

Tetrapropionyloxycalix[4]arene의 구조에 관한 연구

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Structure of Tetrapropionyloxycalix[4]arene

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요 약

Tetrapropionyloxycalix[4]arene($C_{40}H_{40}O_8$)의 결정 및 분자를 X-선 회절법으로 연구하였다. 이 결정은 단사정계이고 공간군은 $P2_1/n$ 이다. 단위세포 길이는 $a=13.921(3)$, $b=13.552(2)$, $c=19.840(5)$ Å이며 $\beta = 110.38(2)^\circ$, $Z=4$ 이다. 회절반점들의 세기는 흑연 단색화 장치가 있는 Enraf-Norius CAD-4 Diffractometer로 얻었으며, Mo-K α X-선($\lambda=0.7107$ Å)을 사용하였다. 분자구조는 직접법으로 풀었으며 최소자승법으로 정밀화하였다. 최종 신뢰도 R값은 2514개의 회절반점에 대하여 0.06이었다.

본 Calixarene은 partial cone conformation을 이루고 있어 세개의 phenyl group들과 나머지 한 개의 phenyl group 사이에 서로 다른 배향을 가지고 있다. 세 개의 phenyloxy group들은 macrocycle로 된 cavity 바깥쪽을 향하여 배열되어 있다.

Abstract

The structure of tetrapropionyloxycalix[4]arene($C_{40}H_{40}O_8$) has been studied by X-ray diffraction method. The crystal is monoclinic $a=13.921(3)$, $b=13.552(2)$, $c=19.840(5)$ Å, $\beta = 110.38(2)^\circ$, $Z=4$, $T=297K$, $D_c=1.23\text{gcm}^{-3}$, $F(000)=1376$, Systematic absences: hkl none, $h0l : h+l=2n$, $0k0 : k=2n$ define space group $P2_1/n$. The structure was solved by direct method and refined by full-matrix least-squares methods to final R of 0.06 for 2514 observed reflections. The macrocycle exists in partial cone conformation. Three propionyl groups direct toward the exterior of the macrocycle cavity.

1. Introduction

In recent years there has been growing interest in inclusion phenomena with natural and synthetic unimolecular receptors with much emphasis on the macrocyclic effect.¹⁾ Among the synthetic matrices which are able to form inclusion complexes with

several guest molecules, calixarenes, the cyclic oligomers, deserve mention.

Calixarene³⁾ are macrocyclic molecules consisting of 4 to 8 phenol units connected via methylene bridges (usually) in the ortho positions with respect to phenolic hydroxyl group. Cyclic oligomers derived from the condensation of phenols and formaldehyde, and recently named calix[n]arenes⁴⁾, are an interesting class of synthetic matrices of different sizes, interesting in their ability to form molecular complexes with neutral organic molecules and, after suitable functionalization, to act as selective catalysts. Because of their flexibility and resultant potential for modification of the cavity size and shape, calixarene of all the numerous cryptants and cavitants were chosen for initial investigations.

The presence of cavities in the calixarenes allows one to attempt to construct systems that mimic the catalytic activity of the enzymes.

Although calix[4]arenes and cyclodextrins have a similar cavity-shaped architecture, there exists a basic difference: the cyclodextrin cavity is conformationally fixed, whereas the conformational freedom still remains in the calix cavity.³⁻⁹⁾ Calix[4]arene is conformationally mobile in solution, although in the solid state it is present exclusively as a "cone" structure due to strong intramolecular hydrogen bonding.

The introduction of substituents on the phenolic groups of calixarenes produces derivatives which have different shapes and conformational mobilities depending on the nature and the number of these substituents.⁹⁾ Calix[4]arenes can easily be functionalized both at the phenolic OH groups (lower rim) and after removed of the tert-butyl groups at the para-positions of the phenol rings (upper rim).^{10,11)} Unmodified p-tert-butylcalix[4]arene adopts a cone conformation because of strong hydrogen-bonding interactions among the OH

Table 1. Summary of Crystal Data.

