Structure Identification of 1,2-Disubstituted Chiral Calix[4]arene: X-Ray and NMR Analysis of 25-(3,5-Dinitrobenzoyloxy)-26-methoxy-27,28-dihydroxycalix[4]arene

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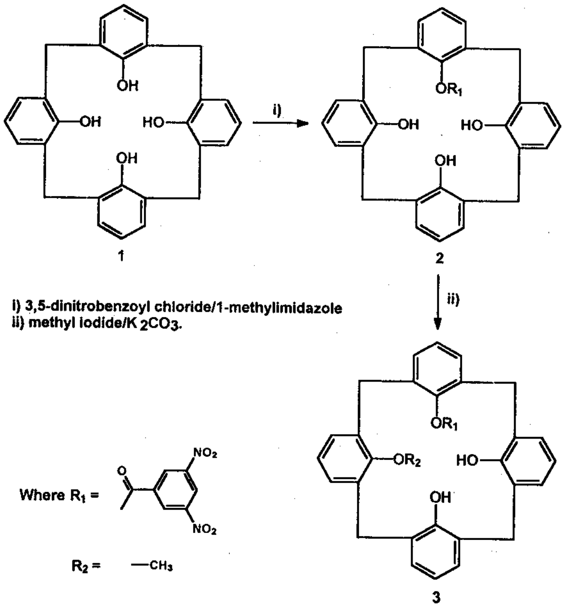
1,2-Disubstituted chiral calix[4]arene "25-(3,5-dinitrobenzoyloxy)-26-methoxy-27,28-dihydroxycalix[4]arene" was synthesized by the reaction of 25-(3,5-dinitrobenzoyloxy)-calix[4]arene with methyl iodide in the presence of K_2CO_3. Methylation was occurred at the 26-position of calix[4]arene. The partial cone conformation and 1,2-substitution were characterized based on the ^{1}H NMR, ^{13}C NMR and X-ray diffraction analysis. The crystal structure has been determined by X-ray diffraction method. The crystals are orthorhombic, Pbca, $a=10.652(1)$, $b=17.687(1)$, $c=32.247(3)$ Å, Z=8, V=6075.4(9) Å^3, $D_c=1.38$ gcm^{-3}. The intensity data were collected on an Enraf-Nonius CAD-4 Diffractometer with a graphite monochromated Cu-Kα radiation. The structure was solved by direct method and refined by full-matrix least-squares methods to a final R value of 0.050 for 2368 observed reflections. The molecule is in the partial cone conformation. It has two strong intramolecular hydrogen bonds of O(1D)-H···O(1C)-H···O(1B).

Introduction

Selective derivatization of calixarene has greatly widened the area of calixarenes in Host-Guest chemistry.[1] Several synthetic procedures for selective derivatization such as 1, 3-alkylation,[2] 1,2-alkylation,[3] monoalkylation,[4] trialkylation,[5] 1, 3-acylation,[6] and triacylation[4a] have been developed. More elegantly mixed derivatives such as alkylated as well as acylated calix[4]arenes have been developed by two step procedures.[7]

Calix[4]arenes have four phenolic units for the selective reaction sites and they could exist as a four possible conformation such as cone, partial cone, 1,3-alternate, and 1,2-alternate. Therefore calixarenes could be an excellent candidate for the chiral compounds by ultilizing selective substitution and conformational variety. Shinkai and his coworkers[8] synthesized several chiral calixarenes by selective dervatization. Recently we developed the synthetic procedure for introducing two different substituents at the lower rim of calix[4]arene by two step reaction.[9] First, 3,5-dinitrobenzoyl group was introduced at the lower rim of calix[4]arene, and then benzyl or allyl groups were introduced at the opposite side of benzoyl group selectively (called 1,3-substitution). They existed as a cone conformation. But when monobenzoylated calix[4]arene treated with methyl iodide in the presence of K_2CO_3, methyl group introduced at the adjacent position (1,2-substitution) to the benzoyl group and it existed as a partial cone conformation. Therefore it is chiral calix[4]arene. Now we report that studies on the substitution pattern and conformational features of this compound in detail with NMR and X-ray analysis.

