

25,26,27,28-테트라아세트옥시시[4]에렌 · 일수화물의 결정 및 분자구조

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The Crystal and Molecular Structure of 25,26,27,28-Tetraacetoxy[4]Arene · Monohydrate

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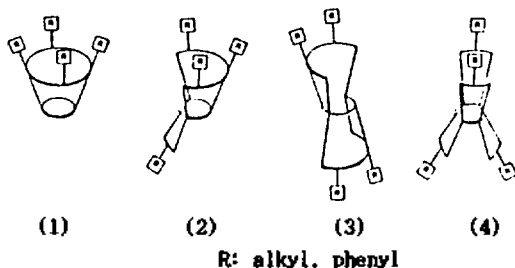
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요 약. 25,26,27,28-테트라아세트옥시시[4]에렌 · 일수화물은 사방정계의 Pbca의 공간군을 갖고 있으며 $a=14.979(4)$, $b=15.154(4)$, $c=27.890(3)$ Å, $Z=8$, $V=6330.6$ Å³, $D_c=1.28$ g·cm⁻³, $\lambda(\text{Mo } K\alpha)=0.71069$ Å, $\mu=0.86$ cm⁻¹, $F(000)=2600$ 이고, 1.0 $\sigma(I)$ 보다 큰 강도를 가진 3376개의 관측된 회절반점에 대하여 최종 R 값은 0.069이다. 직접법에 의하여 구조를 풀었으며, 계단식 대각최소자승법에 의하여 정밀화하여, 모든 C-H 결합길이(=0.96 Å) 및 메틸기와 메틸렌기는 이상적인 기하학적 구조에 맞추어 계산하였다. 큰 고리는 1,3 alternate conformation을 하고 있으며 메틸렌기의 평균 평면으로부터 벤젠고리는 각각 110.7, 68.4, 113.7 및 60.8°를 이루고 있으며, 4개의 각 아세트옥시기는 그들 자신의 벤젠고리와 각각 68.2, 97.6, 78.9 및 71.3°의 각을 만들고 있다. 반대편에 마주 위치한 벤젠고리 (1)과 (3)은 135.6°, (2)과 (4)는 135.2°의 상대적 각을 이루고 있다. 물분자는 메틸렌기를 포함하고 있는 큰고리의 평면의 z -좌표와 거의 같은 높이에 있으며, 분자내의 O(8)부터 2.942(5) Å, 타분자의 O(2)(1/2-x, -1/2+y, z)부터는 2.901 Å의 거리에 있으며, 가장 짧은 분자간 거리는 O(4)와 C(3) (1/2+x, 1/2-y, -z)의 3.193 Å이다.

ABSTRACT. 25,26,27,28-Tetraacetoxy[4]arene·monohydrate is orthorhombic, space group Pbca with $a=14.979(4)$, $b=15.154(4)$, $c=27.890(3)$ Å, $Z=8$, $V=6330.6$ Å³, $D_c=1.28$ g·cm⁻³, $(\text{Mo } K\alpha)=0.71069$ Å, $\mu=0.86$ cm⁻¹, $F(000)=2600$, and $R=0.069$ for 3376 unique observed reflections with $I>1.0$ $\sigma(I)$. The structure was solved by direct methods and refined by cascade diagonal least-squares refinement. All the C-H bond lengths(=0.96 Å), the methyl groups and the methylene groups are fixed and refined as the rigid groups with ideal geometry. The macrocycle exists in the 1,3 alternate conformation (by Conforth) making the angles of 110.7, 68.4, 113.7 and 68.8° between the benzene rings and the methylenic mean plane, and four each acetoxy groups are twisted away from their own benzene rings with the angles of 68.2, 97.6, 78.9 and 71.3°, respectively. The relative dihedral angles between two opposite side of the benzene rings are 135.6° for the rings (1) and (3) and 135.2° for (2) and (4). A water molecule which has nearly the same height of the methylenic plane of the macrocycle in the c -axis, is located within the distances of 2.942(5) Å from the O(8) atom of the carbonyl group and 2.901 Å from, another O(2)(1/2-x, -1/2+y, z). The shortest contact between the molecule is 3.193 Å from the O(4) to the C(3)(1/2+x, 1/2-y, -z).