Formular	C ₄₀ H ₄₀ O ₈
Mw, amu	648
Crystal system	monoclinic
Space group	P2 ₁ /n
a, Å	13.921 (3)
b, Å	13.552 (2)
c, Å	19.840 (5)
β, deg	110.38 (2)
Z	4
V, Å ³	3508.45
μ (Mo-Kα), cm ⁻¹	0.91
Density, gcm ⁻³	1.23 (calc.) 1.21 (meas.)
Diffractionmeter	Enraf-Nonius CAD-4
Radiation	Mo-Kα(λ=0.7107 Å) graphite monochromator
Crystal size, mm	0.23 x 0.26 x 0.43
2θ limits, deg	4 - 46
Scan type	ω - 2θ
Scan range, deg	0.85 + 0.34tanθ
no. of observed reflection	2514 F _o > 3σ F _o
weighting scheme	1.3/(σ ² (F)+0.002(F _o) ²)
R	0.060
Rw	0.064

groups, whereas introduction of alkyl or acyl substituents into the OH group suppresses the conformational freedom because of steric hindrance (i.e. inhibition of the oxygen-through the annulus rotation) and results in conformational isomers that can be categorized in four classes; the cone, the partial cone, the 1,2-alternate and 1,3-alternate conformations¹²⁾.

All of the calixarenes containing free intraannular OH groups are conformationally mobile in solution at room temperature.¹³⁾ That is, the aryl groups of calix[4]arenes can rotate around the axis that passes through the meta carbon atoms bonded to the bridging methylene groups.

Their conformational mobility makes them ephemeral rather than permanent conformers. To convert them into constant calixes, it is necessary to freeze them in any conformation. Conversion into the

Table 2. Fractional Atomic Coordinates($\times 10^4$) and Equivalent Isotropic Thermal Parameters for Non-hydrogen Atoms of Tetrapropionyl-oxycalix[4]arene. The e. s. d.'s are in parentheses. $U_{eq} = 1/3 \sum \sum U_{ij} a_i a_j a_{ij} (\text{\AA}^2)$.

atom	x	y	z	
O(1A)	8506(2)	4405(2)	10735(2)	.055
O(2A)	10001(3)	4983(3)	11510(2)	.084
C(1A)	9023(3)	3683(4)	10487(3)	.050
C(2A)	9476(3)	2896(4)	10920(3)	.052
C(3A)	10001(4)	2234(4)	10641(3)	.064
C(4A)	10057(4)	2358(5)	9971(3)	.071
C(5A)	9543(4)	3126(4)	9546(3)	.062
C(6A)	8999(3)	3808(4)	9787(2)	.053
C(7A)	9405(4)	2748(4)	11659(2)	.058
C(8A)	9083(5)	5053(4)	11244(3)	.062
C(9A)	8432(5)	5816(5)	11415(3)	.086
C(10A)	8919(8)	6232(7)	12145(4)	.140
O(1B)	8143(2)	1095(2)	11108(2)	.058
O(2B)	8438(3)	402(3)	12178(2)	.082
C(1B)	7672(4)	1891(4)	11322(2)	.049
C(2B)	6638(4)	1899(4)	11206(2)	.052
C(3B)	6233(4)	2664(4)	11462(3)	.063
C(4B)	6847(5)	3426(4)	11826(3)	.064
C(5B)	7868(5)	3430(4)	11918(3)	.057
C(6B)	8302(4)	2681(4)	11641(2)	.052
C(7B)	5946(4)	1042(4)	10797(3)	.062
C(8B)	8547(4)	381(4)	11610(3)	.060
C(9B)	9108(6)	-366(5)	11330(4)	.091
C(10B)	9751(8)	-1002(7)	11902(5)	.152
O(1C)	6377(2)	1780(2)	9606(2)	.053
O(2C)	5951(4)	498(3)	8853(3)	.100
C(1C)	5352(4)	1863(4)	9574(3)	.053
C(2C)	4656(4)	2371(4)	9012(3)	.057
C(3C)	3660(4)	2441(5)	8994(3)	.074
C(4C)	3389(4)	2031(5)	9525(4)	.085
C(5C)	4098(5)	1574(4)	10105(4)	.076
C(6C)	5118(4)	1473(4)	10146(3)	.057
C(7C)	5004(4)	2891(4)	8461(3)	.065
C(8C)	6696(5)	1023(4)	9239(3)	.062
C(9C)	7725(4)	975(4)	9377(3)	.072
C(10C)	8016(7)	68(6)	9056(5)	.125
O(1D)	7092(2)	3118(2)	8540(2)	.061
O(2D)	6608(3)	3862(3)	7474(2)	.088
C(1D)	6657(4)	3880(4)	8827(2)	.050
C(2D)	7285(4)	4645(4)	9190(3)	.055
C(3D)	6824(4)	5404(4)	9443(3)	.060
C(4D)	5806(4)	5359(4)	9361(3)	.062
C(5D)	5231(4)	4562(5)	9046(3)	.062
C(6D)	5643(4)	3794(4)	8769(2)	.049
C(7D)	8417(4)	4652(4)	9310(3)	.062
C(8D)	7038(4)	3207(5)	7844(3)	.069
C(9D)	7537(7)	2338(7)	7643(4)	.118
C(10D)	7740(10)	2450(11)	6993(5)	.212

