# Syntheses and NMR Spectroscopic Studies of Bridged and Capped Calix[6]arenes: High-Yield Syntheses of Unimolecular Caged Compounds from Calix[6]arene

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Calix[6]arenes were bridged with a xylenyl unit or capped with a mesitylenyl unit, and their conformational properties were examined by spectroscopic methods. As previously reported by Gutsche et al., the calix[6]arene bridged on 1,4-phenyl units could enjoy slow ring inversion. The calix[6]arene bridged on 1,2-phenyl units also showed the ring inversion behavior, whereas in the calix[6]arene bridged on 1,3-phenyl units, ring inversion was virtually suppressed because of destabilization of the transition state. The capping of 1,3,5-tri-O-alkylated calix[6]arenes with 1,3,5-tris(bromomethyl)benzene gave the products in high yields (80–91%). This advantage was accounted for by the $C_3$ symmetrical complementarity of these two reactants. In these capped products, ring inversion was inhibited under the present measurement conditions, and the presence of a unimolecularly closed inner cavity was suggested on the basis of $^1$H NMR spectroscopy and MM3 calculations.

Calix[*n*]arenes are cyclic oligomers that belong to the class of [$1_n$]metacyclophanes. As calix[*n*]arenes have a cavity-shaped architecture, they are useful as building blocks for host–guest-type receptors and catalysts through appropriate modification of the edges.[1] Functional groups can be introduced either to the upper rim by means of electrophilic substitution reactions[1–5] or to the lower rim by means of Williamson-type OH modifications.[1,6–12] Among them, the $\pi$-basic cavity of calix[4]arenes seems to be too small to accept organic host molecules, whereas those of calix[6]arenes and calix[8]arenes seem to be large enough to include them. It is no doubt that to precisely recognize organic guest molecules the receptor cavity should be rigid and well-delineated. Since calix[*n*]arenes have rotational freedom about their phenyl units,[1] we have to suppress this before we enjoy molecular design of calix[*n*]arene-based receptor molecules. It is now possible to suppress the rotation of phenyl units in calix[4]arenes by bulky O substituents,[1,13] but in calix[6]arenes and calix[8]arenes, it is still a difficult job. Thus, Gutsche et al.[2c] previously described that "even the calix[6]arenes are rather flexible and further insight into their mode of action must await the construction of more rigid and conformationally-defined analogs".

In 1991, Casnati et al.[7c] reported on the $^1$H NMR spectroscopic properties of 5,11,17,23,29,35-hexa-*tert*-butyl-37,39,41-trimethoxy-38,40,42-tris[(*tert*-butoxycarbonyl)methoxy]calix[6]arene. Although the line broadening was scarcely induced by the wide range of temperature,[7c] it was later proven that the phenyl units in this compound still enjoy the rotation, the rate being slower than the NMR time scale.[14,15] Then, how can we immobilize the ring inversion of calix[6]arenes? In 1993, Biali et al.[16] succeeded in the immobilization using two

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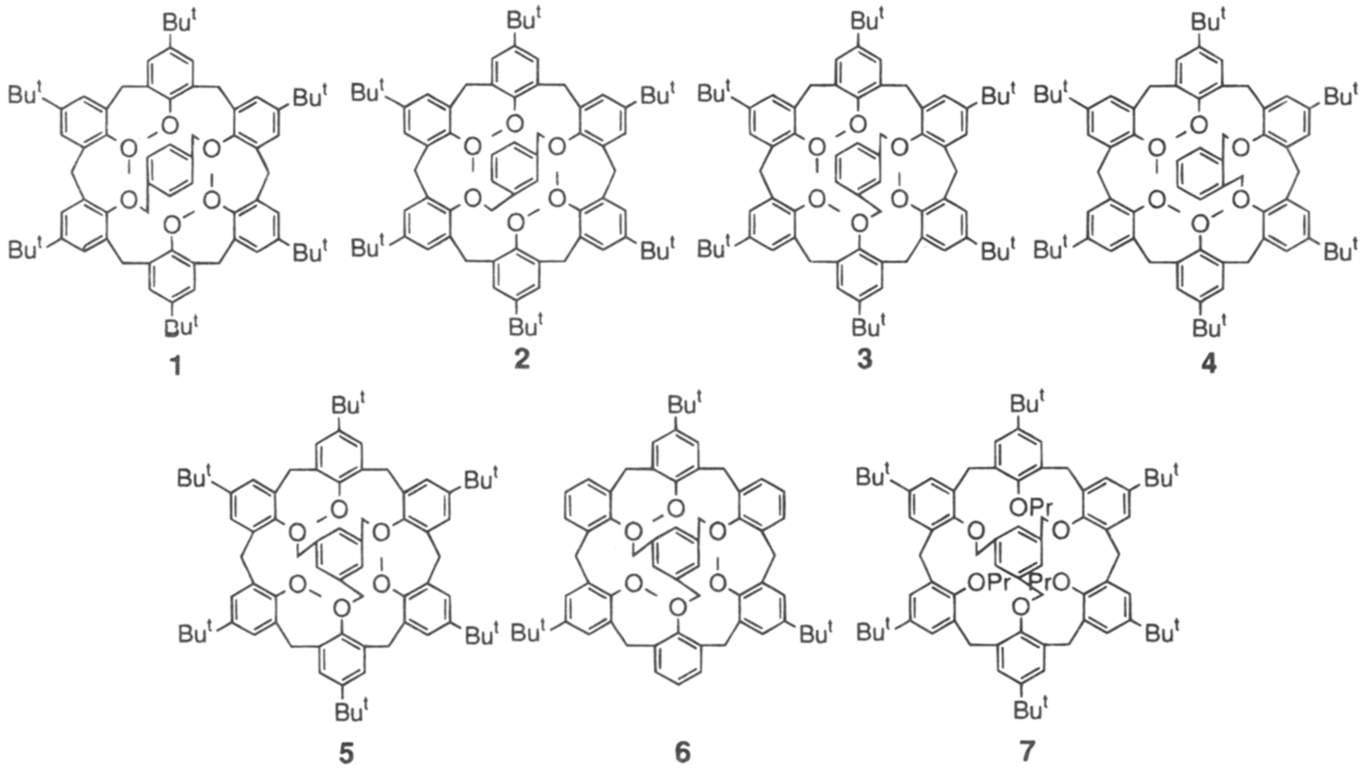
**Chart 1**



