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Synthesis, Conformation and Metal-binding Properties of Calix[6]arene Derivatives

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Abstract—A novel 1,3,5-trimethoxy-2,4,6-tribromoethoxycalix[6]arene (**2**) as a useful intermediate for the design of new host–guest-type receptors of calix[6]arene with C_{3v} symmetrical conformation and two 'biscalix[6]arenes' (**3–4**) has been synthesized by reacting 1,3,5-trimethoxy-*p*-*tert*-butylcalix[6]arene (**1**) with 1,2-dibromoethane in THF in the presence of NaH. Furthermore, several calix[6]arene derivatives **5–7** were then prepared from **2** and their conformational characteristics were studied by dynamic ^{1}H NMR spectroscopy. The complexing properties toward heavy metal ions of the prepared compound **5** are also reported in this paper with the help of fluorescence spectra and UV-visible spectra. It is shown that this ligand can form relatively stable complexes with Cu^{2+} and Sn^{2+}.

Introduction

Over the last decade, an increasing amount of attention has been paid to calixarenes,[1] focussing in particular on calix[4]arenes. Although larger calix[6]arenes are believed to be more useful for the complexation of larger, polyfunctional guest molecules because of their bigger cavity and the presence of six aromatic rings suitable for anchoring binding groups, little is known of the chemistry of calix[6]arenes, which can be confusing owing to their higher degree of functionality and greater conformational flexibility. Their isolation and characterization therefore remains a difficult task.[2]

Since Casnati et al.[3] first reported the synthesis of C_{3v} symmetrically substituted 1,3,5-trimethoxy-*p*-*tert*-butylcalix[6]arene (**1**), a number of findings from research into this compound have been reported.[4–9] Various selectively functionalized calix[6]arene derivatives adopting predominantly the flattened cone conformation have been yielded, enabling further study of the properties and applications of calix[6]arenes. A synthesis will be discussed here which targets 1,3,5-trimethoxy-2,4,6-tribromoethoxy-calix[6]arene (**2**), another useful starting material for the design of new host–guest-type calix[6]arene receptors. From this viewpoint, several 1,3,5-trialkoxy-2,4,6-trisubstituted calix[6]arene derivatives were prepared. Furthermore, studies of the conformational characteristics and complexing properties toward metal ions of these calix[6]arene derivatives are also reported in this paper.

Results and Discussion

Compound **1** was reacted with 1,2-dibromoethane in refluxing THF in the presence of NaH. During this reaction, a total of three compounds, which were separable by chromatography and preparative TLC were obtained in yields of 72, 12 and 5%, respectively. The major product could be easily characterized as the target compound **2** on the basis of its ^{1}H NMR spectrum that indicated two pairs of sharp singlets for *tert*-butyl and aromatic protons at high-field (0.96, 1.30 ppm) and at low-field (6.81, 7.81 ppm), respectively, one 9 H singlet at relatively high field (2.57 ppm) for the three equivalent OMe groups indicating that they were shielded in the cavity, a broad singlet for $ArCH_2Ar$ groups at 3.95 ppm implying the constant inversion of **2** occurring at a rate that was fast on the NMR time scale in solution, and a pair of triplets for the bromoethoxy resonances, in accordance with its C_{3v} symmetry and the conformational mobility of macrocycle.

The remaining two products (**3** and **4**) were very difficult to identify as their ^{1}H NMR spectra were too complicated to assign, even at very low temperature (−40°C), at which the broad spectra split to give sharp resonances. This implies that compound **3** and **4** might adopt a mixture of several conformations in solution. To obtain insight into the analysis of compound **3**, we measured DQF-COSY and 2D-EXSY spectra, which gave us more evidence about the exchanges of the $ArCH_2Ar$ and bromoethoxy protons indicating that there were at least three different

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Keywords: calix[6]arene derivatives; 1,3,5-trimethoxy-2,4,6-tribromoethoxycalix[6]arene; 1,3,5-trimethoxy-*p*-*tert*-butylcalix[6]arene.

