

Synthesis and Molecular Structure of *p*-*tert*-butylcalix[4]arene Hexanoate

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Abstract

Two conformational isomers of *p*-*tert*-butylcalix[4]arene hexanoate were prepared from the reaction of *p*-*tert*-butylcalix[4]arene and hexanoyl chloride in the presence of AlCl_3 in CH_2Cl_2 and their structures were determined by NMR spectra and X-ray diffraction as a cone and a 1,3-alternate conformer, respectively. The crystal of cone conformer ($\text{C}_{68}\text{H}_{96}\text{O}_8 \cdot (\text{CH}_3)_2\text{CO}$) is triclinic. $\text{P}\bar{1}$, $a = 15.066(1) \text{ \AA}$, $b = 16.063(1) \text{ \AA}$, $c = 16.365(1) \text{ \AA}$. $\alpha = 79.75(2)^\circ$, $\beta = 109.95(2)^\circ$, $\gamma = 80.32(0)^\circ$. $V = 3602.7(4) \text{ \AA}^3$, $Z = 2$. The intensity data were collected on Siemens SMART diffractometer/CCD area detector. The structure was solved by direct method and refined by least-squares calculations to a final R value of 0.144 for 4638 observed reflections. The molecular conformation is distorted symmetric cone with the flattening A and D phenyl rings. The crystal of 1,3-alternate conformer ($\text{C}_{68}\text{H}_{96}\text{O}_8 \cdot 2\text{CHCl}_3$) is orthorhombic. $\text{Pca}2_1$, $a = 34.586(5) \text{ \AA}$, $b = 10.207(3) \text{ \AA}$, $c = 20.394(4) \text{ \AA}$, $V = 7199(3) \text{ \AA}^3$, $Z = 4$. The intensity data were collected on an Enraf-Nonius CAD-4 Diffractometer with a graphite monochromated Mo-K radiation. The structure was solved by direct method and refined by least-squares calculations to a final R value of 0.152 for 2241 observed reflections. The molecule has a pseudo mirror symmetric 1,3-alternate conformation.

1. Introduction

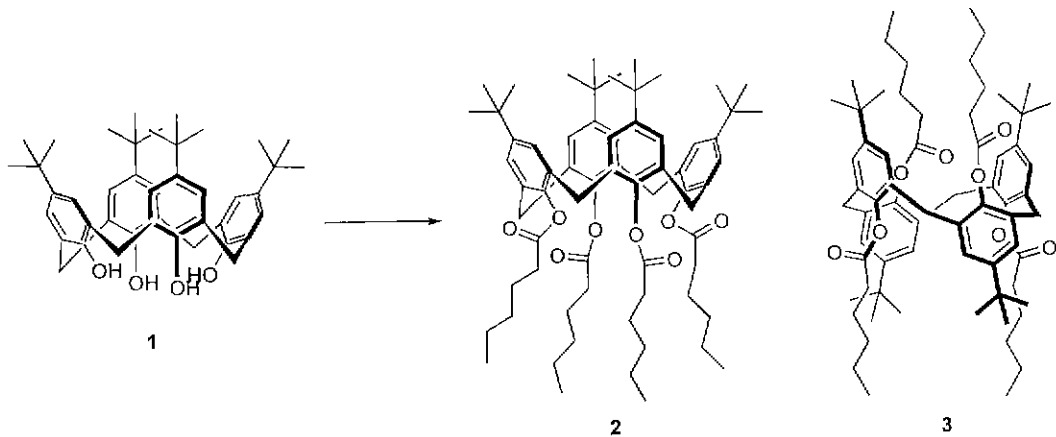
Calixarene is cavity containing macrocyclic compound made up of phenol and formaldehyde building blocks, and has received a great deal of attention in recent years because of its basket shape and its ability to be functionalized in various ways.¹⁻³⁾ The cavity of calixarene is conformationally mobile⁴⁾ in solution at room temperature and exists as four possible conformational isomers; cone, partial cone, 1,2-alternate and 1,3-alternate. All four of the conformers for a calix[4]arene are interchangeable by rotations of the aryl groups around the axis that passes through the meta carbon atoms bonded to the bridge methylene groups. Upon replacement of the phenolic hydrogens with a group larger than ethyl, the calix[4]arenes become conformationally inflexible, existing as discrete entities in one or another of the four possible conformations.^{5,6)}

Shaping the cavity plays a potentially vital role in the design of calixarenes as enzyme mimics, for host-

guest interaction depends on complementarity in shape as well as functionality. In the study of aryl-methylation⁷⁾ and arylation⁸⁾ of calix[4]arene, Gutsche showed that the particular conformation in which calix[4]arene is fixed upon derivatization is dependent on the reaction condition and Shinkai also reported the similar result from the alkylation of calix[4]arene.⁹⁾ We also reported the conformational outcomes in the acylation of calix[4]arene¹⁰⁻¹²⁾ and the present investigation is an extension of these earlier works and involves the structure determination of *p*-*tert*-butylcalix[4]arene hexanoate.