Table 3. Bond Lengths(\AA) for Tetrapropionyl oxycalix[4]arene. The e. s. d.'s are in parentheses.

O(1A)-C(1A)	1.402(6)	O(1A)-C(8A)	1.367(7)
O(2A)-C(8A)	1.204(8)	C(1A)-C(2A)	1.376(8)
C(1A)-C(6A)	1.387(7)	C(2A)-C(3A)	1.388(7)
C(2A)-C(7A)	1.519(7)	C(3A)-C(4A)	1.369(8)
C(4A)-C(5A)	1.373(8)	C(5A)-C(6A)	1.383(7)
C(6A)-C(7D)	1.524(7)	C(7A)-C(6B)	1.525(7)
C(8A)-C(9A)	1.490(9)	C(9A)-C(10A)	1.480(10)
O(1B)-C(1B)	1.404(6)	O(1B)-C(8B)	1.361(6)
O(2B)-C(8B)	1.186(7)	C(1B)-C(2B)	1.377(7)
C(1B)-C(6B)	1.388(7)	C(2B)-C(3B)	1.391(7)
C(2B)-C(7B)	1.516(7)	C(3B)-C(4B)	1.374(8)
C(4B)-C(5B)	1.369(9)	C(5B)-C(6B)	1.389(8)
C(7B)-C(6C)	1.517(8)	C(8B)-C(9B)	1.500(9)
C(9B)-C(10B)	1.458(12)	O(1C)-C(1C)	1.410(6)
O(1C)-C(8C)	1.354(6)	O(2C)-C(8C)	1.192(8)
C(1C)-C(2C)	1.380(8)	C(1C)-C(6C)	1.390(8)
C(2C)-C(3C)	1.378(7)	C(2C)-C(7C)	1.515(8)
C(3C)-C(4C)	1.356(9)	C(4C)-C(5C)	1.376(10)
C(5C)-C(6C)	1.401(8)	C(7C)-C(6D)	1.511(8)
C(8C)-C(9C)	1.499(8)	C(9C)-C(10C)	1.504(10)
O(1D)-C(1D)	1.414(6)	O(1D)-C(8D)	1.361(7)
O(2D)-C(8D)	1.174(7)	C(1D)-C(2D)	1.385(7)
C(1D)-C(6D)	1.380(7)	C(2D)-C(3D)	1.395(8)
C(2D)-C(7D)	1.510(7)	C(3D)-C(4D)	1.371(7)
C(4D)-C(5D)	1.360(8)	C(5D)-C(6D)	1.391(8)
C(8D)-C(9D)	1.491(11)	C(9D)-C(10D)	1.421(13)

ester or ether is the easiest way to accomplish this and it is apparent that the esters and ethers can exist any one of the four conformations. X-ray crystallography provide the surest way to discern which of these conformers is present in a particular case.

The aim of this study is elucidating the crystal structure of tetrapropionyl-oxycalix[4]arene and investigating the structural characteristics, bond distances, bond angles, torsion angles, packing mode and intermolecular interaction of this compound by X-ray diffraction method.

2. Experimental

4Tetrapropionyloxycalix[4]arene was synthesized by Professor Kwanghyun No. The monoclinic crystal were obtained by slow evaporation from a mixture of dichloromethane and acetone solution. The crystal is stable at room temperature.

Preliminary crystal data and space group were

obtained from X-ray Oscillation and Weissenberg photographs and the accurate cell constants were determined by least-squares analysis of 25 reflections in the θ range 18–23°. The crystal system was found to be monoclinic with space group $P2_1/n$. The crystal density was measured to be 1.21 g cm^{-3} by the floatation method in a mixture of methanol and carbon tetrachloride.

