Conformations of Tetrahomodioxa-*p*-phenylcalix[4]arene Alkyl Ethers

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Reaction of tetrahomodioxa *p*-phenylcalix[4]arene with alkyl halide and NaH in DMF leads to the title tetra-alkylated derivatives, 7,13,21,27-tetra-phenyl-29,30,31,32-tetraalkyloxy-2,3,16,17-tetrahomo-3,17-dioxacalix [4]arenes, their preferred conformations were determined by NMR spectra as C-1,2-alternate. The molecular structure of allyl derivative has been solved by X-ray diffraction methods. The molecules have a conformation with pseudo center of symmetry. The benzene ring A is up, ring C is down, B and D rings are flat with respect to the plane of the macrocyclic ring.

Key Words : Homooxacalix[4]arene, Conformation, Crystal structure

Introduction

Calixarenes are synthetic macrocycles with varying ring sizes that have received a great deal of attention in recent years.[1-3] They are of interest both as complexation hosts for ions and molecules and as frameworks for elaborating more complex structures. In contrast to calix[4]arenes, tetrahomodioxacalix[4]arenes which contain two extra oxygen atoms in the macrocyclic ring have received little attention, mainly because they can be synthesized only in relatively low overall yields.[4-6] There have only been limited studies of the solution conformations, solid-state structures and complexation properties of tetrahomodioxacalix[4]arenes.[7-10]

Shaping of cavity plays a potentially vital role in the design of calixarenes, for host-guest interaction depends on complementarity in shape as well as functionality. The interconversion between conformers of calix[4]arene can be sterically inhibited by *O*-substituents bulkier than ethyl group.[11] By using n-propyl bromide as an alkylation reagent, one can thus synthesize a variety of conformational isomer from calix[4]arene. Conformational isomerism in tetrahomodioxacalix[4]arene compounds is expected to be more complicated than in calix[4]arenes, due to reduced symmetry as well as greater mobility. Tetrahomodioxacalix[4]arene containing free intraannular OH groups is conformationally flexible in solution at room temperature and exists five limiting conformations as illustrates in Figure 1.

Masci and coworker[12] reported that the main conformation of tetrahomodioxa-*p*-*tert*-butylcalix[4]arene tetramethyl ether is C-1,2-alternate based on temperature dependent NMR spectral analysis. However the X-ray crystal structure was not reported. In the X-ray crystal structure determination study, Thuery and coworkers[13] reported that *p*-alkyl tetrahomodioxacalix[4]arene is crystallized as distorted cone-like