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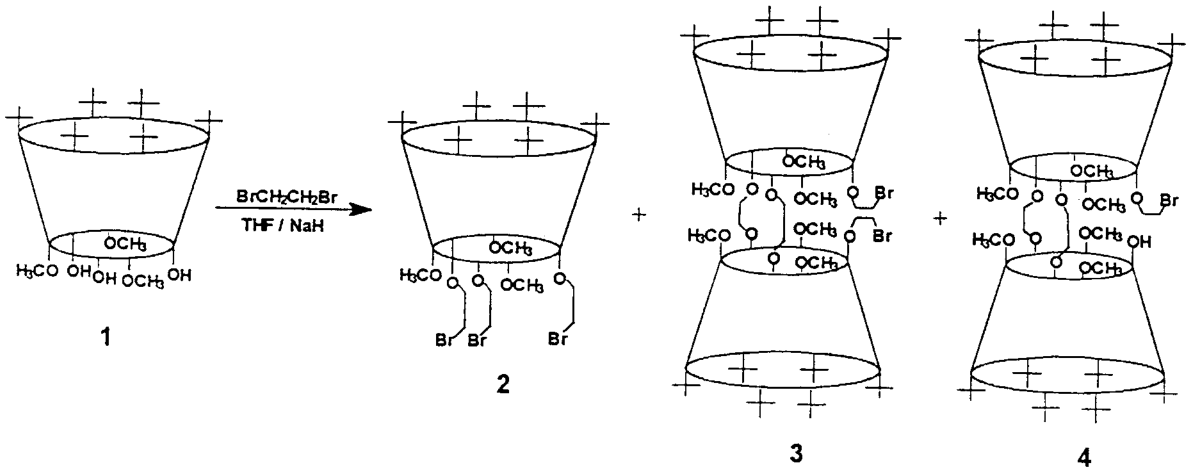


Scheme 1.

conformations in this compound. It was, however, too difficult to interpret these spectra in detail.

In the FAB mass spectra, two molecular ions were observed at 2296 ($[M-1]^+$, 42) and 2228 ($[M+1]^+$ +39 (K), 100), respectively, in accordance with two novel biscalix[6]-arenes as shown in Scheme 1. The structures of **3** and **4** are also well supported by their elemental analytical data.

To further confirm the above results, an attempt was made to obtain ^{1}H NMR spectra of **3** and **4** in which the corresponding signals could be specifically assigned to the structure. The temperature was raised to about 443 K, the broadened sets of resonances of these two compounds, recorded at room temperature, coalesced and finally appeared as an average of the signals (see Figs. 1 and 2) which could be assigned to all the protons of the two biscalixarene **3** and **4** as summarized in the Experimental section.

1,3,5-Trimethoxy-2,4,6,-tribromoethoxy-*p*-*tert*-butylcalix-[6]arene (**2**) represents a key intermediate for preparing various calix[6]arene derivatives possessing C_{3v} symmetry. Starting from this compound, three calix[6]arene derivatives (**5**–**7**) were synthesized in yields of 68, 70 and 75% by reacting **2** with 8-hydroxyquinoline, α-naphthol and *p*-*tert*-butylphenol, respectively, in MeCN in the presence of K_2CO_3 (Scheme 2).

In the ^{1}H NMR spectra of compounds **5**–**7**, the methylene protons appear as two separated resonances (AB system), which points to no or slow interconversion of the aromatic rings. For both the aromatic and *tert*-butyl protons, two singlets are present from the two different aromatic moieties, respectively, indicating a conformation with C_{3v} symmetry. The resonances of the methoxy groups appear at an upfield chemical shift (about 2.0 ppm). This reveals that these groups point toward the aryl groups of the

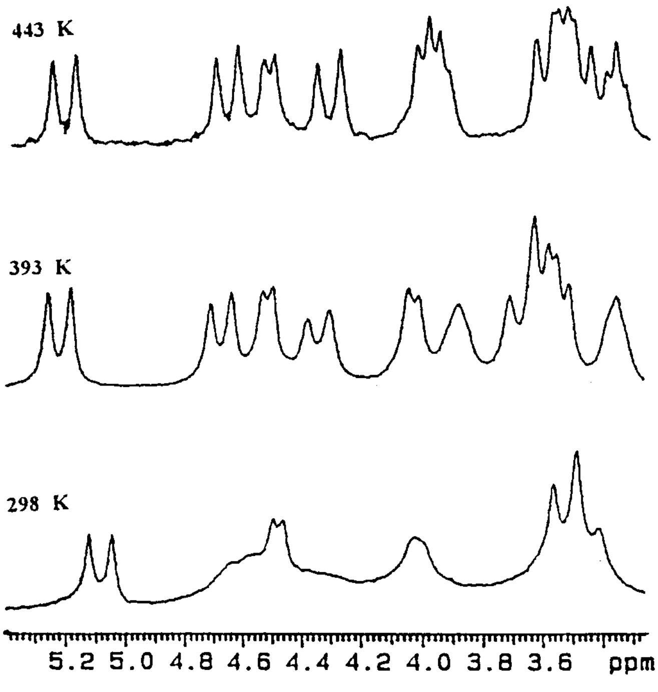


Figure 1. Methylene region of ^{1}H NMR spectrum of compound **3** in $CDCl_3$ or *ortho*-dichlorobenzene-d$_4$ at different temperatures.