Synthesis and NMR Studies of Chiral Calix[4]arene. The 1,2-disubstituted chiral calix[4]arene "25-(3,5-dinitrobenzoyloxy)-26-methoxy-27,28-dihydroxycalix[4]arene" was synthesized from the methylation of monobenzoylated calix[4]arene as shown in Scheme 1. We reported[9] previously that benzyl bromide, allyl bromide, and ethyl bromoacetate reacted with monobenzoylated calix[4]arene **2** in the presence of K_2CO_3 to yield disubstituted calixarenes selectively. Second substitution was occurred only at the 27-position (opposite site of 3,5-dinitrobenzoyl group) of calixarene **2**. But when calixarene **2** was treated with CH_3I in the presence of K_2CO_3 in THF, a different substitution pattern was observed in ^{1}H NMR. Obviously a certain chiral calix[4]arene was synthesized. The proton NMR spectrum shows a typical chiral characteristics of calix[4]arene that is four pairs of doublets at 3.30-4.20 ppm for eight methylene protons and twelve calixarene aromatic protons at 5.80 to 7.50 ppm as shown in Figure 1. Even two OH protons show two different peaks at 7.23 and 8.20 ppm. From the proton NMR spectrum it is clear that the methylated calixarene



Scheme 1.

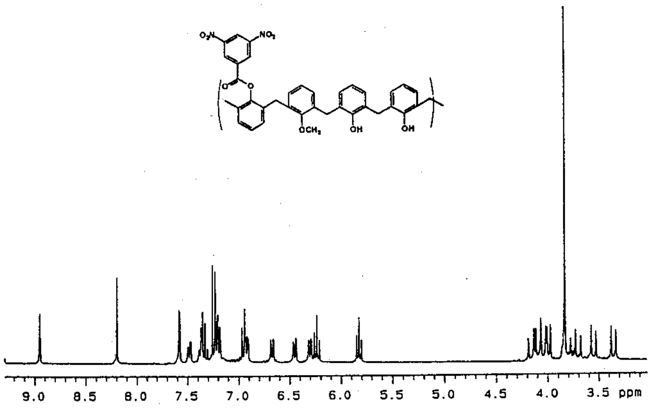


Figure 1. ^1H NMR spectrum of chiral calix[4]arene **3**.

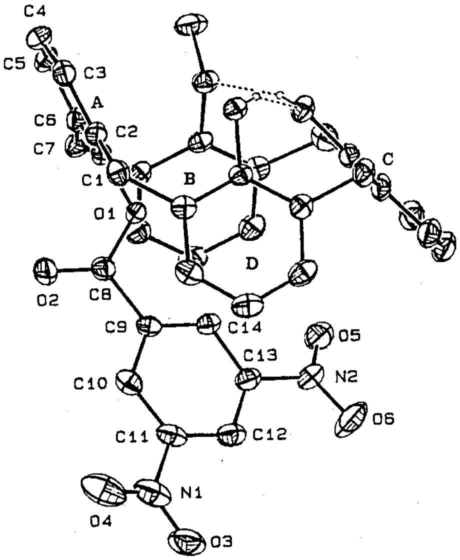


Figure 2. Molecular conformation and atomic numbering. The dotted lines are indicated the intramolecular hydrogen bonds.