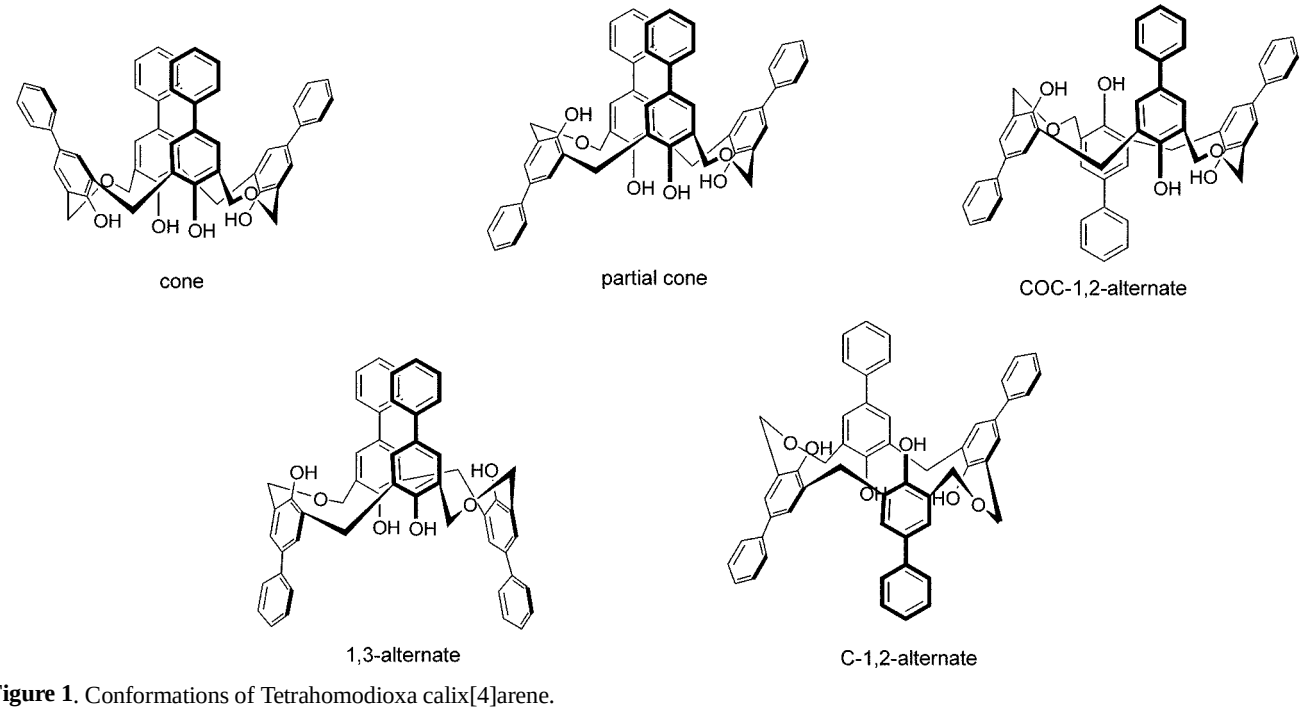
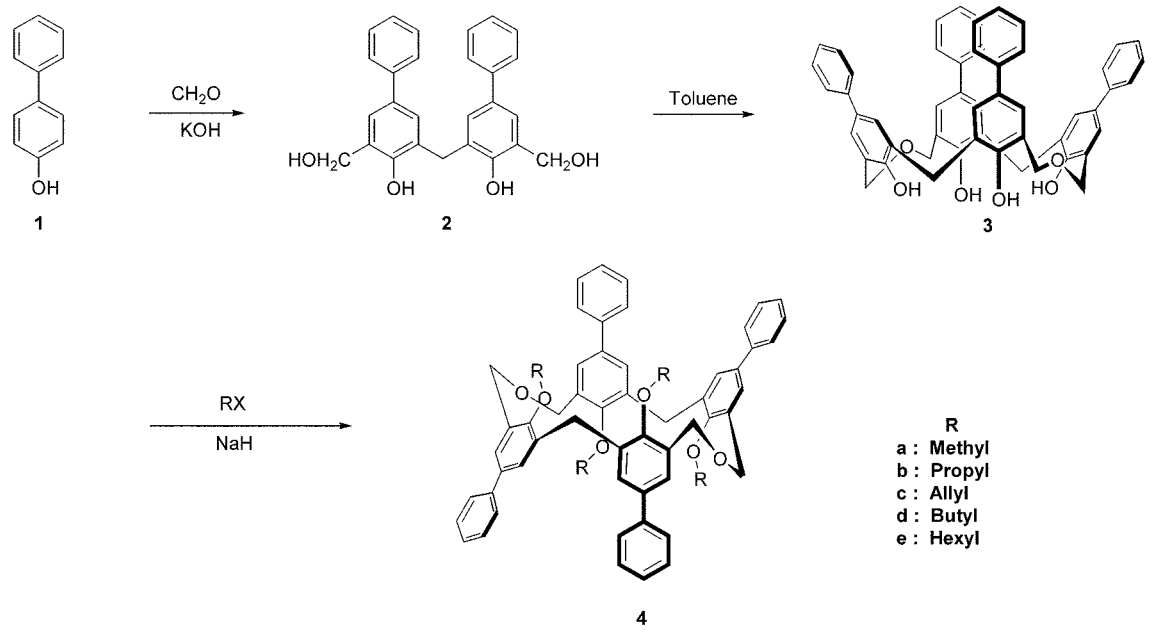


Figure 1. Conformations of Tetrahomodioxa calix[4]arene.



1 2 3 4

Scheme 1

conformation with or without solvent molecules.

Recently, we described a facile two-step synthesis of tetrahomodioxa-*p*-phenyl calix[4]arene by refluxing bis-hydroxymethylated *p*-phenylphenol in xylene[14] and the solid-state structure of its tetraester.[15] We also reported the synthesis of tetrahomodioxa-*p*-phenyl calix[4]arene tetra-amide, its two-phase metal picrate extraction behavior and the solid-state structure of its complex with lead picrate.[16] In a continuation of the homooxacalixarene research, series of tetrahomodioxa-*p*-phenylcalix[4]arene tetraalkyl ethers **4** have been prepared and their conformations were studied by NMR spectral analysis.

