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First C_{3v}-Symmetrical Calix[6](aza)crown

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The first C_{3v}-symmetrical calix[6](aza)crown **8** has been obtained in five steps from $X_6H_3Me_3$ **3**. The key-step introduction of the triple bridge at the small rim has been achieved through reaction of a tris-arylsulfonamide derivative of tren **1** and tris-tosylcalix[6]arene **6**. A ^{1}H NMR study has shown that the tripodal cap rigidifies the whole edifice, preventing ring inversion and constraining the calixarene core in a straight cone conformation.

Introduction

Calix[4]arenes have been extensively studied for host−guest chemistry. However, because of their small size, they have mostly been used as a platform for the preorganization of a binding site. The larger calix[6]-arenes appear more suitable to play the role of a molecular receptor, yet their higher conformational flexibility, due to facile ring inversion,[1] represents an obstacle. We have recently shown that rigidification of the calix[6]arene core could be achieved through the use of coordination chemistry.[2] Indeed, the binding of a metal ion to three amino groups that are covalently linked to the calix[6]arene small rim can constrain the macrocycle into a cone conformation. The so-called *funnel complexes* present a biomimetic environment for Cu or Zn, which can coordinate a neutral guest inside the hydrophobic cavity.[3] We wanted to extend our supramolecular system to the use of a ligand consisting of a calix[6]arene capped with a C_{3v}-symmetrical azacrown bridge. Such a rigidified ligand should possess a reinforced complexation ability because the cap should prevent decomplexation processes by protecting the metal ion from the external medium while maintaining a large degree of flexibility essential for the system in order to act as a biomimetic receptor. The synthesis of calix[4](aza)crowns has already been explored,[4] but only two recent examples of calix[6]arenes including diamide bridges have been reported.[5,6] Furthermore, calix[6]arenes capped with a tripodal bridge are still rare.[7] In this study, we describe the synthesis of the first C_{3v}-symmetrical calix[6](aza)crown, where the small rim is capped with the tris(2-aminoethyl)amine tripodal unit.

Results and Discussion

A classical route for the synthesis of azacrowns consists of the use of a poly-toluenesulfonamide salt for the

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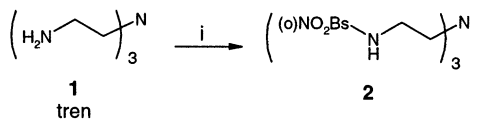
SCHEME 1[a]



[a] (i) (*o*)NO_2BsCl, TEA, THF, 0 °C then rt, 76%.

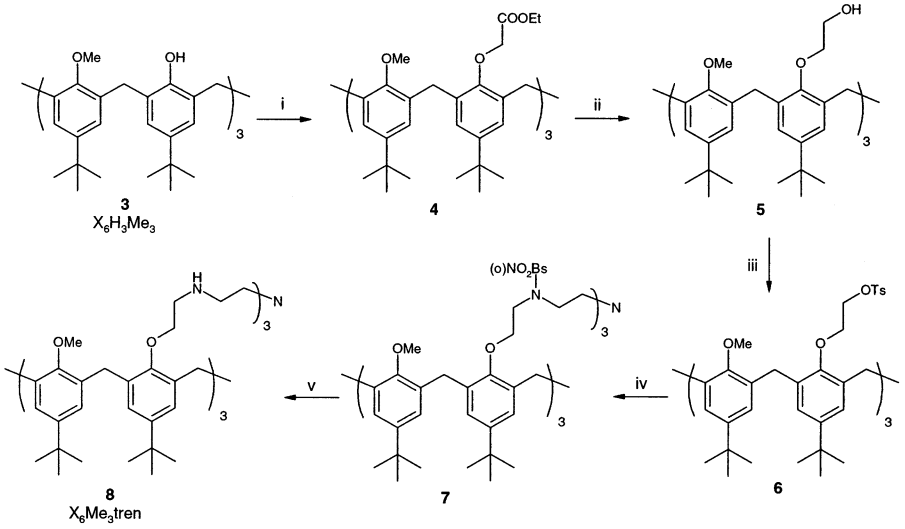
alkylation reaction.[8] Thus, to obtain the desired triply bridged calix[6]arene, we chose to attempt the tris-alkylation reaction between the trianion of a tris-arylsulfonamide derivative of tris(2-aminoethyl)amine (tren) **1** and a tris-tosylcalix[6]arene derivative. For this purpose, we first prepared the tris-protected tren **2** by the reaction between tren **1** and 3.4 equiv of 2-nitrobenzenesulfonyl chloride in the presence of triethylamine (76% yield) (Scheme 1). The 2-nitrobenzenesulfonyl-protected group [(*o*)NO_2Bs] was chosen instead of the more classical tosyl one because it can be removed under milder conditions. It is noteworthy that compound **2** is an amorphous and hygroscopic solid that we were unable to recrystallize; consequently it was only purified by flash chromatography on silica gel.

