

25,27-Bis(5-chloro-3-oxapentyloxy)-*p*-tert-butylcalix[4]arene

Jong S. Kim^{a*}, Jeong A. Rim^a, Sung K. Kim^a, Soo H. Lee^a, Inn H. Kim^a,
Young-S. Kim^b, Geum-H. Choo^c, Jin-G. Kim^d and Il-H. Suh^d

^aDepartment of Chemistry, Konyang University, Nonsan 320-711, Korea

^bDepartment of Cultural Heritage Conservation Science, Kongju National University,
Kongju 314-701, Korea

^cKorea University of Technology and Education, Cheonan PO Box 55, 330-800, Korea

^dDepartment of Physics, Chungnam National University, 305-764, Korea

25,27-Bis(5-chloro-3-oxapentyloxy)-*p*-tert-butylcalix[4]arene

김종승^{a*} · 임정아^a · 김성국^a · 이수현^a · 김인회^a · 김용선^b · 추금홍^c · 김진규^d · 서일환^d

^a건양대학교 화학과, ^b공주대학교 문화재보존학과,

^c한국기술교육대학교, ^d충남대학교 물리학과

요 약

p-tert-Calix[4]arene, tosylate of 2-(2-chloroethoxy)ethanol, K₂CO₃, 그리고 acetonitrile의 혼합물로부터合成된 上記題目的化合物, C₅₂H₇₀Cl₂O₆은 비뚤어진 cone 형태를 띠고 있으며, 分子內 hydroxy group의 酸素原子들과 dichloride 꼬리部分의 酸素原子들간의 두 개의 水素結合에 의해 安定되어 있다.

Abstract

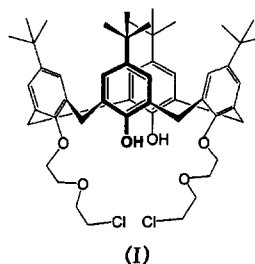
The configuration of the title compound, C₅₂H₇₀Cl₂O₆, synthesized from a mixture of *p*-tert-calix[4]arene, tosylate of 2-(2-chloroethoxy)ethanol, K₂CO₃ and acetonitrile has a distorted cone conformation and the molecule is stabilized by two intramolecular hydrogen bonds between oxygen atoms of hydroxy groups and dichloride tails.

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⁾ We have reported syntheses of calix[4]arene derivatives and their conformational characteristics.⁶⁻¹¹⁾

As a part of a series of structure investigation on calix[4]arene derivatives, we elucidated nine crystal structures⁷⁻¹⁵⁾ of this sort and all of them had a 1,3-alternate conformation. In this paper, a crystal struc-

ture of the title compound I having a cone conformation is reported.



2. Experimental

Synthesis. A mixture of *p*-tert-Calix[4]arene (1.0

g, 1.5 mmol), tosylate of 2-(2-chloroethoxy)ethanol (1.72 g, 6.2 mmol), K_2CO_3 (1.28 g, 9 mmol), and acetonitrile (100 ml) refluxed for 24 h under N_2 . After acetonitrile was removed *in vacuo*, 50 ml of CH_2Cl_2 and 50 ml of 10% aqueous HCl were added. The organic layer was dried over $MgSO_4$. Column chromatography on silica gel with 1:9 EtOAc : hexane as eluents gave **I** as an solid in 52% yield. mp: 147~149°C. IR (KBr, cm^{-1}): 3352, 2965, 2865, 1490, 1359, 1204, 1127, 1042, 864, 741, 671. 1H -NMR (200 MHz, $CDCl_3$): 7.06 (s, 4 H, ArH-calix), 6.77 (s, 4 H, ArH-calix), 4.37 (d, 4 H, Ar- CH_2 -Ar), 4.15-3.71 (m, 16 H, OCH_2CH_2Cl), 3.33 (d, 4 H, Ar- CH_2 -Ar), 2.44 (s, 18 H, $-C(CH_3)_3$), 1.02 (s, 18 H, $-C(CH_3)_3$). FAB-MS m/z (M^+) calcd. 861.01, found 861.05.