X-ray data collection was carried out using an Enraf Nonius CAD-4 diffractometer with graphite monochromator. Mo-K α radiation ($\lambda=0.7107 \text{ \AA}$) with

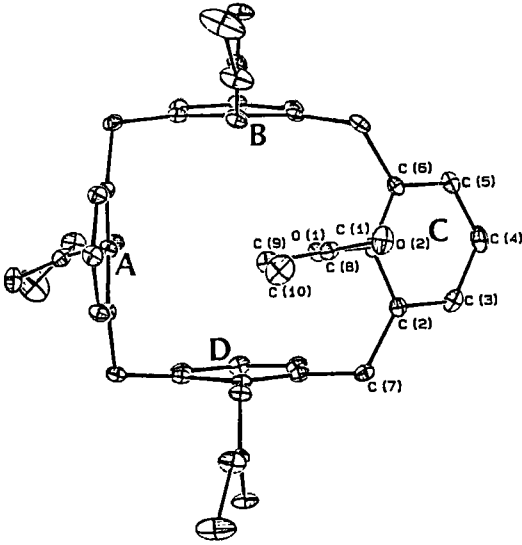


Fig 1. (a) Molecular Conformation with Atomic Numbering in Tetrapropionyloxycalix[4]arene.

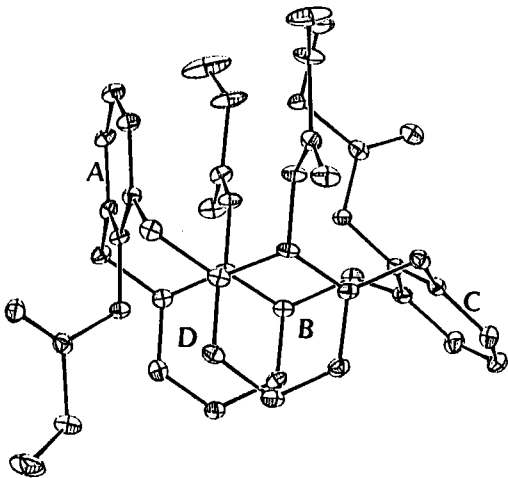


Fig 1. (b). Molecular Conformation of Tetrapropionyloxycalix[4]arene seen from different directions.

Table 4. Bond Angles (°) for Tetrapropionyloxycalix[4]arene. The e. s. d.'s are in parentheses.

