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Calix[6]arene Derivatives Selectively Functionalized at Alternate Sites on the Smaller Rim with 2-Phenylpyridine and 2-Fluorenylpyridine Substituents to Provide Deep Cavities

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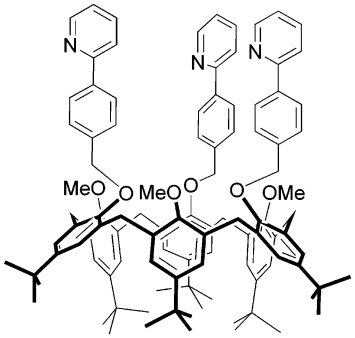

The synthesis is described of calix[6]arene derivatives **4**, **9**, and **14** functionalized at alternate sites on the smaller rim with 4′-(pyrid-2″-yl)phenylmethoxy, (6′-phenylpyrid-3′-ylmethoxy), and {6′-[2-(9,9-di-*n*-hexylfluorenyl)]pyrid-3′-ylmethoxy} substituents, respectively. They were obtained by 3-fold reactions of 2-[4-(bromomethyl)phenyl]pyridine (**3**), 5-(bromomethyl)-2-phenylpyridine (**8**), and 5-(bromomethyl)-2-(9,9-di-*n*-hexylfluorenyl)pyridine (**13**) with the 1,3,5-trimethylether of the *t*-Bu-calix[6]arene in the presence of sodium hydride in THF in 56−75% yields. Detailed analysis of the ^{1}H NMR spectra (including variable-temperature data for **4**) has established that **4**, **9**, and **14** exist predominantly in the C_{3v} cone conformation with minor C_s isomers also observed. The X-ray crystal structure of **4** reveals two molecules of similar cone conformation, with all three 4′-(pyrid-2″-yl)phenylmethoxy substituents stretched in the axial direction. Molecule I has a dimeric capsule structure with (pyrid-2″-yl)phenylmethoxy substituents of one molecule interpenetrating those of its inversion equivalent to form a deep enclosed intermolecular cavity, which contains a CH_2Cl_2 guest molecule. Molecule II forms no such pair: the intramolecular cavity is filled with solvent molecules.

Introduction

Calixarenes are versatile bowl-shaped platforms which can be functionalized to provide a range of interesting molecular architectures with well-defined special arrangements of the substituents.[1] Examples include calix[4]arene derivatives bearing pendent 2,2′-dipyridyl substituents which form stable complexes with Cu(II) ions[2] and analogues which are receptors for lanthanide ions.[3] To obtain higher-level supramolecular architectures, intermolecular interactions of Pd(II) with pyridylcalix[4]arenes have been utilized,[4] and functionalized calix[4]arenes have been synthesized as potential cores for self-assembled dendrimers.[5] Calix[4]arenes substituted at the wider (upper) rim with two diaminotriazine moieties form hydrogen-bonded supramolecular architectures.[6] Recently, calix[4]arene derivatives have been synthesized with redox activity imparted by tetrathiafulvalene substituents.[7] Calix[4]arenes have been tetrafunctionalized at the wider rim with phenylenevinylene and

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phenyleneethynylene oligomers for studies on chromophore−chromophore interactions.[8] Calix[4]arenes functionalized at the wider rim with tetraamide and tetraurea binding sites are anion sensors.[9]

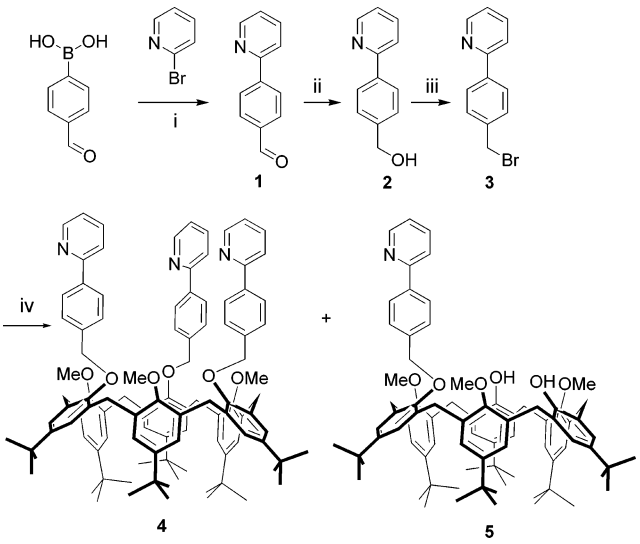
In contrast to the vast number of substituted calix[4]arenes in the literature,[1] functionalization of the calix[5]arene[10] and calix[6]arene platforms[11] have received far less attention. Recent examples are a calix[6]arene bearing three picolyl groups[12] and bridged derivatives which impart rigidity to the calix[6] framework.[13] Sénèque and Reinaud[14] have noted that, compared to calix[4]arenes, calix[6]arenes are much more difficult to functionalize selectively at the smaller rim, due to the higher number of phenol units and the increased flexibility of the calix[6]arene framework.[15] The synthesis of new selectively functionalized derivatives, therefore, poses an interesting challenge.

