Tetra-tert-butyl-tetrapropionyloxycalix[4]arene의 구조

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Structure of
Tetra-tert-butyl-tetrapropionyloxycalix[4]arene

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Abstract

Tetra-tert-butyl-tetrapropionyloxycalix[4] arene ($C_{56}H_{72}O_8$) is Triclinic, space group P1, with a=13.664(5), b=17.585(5), c=12.863(2) Å, α=109.33(2), β=111.97(2), γ=76.45(3)°, Z=2, V=2684.08 Å^3, D_c=1.152g/cm^3, D_m=1.15g/cm^3. The intensity data were collected on an Enraf-Nonius CAD-4 Diffractometer with a graphite monochromated Mo-Kα radiation. The structure was solved by direct methods and refined by least-squares methods. The final R factor was 0.084 for 2561 observed reflections.

The configuration of the molecule from the X-ray crystallographic investigation has the partial cone conformation; three tert-butylphenyls are down and a tert-butylphenyl is up. Three propionyloxy groups direct toward the exterior of the macrocycle cavity.

요 약

Tetra-tert-bytyl-tetrapropionyloxycalix[4] arene ($C_{56}H_{72}O_8$)의 분자 및 결정구조를 X-선 회절법으로 연구하였다. 이 결정은 삼사정계이고 공간군은 P1̄이다. 단위세포 길이는 a=13.664(5), b=17.585(5), c=12.863(2)Å이며 α=109.33(2), β=111.97(2), γ=76.45(3)°, Z=2이다. 회절반점들의 세기는 흑연단색화 장치가 있는 Enraf-Nonius CAD-4 Diffractometer로 얻었으며, Mo-Kα X-선(λ=0.7107Å)을 사용하였다. 분자구조는 직접법으로 풀었으며 최소자승법으로 정밀화하였다. 최종 신뢰도 R값은 2561개의 회절반점에 대하여 0.084이었다.

본 Calixarene은 partial cone conformation을 가져서 세개의 tert-butylphenyl group들과 하나의 tert-butylphenyl group의 상대적인 배열이 다르다. 세개의 propionyloxy group들은 macrocycle로 된 cavity 바깥 쪽을 향하여 배열되어 있다.

INTRODUCTION

X-ray diffraction studies of the individual chemical species in the crystalline state provide the most detailed knowledge concerning molecular structure. Knowledge of structure allows one to understand physical, chemical, or biological properties and activities. It also provides the chemist with useful information for syntheses, modifications and reaction mechanisms, and can also be used to identify very small quantities of scarce material. That the chemist can come to actually see molecules is through the use of X-ray crystallography. X-ray crystallography, in fact, now pervades all of supramolecular chemistry and has become an indispensable.

Calix[n]arenes[1], a class of synthetic macrocycles having phenolic residues in a cyclic array linked by methylene group of organic compounds that are basketlike in shape and possess the potential for forming host-guest complexes[2-5] in which the guest resides in a cavity completely within a single host molecule. The workers with the calixarenes have noted their propersity to form molecular complexes with smaller molecules, a direct consequence of the presence of cavities in the calixarenes. The enzymes are known to possess cavitated active sites, where complex formation with substrate occurs as the first step in the catalytic process. Thus, the calixarenes are particularly attractive compounds for attempting to construct systems that mimic the catalytic activity of the enzymes.[6]

The calixarenes are assuming a place in supramolecular chemistry[7] along side the cyclodextrins, cryptands, cyclophanes and crown ethers. Although the calixarenes have developed much less rapidly than their companions, interest in their potential appears to be increasing and attention to their chemistry is escalating. With respect to the long term goal of calixarene research, i.e, the construction of enzyme mimics, calixarenes involving a variety of functional groups which could act as catalytic sites, are attractive. Calix[4]arenes can easily be functionalized both at the phenolic OH groups (lower rim) and after removal of the tert-butyl groups at the para positions of the phenol rings(upper rim).[8,9] Various OH-derivatives of p-tert-butyl-calix[4]arenes were synthesized and used in conformational analysis, complexation studied and X-ray structure determined by Mckervey[10,11], Andreetti, Ungaro[12], and others.[13,14]

The free hydroxyl containing calix[4]arenes are conformationally flexible molecules, and their conformational behavior is normally discussed in terms of four basic conformations[15], designated as cone, partial cone, 1,3-alternate, and 1,2-alternate, as pictured Figure 1.
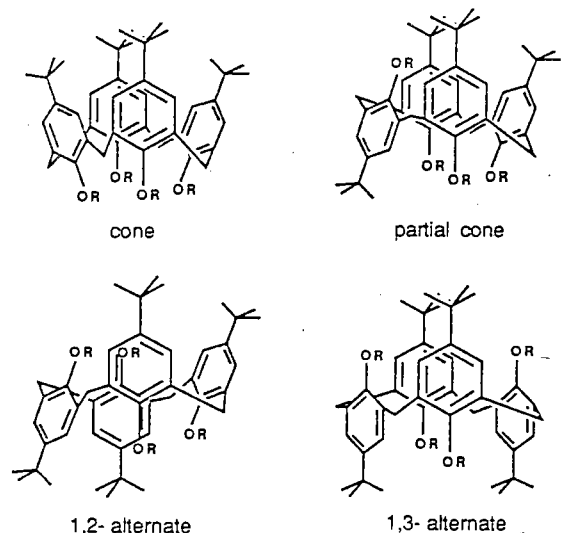

Fig. 1. Conformational isomers of calix[4]arenes

All four of the conformations for a calix[4]arene are accessible by rotations of the aryl groups around the axis that passes through the meta carbon atoms bonded to the bridging methylene groups. All of the calixarenes containing free intraannular OH groups are conformationally mobile in solution at room temperature. Since the pathway for co-

nformational inversion in the calix[4]arenes involves rotation of the aryl groups in a direction that brings the OH groups through the annulus of the macrocyclic ring, the most obvious way to curtail this motion is to replace the OH group with larger moieties. Conversion into the ester or ether is the easiest way to accomplish this, and dozens of such compounds have now been prepared and characterized. Considering the conformational possibilities of the calix[4]arenes, it is apparent that the esters and ethers can exist in any one of the four conformations : cone, partial cone, 1,2-alternate, or 1,3-alternate. X-ray crystallography provides the surest way to discern which of these conformers is present in a particular case.