X-ray Crystallography. Colorless crystal of $C_{52}H_{70}Cl_2O_6$ of approximate $0.36 \times 0.20 \times 0.13$ mm was mounted and aligned on a CAD-4 diffractometer.¹⁶⁾ The accurate triclinic cell parameters : $a = 12.012(4)$ Å, $b = 14.651(2)$ Å, $c = 16.712(4)$ Å, $\alpha = 81.55(1)^\circ$, $\beta = 70.77(3)^\circ$, $\gamma = 66.62(2)^\circ$, $V = 2548(1)$ Å³ were refined from setting angles of 17 reflections with $8.75^\circ < \theta < 11.55^\circ$. Intensities were collected with graphite-monochromatized Mo K α radiation, using the $\omega/2\theta$ scan technique at 290 K. A total of 6029 independent reflections were measured in the range $2 < \theta < 25^\circ$. Three standard reflections were measured every 5 h as orientation and intensity controls; intensity decay, 0%, was observed. L-p and decay corrections were made, and also absorption correction by ϕ -scan was applied.¹⁷⁾ 2081 reflections were assumed as observed by applying the condition $I_o \geq 2\sigma(I_o)$ and space group was $P\bar{1}$ with $Z = 2$ and $\mu = 0.172$ mm⁻¹. The crystallographic data, conditions used for the intensity collection, and some features of the structure refinement are listed in Table 1. The structure was solved by direct methods SHELXS97¹⁸⁾ and the least-squares refinement of the structure was performed by the program SHELXL97.¹⁸⁾ Two H atoms H53 and H54 bound to O5 and O6 were found from difference Fourier synthesis and refined isotropically with fixed coordinates, and the other H atoms were assigned to calculated positions and constrained to ride on their attached atoms with isotropic parameters fixed at $U_{iso} = 1.2U_{eq}$ or $U_{iso} =$

Table 1. Experimental details

Crystal data	
$C_{52}H_{70}Cl_2O_6$	Mo K α Radiation
$M_r = 861.98$	$\lambda = 0.71069$ Å
Triclinic	Cell parameters from 17 reflections
$P\bar{1}$	$\theta = 8.75$ - 11.55°
$a = 12.012(4)$ Å	$\mu = 0.172$ mm ⁻¹
$b = 14.651(2)$ Å	$T = 290$ K
$c = 16.712(4)$ Å	colorless
$\alpha = 81.55(1)^\circ$	$0.36 \times 0.20 \times 0.13$ mm
$\beta = 70.77(3)^\circ$	plate
$\gamma = 66.62(2)^\circ$	$D_x = 1.123$ Mg m ⁻³
$V = 2548(1)$ Å ³	D_m not measured
$Z = 2$	
Data collection	
Enraf-Nonius CAD-4 Diffractometer	$R_{int} = 0.05521$
$\omega/2\theta$ scans	$h = -13 \rightarrow 14$
Reflections collected: 6259	$k = -17 \rightarrow 17$
6029 independent reflections	$l = 0 \rightarrow 19$
$\theta_{max} = 25.0^\circ$	3 standard reflections
2081 reflections with $I \geq 2\sigma(I)$	frequency : 30 min
Absorption correction: semi-empirical	intensity decay : 0%
ψ scans (North <i>et al.</i> , 1968)	
$T_{max} = 0.956$ $T_{min} = 0.9194$	
Refinement	
Refinement on I	$(\Delta/\sigma)_{max} = 0.000$
$R(F)[I > 2\sigma(I)] = 0.047$	$(\Delta/\rho)_{max} = 0.517$ eÅ ⁻³
$\omega R(F) = 0.1102$	$(\Delta/\rho)_{min} = -0.266$ eÅ ⁻³
$S = 0.652$	Extinction correction: none
540 parameters	Scattering factors from International Tables for Crystallography (Vol. C)
H atoms mixed	
$\omega = 1/[\sigma^2(F_o^2) + (0.0490P)^2 + 0.00P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

$1.5U_{eq}$ (for methyl groups) times the equivalent isotropic displacement parameters of their parent atoms. Final reliability factors for 2081 unique observed reflections [$I_o > 2\sigma(I_o)$] were $R = 0.047$ and $\omega R = 0.1102$ with $(\Delta/\sigma)_{max} < 0.001$, $\Delta\rho_{max} = 0.517$, $\Delta\rho_{min} = -0.266$ eÅ⁻³ in $\Delta\rho$ map and $S = 0.652$.