In this article, we describe the efficient synthesis of calix[6]arene derivatives which are selectively functionalized at alternate sites on the small rim with 4′-(pyrid-2″-yl)phenylmethoxy, (6′-phenylpyrid-3′-ylmethoxy), and {6′-[2-(9,9-di-*n*-hexylfluorenyl)]pyrid-3′-ylmethoxy} substituents, viz., compounds **4**, **9**, and **14**, respectively. These compounds present unusually deep cavities. Their conformations have been elucidated by NMR analysis, and an X-ray crystal structure of **4** reveals that interpenetrating dimers form a capsule with an enclosed cavity.

Results and Discussion

Synthesis. Scheme 1 shows the route to the first target calixarene derivative **4**. 4-(Pyridin-2-yl)benzaldehyde **1** was synthesized by a modification of the literature route[16] involving reaction of 4-formylbenzeneboronic acid with 2-bromopyridine under standard Pd-catalyzed Suzuki−Miyaura cross-coupling conditions.[17] Reduction of **1** with sodium borohydride gave the methanol derivative **2** which was converted to the bromomethyl derivative **3** by reaction with phosphorus tribromide. Reaction of **3** (3 equiv) with the 1,3,5-trimethylether of *t*-Bu-calix[6]-

SCHEME 1 [a]



[a] Reagents and conditions: (i) $Pd(PPh_3)_4$, Na_2CO_3, THF, toluene, 80 °C (44% yield); (ii) $NaBH_4$, EtOH, 20 °C (99% yield); (iii) PBr_3, CH_2Cl_2, 20 °C (83% yield); (iv) 5,11,17,23,29,35-hexa-*tert*-butyl-37,39,41-trihydroxy-38,40,42-trimethoxycalix[6]arene, NaH, THF, 66 °C [56% yield (**4**) + 7% yield (**5**)].

arene[18] (namely, 5,11,17,23,29,35-hexa-*tert*-butyl-37,39,41-trihydroxy-38,40,42-trimethoxycalix[6]arene) in the presence of sodium hydride in THF[19] gave the trisubstituted product **4** (56% yield) along with the monosubstituted derivative **5** as a minor byproduct (7% yield).

For our second target calixarene derivative **9**, which is an isomer of **4**, comparable Suzuki−Miyaura methodology gave **6**.[20] Sequential reduction and bromination afforded 5-(bromomethyl)-2-phenylpyridine **8**. By analogy with the synthesis of **4**, 3-fold reaction of **8** with the 1,3,5-trimethylether of *t*-Bu-calix[6]arene gave **9** in 63% yield (Scheme 2). The reaction temperature was kept below 50 °C to avoid decomposition of **8**, which was thermally less stable than its isomer **3**.

The appropriate fluorenylpyridine reagents were synthesized as shown in Scheme 3, from the known fluorenyl-dioxaborolane reagent **10**.[21] The hexyl chains at C(9) of the fluorenyl unit ensured good solubility. A 3-fold reaction of **13**, as above, gave the calix[6]arene derivative **14** in 75% yield.

Calixarene derivatives **4**, **5**, **9**, and **14** were all isolated as air-stable white solids; elemental analysis and MALDI mass spectra established their molecular composition. The symmetry of the ^1H and ^{13}C NMR spectra of **4**, **9**, and **14** confirmed that, in all cases, the ligands were attached at alternate sites, as expected.

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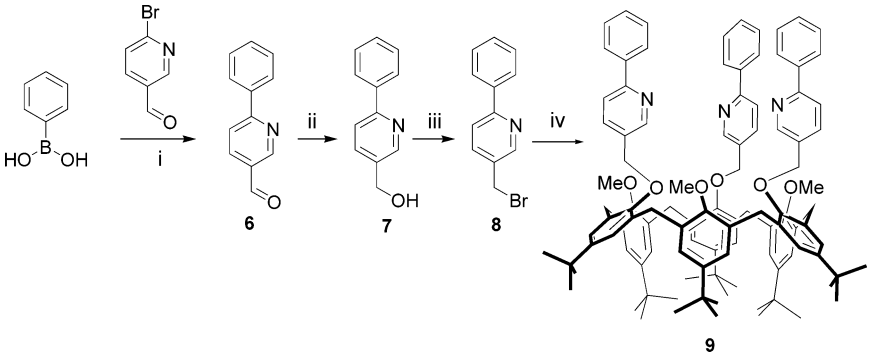
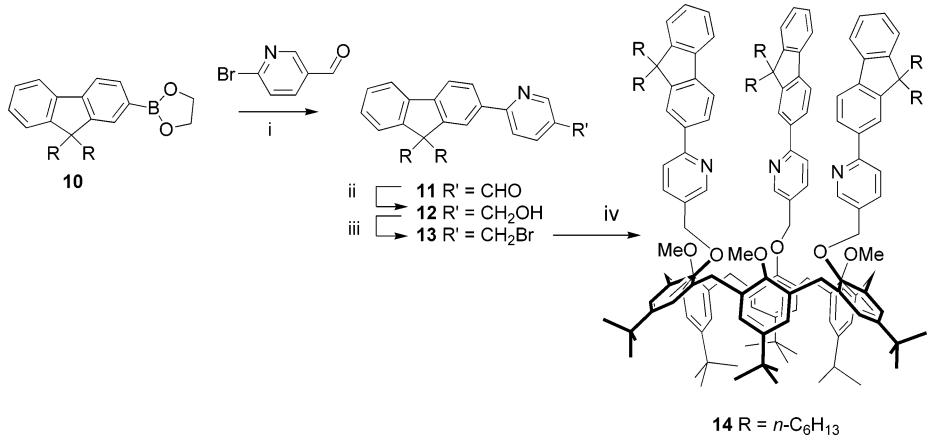
(21) Zhou, X.-H.; Yan, J.-C.; Pei, J. *Org. Lett.* **2003**, *5*, 3543−3546.