1-1. Synthesis

Two conformational isomers of the *p*-*tert*-butylcalix[4]arene hexanoate **2** and **3** were synthesized as shown in Scheme. The cone conformer **2** was prepared using the published procedures.¹³⁾ A solution of the hexanoyl chloride and AlCl_3 in CH_2Cl_2 was added dropwise to a solution of *p*-*tert*-butylcalix[4]arene **1** in CH_2Cl_2 . After refluxing 4h, diluted HCl



Scheme

was added and organic layer was separated, washed with water and then dried. Evaporation of solvent resulted the crude product. Flash chromatographic separation afforded compound **2** (cone conformer) in 77% yield. A faint spot of the compound **3** was shown on the TLC analysis of crude product, however, the isolation of compound **3** was not successful. When the same reaction was carried out by

slightly different method, in which the mixture of *p*-tert-butylcalix[4]arene **1**, AlCl₃ and hexanoyl chloride in CH₂Cl₂ was refluxed for 4h. Flash chromatographic separation of crude product afforded compound **2** (cone conformer) and **3** (1,3-alternate conformer) in 52% and 23% yields respectively, whose conformations were established by inspection of their ¹H and ¹³C NMR spectra. In ¹H NMR spec-

Table 1. Crystal Data of *p*-tert-butylcalix[4]arene hexanoate

	Cone Conformer 2	1,3-Alternate Conformer 3
molecular formula	C ₆₈ H ₉₆ O ₈ · (CH ₃) ₂ CO	C ₆₈ H ₉₆ O ₈ · 2CHCl ₃
molecular weight	1099.53	1280.18
space group	P $\bar{1}$	Pca2 ₁
a, Å	15.066(1)	34.586(5)
b, Å	16.063(1)	10.207(3)
c, Å	16.365(1)	20.394(4)
α, deg.	79.75(2)	90
β, deg.	68.48(1)	90
γ, deg.	80.32(0)	90
Z	2	4
V, Å ³	3602.7(4)	7199 (3)
density (calc.), g/cm ³	1.014	1.181
radiation	Mo-Kα (λ = 0.7107 Å)	Mo-Kα (λ = 0.7107 Å)
crystal size, mm	0.31×0.32×0.21	0.45×0.38×0.80
scan type	ω	ω/2θ
scan range, deg	4~50°	0~44°
no. of unique reflection	6437	4523
no. of observed reflection (F _o > 4σ F _o)	4638	2241
R	0.144	0.152
R _w	0.357	0.377

trum of **2**, protons of aromatic ring and *tert*-butyl groups give one singlet each and those of bridge methylene show two pairs of doublet in 1 : 1 ratio. This pattern is commensurated with cone conformation. ^{13}C NMR spectrum, which shows four peaks from aromatic carbons, one peak from the bridge methylene carbons at 31.08 ppm¹⁴⁾ and single peak from the carbonyl carbon, also supports the result of proton NMR spectrum. Compound **3** shows three sharp singlets from protons of aromatic ring, bridge methylene and *tert*-butyl groups in ^1H NMR spectrum. ^{13}C NMR spectrum shows a single resonance each for the carbonyl carbons, methyl and quaternary carbons of *tert*-butyl groups, and methylene carbons (at 38.49 ppm) of the 'calix' along with four lines for the aryl carbons. Only the 1,3-alternated conformation is commensurated with these spectral data.

1-2. X-ray Structure Analysis

The crystals suitable for the diffraction study were obtained by slow evaporation from an acetone solution for cone conformer, and from a mixture of chloroform and methanol for 1,3 alternate conformer, respectively. Both crystals were unstable in the air and were sealed in the capillary tube in their mother liquor. X-ray intensity data were collected on a Simens SMART¹⁵⁾ diffractometer/CCD area detector for cone conformer and on an Enraf-Nonius CAD-4 diffractometer for 1,3 alternate conformer, respectively. All of the crystal data are summarized in Table 1.

The structures of both conformer were solved by direct method and refined using the program SHELXL-97.¹⁶⁾ Due to the poor crystal, the refinements of the structure were not satisfied. For 1,3 alternate conformer, the refinements of temperature factors of nonhydrogen atoms were performed only isotropically. The final positional and thermal parameters of nonhydrogen atoms are listed in Table 2.

2. Description of the Structure

The selected molecular geometric parameters are listed in Table 3. These values are mainly as expected for the type of bonds involved.