is chiral. But there are many possible structure which could be chiral with two different substituents. One thing is clear from proton NMR and the base hydrolysis that only monomethylation was occurred. To investigate the conformation in detail we examined the ^{13}C NMR spectrum particularly at the 30-40 ppm range. There are all four peaks between 30-40 ppm range as expected as a chiral calix[4]arene. Two peaks are at 31.12 and 31.47, and two peaks at 37.41 and 37.89 ppm. From Mandoza's report[10] if two phenolic rings are syn oriented. Bridge methylene carbon come at around 31 ppm. On the other hand two phenolic rings are anti oriented, bridge methylene carbon come at around 38 ppm. So there are two syn oriented phenols and two anti oriented phenols. If a certain calix[4]arene could have two syn and two anti oriented phenols, it must be a partial cone conformation. Now we can draw one chiral partial cone calix[4]arene which is 25,27-disubstituted and four possible 25,26-disubstituted partial cone calix[4]arene. Ultimate conclusion can come only from X-ray structure analysis. It is 25,26-disubstituted and partial cone as shown in Figure 2 and 3. From our knowledge it is the first example of 1,2-disubstituted chiral calix[4]arene with partial cone conformation.

1,2-Substitution rather than 1,3 as observed for benzylation and allylation can be explained by the steric factor of methyl group. Small methyl group can be substituted at next to large 3,5-dinitrobenzoyl group. On the other hand relatively large benzyl and allyl group can be only substituted at the opposite side to the bulky 3,5-dinitrobenzoyl group. 1,2-Substitution can be favored over 1,3-substitution if sterically allowed, because there are two OH groups remaining next to each other which can be hydrogen bond.[11]

To examine the size effect of substituents for the substitution pattern we expected that ethylation could give an interesting results. But unfortunately ethyl iodide was not reacted with benzoylated calixarene **2** under the same reaction condition. Reaction rate was too late in THF in the presence of K_2CO_3. When different solvent other than THF and K_2CO_3

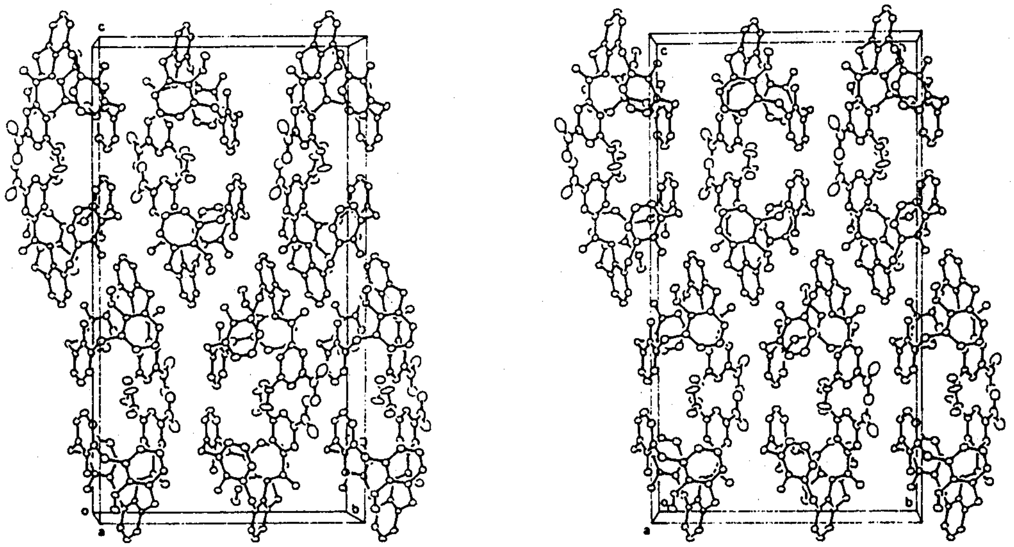


Figure 3. Molecular packing viewed down the *a* axis.

