# Preparation and Conformational Studies of Ethylene-Bridged Calixarene-Analogous Macrocyclic Metacyclophanes

**Takehiko Yamato*, Yoshiyuki Saruwatari, Louis Korbla Doamekpor, Ken-ichi Hasegawa, and Masanori Koike**

Department of Applied Chemistry, Faculty of Science and Engineering, Saga University, Honjo-machi 1, Saga-shi, Saga 840, Japan

Received May 24, 1993

**Key Words:** [(2.1)$_n$]Metacyclophanes, hydroxy- / Calixarenes / Trans-*tert*-butylation / Conformation / Hydrogen bonding, intramolecular

The novel macrocyclic compounds hexahydroxy[2.1.2.1.2.1]- (**7b**) and octahydroxy[2.1.2.1.2.1.2.1]metacyclophane (**7c**) have been prepared from anisole in six steps by using the *tert*-butyl function as a positional protective group on the aromatic ring. Base-catalyzed condensation of 1,2-bis(5-*tert*-butyl-2-hydroxyphenyl)ethane (**5**) with formaldehyde in refluxing xylene does not afford the dimeric product, tetrahydroxy[2.1.2.1]metacyclophane **6a**, but furnishes the larger macrocycles **6b** and **6c** in 70–90% yield. $AlCl_3$/$MeNO_2$-catalyzed trans-*tert*-butylation of **6b** and **6c** in toluene gives the desired metacyclophanes **7b** and **7c** in 60 and 80% yields, respectively, along with *tert*-butyltoluene **8b**. The conformations of the systems such as trimer **6b** and tetramers **6c**, **7c** have been evaluated from their dynamic $^1$H-NMR spectra. The tetramer **6c** is fixed to form a "pleated-loop" conformation like the calix[8]arenes due to the much more stronger intramolecular hydrogen bonding among the hydroxyl groups than in the trimer **6b**.

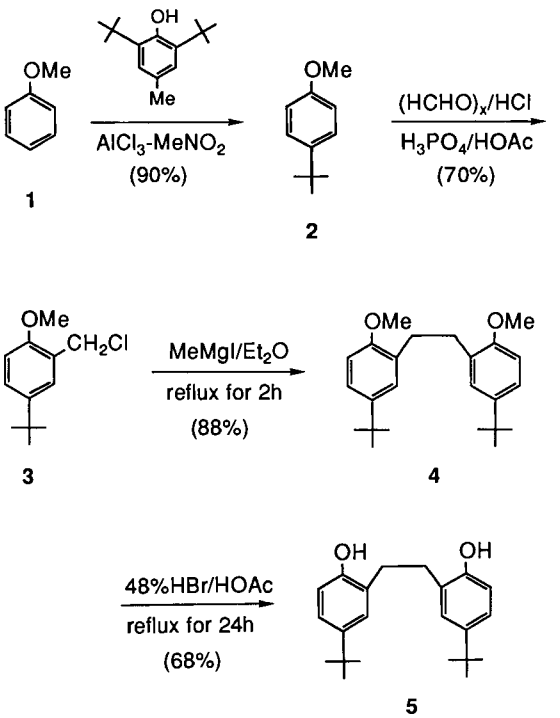
There has been an extensive study of calixarenes in the last decade[1]. Calixarenes are readily obtained from the base-induced condensation of *p*-substituted phenols with formaldehyde[2], and therefore the aromatic rings are invariably connected by methylene groups. Their phenolic hydroxyl groups are ordered in well-shaped cyclic arrays due to the strong intramolecular hydrogen bond[3–6]. Considering this it is surprising that reports on the preparation of calixarenes containing bridges other than methylene groups and characterization of their hydrogen bonding have been very limited except Vögtle's recent work[7]. We have previously reported on the ethylene-bridged calixarene-analogous metacyclophanes such as tetrahydroxy[2.1.2.1]-metacyclophanes by using a conventional sulfur method (8 steps) starting from *p*-*tert*-butylanisole[8]. However, these preparative routes seem to be too long for practical purposes. Therefore, it has been very difficult to obtain a sufficient amount of the above compounds to investigate their chemical behavior.