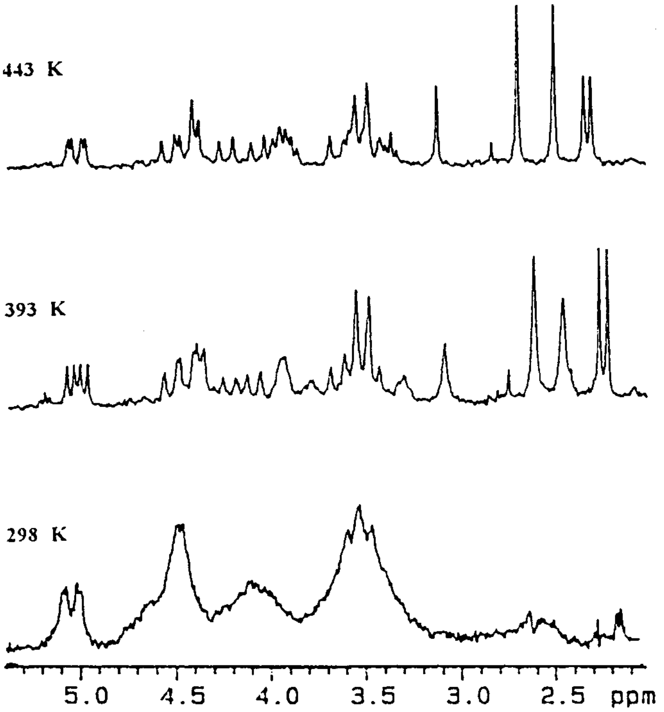
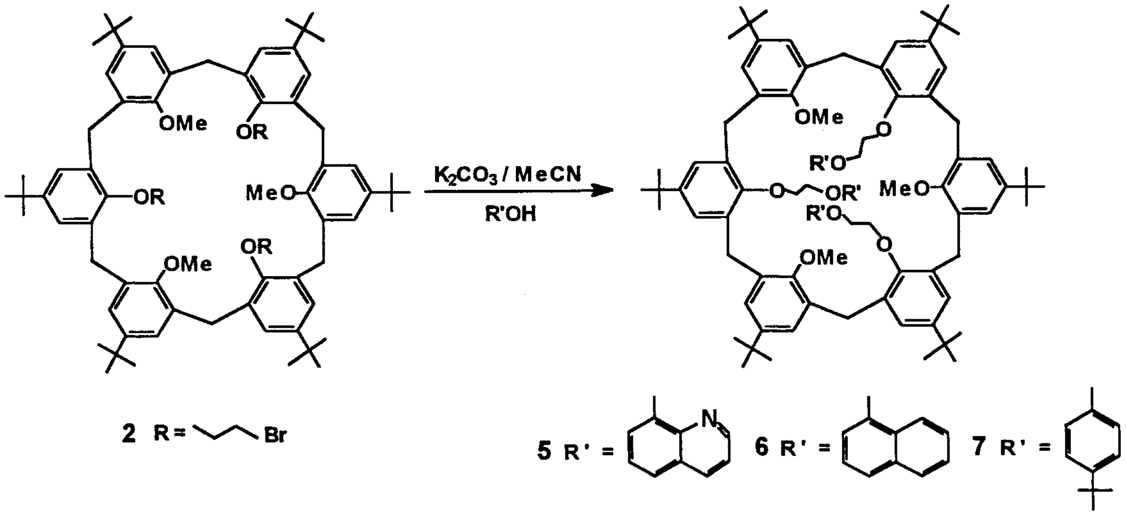


Figure 2. Methylene region of ^{1}H NMR spectrum of compound **4** in $CDCl_3$ or *ortho*-dichlorobenzene-d_4 at different temperatures.

calix[6]arene cavity. The ^{1}H NMR spectral data of compounds **5**–**7** for this conformer are listed in Table 1.