INTRODUCTION

Many of calix[4]arenes¹ and their derivatives² (Greek, calix, chalice; arene, designating the incorporation of aromatic rings) were synthesized and their structures were investigated. The possibility of conformational isomerism in the calix[4]arenes was predicted by Megson³ and Ott and Zinke⁴. Later Conforth⁵ *et al.* pointed out that the four discrete forms could exist, referring to these as the "cone" (1), "partial cone" (2), "1,2 alternate" (3) and "1,3 alternate" (4) conformations, as shown in the Figs. below.



It is also reported that calix[4]arenes form crystalline complexes with a variety of small molecules such as chloroform, toluene⁶ and pyrimidine, indicating that the small molecules are usually located within the calix of the host molecule.

Here we report the crystal structure of 25,26,27,28-tetraacetoxy-calix[4]arene · monohydrate.

EXPERIMENTAL

25,26,27,28-Tetraacetoxy-calix[4]arene was synthesized by published procedure⁷ and transparent crystals of the compound were obtained by slow evaporation of the acetone solution at room temperature. A large block of the crystal was cut and mounted on a Nicolet R3m/E diffractometer with graphite-monochromatized Mo-K α radiation ($\lambda = 0.71069 \text{ \AA}$).

The cell constants were determined by least-squares refinement from 25 reflections within the range ($25 \leq 2\theta \leq 35^\circ$). The space group was determined to be Pbc_a on the basis of the systematic absences ($hk0$; $h = 2n$, $h0l$; $l = 2n$, $0kl$; $k = 2n$, $h00$; $h = 2n$, $0k0$; $k = 2n$, $00l$; $l = 2n$). Table 1 gives crystal data obtained. The θ - 2θ scan method ($2\theta_{\max} =$

Table 1. Crystal data

Chemical formula : C ₃₆ H ₃₂ O ₈ · H ₂ O
Molecular weight : 610.62
Unit cell parameters : $a = 14.979(4) \text{ \AA}$
$b = 15.154(4)$
$c = 27.890(3)$
$V = 6330.6 \text{ \AA}^3$
$Z = 8$
Crystal system : orthorhombic
Space group : Pbc _a
$F(000) = 2600$
$\mu = 0.86 \text{ cm}^{-1}$
$D_c = 1.28 \text{ g.cm}^{-3}$
Crystal size : $0.42 \times 0.44 \times 0.51 \text{ mm}$
$T = 298 \text{ K}$
$\lambda(\text{Mo K}\alpha) = 0.71069 \text{ \AA}$

50°) with the variable scan rates of 4.9 to 29.3°/min. was used to collect the data in the ranges $0 \leq h \leq 15$, $0 \leq k \leq 16$, $0 \leq l \leq 29$. There were no significant intensity variations for three check reflections monitored every 97 reflections. Of the 3850 measured reflections, the 3376 unique observed reflections with $I \geq 1.0 \sigma(I)$ were used. Corrections for Lorentz and polarization effects were applied to the intensity data, while no absorption or extinction correction was carried out.

Structure was solved by direct methods using 200 reflections E values of which were greater than 1.23. All the non-hydrogen atoms except for the oxygen atom of a separate water molecule were found. For refinement all C-H bond lengths were fixed at 0.96 \AA , and the methyl groups and the methylene groups were refined as rigid groups with ideal geometry. The hydrogen-atom coordinates of a separate water molecule, however, were not refined because of large diffusion of its electron density. All the non-hydrogen atoms in the molecule were refined anisotropically and the hydrogen atoms were assigned by a common Ueq of 0.076 \AA^2 . Calculations carried out by cascade block diagonal least-squares on F with the maximum $\sin\theta/\lambda = 0.534 \text{ \AA}^{-1}$ and 407 least-squares parameters, were converged with $R = 0.069$ and $wR = 0.066$, where $w = 1/(\sigma^2(F) + 0.0003 F^2)$; $\sigma^2(F)$ from statistics of counting; goodness of fit = 1.868.