The application of X-ray crystallography to calixarene chemistry has had a powerful impact in providing the definitive proof of structure. Tetra-tert-butyl-tetrapropionyloxycalix[4]arene is afforded as two conformational isomers in the solid state. One of the isomers was investigated by X-ray crystallography. In this paper, we report the crystal structure of tetra-tert-butyl-tetrapropionyloxycalix[4]arene in order to investigate the structural characteristics, bond distances, bond angles, torsion angles, packing mode and intermolecular interaction, and to make detailed comparisons with other structures.

EXPERIMENTAL

Tetra-tert-butyl-tetrapropionyloxycalix[4] arene was synthesised by the similar ways of the previous methods.[8] When this compound was synthesised, it was isolated as two isomer ; the acetone-insoluble compound and the acetone-soluble compound. The acetone-soluble compound was recrystallized as a 1 : 1 complex with acetone*

* The elemental analysis of the crystal results in C : 76. 38 (±0. 21)%, H : 8.31 (±0. 10)%, O : 15. 32 (±0. 16)%. Theoretecal values are C : 76. 13%, H : 8.39%, O : 15. 48%.

by slow evaporation of a mixture of dichloromethane and acetone solution.

Space group and preliminary crystal data were obtained from X-ray Oscillation and Weissenberg photographies and the crystal system was found to be triclinic with space group P$\bar{1}$. And accurate cell constants were determined by least squares analysis of 25 reflections.

X-ray data collection was carried out using an Nonius CAD-4 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.7107$Å) with a crystal of dimension $0.60 \times 0.31 \times 0.08$mm. The intensities were measured using $\omega/2\theta$ scan type over a scan width of $(0.8 + 0.34 \tan \theta)°$. The three standard reflections $(0\ 1\ \bar{6})$, $(\bar{6}\ \bar{2}\ 4)$, $(\bar{4}\ \bar{3}\ 3)$ were measured every 6000 seconds to monitor the intensity and at 200 reflections interval to monitor the orientation of the crystal. There was no significant loss of intensities through out data collection. Among the 4342 independent

Table 1. Summary of crystal data

formula	$C_{56}H_{72}O_8 \cdot CH_3COCH_3$
Mw	930. 6
crystal system	triclinic
space group	P$\bar{1}$
a, Å	13. 664 (5)
b, Å	17. 585 (5)
c, Å	12. 863 (2)
α, deg.	109. 33 (2)
β, deg.	111. 97 (2)
γ, deg.	76. 45 (3)
Z	2
V, Å^3	2684. 08
μ (Mo-Kα), cm^{-1}	0. 82
density, g/cm^3	1. 152 (calc.)
	1. 15 (meas.)
diffractometer	Enraf-Nonius CAD-4
radiation	Mo-Kα (graphite monochromater. λ =0. 7107 Å)
crystal size, mm	0. 60 × 0. 31 × 0. 08
cell-constant determination	25 reflections
2θ range, deg.	4° ⟨ 2θ ⟨ 44°
scan type	ω / 2θ
scan width, deg.	0. 8 + 0. 34 $\tan \theta$
no. of observed reflections	2561 │ F$_o$ │ ⟩ 3σ │ F$_o$ │
R	0. 084
Rw	0. 088

reflections measured in the range of $4°\langle 2\theta\langle 44°$ in the diffractometer, the 2561 reflections with $|F_o|\rangle 3\sigma|F_o|$ were used in structure determinations. Data were corrected for Lorentz and polarization effects, but the absorptions were ignored. All of the crystal data are listed in Table 1.

The crystal density measured by the floatation method in a mixture of carbon tetrachloride and methanol was $1.15 g/cm^3$.

STRUCTURE DETERMINATION AND REFINEMENTS

The structure was solved by direct method of SHELXS-86 program[16] using 519 reflections whose E values were greater than 1.6. The carbon and oxygen atoms except a carbon atom of propionyloxy group were located on the E map. The position of the carbon atom could be found in the

Table 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameter for non-hydrogen atoms of tetra-tert-butyl-tetrapropionyloxycalix(4)arene. $U_{eq}=1/3 \sum_i\sum_j U_{ij}a^*_i a^*_j a_i a_j (Å^2\times 10^{-3})$ The e. s. d. 's are in parentheses.