Like the similar work reported by Reinhoudt et al.,[8] in addition to the C_{3v}-symmetric conformation depicted above, the ^{1}H NMR spectra of compounds **5**–**7** also exhibited another set of signals of low intensity close to the intense signals of the C_{3v} conformer, which were in accordance with a C_s-symmetric 1,2,3-alternate conformation (see Table 2). In the weak signals of this minor conformer, one could observe four signals for *tert*-butyl protons in a 2:1:2:1 integral intensity ratio, a pair of doublets and two singlets for aryl protons at 6.61–7.30 ppm, three pair of doublets (AB system) for $ArCH_2Ar$ protons and two singlets at strong upfield shift (about 2.30 ppm) with a 2:1 intensity ratio for the methoxy groups implying that they also point toward the calix[6]-arene cavity.

The variable temperature NMR studies of **5** elucidate that there is a dynamic equilibrium between the flattened cone and 1,2,3-alternate conformations. The ^{1}H NMR spectra of these compounds did not respond to high temperature at all. Even at temperatures >333 K, almost all the ^{1}H NMR lines remained virtually unchanged. This phenomenon could be contributed to both of the two conformations possessing remarkable kinetic stability and the rate of conformational interconversion between them being very slow. The same was also observed by Reinhoudt et al.[8]



Scheme 2.

Table 1. Selected ^{1}H NMR data of the flattened cone (C_{3v}) conformers of **5–7** in $CDCl_3$ at 298 K

Compound	ArO s (6 H)[a]	ArE s (6 H)[b]	CH_2CH_2 t (12 H)	$ArCH_2Ar$ AB[c] (12 H)	OCH_3 s (9 H)	*t*-Bu (O[d]) s (27 H)	*t*-Bu (E[e]) s (27 H)	ArH[f]
5	7.22	6.55	4.75 (J=5.6 Hz) 4.48 (J=5.6 Hz)	4.60, 3.45	2.22	1.37	0.79	8.82 (dd, J=4.2, 1.7 Hz, 3H), 8.08 (dd, J=1.7 Hz, 3H), 7.25–7.50 12H)
6	7.20	6.67	4.48 (J=6.0 Hz) 4.45 (J=6.0 Hz)	4.65, 3.46	2.25	1.32	0.82	8.18 (d, J=8.3 Hz, 3H), 7.75 (d, J=8.3 Hz, 3H), 7.20–7.42 (m, 15 H)
7	7.27	6.64	4.32 (J=6.0 Hz) 4.27 (J=6.0 Hz)	4.62, 3.42	2.23	1.36	0.78	6.86 (s, 6H), 6.84 (s, 6H)

[a] Aromatic rings substituted with methoxy groups (O rings).

[b] Aromatic rings substituted with substituents other than methoxy groups (E rings).

[c] J=14–16 Hz.

[d] *t*-Butyl groups of O rings.

[e] *t*-Butyl groups of E rings.

[f] Aromatic protons of substituents.

Table 2. Selected ^{1}H NMR data of the 1,2,3-alternate (C_s) conformers of **5–7** in $CDCl_3$ at 298 K

Compound	ArO[a] 2d (4 H) s (2H)	ArE[b] 2d (4H) s (2 H)	$ArCH_2Ar$ AB[c] (12 H)	OCH_3 s (6 H) s (3H)	*t*-Bu (O[d]) s (18 H) s (9H)	*t*-Bu (E[e]) s (18H) s (9H)	ArH[f]
5	7.18, 7.16, 7.13	7.05, 6.79, 6.76	4.49, 3.64, 4.40, 3.52, 4.28, 3.37	2.50, 2.29	1.23, 1.29	0.94, 1.05	[g]
6	7.30, 7.14, 7.03	6.85, 6.81, 6.61	4.80, 3.78, 4.16, 3.68, 4.05, 3.52	2.41, 2.30	1.21, 1.24	1.00, 0.84	[g]
7	7.23, 7.20, 7.13	6.93, 6.74, 6.67	4.47, 3.67, 4.38, 3.48, 4.16, 3.37	2.41, 2.14	1.26, 1.25	1.00, 0.98	[g]

[a] Aromatic rings substituted with methoxy groups (O rings).

[b] Aromatic rings substituted with substituents other methoxy groups (E rings).

[c] J=14–16 Hz.