On the other hand, we have recently demonstrated for the first time the convenient synthesis of the propane-bridged calixarene-analogous metacyclophanes such as tetrahydroxy[3.1.3.1]metacyclophanes using the base-catalyzed condensation of 1,3-bis(5-*tert*-butyl-2-hydroxyphenyl)propane with formaldehyde in refluxing xylene and have disclosed their unique properties[9]. This strategy is supposed to be suitable for the preparation of tetrahydroxy-[2.1.2.1]metacyclophanes. In this paper, we describe the preparation and conformational properties of ethylene-bridged calixarene-analogous macrocyclic metacyclophanes synthesized by the base-catalyzed condensation of 1,2-bis(5-*tert*-butyl-2-hydroxyphenyl)ethane (**5**) with formaldehyde in refluxing xylene.

## Results and Discussion

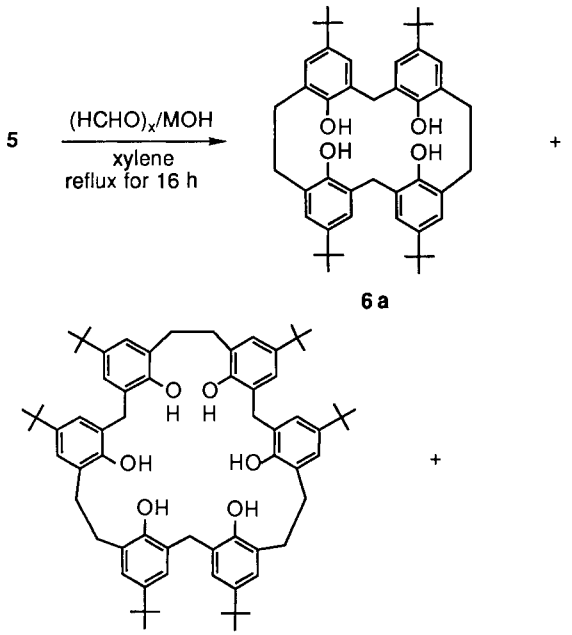
The starting compound **5** is easily prepared in four steps from anisole by using the *tert*-butyl group as a positional protective group on the aromatic ring (Scheme 1)[10–14]. Demethylation of 1,2-bis(5-*tert*-butyl-2-methoxyphenyl)ethane (**4**)[10] with 48% HBr under the conditions of acetic acid reflux for 24 h yields **5** in 68% yield.

Scheme 1



Attempts to prepare the desired tetrahydroxy[2.1.2.1]metacyclophane **6a** by condensation of **5** with formaldehyde in xylene under various alkaline conditions, using the same procedure as our method[8] for the preparation of tetrahydroxy[3.1.3.1]metacyclophanes, have failed. Instead, a mixture of trimer **6b** and tetramer **6c** has been obtained in good yield. This finding seems to be due to the much more strained structure of **6a** than **6b** and **6c** containing the larger ring. These compounds are easily separated from the crude reaction mixture by column chromatography.

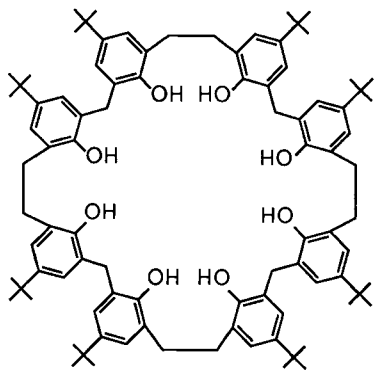
Scheme 2




**6a**




**6b**




**6c**

The structures of **6b** and **6c** have been elucidated on the basis of their elemental analyses and spectral data. For instance, the mass spectral data for **6b** and **6c** ($M^+$ $m/z = 1014$ and 1353) strongly support cyclic trimeric and tetrameric structures, respectively. The calixarenes show concentration-independent hydroxyl stretching bands in the 3200-$cm^{-1}$ region of the infrared spectrum and a signal at $\delta = 9-10$ in the $^1$H-NMR spectrum, indicative of very strong intramolecular hydrogen bonding and the cyclic nature of calixarenes[1]. The IR (KBr) spectra of **6b** and **6c** show the absorption of the hydroxyl stretching vibration around 3298 and 3355 $cm^{-1}$, respectively. The $^1$H-NMR spectra (in $CDCl_3$) exhibit the signals for hydroxyl groups around $\delta = 8.90$ and 9.80, respectively.