atom	x	y	z	Ueq	atom	x	y	z	Ueq.
C(1A)	7789(10)	5905(7)	2930(10)	.040	C(3C)	6290(11)	9106(7)	6104(11)	.048
C(2A)	8699(8)	5759(7)	2634(9)	.034	C(4C)	7258(11)	9241(7)	6985(10)	.043
C(3A)	8617(9)	5411(7)	1463(9)	.055	C(5C)	8154(11)	9168(8)	6663(12)	.053
C(4A)	7695(9)	5215(7)	607(9)	.052	C(6C)	8070(11)	9064(7)	5524(11)	.045
C(5A)	6812(9)	5346(7)	957(9)	.037	C(7C)	7332(13)	9406(9)	8268(11)	.068
C(6A)	6842(10)	5684(7)	2114(9)	.037	C(8C)	8462(16)	9493(14)	9107(13)	.127
C(7A)	7601(9)	4842(7)	-674(9)	.033	C(9C)	6954(21)	8734(12)	8416(15)	.150
C(8A)	6738(10)	5362(7)	-1393(9)	.041	C(10C)	6605(16)	10208(11)	8571(13)	.114
C(9A)	7290(10)	3990(8)	-1082(9)	.049	C(11C)	5109(9)	8757(7)	4011(10)	.041
C(10A)	8654(10)	4803(9)	-906(10)	.062	C(12C)	6678(10)	9686(7)	3263(10)	.047
C(11A)	9802(9)	5877(7)	3583(10)	.042	C(13C)	6818(14)	9597(9)	2107(11)	.081
C(12A)	7877(11)	5968(10)	4830(11)	.051	C(14C)	6868(37)	10313(14)	1953(26)	.316
C(13A)	7831(11)	6573(9)	5939(10)	.059	O(1C)	6968(6)	8953(4)	3526(6)	.041
C(14A)	7934(13)	6187(10)	6856(12)	.081	O(2C)	6383(8)	10282(5)	3858(7)	.072
O(1A)	7797(6)	6355(4)	4057(6)	.033	C(1D)	5393(9)	7240(7)	3194(10)	.041
O(2A)	7979(10)	5270(6)	4629(9)	.095	C(2D)	5430(8)	6443(7)	3188(9)	.031
C(1B)	9543(9)	7414(8)	4406(8)	.035	C(3D)	5008(9)	6335(7)	3953(10)	.041
C(2B)	9676(9)	8094(7)	5337(10)	.041	C(4D)	4523(9)	6981(6)	4671(9)	.036
C(3B)	10314(9)	8002(7)	6433(9)	.035	C(5D)	4562(10)	7747(7)	4655(10)	.042
C(4B)	10773(9)	7255(7)	6641(10)	.037	C(6D)	4999(10)	7910(7)	3947(10)	.043
C(5B)	10549(9)	6591(7)	5665(10)	.036	C(7D)	3993(11)	6808(8)	5424(11)	.050
C(6B)	9942(9)	6650(8)	4559(9)	.036	C(8D)	4814(18)	6308(14)	6191(19)	.149
C(7B)	11401(10)	7181(8)	7856(10)	.049	C(9D)	3651(20)	7577(11)	6233(18)	.151
C(8B)	12349(12)	6509(8)	7838(10)	.065	C(10D)	3067(17)	6377(15)	4662(17)	.148
C(9B)	11863(14)	7957(9)	8661(12)	.100	C(11D)	5818(10)	5710(7)	2358(10)	.048
C(10B)	10659(14)	6944(15)	8302(14)	.135	C(12D)	5177(12)	7373(9)	1369(11)	.057
C(11B)	9078(10)	8934(7)	5220(9)	.040	C(13D)	5771(14)	7485(9)	663(13)	.082
C(12B)	9433(12)	7360(8)	2508(11)	.048	C(14D)	5095(18)	7745(14)	-375(16)	.138
C(13B)	8649(12)	7462(10)	1369(11)	.084	O(1D)	5833(6)	7373(5)	2445(7)	.041
C(14B)	9138(14)	7296(11)	434(11)	.096	O(2D)	4268(10)	7322(10)	1060(9)	.127
O(1B)	8902(6)	7511(5)	3289(6)	.040	O(1S)	9880	807	7501	.153
O(2B)	10350(8)	7157(6)	2700(7)	.061	C(2S)	8979	1119	7107	.129
C(1C)	7084(11)	8996(6)	4701(9)	.032	C(3S)	8629	1129	5867	.130
C(2C)	6164(10)	8986(6)	4938(10)	.040	C(4S)	8205	1586	7852	.179

* List of observed and calculated structure factors, and positional parameters of the hydrogen atoms are available from the auther (YJP)