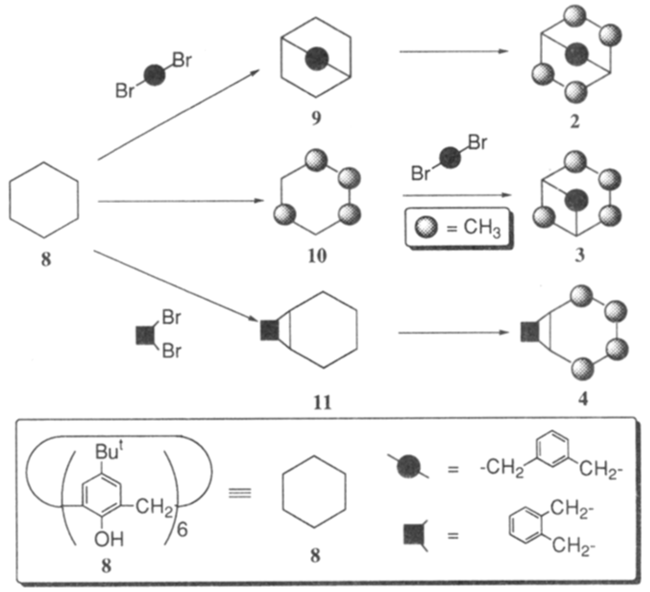
dialkylphosphates which can react with six phenol groups. We considered that the immobilization can be done more conveniently by capping calix[6]arene with regioselectively substituted aromatic compounds.[17-19] Recently, Gutsche et al.[17] synthesized compound **1** in which the 1,4-phenyl units are bridged by a xylenyl unit; **1** is capable of undergoing a conformational transformation in which the bridging moiety becomes threaded through the annulus to produce a "self-anchored rotaxane". More recently, we synthesized calix[6]arenes that are bridged by triple linkages at the upper-rim side or at the lower-rim side.[18] The two-dimensional (2D) EXSY measurements established that, in these calix[6]arenes, the ring inversion is entirely inhibited. The results suggest that the bridging with multiple linkages is more advantageous for suppression of the ring inversion.

To obtain further insights into the relation between the ring inversion in calix[6]arenes and the bridging effect, we synthesized doubly bridged **2**–**4** and triply bridged (i.e., capped) **5**–**7** (Chart 1) and thoroughly studied the $^1$H NMR spectroscopic properties, comparing them with those reported for **1** by Gutsche et al.[17] We have found that the capping to synthesize **5**–**7** proceeds smoothly and in high yields and they possess an inner cavity because of their unique conformation.

## Results and Discussion

**Doubly Bridged Calix[6]arenes.** We previously found that the reaction of 5,11,17,23,29,35-hexa-*tert*-butylcalix[6]arene-37,38,39,40,41,42-hexol (**8**) with α,α′-dibromo-*m*-xylene and α,α′-dibromo-*o*-xylene gives a 1,4-bridged calix[6]arene (**9**) and a 1,2-bridged calix[6]arene (**11**), respectively (Scheme 1).[19] Methylation of **9** and **11** with methyl iodide yields **2** and **4**, respectively. 5,11,17,23,29,35-Hexa-*tert*-butyl-37,38,39,41-tetramethoxy-40,42-dihydroxycalix[6]arene (**10**) can be synthesized via two steps from **8**.[19] The reaction with α,α′-dibromo-*m*-xylene gives a 1,3-bridged calix[6]arene (**3**).