The ratio of the products **6b** and **6c** is governed by the nature of alkali metal hydroxide used as a catalyst as revealed by the results compiled in Table 1.

Table1. Condensation of **5** with paraformaldehyde in the presence of alkali metal hydroxides

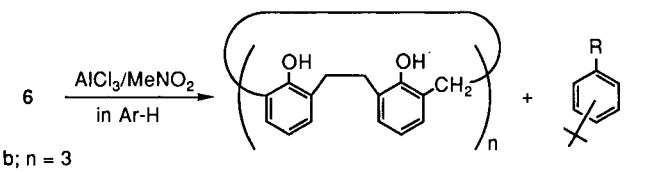
| Run | Alkali hydroxide | Products (%)[a] | | |
|---|---|---|---|---|
| | | **6a** | **6b** | **6c** |
| 1 | NaOH | 0 | 29 | 38 |
| 2 | KOH | 0 | 60 | 25 |
| 3 | CsOH | 0 | 64 | 22 |

[a] Isolated yields.

When cesium hydroxide or potassium hydroxide is used in this reaction, trimer **6b** is obtained as the major product. On the other hand, when sodium hydroxide is used, the yield of tetramer **6c** is higher than that of trimer **6b**. The smaller alkaline metal $Na^+$ obviously gives rise to the formation of a larger macrocyclic compound **6c**, while the action of the larger $K^+$ and $Cs^+$ leads to the production of the smaller macrocycle **6b**. These results seem to indicate that the template effect of the alkaline metal plays an important role in this condensation reaction. Thus, the formation of the 1:2 complex of **6b** with the sodium ion might be possible in a "pleated-loop" conformation like calix[8]arene[4,15].

The $AlCl_3/MeNO_2$-catalyzed trans-*tert*-butylation of **6b** and **6c** in benzene at 20°C for 48 h affords the desired de-*tert*-butylated products **7b** and **7c** in 19 and 60% yield, respectively, along with the recovery of the starting compound and the formation of incompletely de-*tert*-butylated products. In contrast, when toluene is used in place of benzene as an acceptor for the *tert*-butyl group, complete trans-*tert*-butylation is observed to afford **7b** and **7c** in 60 and 80% yield, respectively, along with *tert*-butyltoluene (**8b**). However, raising the reaction temperature to 50°C leads to ring cleavage reactions due to the transbenzylation rather than trans-*tert*-butylation (Table 2).

Scheme 3




The conformations of systems such as trimer **6b** and tetramers **6c**, **7c** have been evaluated by means of dynamic $^1$H-NMR spectroscopy. From the observation of resonances arising from the $ArCH_2Ar$ methylene protons and the

Table 2. $AlCl_3$ $MeNO_2$-catalyzed trans-*tert*-butylation of hexahydroxy-[2.1.2.1.2.1]MCP **6b** and octahydroxy[2.1.2.1.2.1.2.1]MCP **6c** [a]

| Run | Sub-strate | Ar-H | Reaction temp. (°C) | Products (%)[b] |
|---|---|---|---|---|
| 1 | **6b** | Benzene [c] | 20 | **7b** (19)[d] |
| 2 | **6b** | Toluene | 20 | **7b** (60) |
| 3 | **6b** | Toluene | 50 | **7b** (24)[e] |
| 4 | **6c** | Benzene [c] | 20 | **7c** (60)[d] |
| 5 | **6c** | Toluene | 20 | **7c** (80) |

[a] The reaction time was 24h unless indicated otherwise . Catalyst/**6** = 14 [mol/mol] - [b] Isolated yields. - [c] The reaction time was 48h. - [d] Recovery of **6** and formation of incompletely debutylated products were observed. - [e] Formation of ring cleavage reaction products due to the transbenzylation was observed.

Table 3. Coalescence temperature and energy barriers of conformational ring flipping of hexahydroxy[2.1.2.1.2.1]MCP **6b** and octahydroxy[2.1.2.1.2.1.2.1]MCP **6c** and **7c**[a]

| Compound | $T_c$ ($\Delta G_c^{\neq}$) | |
|---|---|---|
| | $-CH_2-$ | $-CH_2CH_2-$ |
| **6b**[b] | -60 | < -100 |
| **6c** | 40 (14.4) | 27 |
| **7c** | 0 (13.6) | -10 |

[a] Key: $T_c$ (°C); $\Delta G_c^{\neq}$ (kcal/mol). $T_c$ and $\Delta G_c^{\neq}$ were determined in $CDCl_3$ by using $SiMe_4$ as reference unless indicated otherwise. [b] Solvent: $CDCl_3/CS_2$ = 1/3.