The required tris-tosyl calix[6]arene was prepared from the known $X_6H_3Me_3$ **3**[9] [obtained by selective 1,3,5-trimethylation of *p*-*t*Bu-calix[6]arene (X_6H_6)[10]] in an efficient three-step sequence (54% overall yield). First, $X_6H_3Me_3$ **3** was converted into the triester derivative **4** by alkylation with an excess of ethylbromoacetate in the presence of NaH in 77% yield.[11] A subsequent reduction by LAH afforded the tris-hydroxy derivative **5** in 82% yield. The latter was reacted at low temperature with an excess of TsCl in a mixture of anhydrous pyridine and chloroform, giving the tris-tosyl calix[6]arene **6** in 86% yield (Scheme 2). This reaction necessitated careful attention to the reaction conditions (essentially the low temperature and reaction time), otherwise unidentified calixarene-type byproducts were formed, lowering the yield. The ^{1}H NMR spectra of compounds **4**, **5**, and **6**, recorded at 298 K in $CDCl_3$, are characteristic of a major flattened cone conformation of C_{3v} symmetry.[12] The high-field shift of the methoxy protons of compounds **4** and **6** (δ_{OMe} = 2.27 and 2.07, respectively) indicates that these groups are included inside the cavity, projecting the bulky ethyl ester or tosyl groups outside. In the case of calix[6]arene **5**, the methoxy groups present a *quasi-normal* resonance (δ_{OMe} = 3.47) suggesting that they are involved in an intramolecular hydrogen bonding network with the hydroxylated arms. This was confirmed by the high-field shift observed for these groups (δ_{OMe} = 3.01) when a protic solvent (CD_3OD) was added. It is also noteworthy that, in contrast to compounds **4** and **5**, sharp signals are observed for the $ArCH_2Ar$ methylene protons of tris-tosyl calix[6]arene **6** (two doublets at 3.29 and 4.40 ppm). It shows that, with these bulky tosyl arms, the cone-cone interconversion of **6** is slower than the NMR time scale.

Key-step formation of the triply bridged calix[6]arene was conducted under standard conditions, reacting **6** and **2** in the presence of Cs_2CO_3 as a base in DMF. After flash chromatography on silica gel, the expected capped calix[6]arene **7** was isolated in 31% yield. Finally, deprotection of the amino groups was performed by SNAr substitution of the (*o*)NO_2Bs groups by thiophenate, giving rise to the desired calix[6]azacrown **8** (X_6Me_3tren) with a 75% yield (Scheme 2).

The ^{1}H NMR spectra of capped calixarenes **7** and **8** are displayed in Figure 1. Their profiles are remarkably simple, attesting to a major C_{3v}-symmetrical rigid cone conformation. Evidence for the rigidification of the cone conformation due to the capping is given by the sharp and well-defined signals corresponding to the $ArCH_2Ar$ methylene protons. Some unusual features, however, are specifically observed for compound **8**. Its methoxy groups are less high-field shifted than for compound **7** (δ_{OMe} = 3.05 instead of 2.40 ppm), suggesting that they are more distant from the C_3 axis. The very small difference of resonance between the two *t*Bu signals of **8** ($\Delta\delta_{tBu}$ = 0.02 ppm) also indicates that all *t*Bu groups have similar orientations. This stands in contrast to the classical alternate *in* and *out* positions adopted by the *t*Bu groups

SCHEME 2[a]



[a] (i) Ethylbromoacetate, NaH, THF, reflux, 77%. (ii) LAH, ether, reflux, 82%. (iii) TsCl, pyridine, $CHCl_3$, −20 °C, 86%. (iv) **2**, Cs_2CO_3, DMF, rt then 90 °C, 31%. (v) PhSH, Na_2CO_3, DMF, 50 °C, 75%.