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters for Nonhydrogen Atoms of *p*-*tert*-butylcalix[4]arene hexanoate. The e. s. d.'s are in parentheses. Ueq. = $1/3 \Sigma \Sigma U_{ij} a_i^2 a_j^2$ (\AA^2)

1. Cone Conformer				
Atom	x	y	z	Ueq
C(1)	6804(15)	-2227(14)	980(14)	0.172(9)
C(2)	7600(15)	-1827(13)	939(16)	0.224(11)
C(3)	7007(15)	-3026(12)	598(17)	0.279(15)
O(1)	6011(12)	-1826(10)	1148(10)	0.216(5)
C(1A)	8040(6)	4371(5)	194(5)	0.061(2)
C(2A)	7409(6)	4930(5)	-126(6)	0.060(2)
C(3A)	7820(6)	5456(5)	-905(6)	0.065(2)
C(4A)	8797(6)	5434(5)	-1354(6)	0.067(2)
C(5A)	9386(6)	4839(5)	-995(6)	0.069(2)
C(6A)	9028(6)	4290(5)	-230(6)	0.061(2)
C(7A)	9681(6)	3591(5)	82(6)	0.068(2)
C(8A)	9178(7)	6022(6)	-2221(7)	0.084(3)
C(9A)	8823(12)	6963(7)	-1987(11)	0.181(7)
C(10A)	8761(11)	5871(11)	-2875(8)	0.156(6)
C(11A)	10253(8)	5928(9)	-2618(8)	0.141(5)
C(12A)	7549(8)	4148(7)	1744(7)	0.087(3)
C(13A)	7054(8)	3597(8)	2550(7)	0.104(3)
C(14A)	6921(17)	3843(14)	3410(11)	0.202(9)
C(15A)	6660(20)	4542(19)	3667(14)	0.275(15)
C(16A)	6690(30)	4650(20)	4550(30)	0.321(19)
C(17A)	6630(30)	5460(20)	4630(20)	0.49(3)
O(1A)	7657(4)	3845(3)	1001(4)	0.071(2)
O(2A)	7872(8)	4784(6)	1720(5)	0.156(4)
C(1B)	9303(6)	2056(5)	207(6)	0.061(2)
C(2B)	9709(5)	2772(5)	-316(6)	0.061(2)
C(3B)	10114(6)	2760(6)	-1211(6)	0.069(2)
C(4B)	10126(6)	2064(6)	-1622(6)	0.072(2)
C(5B)	9671(6)	1385(6)	-1084(6)	0.070(2)
C(6B)	9224(5)	1359(5)	-169(6)	0.061(2)
C(7B)	8677(6)	618(5)	352(6)	0.071(2)
C(8B)	10581(8)	2041(8)	-2612(6)	0.103(3)
C(9B)	11339(13)	1235(11)	-2763(10)	0.203(7)
C(10B)	11116(14)	2790(11)	-3073(9)	0.212(10)
C(11B)	9905(14)	1903(18)	-3015(10)	0.298(14)
C(12B)	9399(7)	1545(5)	1632(7)	0.076(3)
C(13B)	8881(9)	1625(7)	2566(6)	0.103(4)
C(14B)	9399(12)	1071(9)	3166(9)	0.149(6)
C(15B)	8780(30)	1059(16)	4151(17)	0.247(17)
C(16B)	8910(20)	1650(20)	4365(10)	0.330(17)
C(17B)	8598(14)	1821(12)	5338(11)	0.297(7)
O(1B)	8908(4)	2041(3)	1136(4)	0.067(2)
O(2B)	10137(6)	1119(6)	1295(5)	0.118(3)
C(1C)	6941(6)	1142(5)	563(5)	0.063(2)
C(2C)	7774(6)	656(5)	132(6)	0.066(2)
C(3C)	7789(7)	252(5)	-554(6)	0.075(2)
C(4C)	6994(6)	333(6)	-823(6)	0.075(3)
C(5C)	6183(6)	853(5)	-396(6)	0.070(2)
C(6C)	6142(6)	1282(5)	289(6)	0.065(2)