$ArCH_2CH_2Ar$ ethylene protons, the pattern of the spectra becomes a sharp singlet above 40 °C. This behavior indicates that the rate of conformational ring flipping of macrocycles **6b** and **6c** is faster than the NMR time scale above this temperature. However, in trimer **6b** even at −60 °C in $CDCl_3$ the singlet signal of the $ArCH_2CH_2Ar$ ethylene protons remains unsplit, while that of the $ArCH_2Ar$ methylene protons splits into two broad singlets at $\delta = 3.60$ and 4.20. This result suggests that the ring inversion of the ethylene chains may still occur even at this temperature.

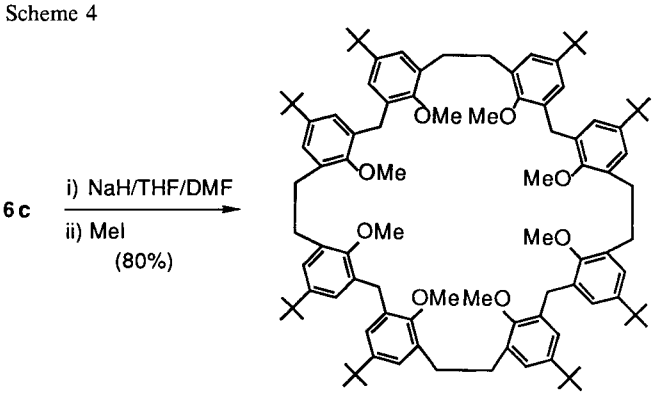
The coalescence temperature and energy barriers of conformational ring flipping of hexahydroxy[2.1.2.1.2.1]MCP **6b** and octahydroxy[2.1.2.1.2.1.2.1]MCPs **6c** and **7c** are compiled in Table 3.

On the other hand, in tetramer **6c** at 0 °C the singlet signal of the methylene protons of $ArCH_2Ar$ splits into two sets of doublets (AB system, $J_{AB}$ 13.48 Hz) at $\delta = 3.46$ and 4.36, and the methylene protons of the ethane bridge are also observed to be split at $\delta = 2.66$ and 2.84. The coalescence temperature of the methylene protons of $ArCH_2Ar$ is 40 °C, and the free energy of activation for inversion is estimated to be 14.4 kcal/mol ($T_c$ = 40 °C, $\Delta\nu$ = 243.53 Hz). The value of the free energy of activation for inversion is smaller than that of calix[8]arene (15.7 kcal/mol)[4]. On the other hand, the coalescence temperature of the ethylene protons of $ArCH_2CH_2Ar$ is 27 °C. Thus, the splitting temperature of the $ArCH_2Ar$ methylene protons is higher than that of $ArCH_2CH_2Ar$ ethylene protons. This result strongly suggests that the intramolecular hydrogen bonding among the hydroxyl groups between the diarylmethane units is stronger than that of 1,2-diarylethane units. A comparison of trimer **6b** with tetramer **6c** reveals that splitting of the signal of the bridged $CH_2$ protons of **6c** occurs at a higher temperature than that of **6b**. This result indicates that tetramer **6c** is fixed to form a "cone-like" conformation similar to that of the calix[8]arenes[3,4] as a result of the much stronger intramolecular hydrogen bonding among the hydroxyl groups and its larger ring size than trimer **6b**. The same results have been obtained for tetramer **7c**. However, in comparison with **6c**, **7c** adopts a much more flexible conformation. These results seem to indicate that the bulky *tert*-butyl groups in **6c** play an important role in the fixation of the conformation.