Table 1. Summary of Crystal Data, Data Collection and Refinement

Crystal Data	
$C_{36}H_{28}O_9N_2$	Cu Kα radiation
Mr=632.6	$\lambda=1.5418$ Å
Orthorhombic	Cell parameters from 24 reflections
Pbca	
$a=10.652$ (1) Å	$\theta=17$-23°
$b=17.687$ (1) Å	$\mu=0.834$ mm^{-1}
$c=32.247$ (3) Å	T=293 K
V=6075.4 (9)Å^3	Prism
Z=8	0.3×0.2×0.4 mm
$D_c=1.38$ gcm^{-3}	yellow
Data Collection	
Enraf-Nonius CAD-4	4500 independent reflections
Diffractometer	2368 observed reflections
ω-2θ scans	$[\vert F_o\vert>4\sigma\vert F_o\vert]$
Absorption correction: none	$\theta_{max}=65°$
4500 measured reflections	$h=0$-11
	$k=0$-17
	$l=0$-32
	3 standard reflections monitored every 400 reflections
Refinement	
Refinement on F	$(\Delta/\rho)_{max}=-2.08$
R=0.050	$\Delta\rho_{max}=0.15$ eÅ^{-3}
wR=0.158	$\Delta\rho_{min}=-0.17$ eÅ^{-3}
S=1.03	Extinction correction; none
2368 reflections	Atomic scattering factors from "International Tables for X-ray Crystallography"[13]
536 parameters	
H-atom parameters refined	

were used, either reaction was not occurred at all or benzoyl group was cleaved before ethylation.

X-Ray Structure Analysis. All of the crystal data, data collection and refinements are summarized in Table 1. The structure was solved by direct method of the program Shelxs-86[12] using 424 reflections whose $|E|$ values were greater than 1.5, and refined by the full-matrix least-squares using the program Shelxl-93.[12] Some of the hydrogen atoms were found in the difference Fourier map, the remaining ones were taken in their calculated positions. The final positional and thermal parameters of nonhydrogen atoms are listed in Table 2.

The bond distances and angles are listed in Table 3. These are mainly as expected for the type of bonds involved. The structure exhibits a partial cone conformation, in which a 3,5-dinitrobenzoyl group is down. This partial cone conformation is mainly determined by two strong intramolecular hydrogen bonds connecting two phenols and one aniosole moieties. As shown in Table 4, the hydroxyl group of phenolic C ring accepts one hydrogen bond from phenolic D ring and donates one hydrogen bond to the anisole B ring. The inclination of the A to D rings with respect to the least-squa-

Table 2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters for Non-hydrogen Atoms.* The e. s. d. 's are in parentheses. $U_{eq.}=1/3\ \sum_j\sum_j U_{ij}\ a_i{}^*a_j{}^*a_{ij}$ (Å^2)

