances from 1.321(7) to 1.395(5) Å with a mean value of 1.378(2) Å, Csp²-Csp³ distances from 1.509(6) to 1.528(6) Å with a mean value of 1.518(2) Å, Csp³-Csp³ distances from 1.409(8) to 1.543(8) Å with a mean value of 1.473(2) Å and Osp³-Csp³ 1.258(6) to 1.431(5) Å with a mean value of 1.402(2) Å, which are all expected values. Bond angles involving the bridging methylenes C2-C30-C29=110.4(3)°, C6-C7-C8=110.7(4)°, C10-C17-C18=110.7(4)°. C22-C24-C25=110.6(4)° are very close to the tetrahedral

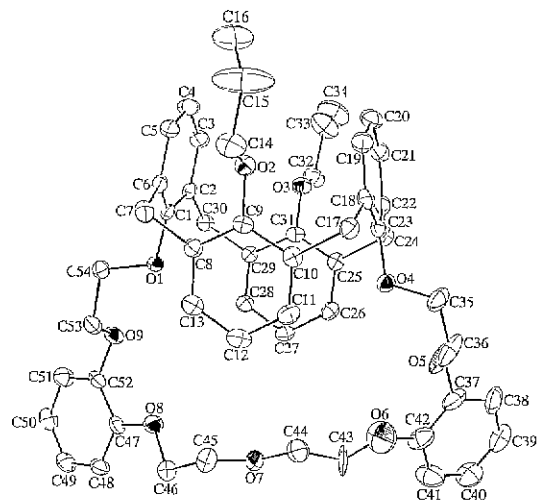


Fig. 1. Molecular structure with atomic numbering scheme showing 50% probability displacement ellipsoids. H atoms are omitted for clarity. The oxygen atoms are expressed with ellipsoids with octant shading.

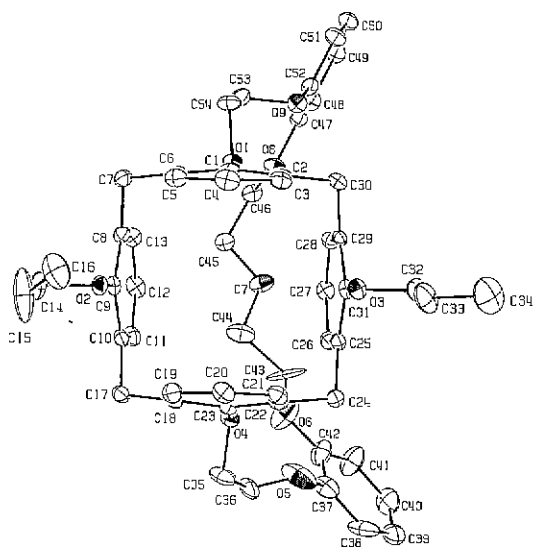


Fig. 2. The calix[4]arene in the title compound offers a square cavity. The oxygen atoms are expressed with ellipsoids with octant shading.

angle.

Two adjacent phenyl rings in the calix[4]arene are almost perpendicular to each other with dihedral angles of 1-2=88.1(1)°, 2-3=89.5(1)°, 3-4=88.6(1)°, 1-4=89.3(3)° so that the calix[4]arene has a fairly perfect square cavity (see Fig. 2). However, two facing rings 1 and 3 are slightly splayed out downwards from the central axis with a dihedral angle of 16.0(2)° leading to C1...C23=5.540(6) Å and C4...C20=4.760(7) 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 2 and 4 are slightly splayed out upwards from the central axis with a dihedral angle of 17.1(2)° leading to C9...C31=5.460(6) Å and C12...C27=4.624(8) 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-C14-C15-C16=37.8(12)° and O3-C32-C33-C34=-175.5(5)° in two propyloxy groups are gauche and trans, respectively. Both torsion angles of O1-C54-C53-O9=77.1(5)° and O4-C35-C36-O5=52.5(9)° in the side ethereal linkage are gauche and those of O6-C43-C44-O7=154.7(7)° and O7-C45-C46-O8=

-88.4(5)° in the bottom ethereal linkage are trans and gauche, respectively, and the dihedral angle of two pairs of benzo groups C37, C38, C39, C40, C41, C42 and C47, C48, C49, C50, C51, C52 in the ethereal linkage is 69.4(2)°.

Oxygen-oxygen distances in the ethereal linkages are O1-O4=6.089(4) Å, O1-O8=4.339(5) Å and O4-O6=4.214(6) Å. Therefore the title macrocyclic molecule contains a somewhat flexible cavity lined with nine O atoms. The closest intermolecular distance O7-H4 ($x, -1+y, z$)=2.587(4) Å involving a H-atom indicates that intermolecular packing is overwhelmed by van der Waals force. The displacement parameters of atoms O5, C15, and C43 indicate disorder (see Fig. 1).

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