Table 2. Continued

Atom	x	y	z	Ueq
C(7C)	5301(6)	1944(4)	654(7)	0.069(3)
C(8C)	7067(7)	-98(6)	-1627(6)	0.080(3)
C(9C)	7858(9)	264(9)	-2448(7)	0.130(4)
C(10C)	6136(8)	30(8)	-1788(7)	0.105(4)
C(11C)	7329(9)	-1062(6)	-1432(9)	0.122(4)
C(12C)	6574(7)	1189(7)	2100(7)	0.077(3)
C(13C)	6246(8)	316(6)	2263(7)	0.097(3)
C(14C)	5894(9)	-24(8)	3222(8)	0.121(4)
C(15C)	5523(11)	-890(9)	3408(9)	0.146(5)
C(16C)	5126(17)	-1199(13)	4349(14)	0.229(10)
C(17C)	-4720(20)	-2018(16)	-4515(18)	0.334(15)
O(1C)	6891(4)	1573(3)	1255(4)	0.071(2)
O(2C)	6548(5)	1580(5)	2668(5)	0.108(2)
C(1D)	5699(5)	3472(5)	481(6)	0.059(2)
C(2D)	5563(5)	2796(5)	111(6)	0.057(2)
C(3D)	5724(6)	2914(5)	-788(6)	0.069(2)
C(4D)	6058(6)	3646(6)	-1334(6)	0.067(2)
C(5D)	6220(5)	4270(5)	-956(6)	0.064(2)
C(6D)	6050(5)	4192(5)	-55(6)	0.060(2)
C(7D)	6337(5)	4894(5)	301(6)	0.066(2)
C(8D)	6271(7)	3716(7)	-2330(7)	0.088(3)
C(9D)	7066(16)	4251(17)	-2850(10)	0.294(13)
C(10D)	6407(18)	2925(10)	-2691(10)	0.254(12)
C(11D)	5453(15)	4239(14)	-2537(10)	0.276(12)
C(12D)	4603(6)	3364(5)	1958(6)	0.070(2)
C(13D)	4577(7)	3174(7)	2912(6)	0.091(3)
C(14D)	3647(9)	2938(10)	3570(8)	0.122(4)
C(15D)	3489(12)	2057(11)	3544(11)	0.173(6)
C(16D)	2530(20)	1765(18)	4350(17)	0.278(13)
C(17D)	2310(30)	1070(20)	4400(30)	0.43(3)
O(1D)	5521(4)	3386(3)	1398(4)	0.069(2)
O(2D)	3936(5)	3484(4)	1711(4)	0.089(2)

2.1.3-Alternate Conformer

C(1)	3629(13)	3520(40)	2980(20)	0.142(15)
Cl(1)	3935(4)	4431(12)	2545(7)	0.137(4)
Cl(2)	3923(3)	2247(10)	3441(5)	0.106(3)
Cl(3)	3439(4)	2339(12)	2287(7)	0.143(5)
C(2)	1323(6)	11800(20)	2942(10)	0.034(5)
Cl(4)	1060(3)	12746(11)	2416(5)	0.117(4)
Cl(5)	1571(5)	12798(15)	3475(9)	0.188(6)
Cl(6)	1002(4)	10721(14)	3330(7)	0.146(5)
C(1A)	1123(7)	8700(20)	1496(11)	0.040(6)
C(2A)	925(7)	7920(20)	1864(11)	0.036(6)
C(3A)	544(8)	8190(30)	2110(14)	0.058(8)
C(4A)	387(7)	9480(20)	1907(11)	0.035(6)
C(5A)	592(7)	1360(20)	1467(12)	0.044(7)
C(6A)	961(7)	9940(20)	1274(11)	0.030(6)
C(7A)	1176(7)	1880(20)	818(12)	0.039(6)
C(8A)	-44(6)	9780(20)	2136(12)	0.042(6)
C(9A)	-321(8)	8750(30)	2027(13)	0.060(8)
C(10A)	-186(8)	11110(30)	1793(13)	0.065(8)
C(11A)	-9(9)	10050(30)	2934(15)	0.075(9)