Table 2 exhibits atomic coordinates and their isotropic thermal parameters, Table 3 selected bond lengths, bond angles and torsion angles, and Table 4 hydrogen-bonding geometry. Software used to prepare material for publication was WinGX.^{19,20)}

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{52}\text{H}_{70}\text{Cl}_2\text{O}_6$ U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
Cl(1)	6039(2)	3822(2)	3042(1)	86(1)
O(1)	5818(6)	2950(4)	1555(4)	83(2)
O(2)	8446(4)	2467(3)	-348(3)	39(1)
O(3)	11782(6)	5068(5)	-863(4)	90(2)
O(4)	10725(4)	4732(4)	-2030(3)	44(1)
O(5)	8472(4)	3973(3)	-1739(3)	37(1)
O(6)	10995(4)	2934(4)	-993(3)	43(1)
C(1)	5206(8)	4436(6)	2311(5)	88(3)
C(2)	4805(9)	3771(8)	1967(5)	95(4)
C(3)	6701(7)	3142(5)	854(5)	54(2)
C(4)	7509(7)	2242(6)	371(5)	58(2)
C(5)	9086(6)	1727(5)	-967(4)	31(2)
C(6)	10272(7)	1032(5)	-953(4)	39(2)
C(7)	10891(6)	303(5)	-1556(4)	33(2)
C(8)	10354(7)	248(5)	-2159(4)	34(2)
C(9)	9198(7)	971(6)	-2144(4)	43(2)
C(10)	8558(6)	1714(5)	-1579(4)	31(2)
C(11)	7321(6)	2532(5)	-1651(4)	36(2)
C(12)	7583(6)	3184(5)	-2416(4)	33(2)
C(13)	8191(6)	3825(5)	-2426(4)	38(2)
C(14)	8501(6)	4377(5)	-3161(5)	36(2)
C(15)	8205(6)	4293(5)	-3867(4)	33(2)
C(16)	7599(7)	3649(6)	-3859(5)	42(2)
C(17)	7324(6)	3096(5)	-3136(5)	35(2)
C(18)	7363(8)	3528(6)	-4667(5)	59(2)
C(19)	6491(8)	3032(7)	-4574(5)	97(3)
C(20)	6899(7)	4477(6)	-5137(5)	76(3)
C(21)	8608(8)	3003(6)	-5345(5)	86(3)
C(22)	9343(7)	4941(5)	-3210(4)	48(2)
C(23)	10702(7)	4264(5)	-3353(5)	44(2)
C(24)	11348(8)	4162(6)	-2763(5)	48(2)
C(25)	12551(8)	3461(6)	-2860(5)	53(2)
C(26)	13147(6)	2849(6)	-3554(5)	56(2)
C(27)	12529(8)	2911(6)	-4150(4)	48(2)
C(28)	11308(8)	3642(6)	-4022(4)	45(2)
C(29)	13181(9)	2221(6)	-4930(5)	63(2)
C(30)	12369(8)	1622(7)	-4858(5)	100(3)
C(31)	13497(9)	2764(6)	-5699(5)	98(3)
C(32)	14503(8)	1484(7)	-4932(5)	96(3)
C(33)	11044(7)	-616(6)	-2808(5)	55(2)
C(34)	10750(7)	-1525(5)	-2351(5)	66(3)
C(35)	12499(7)	-911(6)	-3095(5)	97(3)
C(36)	10610(7)	-304(6)	-3607(5)	71(3)
C(37)	13207(7)	3220(6)	-2173(5)	59(2)
C(38)	13291(8)	2266(7)	-1725(5)	52(2)
C(39)	12140(8)	2156(6)	-1171(5)	47(2)
C(40)	12160(7)	1239(6)	-827(4)	38(2)

Table 2. Continued

	x	y	z	U_{eq}
C(41)	13338(9)	456(7)	-1003(5)	65(3)
C(42)	14449(8)	544(8)	-1512(6)	76(3)
C(43)	14374(8)	1471(8)	-1854(5)	65(3)
C(44)	15753(8)	-381(8)	-1744(6)	80(3)
C(45)	16557(8)	-291(7)	-1287(5)	97(3)
C(46)	15722(8)	-1176(7)	-2133(6)	108(4)
C(47)	16639(8)	-101(7)	-2594(6)	117(4)
C(48)	10981(6)	1092(5)	-332(4)	40(2)
C(49)	10983(8)	5641(6)	-2110(5)	65(2)
C(50)	10937(7)	5844(5)	-1263(4)	93(3)
C(51)	11617(7)	5157(5)	25(4)	97(3)
C(52)	12440(6)	4188(6)	318(5)	99(3)
Cl(2)	14064(2)	4020(2)	-257(2)	101(1)

Table 3. Selected bond lengths (\AA), bond angles ($^\circ$) and torsion angles ($^\circ$) for $\text{C}_{52}\text{H}_{70}\text{Cl}_2\text{O}_6$

Cl(1)-C(1)	1.753(8)
Cl(2)-C(52)	1.800(6)
Cl1-C1-C2-O1	-59.3(9)
C3-O1-C2-C1	-61(1)
C2-O1-C3-C4	-165.6(7)
O1-C3-C4-O2	-178.5(6)
C5-O2-C4-C3	-166.0(6)
O3-C51-C52-Cl2	64.7 (7)
C50-O3-C51-C52	167.0(5)
C51-O3-C50-C49	-169.2(4)
O4-C49-C50-O3	56.8(8)
C24-O4-C49-C50	-148.4(6)