SCHEME 2 [a]



[a] Reagents and conditions: (i) $Pd(PPh_3)_4$, Na_2CO_3, THF, toluene, 80 °C (94% yield); (ii) $NaBH_4$, EtOH, 20 °C (99% yield); (iii) PBr_3, CH_2Cl_2, 20 °C (89% yield); (iv) 5,11,17,23,29,35-hexa-*tert*-butyl-37,39,41-trihydroxy-38,40,42-trimethoxycalix[6]arene, NaH, THF, 46 °C (63% yield).

SCHEME 3 [a]



[a] Reagents and conditions: (i) $Pd(PPh_3)_4$, Na_2CO_3, THF, toluene, 80 °C (88% yield); (ii) $NaBH_4$, EtOH, CH_2Cl_2, 20 °C (100% yield); (iii) PBr_3, CH_2Cl_2, 20 °C (98% yield); (iv) 5,11,17,23,29,35-hexa-*tert*-butyl-37,39,41-trihydroxy-38,40,42-trimethoxycalix[6]arene, NaH, THF, 66 °C (75% yield).

Conformational Analysis. Initial inspection of the ^{1}H NMR spectra revealed a high-field shift of the methoxy groups (e.g., for **4**, δ 2.29, s, 9H at 20 °C) providing clear evidence that the major isomer was the classical C_{3v} cone conformation with the OMe groups projecting inside the aromatic cavity which can be easily assigned from the separation of the six *tert*-butyls [(δ 1.38, 27H, 0.83, 27H (both s))] and the separation of the anisole protons [(δ 7.27, 6H, 6.70, 6H (both s))] as well as the wide separation of the bridging methylene protons [(δ 4.63, 6H, 3.40, 6H (both d, J = 15.2 Hz))] [15] [cf. the monoligand derivative **5**, δ 3.67, 6H and 2.68, 3H (both s, OMe)]. Variable-temperature NMR data for **4** provided more information (see below and Supporting Information). Although compounds **4**, **9**, and **14** possess bulky aryl substituents which are too large to rotate through the annulus, the C_{3v} and C_s conformers interconvert via a transannular motion of the *p-tert*-butyl moiety (Chart 1) affording a significant amount of C_s isomers as judged by their complex but characteristic ^{1}H NMR signals.

In the room-temperature spectra of compounds **4** (Figure 1) and **9**, the protons of the methylene bridges within the calix skeleton of the minor C_s conformers were separated into six pairs of doublets between δ 4.41 and 3.32 ppm with J values of 14.4−16.0 Hz. The *p-tert*-butyl protons of compound **4** were separated into three singlets at δ 1.32, 1.16, and 1.12 ppm in a 1:2:3 ratio. For compound **9**, these protons gave four singlets at δ 1.27, 1.16, 1.00, and 0.99 ppm in a 1:2:1:2 ratio. The aryl protons within the calix platform in compounds **4** and **9** range from δ 7.18 to 6.73 ppm and were separated into four doublets with J values of 2.0−2.4 Hz and two singlets. The methoxy protons were also separated into two singlets with a 2:1 ratio at δ 2.30 and 2.07 ppm for **4** and at δ 2.39 and 2.23 ppm for **9**. The six methylene protons within the three substituents were separated into two doublets with J values of ca. 12.0 Hz and one singlet. Because the proton signals within the aryl substit-

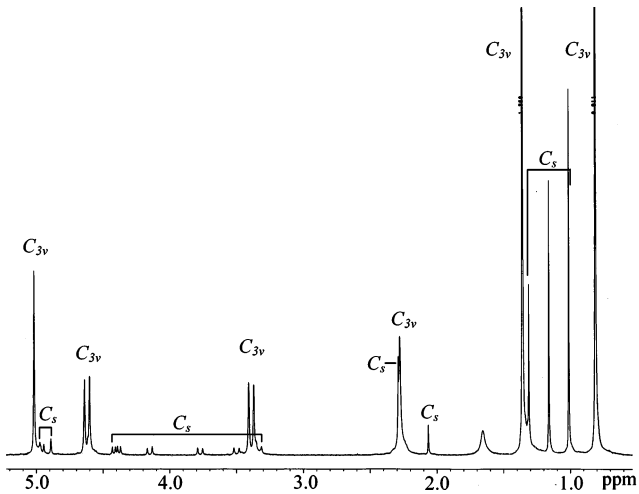


FIGURE 1. Part of the ^{1}H NMR spectrum of compound **4** in $CDCl_3$ at 20 °C.