In a final cycle $(\Delta/\sigma)_{\max}=0.014$ and a difference Fourier map showed the peaks; the highest 0.413, the lowest $-0.335 \text{ e}\text{\AA}^{-3}$. All atomic scattering factors were from "International Tables for X-ray Crystallography"⁸ and all calculations were performed on a Data General Eclips S140 computer using the SHELXTL 5.1 program package⁹(Nicolet Instrument Company).

RESULTS AND DISCUSSION

The final atomic coordinates and equivalent isotropic thermal parameters for non-H atoms of 25,26,27,28-tetraacetoxyalix[4]arene·monohydrate are given in Table 2. A thermal ellipsoid plot of the molecule with the atomic numbering scheme is shown in Fig. 1.

As listed in Table 3 and 4 bond lengths and bond angles in the acetoxy benzene rings well

agree with the values already reported in other compounds^{2,10-13}. The central carbon atoms (C₇, C₁₆, C₂₅, C₃₄) of the acetoxy groups have sp^2 -hybrid

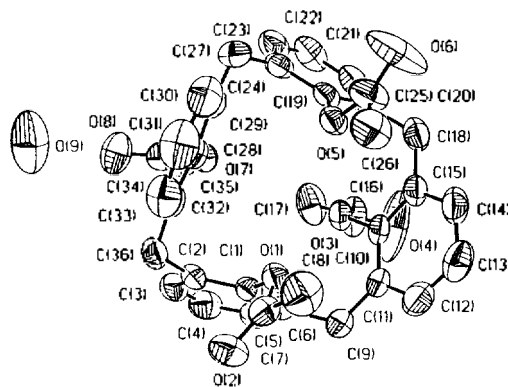


Fig. 1. A molecular conformation with the thermal ellipsoids and atomoc labelling schem for 25,26,27,28-tetraacetoxyalix[4]arene·monohydrate

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters $\times 10^3$ for the non-hydrogen atoms of 25,26,27,28-tetraacetoxyalix[4]arene·monohydrate. The e.s.d.'s are in parentheses

Atom	x	y	z	U^a	Atom	x	y	z	U^a
C(1)	4431(2)	844(2)	701(2)	44(1)	C(24)	4345(2)	3695(2)	1938(1)	54(1)
C(2)	3522(2)	769(2)	800(1)	47(1)	C(25)	6198(3)	2696(3)	2224(1)	69(2)
C(3)	2939(2)	995(2)	435(1)	60(1)	C(26)	6507(3)	1786(2)	2334(1)	76(2)
C(4)	3244(3)	1312(2)	5(1)	69(2)	C(27)	3890(3)	3114(3)	2304(1)	70(2)
C(5)	4140(3)	1402(2)	-73(1)	65(1)	C(28)	3551(2)	1760(2)	1802(1)	43(1)
C(6)	4766(2)	1160(2)	275(1)	50(1)	C(29)	3849(2)	2132(2)	2224(1)	53(1)
C(7)	5197(2)	-189(2)	1197(1)	53(1)	C(30)	4075(2)	1547(3)	2539(1)	75(2)
C(8)	5905(3)	-259(3)	1566(2)	88(2)	C(31)	4003(3)	648(3)	2529(1)	83(2)
C(9)	5755(2)	1218(2)	164(1)	63(1)	C(32)	3721(2)	315(2)	2106(1)	70(1)
C(10)	6175(2)	2495(2)	710(1)	48(1)	C(33)	3492(2)	854(2)	1728(1)	47(1)
C(11)	6355(2)	1666(2)	526(1)	53(1)	C(34)	2485(3)	2462(2)	1295(1)	57(1)
C(12)	7138	1266(3)	676(1)	73(2)	C(35)	2406(3)	3097(3)	896(1)	83(2)
C(13)	7707(3)	1666(3)	993(2)	81(2)	C(36)	3161(2)	444(2)	1271(1)	55(1)
C(14)	7494(2)	2482(3)	1173(1)	68(2)	O(1)	5063(1)	658(1)	1065(1)	52(1)
C(15)	6727(2)	2921(2)	1035(1)	53(1)	O(2)	4781(2)	-791(1)	1033(1)	73(1)
C(16)	5361(3)	3479(3)	217(1)	79(2)	O(3)	5364(1)	2898(1)	574(1)	53(1)
C(17)	4448(3)	3800(3)	113(2)	95(2)	O(4)	6010(2)	3706(3)	24(2)	177(2)
C(18)	6532(2)	3835(2)	1227(1)	66(1)	O(5)	5571(1)	2699(1)	1882(1)	49(1)
C(19)	5177(2)	3504(2)	1746(1)	46(1)	O(6)	6481(3)	3356(2)	2396(1)	141(2)
C(20)	5607(2)	4037(2)	1420(1)	54(1)	O(7)	3348(1)	2346(1)	1424(1)	49(1)
C(21)	5182(3)	4808(2)	1281(2)	70(2)	O(8)	1885(2)	2071(2)	1487(1)	84(1)
C(22)	4364(3)	5027(3)	1470(2)	79(2)	O(9)	-22(3)	2373(3)	1297(2)	174(2)
C(23)	3946(3)	4475(3)	1790(2)	75(2)					