Table 3. Anisotropic temperature factors ($\mathring{A} \times 10^3$) for the non-hydrogen atoms of tetra-tert-butyl-tetrapropionyloxycalix[4]arene. The temperature factor expression used is $\exp[-2n^2(U_{11}h^2 a^{*2} + U_{22}k^2 b^{*2} + \cdots + 2U_{12}hka^*b^*)]$. The e. s. d. 's are in parentheses.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1A)	46(8)	26(7)	37(7)	-9(6)	12(7)	-11(6)	C(3C)	57(10)	43(8)	52(9)	14(7)	28(8)	-3(7)
C(2A)	16(7)	35(7)	36(7)	1(6)	2(6)	-1(6)	C(4C)	43(9)	42(8)	43(8)	20(7)	10(7)	0(7)
C(3A)	39(8)	42(7)	30(7)	6(6)	25(6)	2(6)	C(5C)	50(10)	44(9)	60(10)	13(7)	10(8)	-12(7)
C(4A)	34(7)	39(7)	31(7)	16(6)	13(6)	-5(6)	C(6C)	68(11)	28(7)	36(8)	15(6)	13(8)	4(7)
C(5A)	23(7)	59(8)	33(7)	20(6)	-5(6)	-25(6)	C(7C)	100(13)	70(11)	36(8)	22(8)	20(9)	-7(10)
C(6A)	51(9)	39(7)	27(7)	10(6)	21(7)	-4(7)	C(8C)	120(17)	226(24)	41(10)	51(13)	16(11)	-29(17)
C(7A)	26(7)	40(8)	31(7)	3(6)	11(6)	-6(6)	C(9C)	287(31)	128(18)	71(12)	51(12)	62(16)	-54(19)
C(8A)	50(9)	48(8)	26(7)	1(6)	19(6)	-9(7)	C(10C)	177(20)	96(14)	53(10)	12(10)	66(12)	50(14)
C(9A)	52(9)	59(9)	21(7)	-4(6)	9(6)	-6(6)	C(11C)	46(8)	38(7)	40(7)	11(6)	26(6)	11(6)
C(10A)	54(9)	83(10)	31(7)	-28(7)	26(7)	-19(8)	C(12C)	71(10)	24(7)	38(8)	-1(6)	16(7)	-8(7)
C(11A)	38(8)	37(7)	43(7)	-12(6)	21(6)	-12(6)	C(13C)	161(17)	59(10)	46(9)	20(8)	62(10)	0(11)
C(12A)	50(9)	63(10)	45(9)	28(9)	16(7)	0(8)	C(14C)	783(80)	89(17)	252(32)	-19(19)	406(46)	-73(30)
C(13A)	81(11)	85(11)	25(7)	7(7)	37(7)	-14(9)	O(1C)	52(6)	31(5)	40(5)	5(4)	16(4)	-8(4)
C(14A)	104(14)	104(13)	48(9)	12(9)	41(9)	-22(11)	O(2C)	127(6)	44(6)	62(7)	16(5)	61(5)	12(6)
O(1A)	52(5)	26(4)	23(4)	-6(4)	24(4)	-5(4)	C(1D)	46(6)	41(8)	43(7)	26(6)	11(6)	-4(7)
O(2A)	184(13)	48(7)	61(7)	26(6)	55(7)	13(8)	C(2D)	23(7)	53(8)	20(6)	-1(6)	10(5)	-19(6)
C(1B)	27(7)	67(9)	12(6)	15(6)	2(5)	-7(7)	C(3D)	43(8)	38(8)	41(7)	13(6)	1(6)	-20(7)
C(2B)	30(8)	38(8)	40(8)	-2(6)	11(6)	2(6)	C(4D)	54(9)	15(7)	33(7)	3(6)	25(6)	22(6)
C(3B)	24(7)	36(8)	31(7)	-7(6)	4(6)	-13(6)	C(5D)	40(8)	41(8)	42(8)	7(6)	22(7)	10(7)
C(4B)	39(8)	32(8)	38(7)	16(6)	11(6)	7(6)	C(6D)	45(8)	32(8)	49(8)	17(7)	16(7)	11(7)
C(5B)	29(7)	34(8)	50(8)	11(7)	17(6)	-3(6)	C(7D)	59(10)	70(10)	45(8)	35(8)	35(7)	10(8)
C(6B)	24(7)	55(9)	28(7)	13(6)	2(5)	-11(6)	C(8D)	175(22)	179(21)	176(21)	124(18)	135(19)	65(18)
C(7B)	51(9)	50(8)	30(7)	16(7)	3(7)	14(7)	C(9D)	280(30)	81(13)	167(20)	13(14)	195(22)	11(16)
C(8B)	80(11)	65(10)	33(8)	5(7)	19(7)	10(9)	C(10D)	139(19)	265(28)	107(15)	34(17)	69(15)	-121(20)
C(9B)	136(16)	49(10)	38(9)	-3(8)	-38(10)	-7(10)	C(11D)	45(9)	54(8)	53(8)	-4(7)	43(7)	-3(7)
C(10B)	95(15)	290(29)	62(11)	100(16)	12(11)	-46(7)	C(12D)	53(10)	85(11)	34(9)	15(8)	9(8)	-22(9)
C(11B)	59(9)	40(8)	23(6)	-11(6)	26(6)	-13(7)	C(13D)	133(16)	84(12)	59(10)	19(9)	45(11)	-47(11)
C(12B)	43(10)	56(9)	45(8)	13(7)	15(8)	-7(8)	C(14D)	167(22)	206(24)	89(15)	67(16)	57(15)	-48(18)
C(13B)	87(10)	121(14)	28(8)	26(9)	9(8)	10(11)	O(1D)	49(6)	40(5)	40(5)	3(4)	27(5)	-8(4)
C(14B)	125(15)	127(15)	25(8)	25(9)	3(9)	-27(13)	O(2D)	72(9)	264(18)	73(8)	97(10)	-21(7)	-70(10)
O(1B)	34(5)	46(5)	34(5)	5(4)	8(4)	-8(4)	O(1S)	176(16)	85(10)	123(11)	10(8)	-21(11)	-21(10)
O(2B)	51(7)	82(7)	55(6)	29(5)	21(6)	1(6)	C(2S)	152(22)	53(12)	154(20)	51(13)	-19(17)	-47(14)
C(1C)	69(10)	9(6)	23(7)	11(5)	20(7)	3(6)	C(3S)	168(21)	73(13)	138(18)	44(13)	2(16)	-56(14)
C(2C)	66(10)	21(7)	52(8)	8(6)	36(8)	-12(7)	C(4S)	235(23)	113(18)	216(21)	-33(14)	150(12)	-54(16)

difference Fourier map.

The refinement was carried out by the least-squares method using the program SHELX-76[17] and XTAL.[18] Three cycles of isotropic block-diagonal least-squares refinements decreased R value ($R = \Sigma|F_o - F_c|/\Sigma|F_o|$) from 0.39 to 0.19 for reflections with $F > 4\sigma(F)$. An acetone molecule was found in the difference Fourier map. And then anisotropic thermal parameters were introduced for the carbon and oxygen atoms. After three cycles of anisotropic refinements, R reduced

to 0.10. In the difference Fourier map calculated after anisotropic refinements for non-hydrogen atoms, forty seven hydrogen atoms could be identified. But, any hydrogen atoms attached to the acetone molecule could not be found. The remaining hydrogen atoms except hydrogen atoms attached to the acetone molecule were geometrically fixed on the assumption that C-H=1.08 $\mathring{A}$ and $\angle$H-C-H=109°.

In the final refinement, the positional parameters of all atoms except the hydrogen atoms

and the acetone molecule, the anisotropic thermal parameters for the carbon and oxygen atoms and isotropic thermal parameters for the hydrogen atoms were refined, the positional parameters of the hydrogen atoms and the acetone molecule kept fixed. The final R and Rw values were 0.084 and 0.088 respectively, for the observed reflections.

In the final cycle, $(\Delta/\sigma)_{max}$ for positional and temperature parameters are 0.60 and 0.63 respectively. Final difference Fourier map showed maximum and minimum peaks 0.34 and −0.32 e Å^{-3}. All the atomic scattering factors are from the International Tables of X-ray Crystallography.[19]

The final positional coordinates and thermal parameters for the non-hydrogen atoms are given in Table 2 and Table 3.