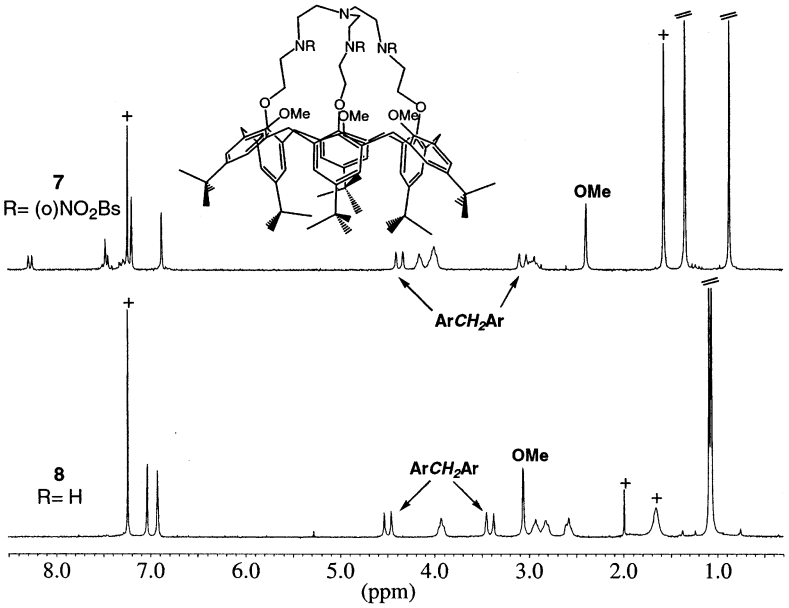


FIGURE 1. ^{1}H NMR spectra of compounds **7** (R = (*o*)NO_2Bs, top) and **8** (R = H, bottom) in $CDCl_3$ at 298 K: (+) residual water or solvent peaks ($CHCl_3$ and CH_3CN; this latter was present in elemental analysis characterization of compound **8**).

of calixarenes with the same symmetry[13] (for example, $\Delta\delta_{t\mathrm{Bu}} = 0.51$, 0.37, 0.63, and 0.47 ppm for calixarenes **4**, **5**, **6** and **7**, respectively). This shows that the skeleton of calix[6]azacrown **8** has a more straight and regular cone conformation. As in the case of compound **5**, these features might well be due to the establishment of hydrogen bonds between the anisole units and their neighboring phenoxy protic substituents, namely, the tren-NH groups in the case of **8**. Indeed, addition of CD_3-OD induced a split of the *t*Bu resonances attesting to a conformational change. Finally, a variable temperature ^{1}H NMR study showed some broadening of the spectra at low temperature. However, the axial and equatorial $ArCH_2Ar$ methylene protons were differentiated over the whole temperature range (240−330 K), indicating that the cone-cone inversion did not occur on the NMR time scale.

In conclusion, we have described the synthesis of the first C_{3v}-symmetrical calix[6](aza)crown **8**. A ^{1}H NMR study has shown that the alternate 1,3,5-azabridge at the small rim rigidifies the whole edifice, preventing ring inversion and constraining the calixarene core in a straight cone conformation. The ability of this novel ligand to coordinate a metal ion together with its host−guest properties (neutral or charged molecules recognition) are under intense investigation.

Experimental Section

General Procedures. THF and ether were distilled over sodium/benzophenone under argon. Pyridine was distilled over KOH under argon. Chloroform was distilled over P_2O_5 under argon. DMF was distilled over $MgSO_4$ and stored over 4 Å molecular sieves under argon. TsCl was recrystallized (dichloromethane/pentane) before use. ^{1}H and ^{13}C NMR spectra were recorded at, respectively, 200 and 50 MHz. Thin-layer chromatographies (TLC) were performed with aluminum plates (0.20 mm) precoated with fluorescent silica gel. Reaction components were then visualized under UV light and dipped in a Dragendorff solution. Silica gel (230−400 mesh) was used for flash chromatography separations. All reactions were performed under an inert atmosphere. Elemental analyses were performed at the Laboratoire de Microanalyse Organique, IRCOF, France.