Atom	x	y	z	U_{eq}
O(1A)	−2704 (2)	1704 (1)	4251 (1)	0.0519 (6)
O(2A)	−3778 (4)	2767 (2)	4349 (1)	0.0999 (12)
O(3A)	−5995 (4)	3040 (2)	2537 (2)	0.137 (2)
O(4A)	−6684 (4)	3233 (3)	3162 (2)	0.145 (2)
O(5A)	−1031 (4)	1386 (2)	2830 (1)	0.1003 (11)
O(6A)	−2407 (4)	1397 (3)	2356 (1)	0.147 (2)
N(1A)	−5918 (5)	2989 (3)	2921 (2)	0.110 (2)
N(2A)	−2076 (5)	1522 (2)	2709 (1)	0.0815 (11)
C(1A)	−2661 (4)	1564 (2)	4686 (1)	0.0511 (9)
C(2A)	−3677 (4)	1194 (2)	4863 (1)	0.0539 (10)
C(3A)	−3559 (5)	1041 (2)	5290 (1)	0.0650 (12)
C(4A)	−2527 (5)	1255 (3)	5510 (1)	0.0712 (12)
C(5A)	−1551 (5)	1612 (2)	5320 (1)	0.0675 (12)
C(6A)	−1599 (4)	1783 (2)	4898 (1)	0.0553 (10)
C(7A)	−554 (5)	2251 (3)	4708 (1)	0.0654 (12)
C(8A)	−3352 (4)	2302 (2)	4121 (1)	0.0616 (11)
C(9A)	−3516 (4)	2296 (2)	3662 (1)	0.0567 (10)
C(10A)	−4555 (5)	2668 (2)	3506 (2)	0.0722 (12)
C(11A)	−4770 (4)	2630 (2)	3084 (2)	0.0726 (13)
C(12A)	−3992 (5)	2258 (3)	2816 (2)	0.0760 (13)
C(13A)	−2961 (4)	1915 (2)	2982 (1)	0.0646 (11)
C(14A)	−2706 (4)	1916 (2)	3403 (1)	0.0566 (10)
O(1B)	235 (3)	727 (1)	4500 (1)	0.0651 (7)
C(1B)	385 (4)	1297 (2)	4202 (1)	0.0545 (10)
C(2B)	−10 (4)	2028 (2)	4292 (1)	0.0561 (10)
C(3B)	106 (4)	2569 (3)	3987 (1)	0.0677 (12)
C(4B)	688 (4)	2394 (3)	3612 (1)	0.0736 (13)
C(5B)	1022 (5)	1666 (3)	3526 (1)	0.0714 (13)
C(6B)	876 (4)	1100 (2)	3820 (1)	0.0602 (10)
C(7B)	1180 (5)	285 (3)	3708 (2)	0.0730 (13)
C(8B)	1269 (7)	679 (4)	4789 (2)	0.092 (2)
O(1C)	−1109 (3)	−315 (2)	4062 (1)	0.0663 (8)
C(1C)	−944 (4)	−338 (2)	3638 (1)	0.0589 (10)
C(2C)	157 (5)	−77 (2)	3455 (1)	0.0639 (11)
C(3C)	258 (6)	−144 (3)	3025 (2)	0.0817 (14)
C(4C)	−698 (6)	−440 (3)	2793 (2)	0.087 (2)
C(5C)	−1770 (6)	−687 (3)	2978 (1)	0.0789 (14)
C(6C)	−1923 (5)	−638 (2)	3408 (1)	0.0657 (11)
C(7C)	−3108 (5)	−891 (2)	3614 (1)	0.0701 (12)
O(1D)	−3385 (3)	−253 (2)	4445 (1)	0.0659 (8)
C(1D)	−4044 (4)	59 (2)	4120 (1)	0.0525 (9)
C(2D)	−3965 (4)	−238 (2)	3723 (1)	0.0600 (11)
C(3D)	−4705 (5)	100 (3)	3416 (1)	0.0770 (14)
C(4D)	−5492 (5)	689 (3)	3501 (2)	0.0804 (14)
C(5D)	−5540 (4)	960 (3)	3895 (2)	0.0684 (12)
C(6D)	−4818 (4)	666 (2)	4214 (1)	0.0579 (10)
C(7D)	−4874 (4)	997 (3)	4647 (1)	0.0631 (11)

*Tables for anisotropic thermal parameters of the non-hydrogenatoms, coordinates of hydrogen atoms and structure factors areavailable from the author (YJP).

Table 3. Bond Distances (Å), Bond Angles (°) and Torsion Angles (°). The e. s. d. 's are in parentheses

	A	B	C	D
C(1)-C(2)	1.388 (6)	1.391 (5)	1.390 (6)	1.388 (5)
C(1)-C(6)	1.377 (6)	1.380 (5)	1.386 (6)	1.387 (5)
C(2)-C(3)	1.407 (5)	1.385 (6)	1.398 (7)	1.399 (6)
C(3)-C(4)	1.363 (7)	1.368 (5)	1.367 (9)	1.365 (8)
C(4)-C(5)	1.364 (7)	1.363 (7)	1.360 (9)	1.360 (9)
C(5)-C(6)	1.394 (5)	1.388 (6)	1.398 (5)	1.385 (7)
C(6)-C(7)	1.516 (6)	1.522 (6)	1.495 (5)	1.515 (5)
O(1)-C(1)	1.425 (5)	1.402 (4)	1.379 (5)	1.377 (5)
O(1)-C(8)	1.330 (4)	1.447 (8)		
O(2)-C(8)	1.193 (5)			
O(3)-N(1)	1.244 (9)			
O(4)-N(1)	1.208 (8)			
O(5)-N(2)	1.205 (7)			
O(6)-N(2)	1.213 (5)		C(7A)-C(2B)	1.514 (5)
N(1)-C(11)	1.475 (7)		C(7B)-C(2C)	1.504 (7)
N(2)-C(13)	1.466 (6)		C(7C)-C(2D)	1.514 (6)
C(8)-C(9)	1.492 (5)		C(2A)-C(7D)	1.496 (6)
C(9)-C(10)	1.383 (7)			
C(9)-C(14)	1.376 (5)			
C(10)-C(11)	1.382 (9)			
C(11)-C(12)	1.365 (8)			
C(12)-C(13)	1.363 (7)			
C(13)-C(14)	1.384 (5)			