^aEquivalent isotropic U defined as one third of the trace of the orthogonalised U tensor. ^bAnisotropic thermal parameters of the non-H atoms and atomic coordinates of hydrogen atoms are available from the first author.

Table 3. Bond lengths (Å) in the non-hydrogen atoms of 25,26,27,28-tetraacetoxy[4]arene·monohydrate. The e.s.d.'s are in parentheses

Acetoxybenzene ring (1)			
C(1)-C(2)	1.393(4)	C(2)-C(3)	1.385(5)
C(3)-C(4)	1.369(5)	C(4)-C(5)	1.367(5)
C(5)-C(6)	1.398(5)	C(6)-C(1)	1.376(5)
C(1)-O(1)	1.415(4)	C(7)-O(1)	1.350(4)
C(7)-C(8)	1.481(5)	C(7)-O(2)	1.195(4)
Acetoxybenzene ring(2)			
C(10)-C(11)	1.384(5)	C(11)-C(12)	1.384(5)
C(12)-C(13)	1.370(6)	C(13)-C(14)	1.372(6)
C(14)-C(15)	1.383(5)	C(15)-C(10)	1.384(5)
C(10)-O(3)	1.412(4)	C(16)-O(3)	1.330(5)
C(16)-C(17)	1.479(5)	C(16)-O(4)	1.164(5)
Acetoxybenzene ring(3)			
C(19)-C(20)	1.377(5)	C(20)-C(21)	1.385(5)
C(21)-C(22)	1.374(6)	C(22)-C(23)	1.374(5)
C(23)-C(24)	1.388(5)	C(24)-C(19)	1.387(5)
C(19)-O(5)	1.407(4)	C(25)-O(5)	1.338(4)
C(25)-C(26)	1.486(5)	C(25)-O(6)	1.188(5)
Acetoxybenzene ring(4)			
C(28)-C(29)	1.379(4)	C(29)-C(30)	1.400(5)
C(30)-C(31)	1.378(6)	C(31)-C(32)	1.351(5)
C(32)-C(33)	1.377(5)	C(33)-C(28)	1.391(4)
C(28)-O(7)	1.411(4)	C(34)-O(7)	1.384(4)
C(34)-C(35)	1.475(5)	C(34)-O(8)	1.203(4)
Methylene linkages			
C(6)-C(9)	1.516(5)	C(9)-C(11)	1.513(5)
C(15)-C(18)	1.515(5)	C(18)-C(20)	1.518(5)
C(24)-C(27)	1.510(5)	C(27)-C(29)	1.505(5)
C(33)-C(36)	1.503(4)	C(36)-C(2)	1.505(5)