RESULTS AND DISCUSSION

The molecular conformation of tetra-tert-butyl-tetrapropionyloxycalix[4]arene, which is drawn by the ORTEP programs[20], is depicted in Figure 2. The bond distances and angles with their estimated standard deviations are listed in Table 4 and Table 5 respectively. These values are mainly as expected for the type of bonds involved.

The dimensions of the calixarene are for the most part in accord with anticipated values. The aromatic C_{sp}^2–C_{sp}^2 distances vary from 1.355(16) Å to 1.411(16) Å with an average value of 1.386 Å and C_{sp}^2–C_{sp}^3 distances vary from 1.484(19) Å to 1.546(16) Å. The C=O distances are 1.153(19) Å, 1.173(18) Å, 1.161(15) Å and 1.169(19) Å respectively for the units A, B, C and D in good agreement with the usual value. The C(1)–O(1) bonds have values of 1.400(13) Å, 1.417(12) Å, 1.437(12) Å and 1.412(12) Å for the units A, B, C and D respectively.

The configuration of the molecule from the X-ray crystallographic investigation has the partial cone conformation as shown in Figure 2; three tert-butylphenyls are down and a tert-butylphenyl is up. The down tert-butylphenyls are splayed out from the central axis.

Selected torsion angles are given in Table 6. The conformation of the propionyloxy groups may be conveniently described by the torsion angles C(1)–O(1)–C(12)–C(13) which are −178.1°, 178.2°,

Table 4. Bond lengths (Å) for tetra-tert-butyl-tetrapropionyloxycalix[4]arene. The e. s. d. 's are in parenthese.

C(1A)	– C(2A)	1.378(15)	C(1A)	– C(6A)	1.370(17)	C(1C)	– C(6C)	1.370(19)	C(1C) – O(1C)	1.437(12)
C(1A)	– O(1A)	1.400(13)	C(2A)	– C(3A)	1.396(15)	C(2C)	– C(3C)	1.392(17)	C(2C) – C(11C)	1.526(17)
C(2A)	– C(11A)	1.551(15)	C(3A)	– C(4A)	1.355(16)	C(3C)	– C(4C)	1.392(19)	C(4C) – C(5C)	1.399(18)
C(4A)	– C(5A)	1.385(15)	C(4A)	– C(7A)	1.526(15)	C(4C)	– C(7C)	1.546(16)	C(5C) – C(6C)	1.378(18)
C(5A)	– C(6A)	1.397(15)	C(6A)	– C(11D)	1.532(16)	C(7C)	– C(8C)	1.526(25)	C(7C) – C(9C)	1.486(23)
C(7A)	– C(8A)	1.523(16)	C(7A)	– C(9A)	1.521(17)	C(7C)	– C(10C)	1.548(25)	C(11C) – C(6D)	1.505(15)
C(7A)	– C(10A)	1.556(16)	C(11A)	– C(6B)	1.506(17)	O(1C)	– C(12C)	1.372(13)	O(2C) – C(12C)	1.161(15)
O(1A)	– C(12A)	1.341(14)	O(2A)	– C(12A)	1.153(19)	C(12C)	– C(13C)	1.522(16)	C(13C) – C(14C)	1.357(26)
C(12A)	– C(13A)	1.484(19)	C(13A)	– C(14A)	1.495(17)	C(1D)	– C(2D)	1.387(16)	C(1D) – C(6D)	1.397(17)
C(1B)	– C(2B)	1.374(17)	C(1B)	– C(6B)	1.376(18)	C(1D)	– O(1D)	1.412(12)	C(2D) – C(3D)	1.392(14)
C(1B)	– O(1B)	1.417(12)	C(2B)	– C(3B)	1.392(16)	C(2D)	– C(11D)	1.508(17)	C(3D) – C(4D)	1.411(16)
C(2B)	– C(11B)	1.536(17)	C(3B)	– C(4B)	1.383(16)	C(4D)	– C(5D)	1.367(14)	C(4D) – C(7D)	1.542(15)
C(4B)	– C(5B)	1.394(17)	C(4B)	– C(7B)	1.508(16)	C(5D)	– C(6D)	1.388(15)	C(7D) – C(8D)	1.514(26)
C(5B)	– C(6B)	1.378(16)	C(7B)	– C(8B)	1.537(20)	C(7D)	– C(9D)	1.504(25)	C(7D) – C(10D)	1.472(25)
C(7B)	– C(9B)	1.521(19)	C(7B)	– C(10B)	1.523(19)	O(1D)	– C(12D)	1.338(16)	O(2D) – C(12D)	1.169(19)
C(11B)	– C(6C)	1.515(18)	O(1B)	– C(12B)	1.373(14)	C(12D)	– C(13D)	1.506(19)	C(13D) – C(14D)	1.459(25)
O(2B)	– C(12B)	1.173(18)	C(12B)	– C(13B)	1.496(19)	O(1S)	– C(2S)	1.214	C(2S) – C(3S)	1.488
C(13B)	– C(14B)	1.502(18)	C(1C)	– C(2C)	1.405(17)	C(2S)	– C(4S)	1.595		

Table 5. Bond Angles(°) for tetra-tert-butyl-tetrapropionyloxycalix[4]arene.
The e. s. d. 's are in parenthese.