**Scheme 1**



The temperature-dependent $^1$H NMR spectra of **2** are shown in Figure 1. It is seen from the spectrum at −30 °C that *tert*-butyl protons and aromatic (calix[6]arene) protons appear in a 1:2 ratio and the methoxy protons appear as a singlet resonance. The ArCH$_2$Ar methylene protons give two pairs of doublets in a 1:2 integral intensity ratio. The results clearly indicate that **2** adopts a cone conformation. Since a 2-H proton (5.48 ppm) (1H)

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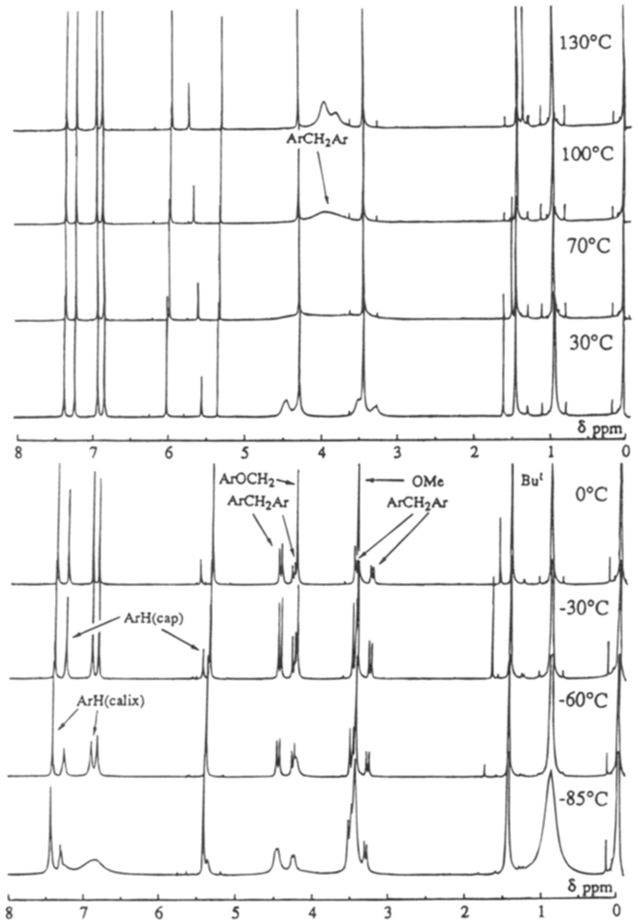


**Figure 1.** Temperature dependence of $^1$H NMR spectra for **2** (400 MHz, $CD_2Cl_2$ below 0 °C and $Cl_2CDCDCl_2$ above 30 °C).

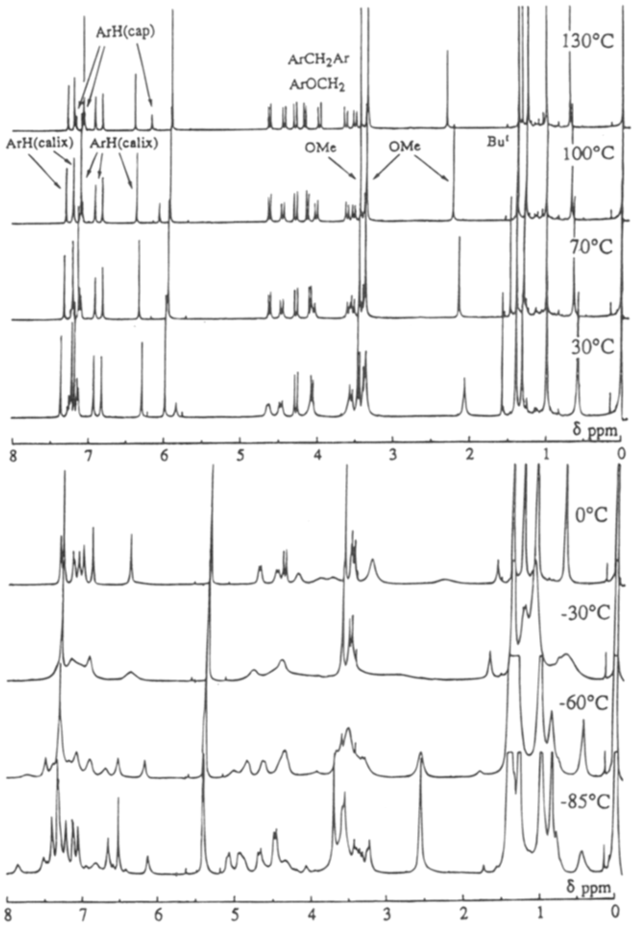
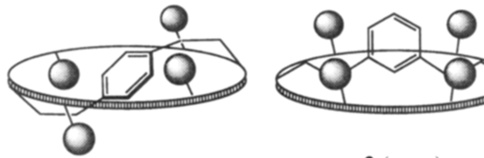


**Figure 3.** Temperature dependence of $^1$H NMR spectra for **3** (400 MHz, $CD_2Cl_2$ below 0 °C and $Cl_2CDCDCl_2$ above 30 °C).