Table 4. Hydrogen-bonding geometry (\AA and $^\circ$) for $\text{C}_{52}\text{H}_{70}\text{Cl}_2\text{O}_6$

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5)-H(53)...O(2)	1.053(4)	1.955(4)	2.961(6)	158.8(3)
O(6)-H(54)...O(4)	0.961(5)	2.142(5)	2.897(7)	134.4(3)

3. Results and Discussion

The title compound comprises the calix[4]arene molecule consisting of four aromatic phenyl groups linked by four methylene groups, four *tert*-butyl groups bonded to the ortho carbon atoms of the four aromatic phenyl groups, two hydroxy groups bonded to the para carbon atoms of the phenyl rings A and C, and two dichloride tails bonded to the para carbon atoms of the phenyl rings B and D (see Fig. 1).

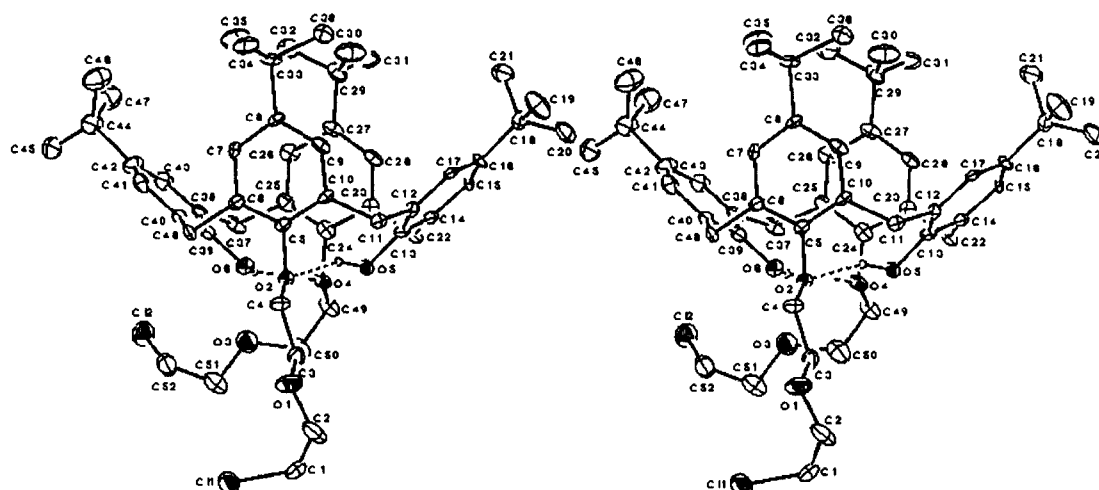


Fig. 1. A stereodrawing²⁰ of the molecule of (I) with the atom-numbering scheme. H atoms are omitted for clarity, apart from those involved in hydrogen bonds, which are drawn as small spheres of an arbitrary radius. Hydrogen bonds are shown as dashed lines and displacement ellipsoids are drawn at the 20% probability level.

All bond lengths and angles are roughly similar to those found in the other calix[4]arene derivatives,^{10,13,15} four phenyl rings in the calix[4]arene are planar within 0.017(5) Å, and bond angles involving the bridging methylenes, C10-C11-C12 = 110.1(5)°, C14-C22-C23 = 112.0(6)°, C6-C48-C40 = 109.3(5)° are close to the tetrahedral angle.

The calixarene is in a distorted cone conformation with all the four phenyl groups lying above the least-squares plane defined by the four bridging methylene groups as clearly illustrated in Fig. 1, and the dihedral angles between each of the four aromatic rings A, B, C, D and the mean plane defined by the four methylenic bridges are 85.5(2), 42.8(2), 87.7(2), and 41.4(2)°, separately. Therefore two facing rings A and C are slightly splayed out upwards from the central axis with a dihedral angle of 6.8(4)° leading to O2...O4 = 5.080(6), C5...C24 = 5.319(9), C8...C27 = 5.626(9) and C29...C33 = 7.397(11) Å, and two rings B and D are so abruptly splayed out upwards from the central axis that they are almost perpendicular to each other with a dihedral angle of 84.2(2)° leading to O5...O6 = 3.365(6), C13...C39 = 5.395(10), C16...C42 = 9.491(11) and C18...C44 = 11.688(12) Å.