In the case of **6c** it has also been found that below −38 °C the singlet signal of the phenolic hydroxyl groups at $\delta = 9.80$ splits into two sets of singlets at $\delta = 9.50$ and 10.50. A similar phenomenon is observed in the debutylated compound **7c**; the singlet signal of the phenolic hydroxyl groups at $\delta$ = 9.55 splits into two sets of singlets at $\delta = 9.31$ and 10.22. These phenomena may be attributed to the formation of two sets of non-equivalent phenolic hydroxyl groups because the conformational fluctuation of the cyclophane ring is frozen below this temperature by the intramolecular hydrogen bonding among the two sets of four hydroxyl groups. The estimated free energy for fluctuation of **6c** is 11.0 kcal/mol ($T_c$ = −38 °C, $\Delta\nu$ = 266.11 Hz). On the basis of the dynamic $^1$H-NMR studies and the Corey-Pauling-Koltun (CPK) model of tetramer **6c**, it is concluded that below −38 °C the conformation of tetramer **6c** is expected to be the "pleated-loop" conformation due to the intramolecular hydrogen bonding among the hydroxyl groups.

On the other hand, in the spectra of octamethoxy derivative **9c**, which has been prepared by methylation of tetramer **6c** with MeI[16], the protons of *tert*-butyl groups, methoxy groups, and methylene bridges appear in the $^1$H-NMR spectrum each as a singlet even below −60 °C. This indicates the much more flexible structure of **9c** than that of the macrocycle **6c**. It is concluded that the calix[8]arene-like intramolecular hydrogen bonds may fix the conformation of octahydroxy[2.1.2.1.2.1.2.1]metacyclophane **6c**.

Scheme 4




**9c**

In conclusion, the ethylene-bridged calixarene-analogous metacyclophanes **6** and **7** may provide rich sources of a new

type of host compounds, especially since these compounds are easily available in reasonable quantities. We are presently testing their behavior as host compounds.

## Experimental

All melting and boiling points are uncorrected. – IR (KBr or NaCl): Nippon Denshi JIR-AQ2OM. – $^1$H NMR: Nippon Denshi Jeol FT-270, in $CDCl_3$, TMS as reference. – MS: Nippon Denshi JMS-01SA-2. – Elemental analysis: Yanaco MT-5.

*1,2-Bis(5-tert-butyl-2-hydroxyphenyl)ethane* (**5**): A solution of 1,2-bis(5-*tert*-butyl-2-methoxyphenyl)ethane (**4**)[10] (6.0 g, 16.92 mmol) and 48% HBr (10 ml) in acetic acid (30 ml) was heated at reflux for 24 h. After cooling the reaction mixture to room temp., it was poured into water (50 ml) and extracted with ether (50 ml). The extract was washed with water (2 × 40 ml), dried ($Na_2SO_4$), and the solvent evaporated in vacuo to leave a residue, which was recrystallized from ethanol to give 3.7 g of **5** (11.3 mmol, 68%) as colorless prisms, m.p. 175–176°C. – IR (KBr): $\tilde{\nu}$ [$cm^{-1}$] = 3325 (OH). – $^1$H NMR ($CDCl_3$): δ = 1.30 (18H, s), 2.85 (4H, s), 6.40 (2H, s), 6.82 (2H, d, *J* = 8.8 Hz), 7.15–7.20 (4H, m). – MS (75 eV), *m/z*: 326 [$M^+$]. – $C_{22}H_{30}O_2$ (326.5): calcd. C 80.94, H 9.26; found C 80.65, H 9.18.

*Base-Catalyzed Condensation. Typical Procedure:* To a mixture of **5** (4.0 g, 12.26 mmol) and paraformaldehyde (0.8 g, 26.0 mmol) in xylene (60 ml) was added under nitrogen and with vigorous stirring aqueous 5 N NaOH (0.6 ml). After the reaction mixture was refluxed for 18 h, it was cooled to room temp., acidified with 1 N HCl (50 ml), and extracted with $CH_2Cl_2$ (2 × 200 ml). The combined extracts were washed with water (2 × 100 ml), dried ($Na_2SO_4$), and condensed under reduced pressure. The residue was chromatographed on silica gel using hexane/benzene (1:1) and benzene as eluents to give 1.58 g of tetramer **6c** (1.17 mmol, 38%) and 1.20 g of trimer **6b** (1.18 mmol, 29%), respectively.