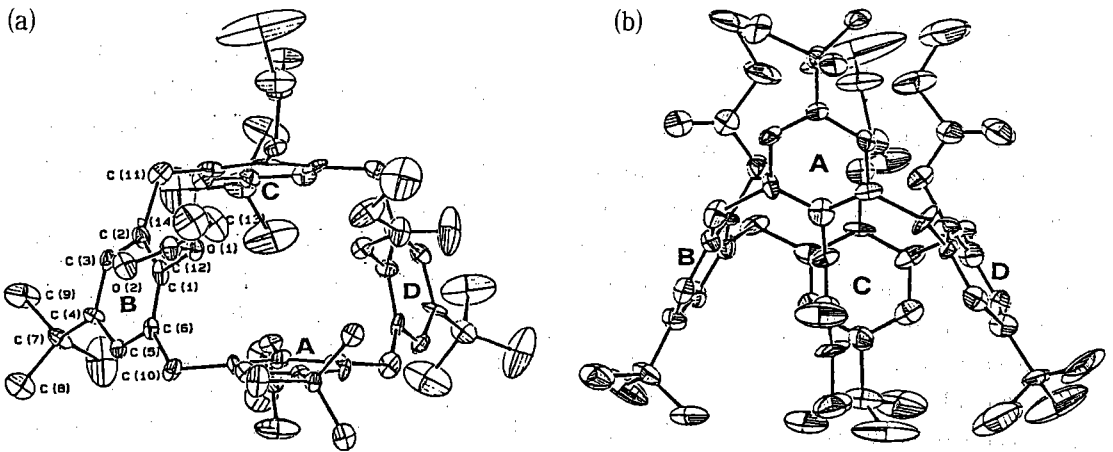|			
C(3A) – C(2A) – C(1A) 117.9(10)	C(4A) – C(3A) – C(2A) 123.7(10)	C(5C) – C(6C) – C(1C) 117.8(12)	C(6C) – C(11B) – C(2B) 108.7(9)
C(5A) – C(4A) – C(3A) 116.1(10)	C(5A) – C(6A) – C(1A) 118.0(11)	C(6C) – C(1C) – C(2C) 124.0(11)	C(6C) – C(5C) – C(4C) 121.5(12)
C(6A) – C(1A) – C(2A) 121.2(10)	C(6A) – C(5A) – C(4A) 123.0(10)	C(7C) – C(4C) – C(3C) 119.8(12)	C(7C) – C(4C) – C(5C) 122.1(12)
C(7A) – C(4A) – C(3A) 123.8(10)	C(7A) – C(4A) – C(5A) 120.1(9)	C(8C) – C(7C) – C(4C) 112.7(12)	C(9C) – C(7C) – C(4C) 110.2(12)
C(8A) – C(7A) – C(4A) 109.0(9)	C(9A) – C(7A) – C(4A) 110.0(9)	C(9C) – C(7C) – C(8C) 108.2(14)	C(10C) – C(7C) – C(4C) 107.2(11)
C(9A) – C(7A) – C(8A) 108.6(9)	C(10A) – C(7A) – C(4A) 112.4(9)	C(10C) – C(7C) – C(8C) 109.1(13)	C(10C) – C(7C) – C(9C) 109.5(15)
C(10A) – C(7A) – C(8A) 107.7(9)	C(10A) – C(7A) – C(9A) 109.1(10)	C(11C) – C(2C) – C(1C) 124.6(10)	C(11C) – C(2C) – C(3C) 119.3(11)
C(11A) – C(2A) – C(1A) 121.0(9)	C(11A) – C(2A) – C(3A) 120.7(9)	O(1C) – C(1C) – C(2C) 117.5(10)	O(1C) – C(1C) – C(6C) 118.5(11)
O(1A) – C(1A) – C(2A) 119.9(10)	O(1A) – C(1A) – C(6A) 118.6(10)	C(13C) – C(12C) – O(1C) 110.2(10)	C(13C) – C(12C) – O(2C) 126.2(11)
O(2A) – C(12A) – O(1A) 123.2(12)	C(12A) – O(1A) – C(1A) 119.5(9)	C(14C) – C(13C) – C(12C) 113.5(17)	C(1D) – C(6D) – C(11C) 120.3(10)
C(13A) – C(12A) – O(1A) 109.3(12)	C(13A) – C(12A) – O(2A) 127.5(13)	C(2D) – C(11D) – C(6A) 120.7(9)	C(3D) – C(2D) – C(1D) 116.2(10)
C(14A) – C(13A) – C(12A) 112.6(13)	C(1B) – C(6B) – C(11A) 124.1(9)	C(4D) – C(3D) – C(2D) 123.4(10)	C(5D) – C(4D) – C(3D) 116.3(10)
C(3B) – C(2B) – C(1B) 118.4(10)	C(4B) – C(3B) – C(2B) 123.2(10)	C(5D) – C(6D) – C(11C) 122.9(10)	C(5D) – C(6D) – C(1D) 116.7(10)
C(5B) – C(4B) – C(3B) 114.8(10)	C(5B) – C(6B) – C(11A) 118.1(11)	C(6D) – C(11C) – C(2C) 108.3(9)	C(6D) – C(1D) – C(2D) 123.2(10)
C(5B) – C(6B) – C(1B) 117.8(10)	C(6B) – C(11A) – C(2A) 119.8(9)	C(6D) – C(5D) – C(4C) 123.9(11)	C(7D) – C(4D) – C(3D) 120.4(9)
C(6B) – C(1B) – C(2B) 121.2(10)	C(6B) – C(5B) – C(4B) 124.3(11)	C(7D) – C(4D) – C(5D) 123.3(10)	C(8D) – C(7D) – C(4D) 108.0(12)
C(7B) – C(4B) – C(3B) 121.3(10)	C(7B) – C(4B) – C(5B) 123.7(10)	C(9D) – C(7D) – C(4D) 111.9(12)	C(9D) – C(7D) – C(8D) 106.3(14)
C(8B) – C(7B) – C(4B) 110.5(9)	C(9B) – C(7B) – C(4B) 112.4(11)	C(10D) – C(7D) – C(4D) 109.4(12)	C(10D) – C(7D) – C(8D) 111.5(15)
C(9B) – C(7B) – C(8B) 106.4(10)	C(10B) – C(7B) – C(4B) 107.1(10)	C(10D) – C(7D) – C(9D) 109.8(15)	C(11D) – C(6A) – C(1A) 126.0(10)
C(10B) – C(7B) – C(8B) 108.6(13)	C(10B) – C(7B) – C(9B) 111.8(12)	C(11D) – C(6A) – C(5A) 115.8(10)	C(11D) – C(2D) – C(1D) 124.1(9)
C(11B) – C(2B) – C(1B) 122.1(10)	C(11B) – C(2B) – C(3B) 119.3(10)	C(11D) – C(2D) – C(3D) 119.5(10)	O(1D) – C(1D) – C(2D) 117.7(9)
O(1B) – C(1B) – C(2B) 118.3(11)	O(1B) – C(1B) – C(6B) 120.3(9)	O(1D) – C(1D) – C(6D) 119.0(10)	O(2D) – C(12D) – O(1D) 123.6(13)
O(2B) – C(12B) – O(1B) 125.0(11)	C(12B) – O(1B) – C(1B) 115.5(9)	C(12D) – O(1D) – C(1D) 116.5(9)	C(13D) – C(12D) – O(1D) 110.2(12)
C(13B) – C(12B) – O(1B) 109.1(11)	C(13B) – C(12B) – O(2B) 125.8(12)	C(13D) – C(12D) – O(2D) 126.2(13)	C(14D) – C(13D) – C(12D) 114.6(15)
C(14B) – C(13B) – C(12B) 113.9(12)	C(1C) – C(6C) – C(11B) 123.0(11)	C(3S) – C(2S) – O(1S) 116.5	
C(3C) – C(2C) – C(1C) 115.7(11)	C(4C) – C(3C) – C(2C) 122.5(12)	C(4S) – C(2S) – C(3S) 118.6	
C(5C) – C(4C) – C(3C) 118.0(11)	C(5C) – C(6C) – C(11B) 118.8(11)		C(4S) – C(2S) – O(1S) 124.6