	A	B	C	D
C(A)-C(1)-O(1)	117.5 (3)	119.3 (3)	121.2 (3)	121.3 (3)
C(A)-C(1)-O(1)	117.8 (3)	118.2 (3)	116.5 (4)	116.6 (3)
C(A)-C(2)-C(1)	115.1 (4)	116.9 (3)	117.3 (4)	117.2 (4)
C(A)-C(3)-C(2)	121.9 (4)	121.7 (5)	121.1 (6)	122.0 (4)
C(A)-C(4)-C(3)	120.5 (3)	120.0 (4)	120.6 (6)	118.6 (5)
C(A)-C(6)-C(1)	116.9 (4)	118.0 (3)	117.8 (4)	117.3 (4)
C(A)-C(1)-C(2)	124.7 (3)	122.4 (3)	122.3 (3)	122.0 (3)
C(A)-C(5)-C(4)	120.8 (4)	120.8 (3)	120.9 (5)	122.7 (5)
C(A)-C(6)-C(1)	123.8 (3)	122.2 (4)	120.9 (3)	121.6 (3)
C(A)-C(6)-C(5)	119.0 (4)	119.7 (4)	121.4 (4)	121.1 (4)
C(A)-O(1)-C(1)	117.7 (3)	113.5 (4)		

O(2A)-C(8A)-O(1A)	123.5 (3)	O(4A)-N(1A)-O(3A)	124.8 (6)
O(6A)-N(2A)-O(5A)	122.5 (4)	C(9A)-C(8A)-O(1A)	111.6 (3)
C(9A)-C(8A)-O(2A)	124.8 (4)	C(10A)-C(9A)-C(8A)	116.8 (4)
C(10A)-C(11A)-N(1A)	117.9 (5)	C(11A)-N(1A)-O(3A)	116.2 (5)
C(11A)-N(1A)-O(4A)	118.9 (6)	C(11A)-C(10A)-C(9A)	117.9 (4)
C(12A)-C(11A)-N(1A)	119.0 (6)	C(12A)-C(11A)-C(10A)	123.1 (5)
C(12A)-C(13A)-N(2A)	119.5 (4)	C(13A)-N(2A)-O(5A)	119.6 (3)
C(13A)-N(2A)-O(6A)	117.7 (5)	C(13A)-C(12A)-C(11A)	117.1 (5)
C(13A)-C(14A)-C(9A)	118.2 (4)	C(14A)-C(9A)-C(8A)	122.2 (3)
C(14A)-C(9A)-C(10A)	120.9 (4)	C(14A)-C(13A)-N(2A)	117.6 (4)
C(14A)-C(13A)-C(12A)	122.8 (4)	C(1B)-C(2B)-C(7A)	122.9 (3)
C(1C)-C(2C)-C(7B)	121.6 (4)	C(1D)-C(2D)-C(7C)	122.7 (3)
C(2B)-C(7A)-C(6A)	119.8 (4)	C(2C)-C(7B)-C(6B)	112.3 (4)
C(2D)-C(7C)-C(6C)	112.6 (3)	C(3B)-C(2B)-C(7A)	120.1 (4)
C(3C)-C(2C)-C(7B)	121.1 (5)	C(3D)-C(2D)-C(7C)	120.1 (3)
C(6D)-C(7D)-C(2A)	119.2 (3)	C(7D)-C(2A)-C(1A)	125.6 (3)
C(7D)-C(2A)-C(3A)	119.2 (4)		