Results and Discussion

As shown on the following Scheme 1 tetrahomodioxacalix [4]arene tetraalkyl ethers **4** can be obtained in a good yield by treatment of a DMF solution of the homooxacalix[4] arene **3** with NaH followed by the alkyl halide (bromide or iodide). Judging from ^{1}H and ^{13}C NMR spectroscopy, compounds **4** were found to be in the C-1,2-alternate conformation.

The NMR spectrum of **4a** could not be obtained due to lack of solubility to most deuterated organic solvent including DMSO. Therefore its conformation can not be determined.

Compound **4b** shows temperature dependent ^{1}H NMR spectra for the methylene protons of $ArCH_2Ar$ and $ArCH_2OCH_2Ar$. At 0 °C in chloroform, the methylene protons of the $ArCH_2Ar$ showed two doublets at δ 4.56 and 3.46 with a geminal coupling constant of 13.7 Hz. An AB pattern for the dimethyleneoxy protons of $ArCH_2OCH_2Ar$ appeared at δ 4.60 and 4.54 with a geminal coupling constant of 10.7 Hz. The methylene protons from propyl groups showed two sets of quartet at δ 3.54, 3.37 and two sets of sextet at δ 1.52, 1.37 and methyl protons appeared as a triplet at δ 0.63. When the temperature was raised, the spectrum became less well resolved and, at 25 °C, AB quartets from bridge methylene protons of $ArCH_2OCH_2OAr$ collapsed into one broad singlet at δ 4.57, and AB quartets from bridge methylene protons of $ArCH_2Ar$ collapsed into two broad singlet at δ 4.57 and 3.45. Obviously, the ease of transformation between conformations via the oxygen-through-the-annulus rotation should be different between $ArCH_2Ar$ rotation and $ArCH_2OCH_2Ar$ rotation. In propyl ether, the interconversion between conformations could occurred through both the $ArCH_2Ar$ and $ArCH_2OCH_2Ar$ rotation, however $ArCH_2OCH_2Ar$ rotation is much easier than $ArCH_2Ar$ rotation. At 50 °C, protons from propyl groups also became three broad singlets at δ 3.45, 1.47 and 0.63. CH_3 signal is upfield shifted with respect to the typical value. The shielding effect experienced by the CH_3 protons of **4b** is not compatible with the cone structure. The obvious interpretation is that the corresponding methyl groups face the benzene ring of *p*-substituted aromatic ring. The ^{13}C NMR spectrum showed a single peak at 75.46 ppm for the $ArCH_2O$ bridge methylene carbons and one peak at 30.70 ppm for the $ArCH_2Ar$ bridge carbons. On extending the criterion first established for calix[4]arenes and successfully applied also to larger homologues to homooxacalixarenes,[17,18] a *syn* arrangement of the aromatic rings can be predicted for the $ArCH_2Ar$ moieties of **4b**. For the partial cone, COC-1,2-alternate and 1,3-alternate conformers, in which two adjacent benzene rings are in an *anti* orientation, an additional methylene bridge carbon peak at around 37 ppm would be anticipated. Thus, the spectral pattern for **4b** is consistent with a C-1,2-alternate conformation in which the two adjacent phenyl rings connected by a dimethyleneoxy group are inverted. The position of the methylenic bridge carbons of $ArCH_2Ar$ at 30.70 ppm indicates that these two adjacent benzene-rings are in *syn* orientation.