(a)

(b)

Fig. 2. a. Molecular conformation with atomic numbering in tetra-tert-butyl-tetrapropionyloxycalix[4]arene.
b. Molecular conformation of Tetra-tert-butyl-tetra-propionyloxycalix[4]arene seen from different direcrions.

Table 6. Selected torsion angles (°) in tetra-tert-bytyl-tetrapropionyloxycalix[4]arene. The e. s. d. 's are in parenthese.

(1) The 16-Membered Macrocyclic Ring

C(6A)	− C(1A)	− C(2A)	− C(11A)	−169.8(17)
C(1A)	− C(2A)	− C(11A)	− C(6B)	−48.8(11)
C(2A)	− C(11A)	− C(6B)	− C(1B)	−44.4(11)
C(11A)	− C(6B)	− C(1B)	− C(2B)	178.4(18)
C(6B)	− C(1B)	− C(2B)	− C(11B)	−169.0(17)
C(1B)	− C(2B)	− C(11B)	− C(6C)	93.6(13)
C(2B)	− C(11B)	− C(6C)	− C(1C)	−103.3(14)
C(11B)	− C(6C)	− C(1C)	− C(2C)	169.5(19)
C(6C)	− C(1C)	− C(2C)	− C(11C)	−168.2(18)
C(1C)	− C(2C)	− C(11C)	− C(6D)	103.3(13)
C(2C)	− C(11C)	− C(6D)	− C(1D)	−89.6(12)
C(11C)	− C(6D)	− C(1D)	− C(2D)	172.3(17)
C(6D)	− C(1D)	− C(2D)	− C(11D)	178.0(17)
C(1D)	− C(2D)	− C(11D)	− C(6A)	45.2(11)
C(2D)	− C(11D)	− C(6A)	− C(1A)	45.6(12)
C(11D)	− C(6A)	− C(1A)	− C(2A)	171.4(18)

(2) The Propionyloxy Group

C(1A)	− O(1A)	− C(12A)	− C(13A)	−178.1(15)
O(1A)	− C(12A)	− C(13A)	− C(14A)	−179.1(16)
C(1B)	− O(1B)	− C(12B)	− C(13B)	178.2(14)
O(1B)	− C(12B)	− C(13B)	− C(14B)	−178.9(16)
C(1C)	− O(1C)	− C(12C)	− C(13C)	167.5(13)
O(1C)	− C(12C)	− C(13C)	− C(14C)	−160.9(21)
C(1D)	− O(1D)	− C(12D)	− C(13D)	−177.6(15)
O(1D)	− C(12D)	− C(13D)	− C(14D)	−161.9(18)

167.5° and −177.6° respectively for the units A, B, C and D indicates an anti conformation. And the torsion angles O(1)−C(12)−C(13)−C(14) are −179.1°, −178.9°, −160.9° and −161.9° respectively for the units A, B, C and D. It is also an anti conformation. This anti conformation not only provides the stable dihedral angle but also makes partial cone most compact so that they can efficiently pack in the crystal lattice.

The phenolic units A, B, C and D make angles of 121.7°, 116.1°, 74.5° and 121.0° respectively with the least-squares plane defined by the four bridging methylene groups. The relative dihedral angles between two adjacent rings are; A−B=79.7°, B−C =94.6°, C−D=93.9° and A−D=76.6° whereas that between two opposite rings are; A−C=163.6° and

B−D=122.4°.