characters which show steric hindrance effect by the $-CH_3$ and the $=C=O$ groups. It is shown that the angles of CH_3-C-O are shifted to smaller values of $111.3(3)-111.7(3)^\circ$ than expected 120° , while in contrast with these, the angles of $CH_3-C=O$ are larger to be $125.7(3)-126.7(4)^\circ$. Four methylenic linkages connecting the acetoxy benzene groups have bond lengths of $1.503(4)-1.518(5)$ Å and bond angles of $118.0(3)-119.6(3)^\circ$ which are larger than those found in other compounds ($108-111^\circ$ for p-t-butylcalix[4]arene¹⁵, $107-114^\circ$ for cyclo[tetrakis [(5-t-butyl-2-acetoxy-1,3-phenylene) methylene]] acetic acid (1:1) clathrate) (CTPA).

Table 5 gives selected torsion angles between

Table 4. Bond angles ($^\circ$) in the non-H atoms of 25,26,27,28-tetraacetoxy[4]arene·monohydrate. The e.s.d.'s are in parentheses

Acetoxybenzene ring(1)			
C(2)-C(1)-C(6)	123.7(3)	C(3)-C(2)-C(1)	116.8(3)
C(4)-C(3)-C(2)	121.3(3)	C(5)-C(4)-C(3)	120.1(5)
C(6)-C(5)-C(4)	121.5(3)	C(1)-C(6)-C(5)	116.3(3)
C(2)-C(1)-O(1)	119.7(3)	C(6)-C(1)-O(1)	116.4(3)
C(7)-O(1)-C(1)	119.0(2)	C(8)-C(7)-O(1)	111.4(3)
O(2)-C(7)-O(1)	122.9(3)	C(8)-C(7)-O(2)	125.7(3)
Acetoxybenzene ring(2)			
C(11)-C(10)-C(15)	123.3(3)	C(12)-C(11)-C(10)	116.8(3)
C(13)-C(12)-C(11)	121.8(4)	C(14)-C(13)-C(12)	119.4(4)
C(15)-C(14)-C(13)	121.6(3)	C(10)-C(15)-C(14)	117.0(3)
C(11)-C(10)-O(3)	117.3(3)	C(15)-C(10)-O(3)	119.2(3)
C(16)-O(3)-C(10)	119.4(3)	C(17)-C(16)-O(3)	111.6(3)
O(4)-C(16)-O(3)	122.5(4)	C(17)-C(16)-O(4)	125.8(4)
Acetoxybenzene ring(3)			
C(20)-C(19)-C(24)	123.6(3)	C(21)-C(20)-C(19)	117.7(3)
C(22)-C(21)-C(20)	120.4(4)	C(23)-C(22)-C(21)	120.5(4)
C(24)-C(23)-C(22)	121.1(4)	C(19)-C(24)-C(23)	116.7(3)
C(20)-C(19)-O(5)	119.4(3)	C(24)-C(19)-O(5)	117.0(3)
C(25)-O(5)-C(19)	119.3(3)	C(26)-C(25)-O(5)	111.7(3)
O(6)-C(25)-O(5)	122.4(4)	C(26)-C(25)-O(6)	125.8(4)
Acetoxybenzene ring(4)			
C(29)-C(28)-C(33)	123.4(3)	C(30)-C(29)-C(28)	116.5(3)
C(31)-C(30)-C(29)	120.8(3)	C(32)-C(31)-C(30)	120.4(4)
C(33)-C(32)-C(31)	121.7(3)	C(28)-C(33)-C(32)	117.2(3)
C(29)-C(28)-O(7)	116.7(3)	C(33)-C(28)-O(7)	119.8(3)
C(34)-O(7)-C(28)	119.2(2)	C(35)-C(34)-O(7)	111.3(3)
O(8)-C(34)-O(7)	122.0(3)	C(35)-C(34)-O(8)	126.7(4)
Methylene linkages			
C(6)-C(9)-C(11)	118.0(3)	C(15)-C(18)-C(20)	119.1(3)
C(24)-C(27)-C(29)	119.6(3)	C(2)-C(36)-C(33)	119.1(3)
C(1)-C(6)-C(9)	123.6(3)	C(5)-C(6)-C(9)	119.9(3)
C(9)-C(11)-C(10)	122.7(3)	C(9)-C(11)-C(12)	120.5(3)
C(10)-C(15)-C(18)	122.9(3)	C(14)-C(15)-C(18)	120.1(3)
C(18)-C(20)-C(19)	122.9(3)	C(18)-C(20)-C(21)	119.3(3)
C(19)-C(24)-C(27)	123.0(3)	C(23)-C(24)-C(27)	120.2(3)
C(27)-C(29)-C(28)	122.9(3)	C(27)-C(29)-C(30)	120.5(3)
C(28)-C(33)-C(36)	123.7(3)	C(32)-C(33)-C(36)	119.1(3)
C(1)-C(2)-C(36)	123.4(3)	C(3)-C(2)-C(36)	119.8(3)