Compound **4c** shows a similar NMR spectral pattern with

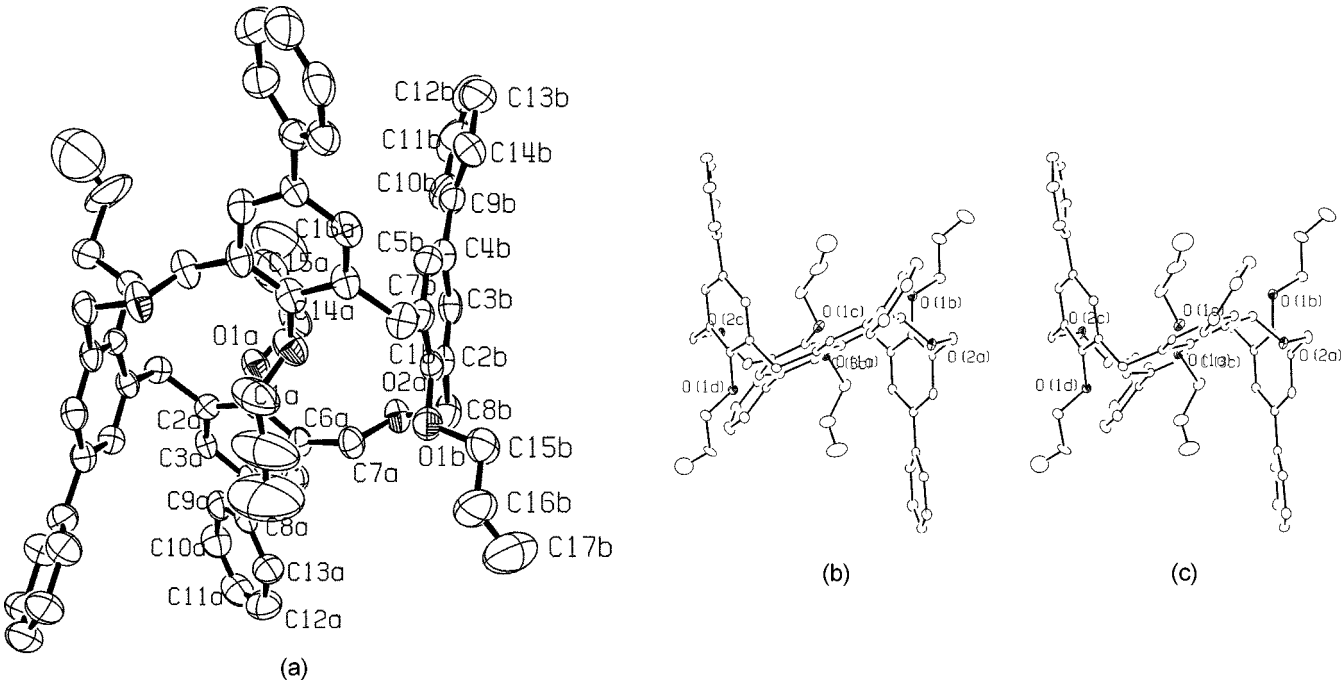


Figure 2. View of the molecular structure and atomic numbering of compound **4c**. Hydrogen atoms have been omitted for clarity.

4b. At -25 °C in chloroform, the methylene protons of the ArC*H*$_2$Ar showed two AB doublets at δ 4.58 and 3.48 with a geminal coupling constant of 13.6 Hz. An AB pattern for the dimethyleneoxy protons of ArC*H*$_2$OC*H*$_2$Ar appeared at δ 4.60 and 4.45 with a geminal coupling constant of 10.3 Hz. When the temperature was raised, the spectrum became less well resolved and, at 0 °C, AB quartets from bridge methyleneoxy protons of ArC*H*$_2$OC*H*$_2$OAr collapsed into broad doublet at δ 4.55, and AB quartets from bridge methylene protons of ArC*H*$_2$Ar collapsed into two broad singlet at δ 4.53 and 3.50. When the temperature was raised to room temperature, the protons of the ArC*H*$_2$Ar and ArC*H*$_2$OC*H*$_2$OAr are appeared as singlet, respectively. Obviously, the transformation between conformations via the oxygen-through-the-annulus rotation should be faster than NMR time scale at room temperature. The ^{13}C NMR spectrum showed a single peak at 75.89 ppm for the ArC*H*$_2$OC*H*$_2$Ar bridge methylene carbons and one peak at 32.27 ppm for the ArC*H*$_2$Ar bridge carbons. Thus, the spectral pattern for **4c** is also consistent with a C-1,2-alternate conformation. The X-ray crystal structure of **4c** is also a positive proof for the C-1,2-alternate conformation. The molecular conformation and atomic numbering (-A-CH$_2$-O-CH$_2$-B-CH$_2$-C-CH$_2$-O-CH$_2$-D-CH$_2$-) of **4c** which is drawn by the ORTEP programs[19] is depicted in Figure 2, showing C-1,2 alternate conformer with a pseudo center of symmetry. All of the crystal data are listed in Table 1.

The molecular conformation may be defined by the angles which the four aromatic rings (A-D) make with the 18-membered macrocyclic ring; A(156.1°), B(86.6°), C(152.9°) and D(76.6°). The relative dihedral angles between two adjacent rings are; A-B = 79.1°, B-C = 85.5°, C-D = 93.4° and A-D = 87.8°. In compound **4c**, ring A and C, and B and D

Table 1. Summary of Crystal Data of tetrahomodioxa *p*-phenylcalix[4]arene tetraallyl ether **4c**