[d] *t*-Butyl groups of O rings.

[e] *t*-Butyl groups of E rings.

[f] Aromatic protons of substituents.

[g] Due to overlap or low abundance of the 1,2,3-alternate conformers, not all resonances could be assigned.

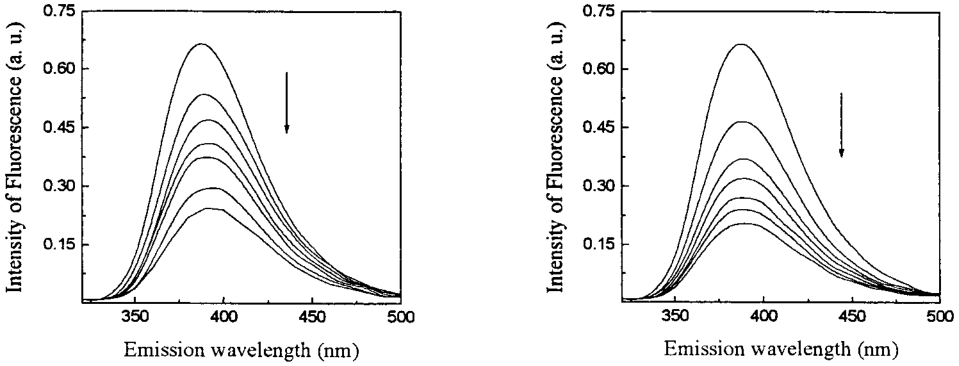


Figure 3. Fluorescence spectra of **5** (3.4×10^{-5} mol dm^{-3}) in MeCN at 25°C with successive addition of $CuCl_2$ (left) (excitation wavelength 386 nm) and $SnCl_2$ (right) (excitation wavelength 392 nm).

The complexation behavior of **5** toward several heavy metal ions was studied with the help of the fluorescence and UV-visible spectra. Fig. 3 shows that the fluorescence of **5** decreased markedly on successive addition of $CuCl_2$ and $SnCl_2$. This suggests that these two metal ions might be transported to the cavity of calix[6]arene **5** to form an inclusion complex. However, there is no visible change of the fluorescence spectra in the presence of Mn^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+} cations.

In order to obtain more evidence for the ability of compound **5** to complex Cu^{2+} and Sn^{2+} cations, UV-visible spectroscopic analyses were also performed. The plot with $C_0/\Delta OD$ versus 1/OD is linear (Fig. 4), supporting the 1:1 stoichiometry of the complex according to the Hildberand–Benesi equation,[10] and also giving the values of the association constants (K_a) of the complexation equilibrium to be 40000 and 3000 mol^{-1} dm^3, respectively, which are indicative of relative stability of these inclusion complexes, especially for **5** with Cu^{2+}. From the data of fluorescence spectra, we can also obtain the same results.

Conclusions

Two novel biscalix[6]arenes **3** and **4** were prepared by treatment of 1,3,5-trimethylated *p-tert*-butylcalix[6]arene (**1**) with 1,2-dibromoethane in the presence of NaH, and they possessed a capsule-like cavity with an entrance. This characteristic structure enables us to believe that they could be very useful for precisely recognizing guest molecules. To the best of our knowledge, although biscalix[4]arenes have been reported extensively, the synthesis of biscalix[6]arenes has hardly been studied except for only two examples so far.[11,12] By the same reaction, a useful intermediate **2** for the synthesis of new host–guest-type receptors of calix[6]arene with a C_{3v} symmetrical conformation was achieved in 72% yield. Starting from this compound, several calix[6]arene derivatives **5–7** were also synthesized. The variable temperature ^{1}H NMR studies indicated that these compounds predominantly adopted a flattened cone conformation. At room temperature this conformation slowly interconverts with a 1,2,3-alternate conformation. Both the fluorescence and UV-visible spectroscopy were employed to determine the complexing ability of compound **5** toward heavy metal ions, and show that this compound could form relatively stable inclusion complexes with Cu^{2+} and Sn^{2+}.