Bond angles involving the bridging methylenes (∠ C2−C11−C6) are 119.8°, 108.7°, 108.3° and 120.7° for units A to D respectively, which the bridging methylenes attached to inversed A ring (∠ C(2A)−C(11A)−C(6B) and ∠ C(6A)−C (11D)−C(2D)) deviate from the value observed in other cyclic oligomers with the cone structure. This shows that the macrocycle conformation is partial cone which a tert-butylphenyl A ring is up. This is also confirmed by the torsion angles involving the bridging methylene carbon atoms (C1−C2−C11−C6) which are −48.8°, 93.6°, 103.3° and 45.2° for units A to D respectively and deviates significantly from the value observed in other cyclic oligomers where the cone structure was essentially determined by strong intramolecular hydrogen bonds.[21]

In the benzene ring, internal angles at the substituted C atoms deviated from the mean value (120°), being more than 120° at EtCOO groups(∠ C2−C1−C6) and less than 120° at tert-butyl groups (∠ C3−C4−C5), these effects being connected with the σ−electron withdrawing or releasing characters of the substituents[22]. We carefully checked several spatial atomic distances where repulsion between two atoms may take place. We found that the distance between C(14A) and C (10B) (3.821(24)Å ; CH₃ in EtCOO in the inversed A phenyl unit and CH₃ in t-Bu in the B phenyl unit) is shorter than 2-fold of a van der Waals· radius for the methyl group of 4.0 Å. The result suggests the presence of steric repulsion between these two carbons.[23] Two tert-butyl groups (C8C−C10C and C8D−C10D) and propionyloxy groups (C12−C14) show a positional disorder. Furthermore, thermal parameters are generally large, which may be characteristic of calixarene crystals.[24]

The calixarenes have the ability to receive and retain neutral organic molecules, e.g., from solvent of crystallization by imprisoning the guest inside

the discrete central cavity, i.e., true clathrate behaviour. But, they also exhibit multimolecular inclusion behaviour in which the guest species is accommodated in continuous channels of layers within the crystal lattice[25]. Figure 3 shows the molecular packing diagram along c axis. The macrocycle exists in the partial cone conformation, where the guest molecule occupies intermolecular cavities of channel type in the host lattice as shown Figure 3. The inclusion behaviour of this
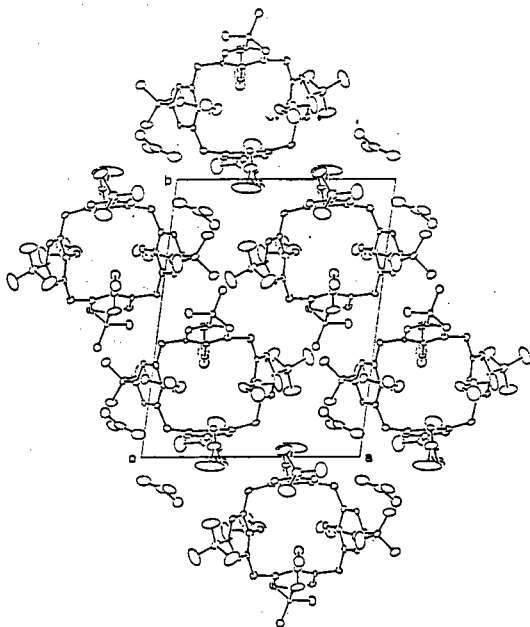

Fig. 3. The crystal structure of tetra-tert-butyl-tetrapropionyloxycalix[4]arene-acetone complex in projection down c-Axis.

compound depends on the conformational rigidity of the macrocycle. True clathrate behaviour obtained from the stability of the cage-type clathrate[7], so it is not possible to have inclusion compounds with the guest interacting inside a host cavity in this compound. At the same time intermolecular cavities suitable for accommodating the guest are formed in the crystals along the c axis. The channels are formed by piles of macrocyclic molecules with the same orientation

and with van der Waals contacts between the acetone and the t-butyl groups and propionyloxy groups which extend outside the 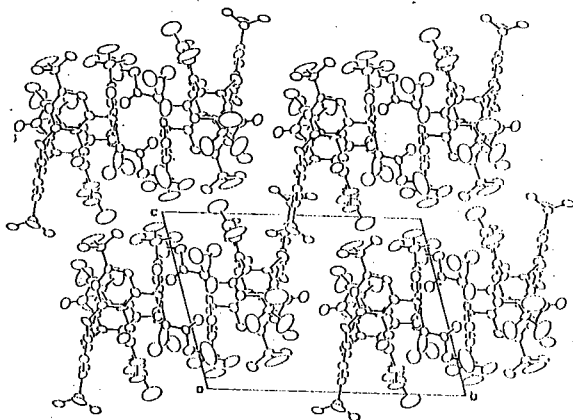macrocycle as shown Figure 4. This study confirms that, although calixarenes are able to include organic molecules, the complexes do not always have intramolecular host-guest character.

Fig. 4. The crystal structure of tetra-tert-butyl-tetrapropionyloxycalix[4]arene-acetone complex in projection down a-Axis.

ough calixarenes are able to include organic molecules, the complexes do not always have intramolecular host-guest character.

The OH group is conformationally mobile, allowing the oxygen through the annulus rotation of each phenol unit whereas O-substituents larger than Et is conformationally immobile because of steric hindrance of these substituents. It is known that unmodified p-tert-butylcalix[4]arene adopts a cone conformation because of strong hydrogen bonding interactions among the OH groups, whereas introduction of alkyl or acylsubstituents into the OH groups suppresses the conformational freedom because of steric hindrance (i.e., inhibition of the oxygen through the annulus rotation) and results in conformational isomers.

The conformational characteristics of calix[4] arenes are conveniently estimated by the splitting pattern of the ArCH₂Ar methylene protons in ¹H NMR spectroscopy[26] as shown in Table 7.

The ¹H NMR spectrum supported by Professor No shows that the acetone-insoluble compound

Table 7. ^{1}H NMR patterns for the CH_2 protons of calix[4]arenes in various conformations.

conformation	^{1}H NMR Pattern
cone	one pair of doublets
partial cone	Two pairs of doublets(ratio 1:1) or one pair of doublets and one singlet (ratio 1:1)
1,2-Alternate	one singlet and two doublet (ratio 1:1)
1,3-Alternate	one singlet

was identified as calix[4]arene in the 1,3-alternate conformation. The acetone-soluble compound was identified as the corresponding partial cone conformer[27] which data is consistent with the conformation of the molecule from the X-ray crystallographic investigation.

ACKNOWLEDGEMENT

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