Table 2. Continued

Atom	x	y	z	Ueq
C(12A)	1794(10)	8950(30)	1636(17)	0.071(10)
C(13A)	2158(10)	8530(30)	1304(16)	0.079(11)
C(14A)	2516(9)	8680(30)	1817(15)	0.070(9)
C(15A)	2915(11)	8530(40)	1487(19)	0.101(12)
C(16A)	3208(9)	8610(30)	1984(14)	0.075(8)
C(17A)	3640(20)	8220(70)	1890(30)	0.22(3)
O(1A)	1507(4)	8483(14)	1310(7)	0.040(4)
O(2A)	1756(6)	9590(20)	2105(11)	0.091(7)
C(1B)	1155(7)	9540(20)	-263(11)	0.031(6)
C(2B)	1347(7)	10430(20)	177(12)	0.035(6)
C(3B)	1729(6)	10735(19)	47(9)	0.019(5)
C(4B)	1875(9)	10410(30)	-498(14)	0.068(9)
C(5B)	1676(8)	9590(20)	-990(12)	0.047(7)
C(6B)	1345(7)	9160(20)	-827(11)	0.032(6)
C(7B)	1119(6)	82000(2)	-1307(11)	0.034(6)
C(8B)	2334(9)	10950(30)	-702(14)	0.065(9)
C(9B)	2287(7)	12400(20)	-867(12)	0.042(6)
C(10B)	2589(10)	10640(30)	-219(17)	0.084(10)
C(11B)	2425(11)	10310(30)	-1410(20)	0.108(12)
C(12B)	505(10)	10020(30)	-173(16)	0.079(11)
C(13B)	100(8)	9330(30)	-61(15)	0.053(8)
C(14B)	-221(8)	10130(30)	-55(13)	0.061(8)
C(15B)	-596(11)	9170(40)	9(18)	0.109(12)
C(16B)	-950(20)	10740(80)	90(40)	0.30(4)
C(17B)	-1339(13)	9960(40)	180(20)	0.141(15)
O(1B)	794(5)	9201(15)	-71(8)	0.042(4)
O(2B)	538(6)	11050(20)	-472(11)	0.087(7)
C(1C)	1123(6)	6100(20)	-612(10)	0.023(5)
C(2C)	911(8)	7020(20)	-1039(12)	0.041(7)
C(3C)	547(6)	6640(20)	-1208(11)	0.032(6)
C(4C)	367(8)	5580(20)	-1030(12)	0.041(7)
C(5C)	566(7)	4740(30)	-639(12)	0.039(7)
C(6C)	959(7)	5020(20)	-390(12)	0.035(6)
C(7C)	1205(8)	4040(20)	-3(13)	0.050(7)
C(8C)	8(8)	5100(30)	-1345(14)	0.063(8)
C(9C)	10(9)	5190(30)	-2072(14)	0.071(9)
C(10C)	-314(10)	6160(30)	-1013(16)	0.087(11)
C(11C)	-131(7)	3730(20)	-1149(12)	0.057(7)
C(12C)	1791(7)	6160(20)	-792(12)	0.040(6)
C(13C)	2171(7)	6500(20)	-517(13)	0.049(7)
C(14C)	2497(11)	6230(30)	-1009(18)	0.096(12)
C(15C)	2888(8)	6680(30)	-690(14)	0.064(8)
C(16C)	3212(14)	6860(40)	-1340(20)	0.151(17)
C(17C)	3590(20)	6910(60)	-840(40)	0.22(3)
O(1C)	1484(5)	6524(15)	-393(8)	0.045(5)
O(2C)	1740(6)	5630(20)	-1339(11)	0.092(7)
C(1D)	1183(7)	5350(20)	1047(11)	0.034(6)
C(2D)	1287(7)	5830(20)	1645(11)	0.038(6)
C(3D)	1704(7)	5430(20)	1818(11)	0.033(6)
C(4D)	1910(5)	4612(17)	1452(9)	0.012(4)
C(5D)	1744(8)	4160(30)	806(15)	0.062(8)
C(6D)	1379(7)	4670(20)	626(11)	0.035(6)
C(7D)	1085(7)	6570(20)	2137(12)	0.042(6)

Table 2. Continued

Atom	x	y	z	Ueq
C(8D)	2270(7)	4080(20)	1627(11)	0.038(6)
C(9D)	2457(9)	4590(30)	2258(16)	0.078(9)
C(10D)	2607(11)	4510(30)	1030(20)	0.094(12)
C(11D)	2233(12)	2500(40)	1620(20)	0.124(16)
C(12D)	470(6)	5030(20)	1078(10)	0.031(5)
C(13D)	116(8)	5720(30)	899(14)	0.058(8)
C(14D)	-235(9)	4600(30)	1037(14)	0.070(8)
C(15D)	-613(7)	5370(20)	789(11)	0.047(6)
C(16D)	-943(9)	4480(30)	722(16)	0.081(9)
C(17D)	-1277(13)	5550(40)	520(20)	0.144(16)
O(1D)	781(5)	5849(16)	956(8)	0.046(5)
O(2D)	530(6)	3870(20)	1209(10)	0.081(6)

Table 3. Selected Geometric Parameters for *p*-*tert*-butylcalix[4]arene hexanoate. The e. s. d.'s are in parentheses.

1. Cone Conformer				
	A	B	C	D
C(1)-O(1)	1.42(1)	1.41(1)	1.40(1)	1.41(1)
C(12)-O(2)	1.20(1)	1.20(1)	1.19(1)	1.20(1)
C(12)-O(1)	1.34(1)	1.36(1)	1.36(1)	1.35(1)
C(12)-C(13)	1.48(2)	1.46(2)	1.52(2)	1.52(2)
C(13)-C(14)	1.46(3)	1.53(2)	1.48(1)	1.47(2)
C(14)-C(15)	1.31(4)	1.46(5)	1.51(2)	1.49(2)
C(15)-C(16)	1.49(6)	1.16(5)	1.48(3)	1.60(4)
C(16)-C(17)	1.27(7)	1.70(4)	1.48(5)	1.16(6)
C(2A)-C(7D)	1.52(1)	C(2C)-C(7B)	1.52(1)	
C(2B)-C(7A)	1.55(1)	C(2D)-C(7C)	1.51(1)	
C(2)-C(1)-O(1)	118.1(7)	119.3(8)	122.1(8)	119.2(7)
C(6)-C(1)-O(1)	117.9(7)	119.0(8)	117.3(8)	120.0(8)
O(2)-C(12)-O(1)	121(1)	121(1)	117(1)	123(1)
O(2)-C(12)-C(13)	126(1)	129(1)	125(1)	127(1)
O(1)-C(12)-C(13)	113(1)	110(1)	118(1)	111(1)
C(14)-C(13)-C(12)	119(2)	112(1)	113(1)	115(1)
C(15)-C(14)-C(13)	129(3)	112(2)	114(1)	112(1)
C(14)-C(15)-C(16)	117(4)	107(4)	114(2)	111(2)
C(17)-C(16)-C(15)	105(5)	128(5)	116(3)	119(4)
C(12)-O(1)-C(1)	116.8(7)	118.1(7)	119.8(7)	118.7(7)
C(6A)-C(7A)-C(2B)	108.5(7)			
C(6B)-C(7B)-C(2C)	110.0(7)			
C(6C)-C(7C)-C(2D)	107.8(8)			
C(6D)-C(7D)-C(2A)	109.4(7)			