atoms, and Table 6 for least-squares planes in the molecule. The mean molecular planes of the benzene groups make angles of 110.7 , 68.4 , 113.7 and 68.8° respectively with the least-squares plane defined by the four bridging methylene groups, which are alternately below and above the plane

Table 5. Selected torsion angles ($^{\circ}$) in 25,26,27,28-tetraacetoxycalix[4]arene monohydrate. The e.s.d.'s are in parentheses

(1) Benzene ring	
C(6)-C(1)-C(2)-C(3)	2.8(5)
C(1)-C(2)-C(3)-C(4)	-2.7(5)
C(2)-C(3)-C(4)-C(5)	0.8(5)
C(3)-C(4)-C(5)-C(6)	1.3(6)
C(4)-C(5)-C(6)-C(1)	-1.3(5)
C(2)-C(1)-C(6)-C(5)	-0.8(5)
C(15)-C(10)-C(11)-C(12)	-1.0(5)
C(10)-C(11)-C(12)-C(13)	0.4(6)
C(11)-C(12)-C(13)-C(14)	0.8(6)
C(12)-C(13)-C(14)-C(15)	-1.4(6)
C(13)-C(14)-C(15)-C(10)	0.9(5)
C(11)-C(10)-C(15)-C(14)	0.4(5)
C(24)-C(19)-C(20)-C(21)	0.5(5)
C(19)-C(20)-C(21)-C(22)	0.5(5)
C(20)-C(21)-C(22)-C(23)	-1.4(6)
C(21)-C(22)-C(23)-C(24)	1.3(6)
C(22)-C(23)-C(24)-C(19)	-0.3(6)
C(20)-C(19)-C(24)-C(23)	-0.6(5)
C(33)-C(28)-C(29)-C(30)	-1.9(5)
C(28)-C(29)-C(30)-C(31)	0.4(5)
C(29)-C(30)-C(31)-C(32)	0.7(5)
C(30)-C(31)-C(32)-C(33)	-0.5(6)
C(31)-C(32)-C(33)-C(28)	-0.9(5)
C(29)-C(28)-C(33)-C(32)	2.1(5)
(2) Methylenic linkages	
C(1)-C(6)-C(9)-C(11)	-50.9(5)
C(5)-C(6)-C(9)-C(11)	131.7(3)
C(6)-C(9)-C(11)-C(10)	-51.1(5)
C(6)-C(9)-C(11)-C(12)	131.3(4)
C(10)-C(15)-C(18)-C(20)	48.8(5)
C(14)-C(15)-C(18)-C(20)	-132.7(4)
C(15)-C(18)-C(20)-C(19)	49.5(5)
C(15)-C(18)-C(20)-C(21)	-133.4(4)
C(19)-C(24)-C(27)-C(29)	-47.0(5)
C(23)-C(24)-C(27)-C(29)	135.0(4)
C(24)-C(27)-C(29)-C(28)	-51.0(5)
C(24)-C(27)-C(29)-C(30)	132.5(3)
C(28)-C(33)-C(36)-C(2)	48.0(4)
C(32)-C(33)-C(36)-C(2)	-134.7(3)
C(1)-C(2)-C(36)-C(33)	51.2(4)
C(3)-C(2)-C(36)-C(33)	-130.1(3)
(3) Acetoxy group	
C(2)-C(1)-O(1)-C(7)	72.7(4)
C(6)-C(1)-O(1)-C(7)	-112.2(3)
C(8)-C(7)-O(1)-C(1)	177.7(3)
O(2)-C(7)-O(1)-C(1)	-2.9(5)

Table 5. Continued.