**1** (1,2,3-alternate)

**2** (cone)

**Figure 2.** Schematic representation of the stable conformations proposed for **1** (1,2,3-alternate)[17] and **2** (cone).

and methylene protons (4.25 ppm) in the *m*-xylenyl cap shift to a higher magnetic field, the aromatic nucleus should stand vertically to the calix[6]arene plane and partly sink in the calix[6]arene cavity (as in Figure 2). This is in marked contrast to **1** which tends to adopt a 1,2,3-alternate conformation with a "self-anchored rotaxane" structure.[17] Conceivably, the *p*-xylenyl bridge is considerably longer than the distance between the 1,4-phenyl units in calix[6]arene and therefore must be distorted into a sigmoidal conformation to allow the cavity accommodate it. This requirement forces the calix[6]arene to adopt a 1,2,3-alternate conformation. In contrast, the *m*-xylenyl bridge is rather comparable with the distance between the 1,4-phenyl units in calix[6]arene; in fact, one can construct a CPK molecular model of **2** without any steric distortion. As shown in Figure 1, two pairs of doublets for the $ArCH_2Ar$ methylene protons coalesce at 80 °C into two singlet resonances in a 1:2 integral intensity ratio. Such a coalescence is not seen for other protons. The findings indicate that **2** can enjoy cone–cone ring inversion; as seen from the high coalescence temperature, however, the rate is much slower than those for conventional calix[6]arenes ($T_c <$ −60 °C; hexamethyl ether of *p*-*tert*-butylcalix[6]arene). This is of course attributed to the bridging effect that suppresses the conformational change from the nondistorted ground state to the sterically distorted transition state.

The temperature-dependent $^1$H NMR spectra of **3** are shown in Figure 3. In the low-temperature region (below 0 °C), the splitting pattern is so complex and so broadened that it seems difficult to assign the conformation adopted by **3**. In the high-temperature region, on the other hand, the splitting pattern becomes simple. The $^1$H NMR spectrum at 130 °C can be easily assigned to **3**, taking the symmetry of this molecule into account; one can observe four different signals for *tert*-butyl protons and aromatic (calix[6]arene) protons in a 1:1:2:2 integral intensity ratio and three different signals for methoxy protons in a 1:1:2 integral intensity ratio. Very interestingly, four pairs of doublets at 3.3–4.7 ppm are firmly maintained even at 130 °C. Three of these AB patterns are assigned to the $ArCH_2Ar$ methylene protons, and one of them is assigned to the $ArOCH_2Ar$ methylene protons in the xylenyl bridge. The result implies that the calix[6]arene ring is not inverted or, even if it is, the rate is much slower than the NMR time scale.[14,17] The correlation of these four pairs of doublets was resolved as in Figure 4 on the basis of 2D COSY $^1$H NMR (400 MHz) spectroscopy. It is known that the methylene protons in the xylenyl bridge usually appear at 4.2–4.6 ppm.[19]

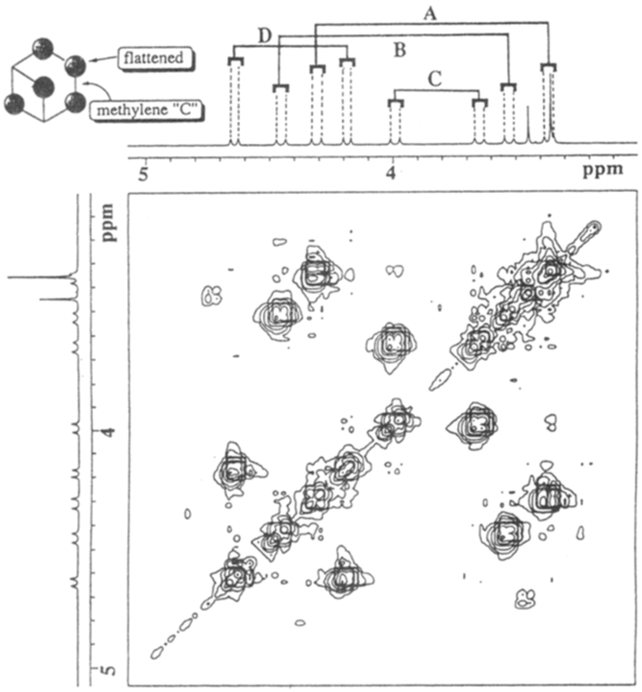


**Figure 4.** Two-dimensional COSY $^1$H NMR (400 MHz) spectrum and correlation of the $ArCH_2Ar$ and $ArOCH_2Ar$ methylene protons in **3**.

Hence, among four pairs (A–D in Figure 4), the D pair should be assigned to the $ArOCH_2Ar$ methylene protons.

The $\Delta\delta_H$ values for the A, B, and C pairs are 0.95, 0.93, and 0.35 ppm, respectively. Since $\Delta\delta_H$ for a regular cone conformation is ca. 0.9 ppm,[1,2] one phenyl unit flanked by the C methylenes is flattened and the five residual phenyl units adopt a regular cone position. Judging from the symmetry and the structure of **3**, we consider that the phenyl unit farthest from the bridgehead is flattened (Figure 4). This is also supported from the chemical shift values of methoxy protons because the methoxy protons in the flattened phenyl unit should shift to a higher magnetic field. Compound **3** gave three different methoxy peaks at 2.32 (3H), 3.36 (6H), and 3.45 (3H) ppm. Hence, the peak at 2.32 ppm can be assigned to the methoxy protons in the flattened phenyl unit.