2. 1,3-Alternate Conformer

	A	B	C	D
C(1)-O(1)	1.42(3)	1.35(2)	1.38(2)	1.49(2)

Table 3. Continued

	A	B	C	D
C(12)-O(2)	1.17(4)	1.23(3)	1.23(3)	1.23(2)
C(12)-O(1)	1.31(3)	1.32(3)	1.38(2)	1.37(2)
C(12)-C(13)	1.47(4)	1.58(4)	1.48(3)	1.46(3)
C(13)-C(14)	1.68(4)	1.34(3)	1.48(4)	1.78(4)
C(14)-C(15)	1.51(4)	1.65(4)	1.52(4)	1.64(4)
C(15)-C(16)	1.42(4)	1.97(9)	1.73(5)	1.54(3)
C(16)-C(17)	1.61(11)	1.60(9)	1.64(6)	1.74(5)
C(2A)-C(7D)	1.57(3)	C(2C)-C(7B)	1.52(3)	
C(2B)-C(7A)	1.53(3)	C(2D)-C(7C)	1.52(3)	
C(2)-C(1)-O(1)	125(2)	114(2)	117(2)	126(2)
C(6)-C(1)-O(1)	112(2)	126(2)	123(2)	105(2)
O(2)-C(12)-O(1)	113(2)	126(3)	123(2)	117(2)
O(2)-C(12)-C(13)	131(3)	117(3)	122(2)	136(2)
O(1)-C(12)-C(13)	107(2)	114(2)	114(2)	107(2)
C(14)-C(13)-C(12)	106(2)	123(2)	117(2)	98(2)
C(15)-C(14)-C(13)	111(3)	108(2)	114(2)	97(2)
C(14)-C(15)-C(16)	111(3)	89(5)	106(2)	107(2)
C(17)-C(16)-C(15)	127(5)	104(7)	99(3)	96(2)
C(12)-O(1)-C(1)	122(2)	116(2)	115(2)	124(2)
C(6A)-C(7A)-C(2B)	121(2)			
C(6B)-C(7B)-C(2C)	120(2)			
C(6C)-C(7C)-C(2D)	115(2)			
C(6D)-C(7D)-C(2A)	114(2)			

Selected Torsion Angle

	Cone Conformer	1,3-Alternate Conformer
C(1A)-C(2A)-C(7D)-C(6D)	-82(1)	-41(3)
C(1A)-C(6A)-C(7A)-C(2B)	84(1)	53(3)
C(1A)-O(1A)-C(12A)-O(2A)	-9(2)	-9(4)
C(1A)-O(1A)-C(12A)-C(13A)	174(1)	-176(2)
O(2A)-C(12A)-C(13A)-C(14A)	1(3)	29(4)
C(6A)-C(1A)-C(2A)-C(7D)	170(1)	-179(2)
C(1B)-C(2B)-C(7A)-C(6A)	-112(1)	44(3)
C(1B)-C(6B)-C(7B)-C(2C)	110(1)	-46(3)
C(1B)-O(1B)-C(12B)-O(2B)	-1(3)	6(4)
C(1B)-O(1B)-C(12B)-C(13B)	179(1)	166(2)
O(2B)-C(12B)-C(13B)-C(14B)	-1(2)	172(2)
C(6B)-C(1B)-C(2B)-C(7A)	172(1)	-177(2)
C(1C)-C(2C)-C(7B)-C(6B)	-85(1)	-54(3)
C(1C)-C(6C)-C(7C)-C(2D)	83(1)	60(2)
C(1C)-O(1C)-C(12C)-O(2C)	180(1)	10(3)
C(1C)-O(1C)-C(12C)-C(13C)	-2(1)	-180(2)
O(2C)-C(12C)-C(13C)-C(14C)	-1(2)	-2(3)