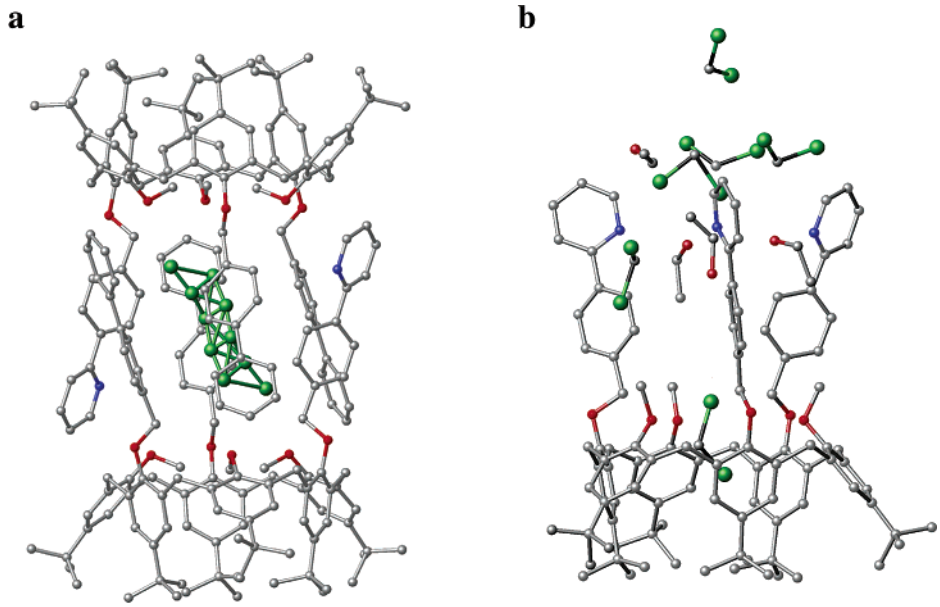


FIGURE 2. X-ray structure of **4**: (a) molecule I and its inversion equivalent, with an encapsulated disordered DCM molecule (light green) and (b) molecule II with DCM and ethanol of crystallization. C atoms and superimposed C and N atoms, gray; O atom, red; N atoms, blue; Cl atoms, green. H atoms and minor positions of disordered groups are omitted for clarity. Note the different conformations of the methoxy groups.

uents overlap with those of their C_{3v} conformers, their signals cannot be fully assigned. The ^{1}H NMR spectrum of the C_s conformer of **14** is much more complex compared with the C_s conformers of **4** and **9** because of the fluorenyl groups. Nonetheless, the methylene bridge protons within the calix skeleton are separated and can still be assigned as six pairs of doublets between δ 4.44 and 3.35 ppm with J values of 14.4−15.6 Hz. The aryl protons within the calix platform of **14** range from 7.19 to 6.78 ppm and are separated into four doublets with $J = 2.4$ Hz and two singlets. The six methylene protons within the three substituents can also be assigned to two doublets at δ 4.92 and 4.73 ppm, respectively, with $J = 12.0$ Hz and one singlet at 4.87 ppm. The nine methoxy protons gave two singlets at δ 2.42 and 2.20 ppm in a 2:1 ratio.

Chart 1 shows the C_{3v} and C_s conformational interconversion of calix[6]arene derivatives. Generally, there are eight conformers in the dynamic equilibrium of calix[6]arene deravitives, i.e., cone, partial cone, 1,2-alternate, 1,3-alternate, 1,4-alternate, 1,2,3-alternate, 1,2,4-alternate, and 1,3,5-alternate.[1c] However, in 37,39,41-trialkoxy-38,40,42-trimethoxycalix[6]arene derivatives, usually only the cone and 1,2,3-alternate (C_s) conformers can be observed if the alkyl substituents are large enough to prevent rotation through the annulus.[15b,22]

To investigate the C_{3v} and C_s conformational exchange, the ^{1}H NMR spectra of compound **4** were recorded at +60, +30, 0, −30, and −60 °C. The data and the spectra are presented in the Supporting Information. Only the C_{3v} and C_s conformers were observed over this temperature range. An explanation is that the conformational change is controlled by the slow transannular motion of the *p-tert*-butyl moiety; the bulky substituents on the phenolic oxygen cannot rotate through the ring. Rotation of the methoxy groups through the annulus is fast even at −60 °C. Therefore, no conformers except the C_{3v} and C_s are observed. The C_{3v} cone conformer of **4** becomes more flattened as the temperature decreases from +60 °C to −60 °C as seen from the increased separation of the *p-tert*-butyl protons (Δ ppm = 0.53 ppm at 60 °C, 0.56 ppm at 0 °C, 0.61 ppm at −60 °C). The upfield shift of the methoxy protons from δ 2.36 to 2.09 ppm means that these groups point more deeply into the cavity with decreasing temperature. It is noteworthy that the ratio of the C_s conformer is lowest (ca. 21.5%) between 30 °C and 0 °C, increasing to 24.8% at 60 °C and to 23.1% at −60 °C (ratios are ±0.2%). This change in the ratio is attributed to a small temperature-dependent change in the flattened cone conformation of both the C_{3v} and C_s conformers. The upfield shift of the methoxy protons with the intensity ratio of 2:1 from δ 2.43 and 2.12 ppm to δ 1.96 and 1.79 ppm shows that the methoxys in the C_s conformer also point further into the cavity due to increased flattening of the cone with a decrease in the temperature from 60 °C to −60 °C. Subtle conformational changes are observed for the C_s conformer at different temperatures. For example, the *tert*-butyl protons give four singlets at −60, 0, +30, and +60 °C, whereas at −30 °C, they are cleanly separated into eight singlets [δ 1.31, 1.29 (9H), 1.16, 1.14 (18H), 1.03, 1.02 (18H), 0.93, 0.91 (9H)] arising from two distinct conformations of the C_s conformer at this temperature.