Crystal data	
$C_{66}H_{60}O_6$	D_x = 1.229 (calc.) g cm^{-3}
Mw = 949.14	Mo Kα radiation
Triclinic, P(-1)	
a = 13.354(7) Å	
b = 14.163(5) Å	μ = 0.077 mm^{-1}
c = 15.026(3) Å	*T* = 293(2) K
alpha = 76.21(3)°	
beta = 70.32(2)°	
gamma = 76.76(5)°	Colorless
V = 2564.2(17) Å^3	0.6 × 0.4 × 0.1 mm
Z = 2	
Data collection	
Enraf-Nonius CAD-4	θ_{max} = 25°
Diffractometer	*h* = 0 → 15
ω / 2θ scan type	*k* = -16 → 16
Absorption correction: none	*l* = -16 → 17
9015 measured reflections	3 standard reflections
	Frequency: 60 min
3186 reflections with $I > 2\sigma(I)$	Intensity decay: negligible
Refinement	
Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0762P)^2 + 0.7341P]$
$R[F^2 > 2\sigma(F^2)] = 0.077$	where $P = (F_o^2 + F_c^2) / 3$
$wR(F^2) = 0.215$	
S = 0.958	$(\Delta / \sigma)_{mean} = 0.052$
9015 reflections	$\Delta\rho_{max}$ = 0.47 eÅ^{-3}
649 parameters	$\Delta\rho_{min}$ = -0.32 eÅ^{-3}
Extinction correction: none	

Atomic scattering factors from *International Table for Crystallography*[22]

Table 2. Conformational Angles around 18-membered macrocyclic ring in **4c**. The e. s. d.'s are in parentheses

C(1A)-C(6A)-C(7A)-O(2A)	-104.4 (6)
C(6A)-C(7A)-O(2A)-C(8B)	175.3 (4)
C(7A)-O(2A)-C(8B)-C(2B)	-79.2 (6)
O(2A)-C(8B)-C(2B)-C(1B)	101.7 (6)
C(8B)-C(2B)-C(1B)-C(6B)	-172.6 (5)
C(2B)-C(1B)-C(6B)-C(7B)	175.4 (5)
C(1B)-C(6B)-C(7B)-C(2C)	-129.5 (5)
C(6B)-C(7B)-C(2C)-C(1C)	64.5 (7)
C(7B)-C(2C)-C(1C)-C(6C)	-173.3 (5)
C(2C)-C(1C)-C(6C)-C(7C)	172.0 (5)
C(1C)-C(6C)-C(7C)-O(2C)	98.0 (6)
C(6C)-C(7C)-O(2C)-C(8D)	175.1 (4)
C(7C)-O(2C)-C(8D)-C(2D)	76.7 (6)
O(2C)-C(8D)-C(2D)-C(1D)	-86.5 (6)
C(8D)-C(2D)-C(1D)-C(6D)	171.6 (5)
C(2D)-C(1D)-C(6D)-C(7D)	-173.3 (5)
C(1D)-C(6D)-C(7D)-C(2A)	128.0 (5)
C(6D)-C(7D)-C(2A)-C(1A)	-66.8 (6)
C(7D)-C(2A)-C(1A)-C(6D)	174.5 (5)
C(2A)-C(1A)-C(6A)-C(7A)	-174.8 (5)

are thus essentially parallel (interplanar angle 9.2° and 10.3 respectively) and rings A and C are tilted so that their allyl ether groups are oriented toward the cavity, while B and D rings are approximately normal to the least-square plane of 18-membered macrocyclic ring. The C-1,2-alternate conformation of the **4c** is also shown in Table 2 of conformational angles.

In ^{1}H NMR spectrum of compound **4d**, at room temperature, the peak from protons of ArCH_2Ar splits into AB system, however that from protons of ArCH_2OCH_2Ar appears as a singlet which splits into AB system on cooling to lower temperature (0 °C). For propyl ether, the ease of conformational transformation should be different between ArCH_2Ar and ArCH_2OCH_2Ar rotation. In case of butyl ether, it can occur only through the CH_2OCH_2 rotation at room temperature. The rotation through ArCH_2Ar is not so fast in NMR time scale even at 50 °C, which showed two singlets in ^{1}H NMR spectrum at that temperature. The ^{13}C NMR spectrum of **4d** showed a similar spectral pattern with **4b**.

For hexyl ether **4e**, in the ^{1}H NMR spectrum, the singlet at 4.56 from bridge methyleneoxy protons of ArCH_2OCH_2OAr at 50 °C splits on cooling to room temperature into AB system at δ 4.57 and 4.53 which indicates the conformational transformation through the ArCH_2OCH_2Ar rotation does not occur at room temperature. The AB pattern of ArCH_2Ar protons remains unchanged up to 50 °C, suggesting the transformation through ArCH_2Ar rotation does not occur even at that temperature. The ^{13}C NMR spectrum of **4e** showed similar spectral pattern with **4b**.