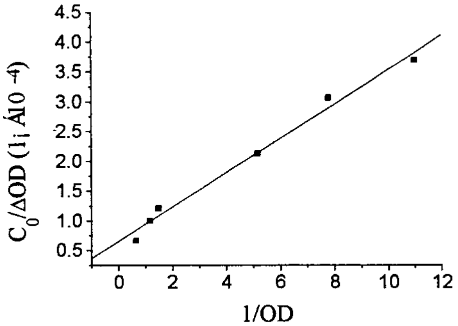


Figure 4. Plot of $C_0/\Delta OD$ vs. 1/OD for the complexation of **5** with Cu^{2+} in MeCN. C_0 represents the concentration of calixarene (3.40×10^{-5} mol dm^{-3}), ΔOD is the absorption intensity change of **5** upon addition of $CuCl_2$ at six different concentrations ($0\sim4.33\times10^{-2}$ mol dm^{-3}).

Experimental

All reactions were carried out under nitrogen. THF was freshly distilled prior to use. All other chemicals were of reagent grade and used without further purification. Melting points were uncorrected. ^{1}H NMR spectra were recorded on a Brucker DPX-400 spectrometer and ^{13}C NMR spectra were recorded on a Varian Unity 200 spectrometer with $CDCl_3$ as solvent and TMS as internal standard, unless otherwise indicated. IR spectra were recorded with a Perkin–Elmer 782 spectrometer. EI and FAB mass spectra were obtained with a KYKY-ZHT-5 instrument. Elemental analyses were performed by the Analytical Laboratory of the Institute. UV–visible spectra were measured with a HITACHI-340 spectrometer. Fluorescence spectra were determined on a HITACHI-850 spectrometer. *p-tert*-Butylcalix[6]arene[13] and 1,3,5-trimethoxy-*p-tert*-butylcalix[6]arene (**1**)[3] were prepared according to literature procedures.

Synthesis of 1,3,5-trimethoxy-2,4,6-tribromoethoxy-*p-tert*-butylcalix[6]arene (2) and biscalix[6]arenes (3-4). A suspension of 1,3,5-trimethoxy-*p-tert*-butylcalix[6]arene **1** (5 g, 4.93 mmol) and NaH (3.6 g, 14.79 mmol) in THF (100 ml) was stirred for 3 h at room temperature. Then 1,2-dibromoethane (5 ml) was added and refluxed for 120 h. The reaction mixture was allowed to cool to room temperature, then water was added dropwise to destroy the remaining NaH until bubbling stopped (CAUTION!). The solvent was removed by evaporation, the residue was treated with 10% HCl (50 ml) and extracted with $CHCl_3$ (3×50 ml). The organic layer was washed with water (2×100 ml) and dried over Na_2SO_4. The crude product was purified by flash column chromatography on silica ($CHCl_3$/Hexane) to give **2–4** as white solids.

2: yield 72%; mp 248–250°C; IR (KBr) ν_{max} (cm^{-1}) 2960, 1480, 1455, 1360, 1010; ^1H NMR δ 7.18 (s, 6H, Ar*H*), 6.81 (s, 6H, Ar*H*), 3.99 (t, *J*=6.0 Hz, 6H, OCH_2), 3.95 (bs, 12H, ArCH_2Ar), 3.52 (t, *J*=6.0 Hz, 6H, CH_2Br), 2.57 (s, 9H, OCH_3), 1.30 (s, 27H, C(CH_3)$_3$), 0.96 (s, 27H, C(CH_3)$_3$); ^{13}C NMR δ 154.28, 151.45, 146.11, 145.73, 133.43, 132.99, 127.20, 124.61 (Ar*C*), 72.11 (OCH_2), 59.99 (OCH_3), 34.17, 34.02, (*C*(CH_3)$_3$), 31.54, 31.22 (C(CH_3)$_3$), 30.49 (CH_2Br), 30.12 (ArCH_2Ar); FAB-MS: *m/e* 1336 (M^+, 100); Anal. Calcd for $C_{75}H_{99}O_6Br_3$: C, 67.41; H, 7.47; Br, 17.94. Found: C, 67.82; H, 7.45; Br, 18.04.