X-ray Molecular Structure of 4. The asymmetric unit of **4** comprises two molecules of similar conformation, with all three 4′-(pyrid-2″-yl)phenylmethoxy substituents stretched in the axial direction. Molecule I and its inversion equivalent (Figure 2a) contact in such a way that the (pyridyl)phenylmethoxy groups of one molecule are plugged between those of the other. Methyl groups are oriented to the interior of the calixarene macrocycle, thus effectively enclosing a prolate intermolecular cavity, in which a highly disordered DCM guest molecule is trapped. This dimer structure acts as a molecular capsule.[23]

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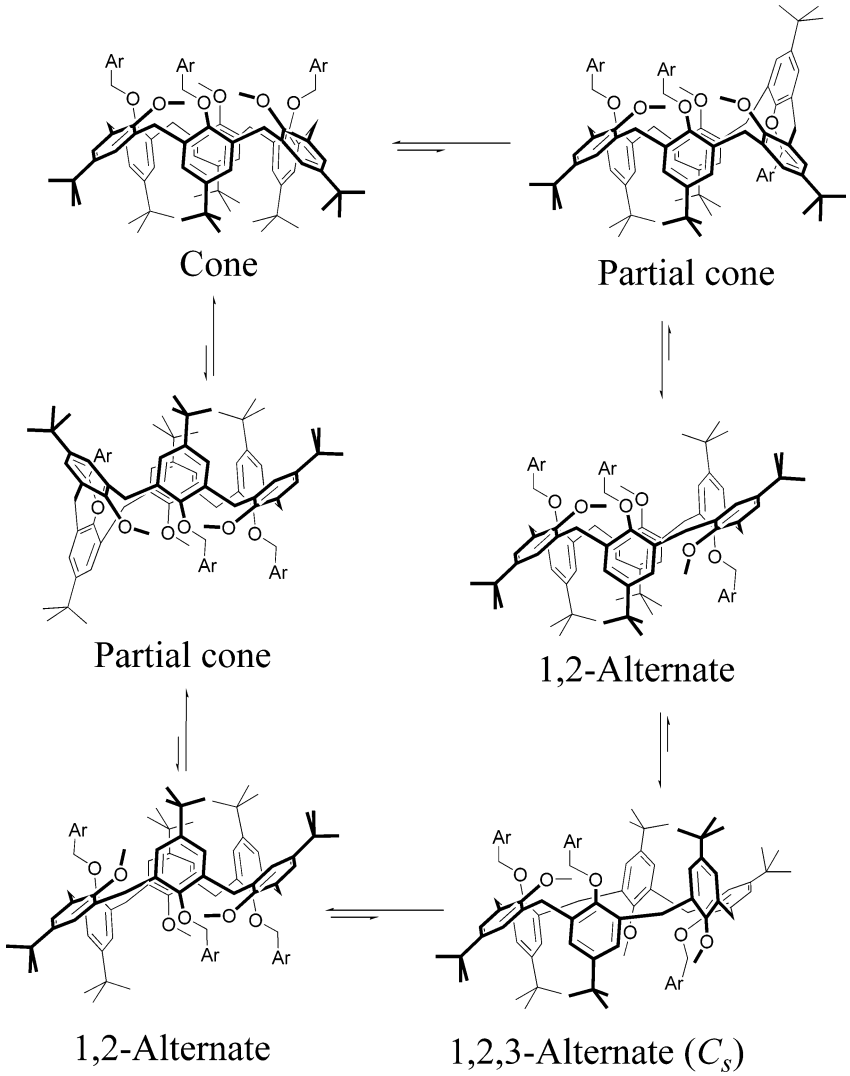
CHART 1. C_{3v} and C_s Conformational Interconversion of 4, 9, and 14 through Transannular Motion of the *p-tert*-Butyl



Calixarene molecule II (Figure 2b) forms no such pair and has both the central cavity and the "slits" between the (pyridyl)-phenylmethoxy groups filled with DCM and ethanol molecules which are partially disordered. Indeed, one DCM molecule lies in the center of the macrocycle, deeply embedded within the cavity, made accessible by the outward orientation of the methyl groups. In molecule I, two out of three pyridyl groups are disordered by a 180° rotation; i.e., N and C atoms are statistically mixed in both ortho positions. In molecule II, all three pyridyls are ordered, with each N atom facing inward and probably stabilized in this orientation by hydrogen bonding with the intracavity ethanol. All (pyridyl)phenyl moieties are slightly twisted, by 13−33° (mean 25°), and their long axes are inclined outward from the 3-fold axes of the calixarene platform by 17−22° (mean 21° in molecule I and 18° in molecule II). The crystal packing in molecules I and II represents two alternative ways to maximize space filling; there are no obvious $\pi-\pi$ interactions or H-bonds between calixarene units in the supramolecular assembly.