To obtain conclusive evidence for the suppression of ring inversion, we measured 2D EXSY in $^1$H NMR spectroscopy that would give us information about the exchange between $H_{ax}$ and $H_{eq}$ in the $ArCH_2Ar$ methylene protons (Brucker ARX-300 instrument, NOESYTP with time proportional phase increment; $[\mathbf{3}] = 10$ mmol dm$^{-3}$, $Cl_2CDCDCl_2$, $\tau_m$ 800 ms). At 30–130 °C, the correlation arising from the exchange between $H_{ax}$ and $H_{eq}$ was not observed. The result reveals that the basket structure of **3** cannot be inverted under this time scale; that is, the single *m*-xylenyl unit suffices to immobilize the conformation if it is bridged on the 1,3-phenyl units in calix[6]arene.

The temperature-dependent $^1$H NMR spectra of **4** are shown in Figure 5. In the high-temperature region (>70 °C), the *tert*-butyl protons and the aromatic (calix[6]arene) protons gave three different signals in a 1:1:1 integral intensity ratio and the methoxy protons gave two different signals in a 1:1 integral intensity ratio. The spectra once became broad at −30 to −60 °C and then sharp again at −85 °C, suggesting the presence of coalescence temperature in this region. However, the splitting pattern at −85 °C is so complex that we cannot assign it to some specific conformation. Judging from the CPK molecular model, two bridgehead phenyl units must adopt a *syn* conformation, and a block composed of these two phenyl units and a *m*-xylenyl bridge unit is conformationally frozen. In contrast, the oxygen-through-the-annulus rotation of the four residual phenyl units is allowed. We consider, therefore, that in **4** ring inversion can take place even though the "block" rotates together and the coalescence for this inversion motion appears at around −50 °C.

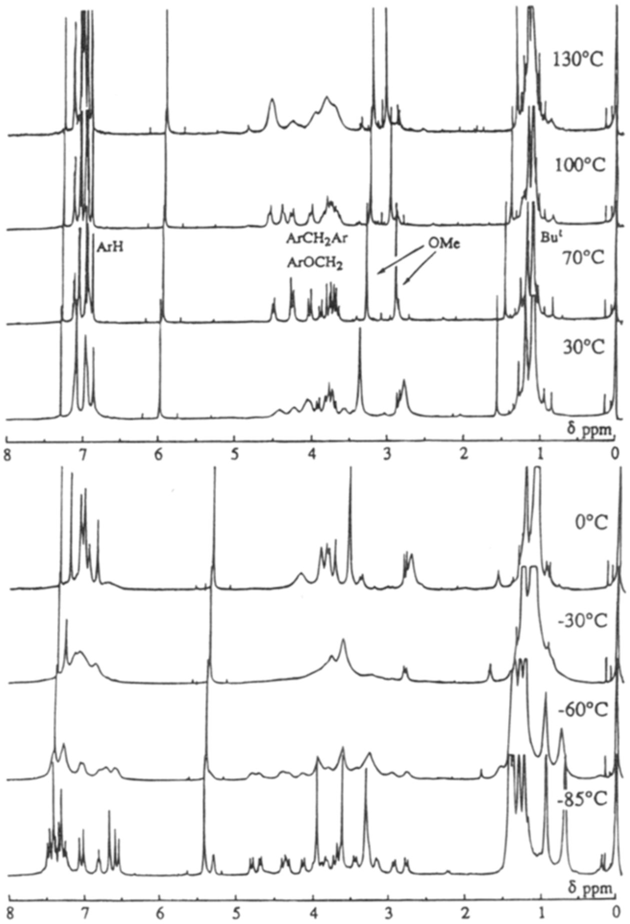
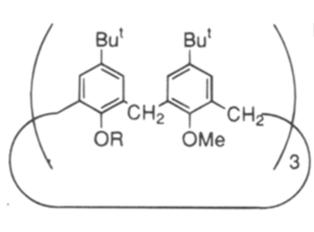


**Figure 5.** Temperature dependence of $^1$H NMR spectra for **4** (400 MHz, $CD_2Cl_2$ below 0 °C and $Cl_2CDCDCl_2$ above 30 °C).