C(2A)-C(1A)-C(6A)-C(7A)	−174.0(6)
C(1A)-C(6A)-C(7A)-C(2B)	−48.7(4)
C(6A)-C(7A)-C(2B)-C(1B)	−49.8(4)
C(7A)-C(2B)-C(1B)-C(6B)	179.8(6)
C(2B)-C(1B)-C(6B)-C(7B)	−173.5(6)
C(1B)-C(6B)-C(7B)-C(2C)	98.3(5)
C(6B)-C(7B)-C(2C)-C(1C)	−77.9(5)
C(7B)-C(2C)-C(1C)-C(6C)	176.6(6)
C(2C)-C(1C)-C(6C)-C(7C)	−178.1(6)
C(1C)-C(6C)-C(7C)-C(2D)	78.4(4)
C(6C)-C(7C)-C(2D)-C(1D)	−100.4(5)
C(7C)-C(2D)-C(1D)-C(6D)	178.9(6)
C(2D)-C(1D)-C(6D)-C(7D)	−178.5(6)
C(1D)-C(6D)-C(7D)-C(2A)	49.7(4)
C(6D)-C(7D)-C(2A)-C(1A)	44.0(4)
C(7D)-C(2A)-C(1A)-C(6A)	175.6(6)
C(8A)-O(1A)-C(1A)-C(2A)	81.5(4)
C(8A)-O(1A)-C(1A)-C(6A)	−100.4(4)
C(1A)-O(1A)-C(8A)-O(2A)	8.5(4)
C(1A)-O(1A)-C(8A)-C(9A)	−169.3(4)
O(1A)-C(8A)-C(9A)-C(10A)	153.5(5)
O(1A)-C(8A)-C(9A)-C(14A)	−24.0(3)
O(2A)-C(8A)-C(9A)-C(10A)	−24.3(4)
O(2A)-C(8A)-C(9A)-C(14A)	158.1(6)
C(8B)-O(1B)-C(1B)-C(2B)	−86.8(5)
C(8B)-O(1B)-C(1B)-C(6B)	95.9(5)

res plan of methylene carbons are 61.7, 111.9, 43.9 and 68.3° respectively. The relative dihedral angles between adjacent rings are: A-B=98.3, B-C=102.9, C-D=71.9 and A-D=78.1°, whereas those between two opposite rings are; A-C=17.9 and B-D=43.6°. The dihedral angle between A ring and 3,5-dinitrobenzene ring is 118.9° with C(1A)-O(1A)-C(8A)-C(9A) torsion angle of −169.3°.

The crystal structure is illustrated in Figure 3. The molecules are packed together by van der Waals forces. The 3,5-dinitrobenzoyloxy parts are packed together along the *a* axis.

Table 4. Intramolecular Hydrogen Bonds

D	H	A	D-H	H···A	D···A	D-H···A
O(1C)-	H(10C)···	O(1B)	0.89(4)	1.898(4)	2.727(4)	158(4)
O(1D)-	H(10D)···	O(1C)	0.87(5)	1.903(5)	2.724(5)	156(4)

Experimental

Melting points of all compounds were measured on a Mel-Temp apparatus without calibration. Infrared (IR) spectra were determined on a Nicolet 520 FT-IR spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 300 AMX spectrometer. Chemical shifts are reported as δ values in parts per million relative to tetramethylsilane (TMS) as an internal standard. Thin layer chromatography (TLC) analyses were carried out silica gel plates. Elemental analyses were performed by EA 1108, Fisons instruments.