Conclusions

The efficient syntheses of the calix[6]arene derivatives **4**, **9**, and **14** functionalized at alternate sites on the smaller rim with 4′-(pyrid-2″-yl)phenylmethoxy, (6′-phenylpyrid-3′-ylmethoxy), and {6′-[2-(9,9-di-*n*-hexylfluorenyl)]pyrid-3′-ylmethoxy} substituents have been accomplished by 3-fold reactions of the corresponding (bromomethyl)aryl precursors with the 1,3,5-trimethylether of *t*-Bu-calix[6]arene. Detailed ^{1}H NMR analysis has established that **4**, **9**, and **14** exist predominantly in the C_{3v} cone conformation with minor C_s isomers also observed. The cone conformation of the these calix[6]arene derivatives provides unusually deep cavities. The X-ray crystal structure of **4** comprises two molecules of similar cone conformation, with all three 4′-(pyrid-2″-yl)phenylmethoxy substituents stretched in the axial direction. Molecule I has a dimeric capsule structure.

The arylpyridine substituents of these calixarenes offer a scope for further studies on intra- and intermolecular behavior. For example, cyclometalated complexes might form with a metal [e.g., Ir(III)] embedded within the ligand cavity. Such complexes could be dopants for electroluminescent devices.[24,25]

Experimental Section

5,11,17,23,29,35-Hexa-*tert*-butyl-37,39,4l-tris[4′-(pyrid-2″-yl)-phenylmethoxy]-38,40,42-trimethoxycalix[6]arene (4) and 5,11,-

(24) Encapsulated cyclometalated phenylpyridine ligands within dendrimers have been described: Lo, S.-C.; Anthopoulos, T. D.; Namdas, E. B.; Burn, P. L.; Samuel, I. D. W. *Adv. Mater*. **2005**, *17*, 1945−1948.

17,23,29,35-Hexa-*tert*-butyl-37-[4′-(pyrid-2″-yl)phenylmethoxy]-39,41-dihydroxy-38,40,42-trimethoxycalix[6]arene (5). To a solution of 5,11,17,23,29,35-hexa-*tert*-butyl-37,39,41-trihydroxy-38,40,42-trimethoxycalix[6]arene (649 mg, 0.64 mmol) in THF (70 mL) was added NaH (60% dispersion in mineral oil, 171 mg, 4.30 mmol) in one portion. The resulting suspension was heated to 66 °C for 30 min, and then a solution of compound **3** (500 mg, 2.02 mmol) in THF (50 mL) was added dropwise. The reaction mixture was stirred at 66 °C overnight. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (50 mL) and water (50 mL). The solution was stirred at room temperature for 30 min. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (3 × 30 mL). The combined organic phases were dried (anhydrous $MgSO_4$); the solvent was removed under reduced pressure; and the yellow residue was purified by column chromatography (silica gel, DCM/acetone, from 100:2 to 100:8 v/v). Compound **4** (542 mg, 56% yield) was obtained as a white powder, followed by compound **5** (50 mg, 7% yield) as a white powder.

Compound **4**: mp 175−176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) C_{3v} conformer, 8.69 (m, 3H), 8.01 (d, 6H, J = 8.0 Hz), 7.75 (m, 6H), 7.64 (d, 6H, J = 8.0 Hz), 7.27 (s, 6H), 7.21 (dd, 3H, J = 8.4 Hz, 4.0 Hz), 6.70 (s, 6H), 5.04 (s, 6H), 4.63 (d, 6H, J = 15.2 Hz), 3.40 (d, 6H, J = 15.2 Hz), 2.29 (s, 9H), 1.38 (s, 27H), 0.83 (s, 27H); C_s conformer, 7.95 (d, 4H, J = 8.4 Hz), 7.75 (m, 6H), 7.74 (m, 6H), 7.56 (d, 2H, J = 8.4 Hz), 7.51 (d, 4H, J = 8.4 Hz), 7.16 (s, 2H), 7.10 (d, 2H, J = 2.4 Hz), 7.04 (d, 2H, J = 2.4 Hz), 6.78 (s, 2H), 6.73 (d, 2H, J = 2.4 Hz), 4.95 (d, 2H, J = 12 Hz), 4.90 (s, 2H), 4.59 (d, 2H, J = 12 Hz, overlapped with C_{3v} conformer), 4.41 (d, 2H, J = 16.0 Hz), 4.38 (d, 2H, J = 16.0 Hz), 4.14 (d, 2H, J = 15.6 Hz), 3.78 (d, 2H, J = 14.4 Hz), 3.50 (d, 2H, J = 14.8 Hz), 3.32 (d, 2H, J = 16.0 Hz), 2.30 (s, 6H), 2.07 (s, 3H), 1.32 (s, 9H), 1.16 (s, 18H), 1.12 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) 157.3, 154.6, 151.7, 149.6, 145.9, 138.9, 138.6, 136.7, 133.8, 133.2, 128.4, 128.0, 127.7, 127.0, 126.8, 123.7, 122.0, 120.6, 120.5, 74.3, 60.3, 34.2, 31.6, 31.2, 30.0, 18.4; MS (MALDI) *m*/*z* 1518.0 (calcd 1517.9). Anal. Calcd for $C_{105}H_{117}N_3O_6{\cdot}H_2O$: C, 82.15; H, 7.81; N, 2.74. Found: C, 82.35; H, 7.93; N, 2.70.