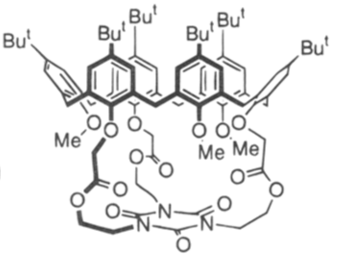
**Triply Bridged Calix[6]arenes.** Compounds **5**–**7** were synthesized by the reaction of 1,3,5-tris(bromomethyl)benzene with corresponding 1,3,5-tri-*O*-substituted calix[6]arenes. We found that the yields of this reaction are surprisingly high: 91% for **5**, 80% for **6**, and 60% for **7**. Previously, we synthesized two triply bridged calix[6]arenes by esterification or by alkylation, but the yields were very low (2.5–28%).[18] In the present system, the reaction was carried out under high-dilution conditions, but even if the concentrations of reactants were enhanced (see the Experimental Section), it gave a considerably high yield (82%). The results imply that in the present reaction the intramolecular second and third O-alkylation processes are faster than the intermolecular O-alkylation processes. We consider that the advantage of the intramolecular processes stems from the $C_3$ symmetrical complementarity and the similar size between the calix[6]arene cavity and the 1,3,5-tris(bromomethyl)benzene cap. When 1,3,5-trimethyl-2,4,6-tris(bromomethyl)benzene was used instead of 1,3,5-tris(bromomethyl)benzene, the triply bridged calix[6]arene was not isolated at all. Compounds **5** and **6** are already sterically crowded, so that the further increase in the steric crowding is unfavorable for the capping reaction. This view elucidates the low yield (60%) of **7** with propoxy groups relative to those of **5** and **6**.

The temperature-dependent $^1$H NMR spectra showed that a pair of doublets for the $ArCH_2Ar$ protons consistently appears from −85 to 130 °C. The result indicates that **5** firmly maintains a cone conformation. However, this fact is not sufficient for the freezing of the conformation, for the rate of cone−cone ring inversion may be only slower than the NMR time scale.[14] The direct evidence for immobilization is obtained from 2D EXSY (Brucker ARX-300 instrument, NOESYTP with time proportional phase increment; $[\mathbf{5}] = 10$ mmol dm$^{-3}$, $Cl_2CDCDCl_2$, $\tau_m$ 800 ms) in $^1$H NMR spectroscopy;[14,18] at 30−130 °C, the correlation arising from the exchange between $H_{ax}$ and $H_{eq}$ in the $ArCH_2Ar$ methylene protons was not observed. The result reveals that **5** is immobilized in a cone conformation and that flip-flop-type ring inversion does not take place under the present measurement conditions. Similar results were obtained from **6** and **7**.

Previously, Casnati et al.[7c] and Duynhoven et al.[15] synthesized a number of 1,3,5-tri-O-substituted calix[6]arene derivatives (**12**). In these molecules, the $\delta_H$ values for the methoxy protons appear at a high magnetic field (2.15−2.31 ppm), indicating that these methoxy groups are flattened into the cavity. We synthesized a triply capped calix[6]arene (**13**).[18a,20] The $\delta_H$ values appear again at a high magnetic field (2.69 ppm), indicating that the conformation is not changed by the capping. In contrast, the $\delta_H$ for **5** appears at a relatively low magnetic field (3.85 ppm). The $\delta_H$ values for the *tert*-butyl protons in anisole units and bridged phenyl units appear at 0.72 and 1.41 ppm, respectively; the shifts of these protons are opposite from those in **12** and **13** (1.24 −1.47 ppm for anisole units and 0.71−0.94 ppm for bridged phenyl units). The results indicate that in **5** bridged phenyl units are flattened and anisole units stand up. Figure 6 shows an energy-minimized structure of **5** estimated on the basis of MM3(92).[21,22] It is clearly seen from Figure 6 that both the upper rim and the lower rim are very crowded. At the upper rim, *tert*-butyl groups occupy an interior space and an exterior space of the edge alternately and three *tert*-butyl groups in the anisole units apparently act as a lid of the cavity. On the other hand, the 1,3,5-trisubstituted benzene acts as a lid at the lower rim. As shown by the $^1$H NMR spectral data, the bridged phenyl units are flattened and the anisole units stand up. The three methylene groups in the mesitylenyl cap provide diastereotopic protons. To test this possibility, we measured the $^1$H NMR spectrum at −85 °C but could not find the split of the peak. This implies that the exchange of these protons (if it exists) is much faster than the NMR time scale.



**12**



**13**

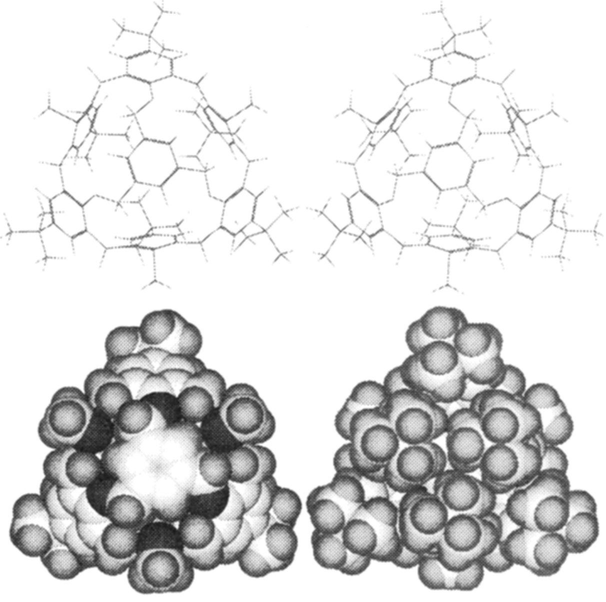


**Figure 6.** Energy-minimized structure of **5** with an inner cavity: bottom view (left) and top view (right).

It is seen from Figure 6 that compound **5** possesses a capsule-like closed cavity. This characteristic structure tempted us to investigate the inclusion properties. The preliminary study using $^1$H NMR spectroscopy shows that **5** is capable of including $Ag^+$, $Cs^+$, $RNH_3^+$, etc.[23]