25-(3,5-Dinitrobenzoyloxy)-26,27,28-trihydroxycalix[4]arene 2. To a solution of 1.6 g (3.9 mmol) of **1** in 40 mL of acetonitrile 4.8 mL of 1-methylimidazole and 1.2 g of 3,5-dinitrobenzoyl chloride (5.2 mmol) was added. The mixture was stirred at room temperature for 6h, acidified, and extracted with $CHCl_3$. After removed the solvents, the residue triturated with methanol. The crude product was recrystallized from $CHCl_3$-MeOH to yield 1.47 g (63%) of pale yellow crystalline **2**; mp 288 ℃ dec., ^{1}H NMR ($CDCl_3$) 9.11 and 8.10 (t and d, 3H, O_2NArH, J=2.1 Hz), 6.16-7.61 (m, 12H, ArH), 3.60-4.02 (two pairs of d, 8H, $ArCH_2Ar$, J= 14.2 Hz). ^{13}C NMR (DMSO-d_6) 162.08 (-CO_2-), 156.49, 153.95, 148.47, 144.91, 136.44, 133.31, 132.74, 130.12, 129.69, 129.38, 129.33, 128.23, 128.15, 127.86, 127.51, 125.75, 122.88, 122.83, 122.05, 118.05, and 116.00 (Ar), 33.00 and 32.05 ($ArCH_2Ar$). IR (KBr) 3450 cm^{-1} (OH), 1730 cm^{-1} (-CO_2-). Anal. Calcd for $C_{35}H_{26}O_9N_2$: C, 67.96; H, 4.24; N, 4.53; O, 23.28. Found: C, 67.79; H, 4.01; N, 4.46; O, 23.74.

25-(3,5-dinitrobenzoyloxy)-26-methoxy-27,28-dihydroxycalix[4]arene 3. A mixture of 500 mg (0.8 mmol) of **2**, 340 mg of K_2CO_3 and 230 μL of CH_3I in 50 mL of THF was refluxed for 15h and the solvents were removed. The residue was recrysyallized from toluene to yield 280 mg (54%) of pale yellow crystalline **3**. mp 285 ℃ dec. ^{1}H NMR ($CDCl_3$) 8.95 (t, 1H, O_2NArH), 8.20 (s, 1H, OH), 7.60 (d, 2H, O_2NArH, J=2.1 Hz), 7.46 (d, 1H, ArH), 7.37 (d, 1H, ArH), 7.31 (t, 1H, ArH), 7.23 (s, 1H, OH), 7.18 (d×2, 2H, ArH), 6.94 (t, 1H, ArH), 6.91 (d, 1H, ArH), 6.66 (d, 1H, ArH), 6.44 (d, 1H, ArH), 6.29 (d, 1H, ArH), 6.21 (t, 1H, ArH), 5.80 (t, 1H, ArH), 4.14, 4.07, 4.01, 3.98, 3.78, 3.68, 3.53, and 3.34 (four pairs of d, 8H, $ArCH_2Ar$, J=13.2 Hz), 3.82 (s, 3H, -OCH_3). ^{13}C NMR ($CDCl_3$) 159.48 (-CO_2-), 152.02, 150.74, 147.69, 147.05, 134.85, 133.51, 132.79, 132.17, 131.67, 130.81, 129.93, 129.74, 129.61, 129.39, 129.10, 128.89, 128.62, 128.51, 128.06, 127.52, 126.64, 125.43, 124.69, 122.01, 121.50, and 119.60 (Ar), 61.21 (-OCH_3), 37.89, 37.41, 31.47, and 31.12 ($ArCH_2Ar$). IR (KBr) 3300 cm^{-1} (OH), 1738 cm^{-1} (-CO_2-). Anal. Calcd for $C_{36}H_{28}O_9N_2$: C, 68.35; H, 4.46; N, 4.43; O, 22.76. Found: C, 68.29; H, 4.50; N, 4.36; O, 22.85.

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