*5,12,20,27,35,42-Hexa-tert-butyl-8,15,23,30,38,45-hexahydroxy-[2.1.2.1.2.1]metacyclophane* (**6b**): Colorless prisms ($CHCl_3$/MeOH, 1:1), m.p. >300°C. – IR (KBr): $\tilde{\nu}$ [$cm^{-1}$] = 3298 (OH). – $^1$H NMR ($CDCl_3$, 20°C): δ = 1.27 (54H, s), 2.93 (12H, s), 3.98 (6H, s), 6.98 (6H, d, *J* = 2.93 Hz), 7.20 (6H, d, *J* = 2.93 Hz), 8.90 (6H, s). – MS (75 eV, *m/z*: 1014 [$M^+$]. – $C_{69}H_{90}O_6$ (1015.5): calcd. C 81.61, H 8.93; found C 81.90, H 8.70.

*5,12,20,27,35,42,50,57-Octa-tert-butyl-8,15,23,30,38,45,53,60-octahydroxy[2.1.2.1.2.1.2.1]metacyclophane* (**6c**): Colorless prisms ($CHCl_3$/MeOH, 1:1), m.p. 241–246°C. – IR (KBr): $\tilde{\nu}$ [$cm^{-1}$] = 3355 (OH). – $^1$H NMR ($CDCl_3$, 20°C): δ = 1.28 (72H, s), 2.73 (16H, broad s), 3.58 (4H, broad s), 4.45 (4H, braod s), 7.00 (8H, d, *J* = 2.44 Hz), 7.22 (8H, d, *J* = 2.44 Hz), 9.80 (8H, s); ($CDCl_3$, –60°C): δ = 1.28 (72H, s), 2.73 (16H, broad s), 3.58 (4H, d, *J* = 13.48 Hz), 4.45 (4H, d, *J* = 13.48 Hz), 7.00 (8H, d, *J* = 2.44 Hz), 7.22 (8H, d, *J* = 2.44 Hz), 9.50 (4H, s), 10.50 (4H, s). – MS (75 eV), *m/z*: 1353 [$M^+$]. – $C_{92}H_{120}O_8$ (1354.0): calcd. C 81.61, H 8.93; found C 81.75, H 8.90.

*Trans-tert-butylation of* **6**. *Typical Procedure:* To a solution of **6c** (600 mg, 0.443 mmol) in toluene (80 ml) was added a solution of $AlCl_3$ (0.83 g, 6.23 mmol) in nitromethane (1.5 ml) at 20°C. After stirring of the reaction mixture at 20°C for 24 h, it was poured into ice/water (100 ml) and extracted with benzene (2 × 100 ml). The combined extracts were washed with water (2 × 100 ml), dried ($Na_2SO_4$), and the solvent was evaporated in vacuo to leave a residue. The residue was chromatographed on $SiO_2$ by using benzene as the eluent to give 320.4 mg of *8,15,23,30,38,45,53,60-octahydroxy[2.1.2.1.2.1.2.1]metacyclophane* (**7c**) (0.354 mmol, 80%) as colorless prisms ($CHCl_3$/MeOH, 1:1), m.p. >300°C. – IR (KBr): $\tilde{\nu}$ [$cm^{-1}$] = 3281 (OH). – $^1$H NMR ($CDCl_3$): δ = 2.76 (16H, broad s), 3.94 (8H, broad s), 6.81 (8H, t, *J* = 7.32 Hz), 6.99 (8H, d, *J* = 7.32 Hz), 7.20 (8H, d, *J* = 7.32 Hz), 9.71 (8H, s). – MS (75 eV), *m/z*: 905 [$M^+$]. – $C_{60}H_{56}O_8$ (905.1): calcd. C 79.62, H 6.24; found C 79.90, H 6.10.

A similar treatment of **6b** with benzene or toluene in the presence of $AlCl_3$/$MeNO_2$ afforded **7b**. The yields are compiled in Table 2.

*8,15,23,30,38,45-hexahydroxy[2.1.2.1.2.1]metacyclophane* (**7b**): Colorless prisms ($CHCl_3$/MeOH, 1:1), m.p. >300°C. – IR (KBr): $\tilde{\nu}$ [$cm^{-1}$] = 3328 (OH). – $^1$H NMR ($CDCl_3$): δ = 2.95 (12H, broad s), 4.02 (6H, broad s), 6.82 (6H, t, *J* = 7.32 Hz), 6.97 (6H, d, *J* = 7.32 Hz), 7.21 (6H, d, *J* = 7.32 Hz), 9.04 (6H, s). – MS (75 eV), *m/z*: 678 [$M^+$]. – $C_{45}H_{42}O_6$ (678.8): calcd. C 79.62, H 6.24; found C 79.85, H 6.15.