(3) Acetoxy group	
C(11)-C(10)-O(3)-C(16)	-97.3(4)
C(15)-C(10)-O(3)-C(16)	85.8(4)
C(17)-C(16)-O(3)-C(10)	177.5(3)
O(4)-C(16)-O(3)-C(10)	-3.8(6)
C(20)-C(19)-O(5)-C(25)	82.7(4)
C(24)-C(19)-O(5)-C(25)	-100.0(4)
C(26)-C(25)-O(5)-C(19)	177.5(3)
O(6)-C(25)-O(5)-C(19)	-5.1(5)
C(29)-C(28)-O(7)-C(34)	-109.9(3)
C(33)-C(28)-O(7)-C(34)	73.6(4)
C(35)-C(34)-O(7)-C(28)	179.8(3)
O(8)-C(34)-O(7)-C(28)	-1.1(5)

by -0.0278 , 0.0279 , -0.0523 and 0.0278 Å. The inclinations of the benzene ring with respect to the mean methylenic plane are observed in the different conformational parameters, depending on the nature of its substituents in the benzene group or on inclusion complexes: $39.3\sim 97.5^{\circ}$ in CTPA and $43.5\sim 89.5^{\circ}$ in *p*-*t*-butylcalix[4]arene tetraamide (1 : 1) KSCN. Two benzene rings which are located diametrically-ring (1) and (3), ring (2) and (4)-are tilted by 135.6 and 135.2° , respectively, and the relative dihedral angles between two adjacent benzene rings are 96.4° for the ring (1) and (2), 98.4° for (2) and (3), 98.9° for (3) and (4), 98.5° for (1) and (4).

Consequently, the molecule which has a V-shape with the angle of 135° with respect to the diametrical benzene rings consists of a 1,3 alternate conformation^{14,5} with the acetoxy benzene groups on one side and on the other side of the plane containing the bridging methylene groups of the macrocycle. However, the large pendant acetoxy group, which can make the transformation impossible, are twisted away from their own benzene rings by making the angles of 68.2 , 97.6 , 78.9 and 71.3° , respectively. It seems that tilting of the acetoxy benzene groups mentioned above are such as to increase the intramolecular separation, and to reduce hindrance between their groups in the molecule. In cyclo[tetrakis [(5-*t*-butyl-2-acetoxy-1,3-phenylene)methylene]]acetic acid (1 : 1) clathrate, these are reported to be between 82

Table 6. Least squares planes and deviations of each atom from the planes in 25,26,27,28-tetraacetyoxycalix[4]-arene·monohydrate. The equation of the plane is expressed in the form of $Ax+By+Cz=D$, where x , y and z are in Å