**Conclusions.** The present spectroscopic studies demonstrate that the *m*-xylenyl unit bridged on the 1,3-phenyl units can inhibit ring inversion of calix[6]arenes and that the 1,3,5-mesitylenyl unit capped on the 1,3,5-phenyl units can immobilize the conformation of calix[6]arenes. It is also worthy to mention that the yields of **5** and **6** are very high because of the complementarity between the calix[6]arene and the cap. The cavities provided by these bridged and capped calix[6]arenes should be very rigid and conformationally defined. We believe that they are useful for precisely recognizing guest molecules. Further studies are currently under way in this laboratory.

## Experimental Section

**Materials.** The synthesis of compounds **2** and **4** was reported previously.[19]

**Compound 3.** 5,11,17,23,29,35-Hexa-*tert*-butyl-37,38,39,41-tetramethoxy-40,42-dihydroxycalix[6]arene[19] (200 mg, 0.24 mmol) was dispersed in acetone (250 mL) containing α,α′-dibromo-*m*-xylene (84 mg, 0.24 mmol) and $Cs_2CO_3$ (2.3 g, 7.08 mmol), and the mixture was refluxed for 24 h under a nitrogen stream. After evaporation, the solid residue was dispersed in aqueous HCl solution (0.1 mol dm$^{-3}$) and extracted with

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(20) Other examples for capping of calix[6]arenes (although their purposes are not necessarily immobilization of the conformation): (a) Janseen, R. G.; Verboom, W.; van Duynhoven, J. P. M.; van Velzen, E. J. J.; Reinhoudt, D. N. *Tetrahedron Lett.* **1994**, *35*, 6555. (b) Kraft, K.; Böhmer, V.; Vogt, W.; Ferguson, G.; Gallagher, J. F. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1221.

(21) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551, 8566, and 8576. The MM3(92) program for the UNIX system was obtained from Technical Utilization Corp., Inc., 235 Glen Village Court, Powell, OH 43065. See manual and references cited therein.

(22) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1994.

(23) Otsuka, H.; Shinkai, S., to be submitted for publication.

chloroform. The chloroform layer was separated, washed with water, and dried over $MgSO_4$. The solution was evaporated to dryness, the residue being purified by reprecipitation from chloroform to methanol: mp >280 °C dec; yield 93%; IR (Nujol) no $\nu_{OH}$; $^1$H NMR ($CDCl_3$, 25 °C) $\delta$ 0.66, 1.05, 1.25, and 1.39 (*t*-Bu, s each, 9H, 18H, 9H, and 18H, respectively), 2.35, 3.21, and 1.39 ($OCH_3$, s each, 3H, 6H, and 3H, respectively), 3.45, 3.53, 3.74, 3.95, 4.37, and 4.43 ($ArCH_2Ar$, d each, 2H each), 4.21 and 4.67 ($ArOCH_2$, d, 2H each), 6.19, 7.07, and 7.20 (ArH-(bridge), s, d, and t, respectively, 1H, 2H, and 1H, respectively), 6.37, 6.87, 6.97, 7.09, 7.23, and 7.31 (ArH(calixarene), s, d, d, s, d, and d, respectively, 2H each). Anal. Calcd for $C_{78}H_{98}O_6$: C, 82.79; H, 8.73. Found: C, 82.41; H, 8.70.

**Compound 5.** A THF solution (50 mL) containing 5,11,17,23,29,35-hexa-*tert*-butyl-37,39,41-trimethoxy-38,40,42-trihydroxycalix[6]arene[7c,15] (200 mg, 0.19 mmol) and an acetone solution (50 mL) containing 1,3,5-tris(bromomethyl)benzene (69 mg, 0.19 mmol) were deposited in two different dropping funnels, and they were dropped simultaneously into a refluxed acetone solution (250 mL) containing $Cs_2CO_3$ (1.9 g, 5.83 mmol) under a nitrogen atmosphere. The addition took 6 h. The reaction at the refluxed temperature was continued for 12 h. After evaporation, the solid residue was dispersed in aqueous HCl solution (0.1 mol dm$^{-3}$) and extracted with chloroform. The chloroform layer was separated, washed with water, and dried over $MgSO_4$. The solution was concentrated to dryness, the residue being purified by reprecipitation from chloroform to methanol: mp > 320 °C dec; yield 91%; IR (Nujol) no $\nu_{OH}$; $^1$H NMR ($(CDCl_2)_2$, 30 °C) $\delta$ 0.67 and 1.39 (*t*-Bu, s each, 9H each), 3.55 and 4.77 ($ArCH_2Ar$, d each, $J$ = 15.8 Hz for all peaks, 2H each), 3.84 ($OCH_3$, s, 3H), 4.82 ($ArOCH_2$, s, 2H), 6.37 and 7.23 (ArH(calixarene), s each, 2H each), 7.53 (ArH(cap), s, 1H); $^{13}$C NMR ($CDCl_3$, 30 °C) $\delta$ 31.1, 31.5, 31.7, 33.7, 34.2, 71.2, 76.2, 122.4, 128.1, 128.4, 131.6, 133.2, 137.5, 145.5, 145.7, 151.9, 153.3. Anal. Calcd for $(C_{26}H_{32}O_2)_3 \cdot 1.2H_2O$: C, 84.66; H, 8.29. Found: C, 84.34; H, 8.21. To estimate if the high-dilution method is indispensable to the present reaction, three reactants were directly mixed in acetone (120 mL) and treated in a manner similar to that described above. The yield of **5** was 82%.