The formation of *tert*-butylbenzene (**8a**) and *tert*-butyltoluene (**8b**) was confirmed by GLC (Shimadzu gas chromatograph, GC-14A, Silicone OV-1, 2 m, programmed temperature rise 12°C/min; carrier gas nitrogen 25 ml/min).

*5,12,20,27,35,42,50,57-Octa-tert-butyl-8,15,23,30,38,45,53,60-octamethoxy[2.1.2.1.2.1.2.1]metacyclophane* (**9c**): To a suspension of NaH (1.08 g, 45.0 mmol) in THF (5 ml) was added a solution of **6c** (500 mg, 0.37 mmol) in a mixture of DMF (5 ml) and THF (15 ml) under nitrogen, and the reaction mixture was stirred at room temp. for 1 h. Then MeI (3.25 ml, 43.0 mmol) was added and the mixture heated at reflux for 16 h. After cooling of the reaction mixture to room temp., water was added, and the mixture was extracted with $CH_2Cl_2$ (2 × 200 ml). The combined extracts were washed with water (2 × 100 ml), dried ($Na_2SO_4$), and condensed under reduced pressure. The residue was chromatographed on $SiO_2$ by using THF as the eluent to give 461.1 mg of **9c** (0.315 mmol, 85%) as colorless prisms ($CHCl_3$/MeOH, 1:1), m.p. 238–242°C. – $^1$H NMR ($CDCl_3$): δ = 1.19 (72H, s), 2.92 (16H, s), 3.53 (24H, s), 3.99 (8H, s), 6.94 (8H, d, *J* = 1.83 Hz), 7.20 (6H, d, *J* = 1.83 Hz). – $C_{100}H_{136}O_8$ (1466.2): calcd. C 81.92, H 9.35; found C 82.10, H 9.10.

[1] For a comprehensive review of all aspects of calixarene chemistry see: C. D. Gutsche, *Calixarenes*, Royal Society of Chemistry, Cambridge, **1989**.
[2] C. D. Gutsche, B. Dhawan, K. H. No, R. Muthukrishnan, *J. Am. Chem. Soc.* **1981**, *103*, 3782–3792.
[3] C. D. Gutsche, *Acc. Chem. Res.* **1983**, *16*, 161–170.
[4] C. D. Gutsche, L. J. Bauer, *J. Am. Chem. Soc.* **1985**, *107*, 6052–6059.
[5] J. D. van Loon, L. C. Groenen, S. S. Wijmenga, W. Verboom, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1991**, *113*, 2378–2384.
[6] L. C. Groenen, J. D. van Loon, W. Verboom, S. Harkema, A. Casnati, R. Ungaro, A. Pochini, F. Ugozzoli, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1991**, *113*, 2385–2392.
[7] F. Vögtle, J. Schmitz, M. Nieger, *Chem. Ber.* **1992**, *125*, 2523–2531.
[8] M. Tashiro, A. Tsuge, T. Sawada, T. Makishima, S. Horie, T. Arimura, S. Mataka, T. Yamato, *J. Org. Chem.* **1990**, *55*, 2404–2409.
[9] T. Yamato, Y. Saruwatari, S. Nagayama, K. Maeda, M. Tashiro, *J. Chem. Soc., Chem. Commun.* **1992**, 861–862.
[10] M. Tashiro, T. Yamato, *J. Org. Chem.* **1978**, *43*, 1413–1420.
[11] M. Tashiro, *Synthesis* **1979**, 921–936.
[12] M. Tashiro, T. Yamato, K. Kobayashi, T. Arimura, *J. Org. Chem.* **1987**, *52*, 3196–3199.
[13] T. Yamato, T. Arimura, M. Tashiro, *J. Chem. Soc., Perkin Trans. 1*, **1987**, 1–7.
[14] T. Yamato, J. Matsumoto, K. Tokuhisa, K. Suehiro, M. Tashiro, *Chem. Ber.* **1992**, *125*, 2443–2454.
[15] S. Shinkai, K. Araki, O. Manabe, *J. Am. Chem. Soc.* **1988**, *110*, 7214–7215.
[16] C. D. Gutsche, B. Dhawan, J. A. Levine, K. H. No, L. J. Bauer, *Tetrahedron* **1983**, *39*, 409–426.

[155/93]