O(2A)-C(8A)-O(1A)	122.2(5)	C(2A)-C(1A)-O(1A)	120.1(5)
C(3A)-C(2A)-C(1A)	116.3(5)	C(4A)-C(3A)-C(2A)	121.5(5)
C(5A)-C(4A)-C(3A)	119.7(5)	C(5A)-C(6A)-C(1A)	116.0(5)
C(6A)-C(1A)-O(1A)	115.4(4)	C(6A)-C(1A)-C(2A)	124.4(5)
C(6A)-C(5A)-C(4A)	121.7(5)	C(7A)-C(2A)-C(1A)	122.3(4)
C(7A)-C(2A)-C(3A)	121.3(5)	C(8A)-O(1A)-C(1A)	117.8(4)
C(9A)-C(8A)-O(1A)	111.5(5)	C(9A)-C(8A)-O(2A)	126.3(5)
C(10A)-C(9A)-C(8A)	112.3(6)	O(2B)-C(8B)-O(1B)	121.5(5)
C(1B)-C(6B)-C(7A)	121.8(5)	C(2B)-C(1B)-O(1B)	120.2(4)
C(3B)-C(2B)-C(1B)	117.0(5)	C(4B)-C(3B)-C(2B)	121.1(5)
C(5B)-C(4B)-C(3B)	120.0(5)	C(5B)-C(6B)-C(7A)	121.4(5)
C(5B)-C(6B)-C(1B)	116.8(5)	C(6B)-C(7A)-C(2A)	112.9(3)
C(6B)-C(1B)-O(1B)	116.3(4)	C(6B)-C(1B)-C(2B)	123.5(5)
C(6B)-C(5B)-C(4B)	121.3(5)	C(7B)-C(2B)-C(1B)	122.6(5)
C(7B)-C(2B)-C(3B)	120.4(5)	C(8B)-O(1B)-C(1B)	116.2(4)
C(9B)-C(8B)-O(1B)	110.1(5)	C(9B)-C(8B)-O(2B)	128.5(5)
C(10B)-C(9B)-C(8B)	111.6(6)	O(2C)-C(8C)-O(1C)	122.5(6)
C(1C)-C(6C)-C(7B)	121.1(5)	C(2C)-C(1C)-O(1C)	119.4(5)
C(3C)-C(2C)-C(1C)	118.2(5)	C(4C)-C(3C)-C(2C)	120.1(5)
C(5C)-C(4C)-C(3C)	121.5(5)	C(5C)-C(6C)-C(7B)	122.7(5)
C(5C)-C(6C)-C(1C)	115.9(5)	C(6C)-C(7B)-C(2B)	108.9(4)
C(6C)-C(1C)-O(1C)	117.0(5)	C(6C)-C(1C)-C(2C)	123.4(5)
C(6C)-C(5C)-C(4C)	120.6(6)	C(7C)-C(2C)-C(1C)	120.3(5)
C(7C)-C(2C)-C(3C)	121.4(5)	C(8C)-O(1C)-C(1C)	116.7(4)
C(9C)-C(8C)-O(1C)	110.7(5)	C(9C)-C(8C)-O(2C)	126.8(6)
C(10C)-C(9C)-C(8C)	112.2(5)	O(2D)-C(8D)-O(1D)	122.5(5)
C(1D)-C(6D)-C(7C)	122.9(5)	C(2D)-C(1D)-O(1D)	118.4(4)
C(2D)-C(7D)-C(6A)	113.1(4)	C(3D)-C(2D)-C(1D)	116.9(5)
C(4D)-C(3D)-C(2D)	120.7(5)	C(5D)-C(4D)-C(3D)	120.6(5)
C(5D)-C(6D)-C(7C)	120.0(5)	C(5D)-C(6D)-C(1D)	117.0(5)
C(6D)-C(7C)-C(2C)	112.0(4)	C(6D)-C(1D)-O(1D)	118.3(4)
C(6D)-C(1D)-C(2D)	123.3(5)	C(6D)-C(5D)-C(4D)	121.2(5)
C(7D)-C(6A)-C(1A)	122.5(4)	C(7D)-C(6A)-C(5A)	121.5(4)
C(7D)-C(2D)-C(1D)	121.5(5)	C(7D)-C(2D)-C(3D)	121.6(5)
C(8D)-O(1D)-C(1D)	117.6(4)	C(9D)-C(8D)-O(1D)	109.6(5)
C(9D)-C(8D)-O(2D)	127.8(6)	C(10D)-C(9D)-C(8D)	114.7(9)

a colorless crystal of dimension 0.23 x 0.26 x 0.43 mm. The intensity data were collected using ω - 2θ scan mode with an ω -scan width of $(0.8 + 0.34\tan \theta)^\circ$

The intensities of three standard reflections (8 2 $\bar{2}$), (4 4 $\bar{9}$), (3 $\bar{2}$ $\bar{9}$) were measured every 6000 seconds. Data were collected for a total 3595 reflections of which 3592 were nonzero and the 2514 reflections with the $|F_o| > 3\sigma|F_o|$ were used in the structure determinations and refinement. Data were corrected for Lorentz and polarization factors, but absorption was ignored. All of the crystal data are listed in Table 1.

The structure was solved by direct method of the program SHELXS-86¹⁴ using 895 reflections whose

$|E|$ values were greater than 1.2. All the nonhydrogen atoms were located on the resulting E-map.

The refinement was carried out in the two blocks of full-matrix least-squares using the program SHELX-76.¹⁵ Two cycles of isotropic full-matrix least-squares refinements lowered R value ($R = \sum|F_o - F_c|/\sum|F_o|$) from 0.28 to 0.13 for reflections with $F > 4\sigma|F_o|$. After eight cycles of anisotropic refinement of the nonhydrogen atomic positions, the most of hydrogen atoms could be obtained on the difference map ($R = 0.093$). The remaining hydrogen atoms were included in the later refinement in the geometrically calculated positions. In the final cycle the positional parameters of all atoms, anisotropic temperature factor for the nonhydrogen atoms and isotropic thermal parameters for the hydrogen atoms were refined. The final R and R_w values were 0.060 and 0.064 respectively for the 2514 reflections, in the final refinement, $(\Delta/\sigma)_{\max}$ values for positional and temperature parameters are 0.128 and 0.319 respectively. Final difference Fourier map showed maximum and minimum electron densities of 0.21 and $-0.19e\text{\AA}^{-3}$ respectively. All the atomic scattering factors are from the International Tables of X-Ray Crystallography.¹⁶ The final positional coordinates for the nonhydrogen atoms are given in Table 2. The thermal parameters for the nonhydrogen atoms, the atomic coordinates of hydrogen atoms and the structure factor tables are available from the author(YJP).