Temperature dependant ^{1}H NMR spectral patterns of ArCH_2OCH_2Ar and ArCH_2Ar protons of compound **4** are summarized in Table 3.

Table 3. Temperature dependant ^{1}H NMR spectral patterns of CH_2OCH_2 and ArCH_2Ar protons of compound **4**

	CH_2OCH_2				ArCH_2Ar			
R\Temp (°C)	-25	0	25	50	-25	0	25	50
allyl	AB	br.d	s	s	AB	two s	s	s
propyl	AB	AB	s	s	AB	AB	two s	two s
butyl	AB	AB	s	s	AB	AB	AB	two s
hexyl	AB	AB	AB	s	AB	AB	AB	AB

In conclusion, five tetrahomodioxacalix[4]arene tetra alkylethers were synthesized by the treatment of tetrahomodioxa-*p*-phenylcalix[4]arene with alkyl halide and NaH in DMF. From ^{1}H, ^{13}C NMR and crystal structure they were found to be in the C-1,2-alternate conformation. The butyl group is not bulky enough for the sterical inhibition of the conformational interconversion of tetrahomodioxacalix[4] arene at room temperature.

Experimentals Section

Unless otherwise noted, reagents were obtained from commercial suppliers and used without further purification. Melting points were taken in evacuated and sealed capillary tubes with a Mel-Temp apparatus. IR spectra were determined with a Nicolet Impact 400 FT-IR spectrometer as KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AMX 600 spectrometer. Chemical shifts are recorded in parts per million relative to TMS as an internal standard.

The 3-(3-hydroxymethyl-5-phenylsalicyl)-5-phenyl-2-hydroxybenzyl alcohol (**2**) was prepared in 55% yield following the published procedure.[20] The 7,13,21,27-tetraphenyl-29,30,31,32-tetrahydroxy-2,3,16,17-tetrahomo-3,17-dioxacalix[4] arene (**3**) was prepared in 79% yield from bishydroxymethylated dimer of *p*-phenylphenol as described elsewhere;[14] *mp* 236-237 °C (lit.[14] 236-237 °C).

General method for the synthesis of 7,13,21,27-tetraphenyl-29,30,31,32-tetraalkyloxy-2,3,16,17-tetrahomo-3,17-dioxacalix[4]arenes 4a-d. To heated suspension of compound **3** (1.00 mmole) and NaH (537 mg, 60% oil dispersion) in dry DMF (30 mL), alkyl iodide or bromide (12.0 mmole) was added under Ar and then the reaction mixture was heated at 70 °C for 24-48 h. After small amount of methanol was added to destroy the excess NaH, solvent was removed *in vacuo* and then the organic material was extracted with methylene chloride. The organic layer was washed with water, dried and evaporated to afford slightly brown colored residue, which was subjected to purification.

7,13,21,27-Tetraphenyl-29,30,31,32-tetramethyloxy-2,3,16,17-tetrahomo-3,17-dioxacalix[4]arene 4a. The reaction residue was stirred with methylene chloride. The methylene insoluble material was collected by filtration, washed with water and then dried to afforded 724 mg (84.5%) of the colorless crystalline material. The filtrate and washing were washed with water, dried and evaporated to afford additional 85 mg of colorless solid. The total yield

was 94.4%. Analytical sample was obtained by recrystallization from CH_2Cl_2 and methanol. mp 270-271 °C; Anal. Calcd. For $C_{58}H_{52}O_6$: C, 82.44; H, 6.20. Found: C, 82.58; H, 6.12.