Table 3. Continued

C(6C)-C(1C)-C(2C)-C(7B)	171(1)	-177(2)
C(1D)-C(2D)-C(7C)-C(6C)	-114(1)	47(3)
C(1D)-C(6D)-C(7D)-C(2A)	114(1)	-58(3)
C(1D)-O(1D)-C(12D)-O(2D)	-6(1)	-2(3)
C(1D)-O(1D)-C(12D)-C(13D)	174(1)	-174(2)
O(2D)-C(12D)-C(13D)-C(14D)	13(2)	9(3)
C(6D)-C(1D)-C(2D)-C(7C)	172(1)	170(2)

The conformation of the cone conformer shown in Fig. 1 is distorted as compared with the ideal four-fold symmetry found for *tert*-butylcalix[4]arene.¹⁷⁾ The inclination of the phenyl rings, A to D, with respect to the least-squares plane of the four methylene carbons are 52°, 80°, 126° and, 95° respectively. Ring B and D are thus approximately normal to the plane, and Ring A and C are tilted. Four hex-

anoate groups are oriented away from the macrocyclic cavity center.

The molecule of 1,3 alternate conformer is pseudo mirror symmetric. The dihedral angle between the four aromatic rings and mean plane of the macrocyclic CH₂ groups are; A (115°), B (-112°), C (110°), D (113°). The dihedral angles between two adjacent rings are; A-B = 99°, B-C = 98°, C-D = 84°, D-A = 80°, whereas those between two opposite rings are A-C = 45° and B-D = 45°. Four hexanoate are almost planar zigzag chains. Each hexanoate least-square plan makes angles of 73, 62, 64 and 74° with its benzene ring planes A to D, respectively.

Fig. 2 shows the stereopacking diagram of the molecules in the unit cell. The crystal structure of cone conformer has one solvent acetone molecules in the unit cell, and two chloroform molecules are

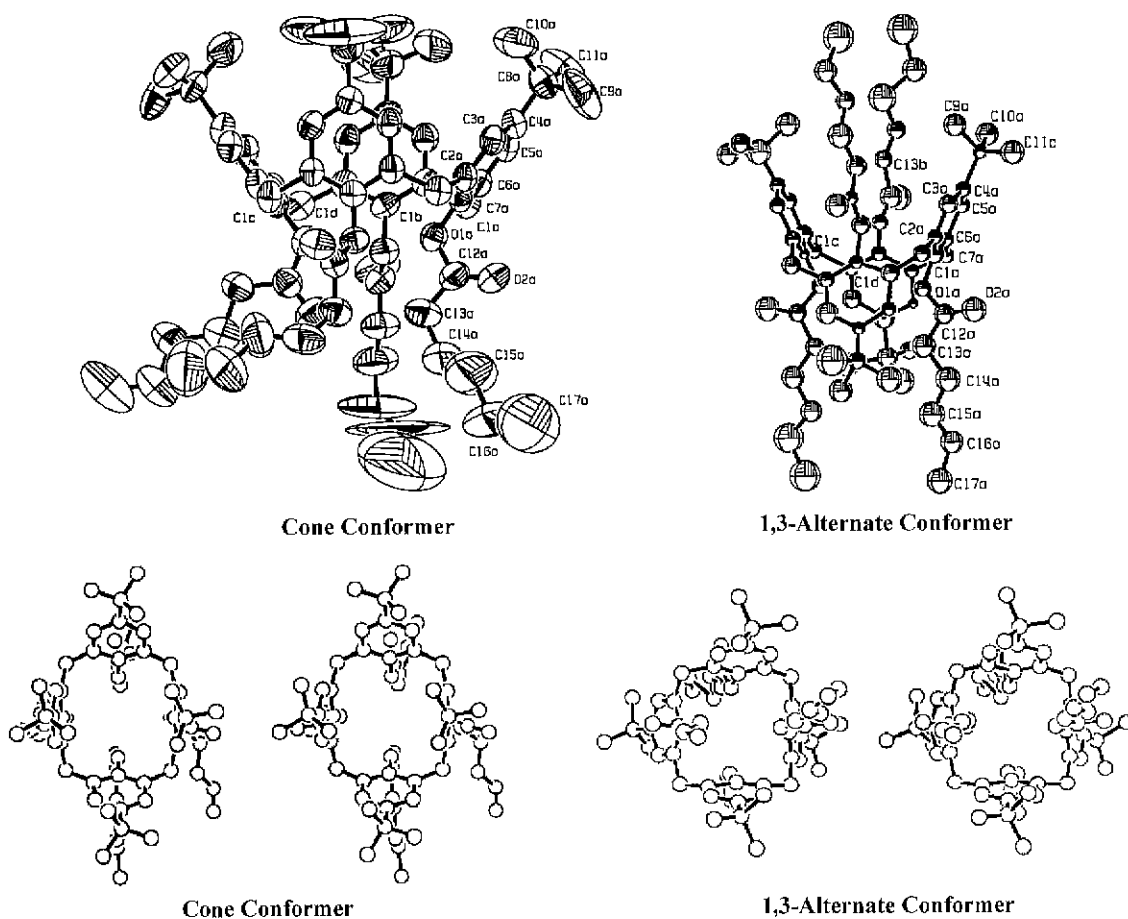


Fig. 1. Molecular conformation with atomic numbering drawn by ORTEP¹⁷⁾.