Atoms in plane	Atoms out of plane	Distances(Å) from best plane	Given constants	Atoms in plane	Atoms out of plane	Distances(Å) from best plane	Given constants
Benzene ring(1)				Benzene ring(4)			
C(1)		-0.010	$A = -0.369$	C(31)		-0.023	$D = 3.287$
C(2)		0.017	$B = 14.129$	C(32)		0.001	
C(3)		-0.010	$C = 10.056$	C(33)		0.008	
C(4)		-0.004	$D = 1.744$		C(34)	-1.070	
C(5)		0.012			C(35)	-0.836	
C(6)		-0.004			C(27)	-0.046	
	C(7)	0.999			C(36)	-0.020	
	C(8)	-0.753			O(7)	0.031	
	C(9)	-0.071			O(8)	-2.082	
	C(36)	-0.042		Acetoxy group(1)			
	O(1)	0.070		O(1)		-0.001	$A = 10.271$
	O(2)	-1.999		O(2)		-0.001	$B = -1.554$
Benzene ring(2)				C(7)		0.003	$C = -20.099$
C(10)		0.005	$A = 7.402$	C(8)		-0.001	$D = 2.952$
C(11)		-0.006	$B = 6.434$		C(1)	0.052	
C(12)		-0.002	$C = -21.159$		C(2)	-1.067	
C(13)		0.007	$D = 4.668$		C(6)	1.204	
C(14)		-0.007		Acetoxy group(2)			
C(15)		0.001		O(3)		0.002	$A = 1.730$
	C(16)	1.079		O(4)		0.003	$B = 11.215$
	C(17)	0.830		C(16)		-0.007	$C = 13.478$
	C(9)	0.029		C(17)		0.002	$D = 5.237$
	C(18)	0.038			C(11)	-1.298	
	O(3)	-0.048			C(10)	-0.058	
	O(4)	2.114			C(15)	1.114	
Benzene ring(3)				Acetoxy group(3)			
C(19)		0.005	$A = 6.637$	O(5)		0.004	$A = 10.504$
C(20)		-0.001	$B = 7.374$	O(6)		0.005	$B = 0.968$
C(21)		-0.005	$C = 20.998$	C(25)		-0.013	$C = -19.804$
C(22)		0.008	$D = 9.681$	C(26)		0.004	$D = 2.381$
C(23)		-0.004			C(19)	-0.062	
C(24)		-0.003			C(20)	1.087	
	C(25)	1.090			C(24)	-1.298	
	C(26)	0.856		Acetoxy group(4)			
	C(18)	0.057		O(7)		-0.002	$A = -1.331$
	C(27)	0.034		O(8)		-0.002	$B = 11.290$
	O(5)	-0.041		C(34)		0.005	$C = 18.437$
	O(6)	2.127		C(35)		-0.002	$D = 4.830$
Benzene ring(4)					C(28)	0.007	
C(28)		-0.011	$A = 14.120$		C(29)	1.165	
C(29)		0.005	$B = -0.371$		C(33)	-1.144	
C(30)		0.009	$C = -9.282$				

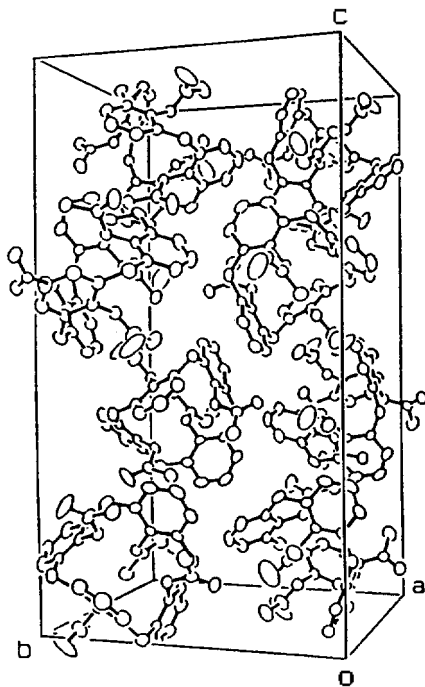


Fig. 2. The unit cell packing diagram of molecules.

and 88° . A water molecule which was found unexpectedly, occupies the void outside the macromolecular ring (probably a water molecule was picked during recrystallization of 25,26,27,28-tetraacetoxycalix(4)arene in an acetone solution). The addition of the water molecule reduced the R -values by about 0.04 in the final refinement. Its oxygen atom (O(9)), which is located at the distances of $2.942(5) \text{ \AA}$ from O(8) and $2.901(5) \text{ \AA}$ from O(2)($1/2-x, -1/2+y, z$) has nearly the same height in the z -coordinate as that of the plane of the macrocycle. Considering these distances, its large thermal parameters and no strong peaks around the O(9) atom during the final refinement, the water molecule seems to be in large thermal motion.

Fig. 2 shows a molecular packing diagram in the unit cell. The shortest contact between molecules is $3.193(5) \text{ \AA}$ from the O(4) atom to the C(3)($1/2+x, 1/2-y, -z$).

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