Compound **5**: mp 172−173 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 8.71−8.68 (m, 1H), 8.04 (d, 2H, J = 8.0 Hz), 7.79 (d, 1H, J = 8.0 Hz), 7.74 (td, 1H, J = 7.6 Hz, 2.0 Hz), 7.50 (d, 2H, J = 8.0 Hz), 7.23−7.21 (m, 1H), 7.20 (s, 2H), 7.17 (s, 2H), 7.07 (d, 2H, J = 2.4 Hz), 6.95 (s, 4H), 6.94 (s, 2H), 6.88 (d, 2H, J = 2.4 Hz), 4.72 (s, 2H), 4.30 (d, 2H, J = 14.4 Hz), 3.94 (d, 2H, J = 14.4 Hz), 3.86 (d, 2H, J = 15.6 Hz), 3.82 (d, 2H, J = 14.4 Hz), 3.75 (d, 2H, J = 15.2 Hz), 3.72 (d, 2H, J = 13.6 Hz), 3.67 (s, 6H), 2.68 (s, 3H), 1.27 (s, 9H), 1.18 (s, 18H), 1.12 (s, 9H), 0.97 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) 157.5, 153.4, 152.8, 152.3, 149.8, 149.5, 146.7, 146.5, 146.2, 142.1, 139.0, 138.5, 136.7, 133.2, 132.7, 132.5, 128.2, 127.1, 127.0, 126.9, 126.6, 126.0, 125.34, 125.29, 125.1, 121.9, 120.6, 74.7, 61.4, 60.5, 34.2, 34.1, 33.8, 31.8, 31.5, 31.4, 31.2, 30.8; MS (MALDI) *m*/*z* 1182.7 (calcd 1182.7). Anal. Calcd for $C_{81}H_{99}NO_6$: C, 82.26; H, 8.44; N, 1.18. Found: C, 82.50; H, 8.52; N, 1.15.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,39,4l-tris(6′-phenylpyrid-3′-ylmethoxy)-38,40,42-trimethoxycalix[6]arene (9). To a solution of 5,11,17,23,29,35-hexa-*tert*-butyl-37,39,41-trihydroxy-38,40,42-trimethoxycalix[6]arene (1.02 g, 1.0 mmol) in THF (150 mL) was added NaH (60% dispersion in mineral oil, 342 mg, 8.55 mmol) in one portion. The resulting suspension was heated to 46 °C for 30 min, and then compound **8** (756 mg, 3.05 mmol) was added in one portion. The reaction mixture was stirred at 46 °C overnight. Workup as described for **4** gave **9** as a white powder (0.953 g, 63% yield). A sample was crystallized from dichloromethane and ethanol: mp 191−192 °C; ^{1}H NMR (400 MHz, $CDCl_3$) C_{3v} conformer, 8.73 (dd, 3H, J = 2.0 Hz, 0.8 Hz), 8.01 (dd, 3H, J = 8.0 Hz, 2.0 Hz), 7.99−7.97 (m, 6H), 7.77 (dd, 3H, J = 8.0 Hz, 0.8 Hz), 7.49−7.40 (m, 9H), 7.27 (s, 6H), 6.71 (s, 6H), 5.03 (s, 6H), 4.60 (d, 6H, J = 15.2 Hz), 3.40 (d, 6H, J = 15.2 Hz), 2.28 (s, 9H), 1.37 (s, 27H), 0.83 (s, 27H); C_s conformer, 8.69 (d, 1H, J = 1.6 Hz), 8.67 (d, 2H, J = 1.6 Hz), 7.85 (dd, 1H, J = 8.4 Hz, 2.0 Hz), 7.81 (dd, 2H, J = 8.4 Hz, 2.0 Hz), 7.70 (dd, 1H, J = 8.4 Hz, 0.4 Hz), 7.64 (dd, 2H, J = 8.0 Hz, 0.4 Hz), 7.18 (d, 2H, J = 2.0 Hz), 7.12 (s, 2H), 7.05 (d, 2H, J = 2.0 Hz), 6.93 (d, 2H, J = 2.4 Hz), 6.77 (bs, 4H), 4.91 (d, 2H, J = 11.6 Hz), 4.84 (s, 2H), 4.65 (d, 2H, J = 11.6 Hz), 4.40 (d, 2H, J = 15.2 Hz), 4.33 (d, 2H, J = 15.2 Hz), 4.12 (d, 2H, J = 14.8 Hz), 3.67 (d, 2H, J = 15.2 Hz), 3.47 (d, 2H, J = 15.2 Hz), 3.33 (2H, partially overlapped with C_{3v} conformer), 2.39 (s, 6H), 2.23 (s, 3H), 1.27 (s, 9H), 1.16 (s, 18H), 1.00 (s, 9H), 0.99 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) 157.2, 154.4, 152.3, 151.4, 149.1, 146.2, 145.9, 139.2, 136.8, 133.7, 133.0, 131.6, 129.0, 128.7, 127.0, 123.8, 120.5, 120.2, 72.0, 60.2, 34.1, 31.6, 31.3, 30.0, 15.3; MS (MALDI) *m*/*z* 1517.9 (calcd 1517.9). Anal. Calcd for $C_{105}H_{117}N_3O_6{\cdot}CH_2Cl_2$: C, 79.47; H, 7.49; N, 2.62. Found: C, 79.65; H, 8.78; N, 2.65.