**Compound 6.** This compound was synthesized from 5,17,29-tri-*tert*-butyl-37,39,41-trimethoxy-38,40,42-trihydroxycalix[6]arene[18] and 1,3,5-tris(bromomethyl)benzene in a manner similar to that described for **5**: mp >280 °C dec; yield 80%; IR (Nujol) no $\nu_{OH}$; $^1$H NMR ($CDCl_3$, 25 °C) $\delta$ 0.73 (*t*-Bu, s, 9H), 3.59 and 4.82 ($ArCH_2Ar$, d each, $J$ = 15.9 Hz for all peaks, 2H each), 3.85 ($OCH_3$, s, 3H), 4.90 ($ArOCH_2$, s, 2H), 6.40, 7.11, and 7.27 (ArH(calixarene), s, t, and d, respectively, 2H, 1H, and 2H, respectively), 7.70 (ArH(cap), s, 1H). Anal. Calcd for $(C_{22}H_{24}O_2)_3 \cdot 2.3H_2O$: C, 79.06; H, 7.70. Found: C, 79.06; H, 7.60.

**Compound 7.** 5,11,17,23,29,35-Hexa-*tert*-butyl-37,39,41-tripropoxy-38,40,42-trihydroxycalix[6]arene was synthesized from 5,11,17,23,29,35-hexa-*tert*-butylcalix[6]arene-37,38,39,40,41,42-hexol and propyl iodide in a manner similar to that used for the methyl derivative:[7c,15] mp 179−181 °C; yield 22%; IR (Nujol) $\nu_{OH}$ 3300 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 25 °C) $\delta$ 0.63 ($OCH_2CH_2CH_3$, t, 3H), 1.10 and 1.19 (*t*-Bu, s each, 9H each), 1.62 ($OCH_2CH_2CH_3$, m, 2H), 3.58 ($OCH_2CH_2CH_3$, t, 2H), 3.89 ($ArCH_2Ar$, s, 4H), 6.64 (OH, s, 1H), 6.97 and 7.02 (ArH, s each, 2H each), 7.53 (ArH(cap), s, 1H). Anal. Calcd for $(C_{25}H_{34}O_2)_3 \cdot 0.15CHCl_3$: C, 82.79; H, 8.73. Found: C, 82.41; H, 8.70. Recently, the synthesis of 5,11,17,23,29,35-hexa-*tert*-butyl-37,39,41-tripropoxy-38,40,42-trihydroxycalix[6]arene was also reported by an Italian group.[24] This compound was treated with 1,3,5-tris(bromomethyl)benzene and $Cs_2CO_3$ in a manner similar to that described for **5**: mp >310 °C dec; yield 60%; IR (Nujol) no $\nu_{OH}$; $^1$H NMR ($CDCl_3$, 25 °C) $\delta$ 0.71 and 1.42 (*t*-Bu, s each, 9H each), 1.19 ($OCH_2CH_2CH_3$, t, 3H), 1.94 ($OCH_2CH_2CH_3$, m, 2H), 3.55 and 4.84 ($ArCH_2Ar$, d each, $J$ = 15.6 Hz for all peaks, 2H each), 3.86 ($OCH_2CH_2CH_3$, t, 2H), 4.92 ($ArOCH_2$, s, 2H), 6.40 and 7.34 (ArH(calixarene), s each, 2H each), 7.53 (ArH(cap), s, 1H). Anal. Calcd for $(C_{28}H_{36}O_2)_3$: C, 83.12; H, 8.97. Found: C, 82.48; H, 8.95.

**Miscellaneous.** $^1$H NMR, IR, 2D COSY NMR, and 2D EXSY NMR spectroscopic measurements were carried out with a Bruker AC 250P spectrophotometer, a JASCO A-100 infrared spectrometer, a JEOL GSX-400 spectrometer, and a Brucker ARX-300 instrument, respectively. MM3(92) calculation was performed on a UNIX workstation system: SUN 4/2 GX-IRIS 4D/35G.

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[24] Neri, P.; Condoli, G. L. M. *Tetrahedron Lett.* **1994**, *35*, 2795.