7,13,21,27-Tetraphenyl-29,30,31,32-tetrapropyloxy-2,3,16,17-tetrahomo-3,17-dioxacalix[4]arene 4b. The reaction residue was recrystallized from CH_2Cl_2 and methanol to produce 1.08 g (89%) of the product **4b** as crystalline solid. mp 250-251 °C; ^{1}H NMR ($CDCl_3$, 0 °C) δ 7.56-7.27 (m, 28, Ar*H*), 4.60 (d, 4, ArCH_2O, J = 10.7 Hz), 4.56 (d, 2, ArCH_2Ar, J = 13.7 Hz), 4.54 (d, 4, ArCH_2O, J = 10.7 Hz), 3.54 (q, 4, CH_2, J = 7.0 Hz), 3.46 (d, 2, ArCH_2Ar, J = 13.7 Hz), 3.37 (q, 4, CH_2, J = 7.0 Hz), 1.52 (sextet, 4, CH_2, J = 6.8 & 7.3 Hz), 1.37 (sextet, 4, CH_2, J = 6.8 & 7.3 Hz), 0.63 (t, 12, CH_3, J = 7.3 Hz). (25 °C) 7.55-7.26 (m, 28, Ar*H*), 4.57 (s, 10, ArCH_2O & ArCH_2Ar), 3.55-3.39 (br. m, 10, OCH_2 & ArCH_2Ar), 1.50 (br. 4, 8, CH_2), 1.37 (br. 4, 8, CH_2), 0.62 (br. s, 12, CH_3). ^{13}C NMR ($CDCl_3$): δ 156.50, 140.71, 136.02, 135.21, 130.63, 129.09, 128.58, 126.85, 126.74 (Ar), 76.89, 66.80 (O*C*H_2), 30.70 (Ar*C*H_2Ar), 23.03(*C*H_2), 10.39 (*C*H_3). Anal. Calcd. For $C_{66}H_{68}O_6$: C, 82.81; H, 7.16. Found: C, 82.88; H, 7.04.

7,13,21,27-Tetraphenyl-29,30,31,32-tetraallyloxy-2,3,16,17-tetrahomo-3,17-dioxacalix[4]arene 4c. The reaction residue was recrystallized from CH_2Cl_2 and methanol to produce 792 mg (82.3%) of the product **4** as crystalline solid. mp 244-245 °C; ^{1}H NMR ($CDCl_3$, 50 °C) δ 7.50-7.25 (m, 28, Ar*H*), 5.75 (m, 4, C*H* =), 4.98 (d, 4, = CH_2, J = 17.2 Hz), 4.82 (d, 4, = CH_2, J = 10.4 Hz), 4.53 (s, 8, ArCH_2O), 4.00 (br, 4, ArCH_2Ar), 3.96 (d, 8, OCH_2C =, J = 5.6 Hz); (-25 °C) 7.50-7.25 (m, 28, Ar*H*), 5.75 (m, 4, C*H* =), 5.01 (d of d, 4, = CH_2, J = 17.2 & 1.6 Hz), 4.84 (d, 4, = CH_2, J = 10.4 Hz), 4.60 (d, 4, ArCH_2O, J = 10.3 Hz), 4.58 (d, 2, ArCH_2Ar, J = 13.6 Hz), 4.45 (d, 4, ArCH_2O, J = 10.3 Hz), 4.05 (br, 4, OCH_2C =), 3.89 (br, 4, OCH_2C =), 3.48 (d, 2, ArCH_2Ar, J = 13.6 Hz); ^{13}C NMR ($CDCl_3$): δ 156.30, 141.01, 136.77, 135.48, 134.29, 131.31, 129.55, 129.03, 128.69, 127.18, 126.93 (Ar, H*C* =), 116.99 (= *C*H_2), 75.89, 67.14 (O*C*H_2), 32.27 (*C*H_2). Anal. Calcd. For $C_{66}H_{60}O_6$: C, 83.52; H, 6.37. Found: C, 83.45; H, 6.29.

7,13,21,27-Tetraphenyl-29,30,31,32-tetrabutyloxy-2,3,16,17-tetrahomo-3,17-dioxacalix-[4]arene 4d. The reaction residue was recrystallized from CH_2Cl_2 and methanol to produce 968 mg (94%) of the product **4** as crystalline solid. mp 227-228 °C; ^{1}H NMR ($CDCl_3$, 25 °C) δ 7.57-7.25 (m, 28, Ar*H*), 4.53 (s, 8, ArCH_2O), 4.55 (d, 2, ArCH_2Ar, J = 13.6 Hz), 3.58 (t, 4, CH_2, J = 7.2 Hz), 3.42 (t, 4, CH_2, J = 7.2 Hz), 3.38 (d, 2, ArCH_2Ar, J = 13.6 Hz), 1.45 (quintet, 4, CH_2, J = 7.2 & 8.0 Hz), 1.35 (quintet, 4, CH_2, J = 7.2 & 8.0 Hz), 1.05 (sextet, 8, CH_2, J = 7.2 & 8.0 Hz), 0.54 (t, 12, CH_3, J = 7.2 Hz). (0 °C) δ 7.56-7.28 (m, 28, Ar*H*), 4.56 (d, 4, ArCH_2O, J = 10.6 Hz), 4.55 (d, 2, ArCH_2Ar, J = 13.7 Hz), 4.52 (d, 4, ArCH_2O, J = 10.6 Hz), 3.59 (t, 2, CH_2, J = 7.2 Hz), 3.58 (t, 2, CH_2, J = 7.2 Hz), 3.45 (d, 2, ArCH_2Ar, J = 13.7 Hz), 3.39 (t, 2, CH_2, J = 7.2 Hz), 3.38 (t, 2, CH_2, J = 7.2 Hz), 1.46 (m, 4, CH_2), 1.36 (m, 4, CH_2), 1.05 (sextet, 8, CH_2, J = 7.2 Hz), 0.54 (t, 12, CH_3, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$): δ 156.61, 140.59, 135.87, 135.20, 130.60, 128.96, 128.81, 128.57, 126.76 (Ar), 75.46, 67.03 (O*C*H_2), 32.11 (Ar*C*H_2Ar), 30.85 (*C*H_2), 19.15 (*C*H_2), 13.77 (*C*H_3). Anal. Calcd. For $C_{70}H_{76}O_6$: C, 82.97; H, 7.56. Found: C, 82.88; H, 7.62.