3. Results and Discussion

The molecular conformation of tetrapropionyloxy-calix[4]arene which is drawn by the ORTEP programs¹⁷ is depicted in Figure 1. The bond distances and angles with their estimated standard deviations are listed in Table 3 and 4 respectively.

Table 5. Selected Torsion Angles($^\circ$) in Tetrapropionyl-oxycalix[4]arene. The e. s. d.'s are in parentheses.

(1) The 16-Membered Macrocyclic Ring	
C(6A)-C(1A)-C(2A)-C(7A)	-174.7(8)
C(1A)-C(2A)-C(7A)-C(6B)	57.7(5)
C(2A)-C(7A)-C(6B)-C(1B)	67.5(5)
C(7A)-C(6B)-C(1B)-C(2B)	-170.6(8)
C(6B)-C(1B)-C(2B)-C(7B)	124.3(8)
C(1B)-C(2B)-C(7B)-C(6C)	-120.1(6)
C(2B)-C(7B)-C(6C)-C(1C)	68.5(6)
C(7B)-C(6C)-C(1C)-C(2C)	-171.8(8)
C(6C)-C(1C)-C(2C)-C(7C)	171.8(8)
C(1C)-C(2C)-C(7C)-C(6D)	-71.0(6)
C(2C)-C(7C)-C(6D)-C(1D)	116.7(6)
C(7C)-C(6D)-C(1D)-C(2D)	-171.5(8)
C(6D)-C(1D)-C(2D)-C(7D)	173.2(8)
C(1D)-C(2D)-C(7D)-C(6A)	-64.3(5)
C(2D)-C(7D)-C(6A)-C(1A)	-59.6(5)
C(7D)-C(6A)-C(1A)-C(2A)	175.2(8)
(2) The Propionyloxy Group	
C(1A)-O(1A)-C(8A)-C(9A)	176.0(6)
O(1A)-C(8A)-C(9A)-C(10A)	154.8(8)
C(1B)-O(1B)-C(8B)-C(9B)	-174.6(6)
O(1B)-C(8B)-C(9B)-C(10B)	154.8(8)
C(1C)-O(1C)-C(8C)-C(9C)	-174.8(6)
O(1C)-C(8C)-C(9C)-C(10C)	172.7(7)
C(1D)-O(1D)-C(8D)-C(9D)	179.8(7)
O(1D)-C(8D)-C(9D)-C(10D)	-166.3(10)

The configuration of tetrapropionyloxy-calix[4]arene from the X-ray crystallographic investigation is the partial cone conformer as shown in Figure 1; three propionyloxy groups are up and one propionyloxy group is down. The up propionyl groups direct toward the exterior of the macrocycle cavity.

In the macrocyclic ring of this compound, the aromatic $C_{sp^2} - C_{sp^2}$ distances vary from 1.356(9) Å to 1.401(7) Å with an average value of 1.376 Å and the $C_{sp^2} - C_{sp^3}$ distances vary from 1.510(7) Å to 1.525(7) Å. The C=O distances are 1.204(8) Å, 1.186(7) Å, 1.192(8) Å and 1.174(7) 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 1.402(6) Å, 1.404(6) Å, 1.410(6) Å and 1.414 Å for the units A, B, C and D respectively.

The four ester groups of this compound define a central cavity with a 3.197(5) - 3.268(5) Å separation between adjacent phenolate oxygen atoms. The molecular conformation may be defined by the angles which the four aromatic rings(A-D) make with the macrocyclic ring CH_2 groups; A(82.4°), B(93.0°), C(142.9°) and D(91.7°). These data were compared with those of tetra-tert-butyl-tetrapropionyloxycalix[4]arene¹⁸⁾ which was already solved in Table 5. The relative dihedral angles between two adjacent rings are; A-B=88.8°, B-C=89.0°, C-D=88.7° and A-D=90.8°.