This geometry enables O5 and O6 atoms of two

hydroxy groups to be directed towards the inside of the molecule and to form hydrogen bonds with O2 and O4 of dichloride tails as shown in Table 4 and Fig. 1, and the two intramolecular hydrogen bonds stabilize the molecule. The closest intermolecular distance is O2...H51B (2 - x, 1 - y, -z) = 2.655 Å.

The similar cone structures have been found in calix[4]arene piperidinium salt²¹) and 5,11,17,23-tetra-*tert*-butyl-25,27-bis(carboxymethoxy)-26,28-bis(2-methoxyethoxy) calix[4]arene-methanol (1/1).²²)

Acknowledgment

This work was supported by Grant 2000-1-12300-001-3 from the Basic Research Program of the Korea Science and Engineering Foundation.

References

- 1) Gutsche, C. D., *Calixarene, Monographs in Supramolecular Chemistry*, 1, Stoddart, J. F. Ed., Cambridge: The Royal Society of Chemistry (1989).
- 2) Guelzim, A., Khrifi, S., Baert, F., Saadioui, M., Asfari, Z. and Vicens, J., *Acta Cryst.*, **C53**, 1958 (1997).

- 3) Harkema, S., van Loon, J. D., Verboom, W. and Reinhoudt, D., *Acta Cryst.*, **C54**, 269 (1997).
- 4) Ungaro, R. and Pochini, A., *Frontiers in Supramolecular Organic Chemistry and Photochemistry*, Schneider, H.-J. Ed., pp. 57-81. Weinheim: VCH Publishers (1991).
- 5) Kim, H. J., No, K. H., Park, Y. J. and Suh, I. H., *Korean J. of Crystallography*, **4**, 25 (1993).
- 6) Kim, J. S., Pang, J. H., Suh, I. H., Kim, D. W. and Kim, D. W., *Synthetic Communications*, **28**, 677 (1998).
- 7) Kim, J. S., Yu, I. Y., Suh, I. H., Ra, D. Y. and Kim J. W., *Synthetic Communications*, **28(16)**, 2937 (1998).
- 8) Kim, J. S., Suh, I. H., Kim, J. K. and Cho, M. H., *J. Chem. Soc. Perkin Trans. 1*, 2307 (1998).
- 9) Kim, J. S., Cho, M. H., Yu, I. Y., Pang, J. H., Kim, E. T., Suh, I. H., Oh, M. R., Ra, D. Y. and Cho, N. S., *Bull. Korean Chem. Soc.*, **18(6)**, 677 (1997).
- 10) Kim, J. S., Kim, M. J., Lee, J. H., Kim, J. G. and Suh, I. H., *Korean J. of Crystallography*, **10(1)**, 28 (1999).
- 11) Kim, J. S., Choo, G. H., Lee, J. H. and Suh, I. H., *Korean J. of Crystallography*, **10(1)**, 66 (1999).
- 12) Kim, J. S., Jensen, W. P., Lee, C. H., Lee, J. H., Kim, M. J. and Suh, I. H., *Acta Cryst.*, **C56**, 379 (2000).
- 13) Kim, J. S., Shon, O. J., Sim W., Kim, S. K., Cho, M. H., Kim, J. G., Suh, I. H. and Kim, D. W., *J. Chem. Soc. Perkin Trans. 1*, 31 (2001).
- 14) Kim, J. S., Choo, G. H., Lee, C. H., Lee, J. H., Kim, M. J., Kim, J. G. and Suh, I. H., *Korean J. of Crystallography*, **10(2)**, 114 (1999).
- 15) Kim, J. S., Lee, W. K., Choo, G. H., Lee, C. H., Lee, J. H., Kim, M. J., Kim, J. G. and Suh, I. H., *Korean J. Crystallography*, **10(2)**, 130 (1999).
- 16) Enraf-Nonius., *CAD-4 EXPRESS*. Enraf-Nonius, Delft, the Netherlands (1994).
- 17) Harms, K. and Wocadlo, S., *XCAD4*. University of Marburg, Germany (1995).
- 18) Sheldrick, G. M., *SHELXS97, SHELXL97*, University of Goettingen, Germany (1997).
- 19) Farrugia, L. J., WinGX. University of Glasgow, Scotland (1999).
- 20) Farrugia, L. J., *J. Appl. Cryst.*, **30**, 656 (1997).
- 21) Francine, F., Nacthigall, I. V., Marcio, L. and Faruk, N., *Acta Cryst.*, **C54**, 1007 (1998).
- 22) Thuery, P., Nierlich, M., Asfari, Z. and Vicens, J., *Acta Cryst.*, **C56**, 343 (2000).