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,39,4l-tris{6′-[2-(9,9-di-*n*-hexylfluorenyl)]pyrid-3′-ylmethoxy}-38,40,42-trimethoxycalix-[6]arene (14). To a solution of 5,11,17,23,29,35-hexa-*tert*-butyl-37,39,41-trihydroxy-38,40,42-trimethoxycalix[6]arene (1.27 g, 1.25 mmol) in THF (100 mL) was added NaH (60% dispersion in mineral oil, 342 mg, 8.55 mmol) in one portion. The resulting suspension was heated to 60 °C for 30 min. Then a solution of **13** (1.95 g, 3.86 mmol) in THF (30 mL) was added dropwise, and the resulting mixture was stirred at 66 °C for 6 h. The reaction was quenched by the dropwise addition of ethanol (5 mL). Workup as described for **4**, with column chromatography (silica gel, DCM/acetone, from 100:1 to 100:3 v/v) gave compound **14** (2.13 g, 75% yield) as a white powder: mp 140−141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) C_{3v} conformer, 8.77 (d, 3H, J = 2.0 Hz), 8.06 (dd, 3H, J = 8.0 Hz, 2.0 Hz), 8.04−7.99 (m, 9H), 7.87 (d, 3H, J = 8.0 Hz), 7.77 (d, 3H, J = 8.0 Hz), 7.74 (dd, 3H, J = 6.8 Hz, 1.6 Hz), 7.36−7.30 (m, 6H), 7.29 (s, 6H), 6.71 (s, 6H), 5.07 (s, 6H), 4.60 (d, 6H, J = 15.2 Hz), 3.38 (d, 6H, J = 15.2 Hz), 2.27 (s, 9H), 2.06−1.94 (m, 12H), 1.39 (s, 27H), 1.09−0.94 (m, 36H), 0.81 (s, 27H), 0.69 (t, 18H, J = 6.8 Hz), 0.67−0.55 (m, 12H); C_s conformer, 7.19 (d, 2H, J = 2.4 Hz), 7.16 (s, 2H), 7.10 (d, 2H, J = 2.4 Hz), 6.98 (d, 2H, J = 2.4 Hz), 6.81 (s, 2H), 6.78 (d, 2H, J = 2.4 Hz), 4.92 (d, 2H, J = 12.0 Hz), 4.87 (s, 2H), 4.73 (d, 2H, J = 12.0 Hz), 4.44 (d, 2H, J = 15.6 Hz), 4.37 (d, 2H, J = 15.6 Hz), 4.15 (d, 2H, J = 14.4 Hz), 3.72 (d, 2H, J = 14.8 Hz), 3.54 (d, 2H, J = 14.4 Hz), 3.35 (2H, partially overlapped with C_{3v} conformer), 2.42 (s, 6H), 2.20 (s, 3H), 1.30 (s, 9H), 1.19 (s, 18H), 1.05 (s, 9H), 1.00 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) 157.6, 154.6, 154.5, 151.6, 151.4, 149.1, 146.2, 145.8, 142.2, 140.7, 136.8, 133.7, 133.0, 131.4,128.1, 127.3, 126.8, 126.0, 123.8, 123.0, 121.3, 120.5, 120.2, 120.0, 119.9, 72.2, 60.3, 55.3, 40.4, 34.3, 34.1, 31.7, 31.49, 31.46, 30.0, 29.7, 23.8, 22.6, 14.0; MS (MALDI) *m*/*z* 2286.7 (calcd 2286.4). Anal. Calcd for $C_{162}H_{201}N_3O_6{\cdot}H_2O$: C, 84.44; H, 8.88; N, 1.82. Found: C, 84.60; H, 8.72; N, 1.90.

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Supporting Information Available: Synthetic details and characterization data for compounds **1**−**3**, **6**−**8**, and **11**−**13**; a table of variable-temperature ^{1}H NMR data and copies of the spectra for compound **4** at +60, +30, 0, −30, and −60 °C; and an X-ray crystallographic file for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) Cyclometalated fluorenylpyridine complexes have been described: (a) Ostrowski, J. C.; Robinson, M. R.; Heeger, A. J.; Bazan, G. C. *Chem. Commun.* **2002**, 784−785. (b) Tavasli, M.; Bettington, S.; Bryce, M. R.; Al Attar, H. A.; Dias, F. B.; King, S.; Monkman, A. P. *J. Mater. Chem.* **2005**, *15*, 4963−4970.