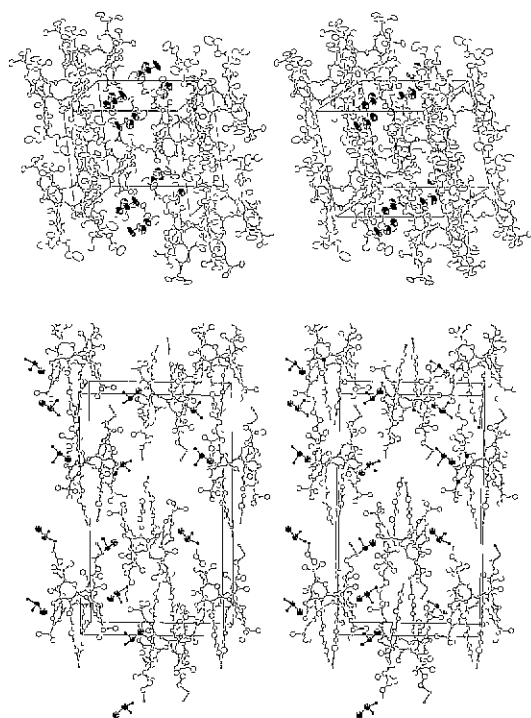


Fig. 2. The Crystal Structure. The solvent molecules are expressed as octant shading ellipsoid. Top: Cone Conformer. Bottom: 1,3-Alternate Conformer.

in unit cell of 1,3 alternate conformer crystal.

3. Experimental

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Melting points of all compounds were taken in sealed and evacuated capillary tubes on an Mel-temp apparatus and were not corrected for temperature. IR spectra were measured with a Nicolet Impact 400 FT-IR spectrometer on samples in KBr pellet. ^1H and ^{13}C NMR spectra were recorded on Varian Gemini 300 (300 and 75 MHz) and Bruker AMX 500 instrument. Chemical shifts are recorded as values in parts per million relative to TMS (δ 0.0) as an internal standard. TLC analyses were carried out on silica gel plates (absorbent thickness 250 μm). Flash chromatography was carried out with E. Merck silica gel (230–400 mesh ASTM). Elution rate was 2 ml/min.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrahydro-

xycalix[4]arene 1 was prepared in 52% yield from *p*-*tert*-butylphenol and formaldehyde as described elsewhere¹⁹; mp 344–346°C (lit¹⁹ 344–346°C).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrahexanoxyloxyalix[4]arene 2 (cone conformer) was prepared in 77% yield from compound 1 and hexanoyl chloride using the published procedure¹³; mp 275–276°C (lit¹³ 275–276°C).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrahexanoxyloxyalix[4]arene 3 (1,3-alternate conformer). A mixture of *p*-*tert*-butylcalixarene **1** (1.80 g, 2.43 mmole), hexanoyl chloride (6.3 mL, 4 mole equivalent per OH group) and AlCl_3 (2.0 g) in CH_2Cl_2 (100 mL) was refluxed for 4 h and then poured into 200 mL of 2 M HCl and ice mixture. The organic layer was then separated, washed several times with water and dried over MgSO_4 . The slightly waxy solid, obtained from the evaporation of CH_2Cl_2 , was triturated with methanol to produce the crude product which was purified by the flash chromatography (eluent was 5 : 3 mixture of hexane and chloroform) to afford **2** (1.25 g, 52%) and **3** (553 mg, 23%) as colorless crystalline solids; **3** (1,3-alternate conformer) mp 349–350°C; IR (KBr) 1735 cm^{-1} (C=O); ^1H NMR (CDCl_3) δ 6.98 (s, 8, ArH), 3.71 (s, 4, ArCH_2Ar), 1.60 (l. 8, COCH_2 , $J=7.3$ Hz), 1.30 (m, 8, CH_2), 1.28 (s, 36, tBu), 1.18 (m, 8, CH_2), 0.89 (t, 12, CH_3 , $J=7.3$ Hz); ^{13}C NMR (CDCl_3) 170.84 (C=O), 147.29, 146.23, 132.58, 125.58 (Ar), 38.49 (ArCH_2Ar), 34.21 ($\text{C}(\text{CH}_3)_3$), 32.62 (CH_2), 31.54 ($\text{C}(\text{CH}_3)_3$), 31.27 (CH_2), 23.76 (CH_2), 22.84 (CH_2), 13.93 (CH_3).

Acknowledgement

This work was supported by the Ministry of Science and Technology (KISTEP; 98-N6-02-01-A-02).

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