3: yield 12%; mp>300°C (dec.); IR (KBr) ν_{max} (cm^{-1}) 2960, 1480, 1450, 1360, 1010; ^1H NMR (*o*-$C_6D_4Cl_2$, 170°C) δ 7.42 (s, 8H, Ar*H*), 7.22 (s, 8H, Ar*H*), 7.02 (s, 4H, Ar*H*), 6.79 (s, 4H, Ar*H*), 5.21 (d, *J*=14.9 Hz, 4H, ArCH_2Ar), 4.67 (d, *J*=14.6 Hz, 4H, ArCH_2Ar), 4.53 (t, *J*=6.8 Hz, 4H, OCH_2), 4.33 (d, *J*=15.2 Hz, 4H, ArCH_2Ar), 4.00 (t, *J*=7.0 Hz, 8H, OCH_2CH_2O), 3.63 (d, *J*=14.2 Hz, 4H, ArCH_2Ar), 3.58 (d, *J*=12.9 Hz, 4H, ArCH_2Ar), 3.53 (d, *J*=14.6 Hz, 4H, ArCH_2Ar), 3.40 (t, *J*=6.5 Hz, 4H, CH_2Br), 2.55 (s, 12H, OCH_3), 2.40 (s, 6H, OCH_3), 1.58 (s, 18H, C(CH_3)$_3$), 1.35 (s, 36H, C(CH_3)$_3$), 1.05 (s, 36H, C(CH_3)$_3$), 0.92 (s, 18H, C(CH_3)$_3$); FAB-MS: *m/e* 2296 ($[M-1]^+$, 42); Anal. Calcd for $C_{146}H_{190}O_{12}Br_2$; C, 76.34; H, 8.34; Br, 6.96. Found: C, 76.67; H, 8.39; Br, 7.05.

4: yield 5%; mp>300°C (dec.); IR (KBr) ν_{max} (cm^{-1}) 3423 (OH), 2921, 1637, 1455, 1383, 1024; ^1H NMR (*o*-$C_6D_4Cl_2$, 170°C) δ 7.42 (s, 4H, Ar*H*), 7.41 (s, 4H, Ar*H*), 7.24 (s, 4H, Ar*H*), 7.11 (s, 4H, Ar*H*), 7.05 (s, 2H, Ar*H*), 7.03 (s, 2H, Ar*H*), 6.82 (s, 2H, Ar*H*), 6.79 (s, 2H, Ar*H*), 5.20 (d, *J*=15.2 Hz, 2H, ArCH_2Ar), 5.17 (d, *J*=15.2 Hz, 2H, ArCH_2Ar), 4.45–4.67 (4d, *J*=14–15 Hz, 8H, ArCH_2Ar), 4.32 (d, *J*=14.2 Hz, 2H, ArCH_2Ar), 4.20 (d, 2H, *J*=15.2 Hz, 2H, ArCH_2Ar), 4.02 (t, *J*=6.5 Hz, 4H, OCH_2CH_2O), 3.87 (t, *J*=6.5 Hz, 2H, OCH_2), 3.55–3.80 (4d, 14–15 Hz, 8H, ArCH_2Ar), 3.40 (t, *J*=6.6 Hz, 2H, OCH_2CH$_2$O), 3.35 (t, *J*=6.5 Hz, 2H, CH_2Br), 3.12 (t, *J*=6.6 Hz, 2H, OCH$_2$$CH_2$O), 2.72 (s, 6H, O$CH_3$), 2.52 (s, 6H, O$CH_3$), 2.34 (s, 3H, O$CH_3$), 2.30 (s, 3H, O$CH_3$), 1.62 (s, 9H, C($CH_3$)$_3$), 1.60 (s, 9H, C($CH_3$)$_3$), 1.39 (s, 18H, C($CH_3$)$_3$), 1.32 (s, 18H, C($CH_3$)$_3$), 1.08 (s, 18H, C($CH_3$)$_3$), 1.06 (s, 18H, C($CH_3$)$_3$), 1.02 (s, 9H, C($CH_3$)$_3$), 0.95 (s, 9H, C($CH_3$)$_3$); FAB-MS: *m/e* 2228 ($[M+1+K]^+$, 100); Anal. Calcd for $C_{144}H_{187}O_{12}Br$: C, 78.98; H, 8.61; Br, 3.65. Found: C, 78.74; H, 8.75; Br, 3.31.