7,13,21,27-Tetraphenyl-29,30,31,32-tetrahexyloxy-2,3,16,17-tetrahomo-3,17-dioxacalix[4]arene 4e. To heated suspension of compound **3** (804 mg, 1.02 mmole) and NaH (800 mg, 60% oil dispersion) in dry DMF (30 mL), hexyl iodide (2.5 mL, mmole) was added under Ar and then the reaction mixture was heated at 70 °C for 48 h. A second portion of hexyl iodide (2.5 mL) and NaH (750 mg) were then added, and heating was continued for an additional 48 h. After small amount of ethanol was added to destroy the excess NaH, solvent was removed *in vacuo* and then the organic material was extracted with methylene chloride. The organic layer was washed with water, dried and evaporated to afford slightly brown colored residue, purified by recrystallization from methylene chloride and methanol to afford tetrahexylated product **3** (978 mg, 85.3%) as white crystalline solid. mp 197-198 °C. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.56-7.27 (m, 28, Ar*H*), 4.57 (d, 4, ArCH_2O, J = 10.9 Hz), 4.56 (d, 2, ArCH_2Ar, J = 13.7 Hz), 4.53 (d, 4, ArCH_2O, J = 10.9 Hz), 3.45 (d, 2, ArCH_2Ar, J = 13.7 Hz), 3.57 (t, 2, CH_2O, J = 8.6 Hz), 3.55 (t, 2, CH_2O, J = 8.6 Hz), 3.40 (t, 2, CH_2O, J = 8.6 Hz), 3.39 (t, 2, CH_2O, J = 8.6 Hz), 1.51 (br, 4, CH_2), 1.35 (br, 4, CH_2), 1.03-0.89 (m, 24, CH_2), 0.66 (t, 12, CH_3, J = 6.7 Hz). (50 °C) δ 7.56-7.27 (m, 28, Ar*H*), 4.59 (d, 2, ArCH_2Ar, J = 13.4 Hz), 4.56 (s, 8, ArCH_2O), 3.59 (t, 2, CH_2O, J = 8.7 Hz), 3.56 (t, 2, CH_2O, J = 8.7 Hz), 3.45 (d, 2, ArCH_2Ar, J = 13.4 Hz), 3.43 (t, 2, CH_2O, J = 8.7 Hz), 3.41 (t, 2, CH_2O, J = 8.7 Hz), 1.52 (m, 4, CH_2), 1.36 (m, 4, CH_2), 1.07-0.94 (m, 24, CH_2), 0.68 (t, 12, CH_3, J = 6.9 Hz). ^{13}C NMR ($CDCl_3$): δ 156.65, 140.55, 135.85, 135.23, 130.53, 128.99, 128.78, 128.57, 126.75 (Ar), 75.77, 67.03 (O*C*H_2), 31.74 (Ar*C*H_2Ar), 30.84, 29.97, 25.65, 22.37(*C*H_2), 14.00 (*C*H_3). Anal. Calcd. For $C_{78}H_{92}O_6$: C, 83.23; H, 8.24. Found: C, 83.16; H, 8.15.

Solid state structure. The crystals were obtained by slow evaporation from a 1-pentanol solution. X-ray data collection was carried out using an Enraf Nonius CAD-4 diffractomer with graphite monochromator Mo-Kα radiation (λ = 0.7107 Å). All of the crystal data are listed in Table S1. The structure was solved and refined by the program SHELXL-97.[21]

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