In tetrapropionyloxycalix[4]arene, ring B and D are thus essentially parallel (interplanar angle 2.6°) and ring A is approximately normal to the four bridging methylene groups. Ring C is tilted so that its phenolate oxygen atom is oriented away from the cavity center. In tetra-tert-butyl-tetrapropionyloxycalix[4]arene, ring B and D are tilted so that their propionyloxy group is oriented toward the cavity, i.e. tert-butyl groups are oriented away from the cavity, because of the steric repulsion of tert-butyl groups. On the other hand,

Table 5. The Angles which the Phenolic Units(A-D) make with the Macrocyclic Ring CH_2 Groups in Tetrapropionyloxycalix[4]arene and Tetra-tert-butyl-tetrapropionyloxycalix[4]arene.

	Tetra-tert-butyl-tetrapropionyloxy-calix[4]arene (°)	Tetrapropionyloxy-calix[4]arene (°)
Ring A	121.7	82.4
Ring B	116.1	93.0
Ring C	74.5	142.9
Ring D	121.0	91.7

ring C is less flattened than that of tetrapropionyloxycalix[4]arene.

In the benzene ring, internal angles at the substituted C atoms deviated from the mean value(120°), being more than 120° at EtCOO groups($\angle C2-C1-C6$) these effects being connected with the σ -electron withdrawing or releasing characters of the substituents.¹⁹⁾ The propionyl groups (C8-C10) have the large thermal parameters which may be characteristic of calixarene crystals.²⁰⁾

Bond angles involving the bridging methylenes ($\angle C2-C7-C6$) are 112.9°, 108.9°, 112° and 113.1° for units A to D respectively. Angles at methylene bridges have values close to 112°. This shows that the macrocycle conformations, in the absence of any intramolecular hydrogen bonds, is mainly determined by steric interaction between the ester chains.¹⁹⁾

The partial cone conformation is confirmed by comparing the torsion angles involving the bridging methylene carbon atoms(C(1)-C(2)-C(7)-C(6)) which are 57.5°, -120.1°, -17.0°, 64.3° for units A to D with the values observed in other cycle oligomers where the cone structure was essentially determined by strong intramolecular hydrogen bonds.¹³⁾

Some torsional angles show the geometry around the CH_2 bridges as well as the relative positions of propionyl group versus phenolic ring planes. The torsion angle C(1)-O(1)-C(8)-C(9) are 176.0°, -

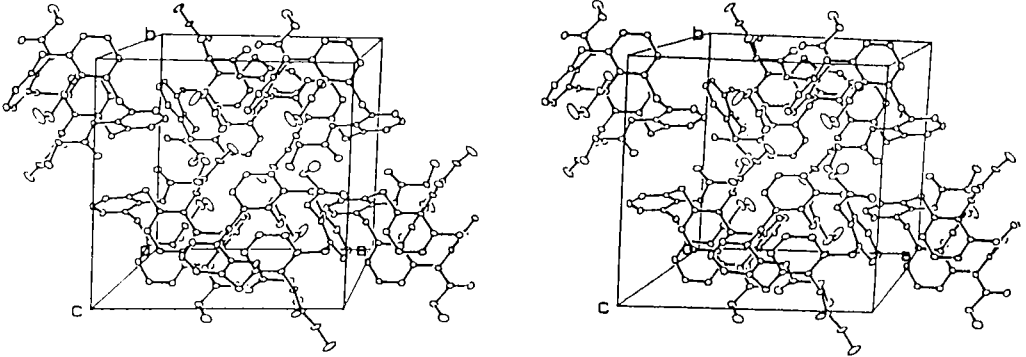


Fig 2. Molecular Packing in Tetrapropionyloxycalix[4]arene Viewed down the *c*-Axis

174.6°, -174.8° and 179.8° respectively for the units A, B, C and D and this data indicate an anti conformation. The conformation of the torsion angles O(1)-C(8)-C(9)-C(10) which are 154.8°, 154.8°, 172.7° and -166.3° respectively for the units A, B, C and D is also an anti conformation. This anti conformation makes partial cone most compact so that they can efficiently pack in the crystal lattice.²¹⁾

Figure 2 shows the stereo packing diagram viewed down *c*-axis of the molecules in the unit cell. The molecules are held by van der Waals force in the crystal.

There are several intermolecular distances of less than 4.0Å (2-fold of a van der Waals radius for the methyl group, 4.0Å = 2x2.0Å), of which shortest is C(7A)-C(7C) of 3.485Å. Geometric calculations of the molecular structure were done using GEOM program.²²⁾

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