5,11,17,23,29,35-Hexa-*tert*-butyl-38,40,42-trimethoxy-37,39,41-tris(8′-quinolinoxyethoxy)calix[6]arene (5). A suspension of 8-hydroxyquinoline (0.1 g, 0.69 mmol) and K_2CO_3 (0.14 g, 1.04 mmol) in CH_3CN (30 ml) was refluxed for 30 min. Then **2** (0.3 g, 0.23 mmol) was added and refluxing was continued for 18 h. After evaporation of the solvent, the residue was extracted with $CHCl_3$ and then submitted to preparative thin layer chromatography on silica ($CHCl_3$/AcOEt=3/2). The obtained product was further purified by recrystallization from $CHCl_3$/MeOH to afford pure **5** as colorless crystalline needles: yield 68%; mp 220–221°C; IR (KBr) ν_{max} (cm^{-1}) 2956, 1571, 1478, 1260, 1110; ^1H NMR spectra data was summarized in Tables 1 and 2; ^{13}C NMR (C_{3v} conformer) δ 154.54, 154.41, 151.61, 149.12, 145.73, 145.62, 140.03, 135.88, 133.47, 133.04, 129.50, 127.92, 126.74, 123.45, 121.45 120.02, 109.62 (Ar*C*), 70.95 (OCH_2), 67.78 (OCH_2), 60.03 (OCH_3), 34.19, 33.92 (*C*(CH_3)$_3$), 31.61, 31.10 (C(CH_3)$_3$), 29.68 (ArCH_2Ar); EI-MS; *m/e* 1568 ($[M+1+K]^+$, 1); Anal. Calcd for $C_{102}H_{117}N_3O_9$: C, 80.12; H, 7.71; N, 2.75. Found: C, 79.61; H, 7.74; N, 2.77.

5,11,17,23,29,35-Hexa-*tert*-butyl-38,40,42-trimethoxy-37,39,41-tris(α-naphthaoxyethoxy)calix[6]arene (6). According to the procedure described above for the preparation of **5**, α-naphthol (33 mg, 0.23 mmol) was dissolved in CH_3CN (15 ml) and treated with K_2CO_3 (80 mg, 0.35 mmol) followed by **2** (100 mg, 0.0075 mmol). The mixture was heated at reflux for 24 h and then worked up as described above to yield a crude product. Preparative thin layer chromatography on silica of the residue afforded pure **6** a white solid after recrystallization from $CHCl_3$/MeOH: yield 70%; mp 195–196°C; IR (KBr) ν_{max} (cm^{-1}) 2958, 1480, 1461, 1269, 1020; ^1H NMR spectra data was summarized in Tables 1 and 2; ^{13}C NMR (C_{3v} conformer) δ 154.55, 151.86, 145.72, 145.68, 134.46, 133.65, 133.54, 133.02, 127.99, 127.21, 126.31, 125.73, 125.65, 125.09, 123.56, 122.36, 120.40, 104.58 (Ar*C*), 71.14 (OCH_2), 67.83 (OCH_2), 60.31, (OCH_3), 34.17, 33.99 (*C*(CH_3)$_3$), 31.59, 31.19 (C(CH_3)$_3$), 29.88 (ArCH_2Ar); EI-MS: *m/e* 1549 ($[M+1+Na]^+$, 30); Anal. Calcd for $C_{105}H_{120}O_9$: C, 82.64; H, 7.93. Found: C, 81.95; H, 7.95.

5,11,17,23,29,35-Hexa-*tert*-butyl-38,40,42-trimethoxy-37,39,41-tris(*p*-*tert*-butylphenoxyethoxy)calix[6]arene (7). According to the procedure described above for the preparation of **5**, *p*-*tert*-butylphenol (35 mg, 0.23 mmol) was dissolved in CH_3CN (15 ml) and treated with K_2CO_3 (80 mg, 0.35 mmol) followed by **2** (100 mg, 0.0075 mmol). The mixture was heated at reflux for 24 h and then worked up as described above to yield a crude product. Recrystallization of the residue from $CHCl_3$/MeOH gave pure **7** as a white powder: yield 75%; mp 114–115°C; IR (KBr) ν_{max} (cm^{-1}) 2960, 1513, 1480, 1247, 1017; ^1H NMR spectra data was summarized in Tables 1 and 2; ^{13}C NMR (C_{3v} conformer) δ 156.49, 154.54, 151.63, 145.65, 143.50, 133.60, 133.16, 127.98, 126.16, 125.96, 123.51, 114.11 (Ar*C*), 71.09 (OCH_2), 67.14 (OCH_2), 60.13 (OCH_3), 34.21, 34.04 (*C*(CH_3)$_3$), 31.52, 31.15 (C(CH_3)$_3$), 29.80 (ArCH_2Ar); EI-MS: *m/e* 1567 ($[M+1+Na]^+$, 12); Anal. Calcd for $C_{105}H_{138}O_9$: C, 81.67; H, 9.01. Found: C, 81.23; H, 9.05.

Acknowledgements

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