***N,N′,N″*-Tri-2-nitrobenzenesulfonyl-2,2′,2″-nitrilotriethylamine 2.** At 0 °C, TEA (3.9 mL, 27.75 mmol) was added to a solution of tren (1.0 mL, 6.68 mmol) in 20 mL of anhydrous THF. (*o*)NO_2BsCl (5.03 g, 22.7 mmol) was added by small portions over the course of 20 min time, and then the reaction mixture was stirred for 16 h at room temperature. After removal of the solvent under reduced pressure, addition of water, and extraction with dichloromethane, the resulting crude residue was purified by flash chromatography, yielding **2** (3.56 g, 76%) as an amorphous yellow solid that we were unable to recrystallize. Mp: 85−88 °C (decomp). IR ($CHCl_3$): ν 3340, 1542, 1362 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.63 (t, J = 5.5 Hz, 6H), 3.10 (q, J = 5.5 Hz, 6H), 5.76 (t, J = 5.5 Hz, 3H), 7.69−7.87 (m, 9H), 8.04−8.13 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 41.77, 54.78, 125.7, 131.0, 133.1, 133.2, 133.9, 148.2. MS (FAB) *m*/*z*: 702.4 (M − H$^+$, calcd 702.1).

5,11,17,23,29,35-Hexa-*tert*-butyl-37,39,41-trimethoxy-38,40,42-tris(2-hydroxyethoxy)calix[6]arene 5. To a solution of **4** (4.15 g, 3.26 mmol) in 350 mL of anhydrous Et_2O was added LAH (1.43 g, 37.6 mmol) at −4 °C. After 16 h of refluxing, the reaction mixture was cooled to 0 °C and 50 mL of an aqueous solution of HCl (4 M) was added slowly. After dichloromethane (500 mL) extraction, the organic layer was washed twice with 50 mL of an aqueous solution of HCl (4 M). The solvent was removed under reduced pressure, and the resulting residue was dissolved in 200 mL of chloroform. The

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insoluble material was removed by filtration and the chloroform was removed under reduced pressure, giving a white solid that was purified by recrystallization in ethanol. Thus, pure compound **5** (3.06 g, 82%) was obtained as a white solid. Mp: 227 °C (decomp). IR ($CHCl_3$): ν 3660 to 3120, 1480 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.91 (s, 27H), 1.28 (s, 27H), 3.30 (s_l, 6H), 3.43 (s_l, 6H), 3.47 (s, 9H), 3.92 (s_l, 12H), 6.65 (s, 6H), 7.13 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 30.90, 31.36, 31.64, 34.12, 34.15, 34.31, 60.33, 61.73, 75.23, 124.4, 127.2, 133.1, 133.2, 145.8, 146.2, 153.2, 153.4. Anal. Calcd for $C_{75}H_{102}O_9$, 2 EtOH: C, 76.54; H, 9.27. Found: C, 76.74; H, 9.04.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,39,41-trimethoxy-38,40,42-tris(2-tosylethoxy)calix[6]arene 6. TsCl (0.997 g, 5.23 mmol) was added to a solution of **5** (1.00 g, 0.87 mmol) in 1 mL of anhydrous $CHCl_3$, and then, at −10 °C, anhydrous pyridine (3.0 mL, 36.79 mmol) was slowly added under vigorous stirring. The flask containing the reaction mixture was placed in a freezer at −20 °C for 16 h. The solvents were removed under high vacuum, and 10 mL of ethanol was added to the crude residue. The resulting solid was isolated by filtration and washed twice with cold ethanol, yielding compound **6** (1.20 g, 86%) as a white solid. Mp: 153−154 °C. IR ($CHCl_3$): ν 1598, 1482, 1361, 1175 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.74 (s, 27H), 1.37 (s, 27H), 2.07 (s, 9H), 2.37 (s, 9H), 3.29 (d, J = 15.6 Hz, 6H), 4.11 (t, J = 4.7 Hz, 6H), 4.40 (d, J = 14.9 Hz, 6H), 4.42 (t, J = 4.7 Hz, 6H), 6.58 (s, 6H), 7.21 (s, 6H), 7.28 (d, J = 7.8 Hz, 6H), 7.82 (d, J = 7.8 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 21.77, 29.67, 31.18, 31.76, 34.06, 34.36, 60.05, 68.97, 70.16, 123.7, 128.1, 130.1, 132.9, 133.5, 145.2, 146.0, 146.3, 151.1, 154.4. Anal. Calcd for $C_{96}H_{120}O_{15}S_3$, 2 H_2O: C, 70.04; H, 7.59. Found: C, 70.37; H, 7.22.

Capped Calix[6]arene 7. Cs_2CO_3 (0.815 g, 2.50 mmol) was added to a solution of **6** (1.152 g, 0.715 mmol) in 25 mL of anhydrous DMF at room temperature. The reaction mixture was vigorously stirred, and a solution of **2** (0.506 g, 0.721 mmol) in 25 mL of anhydrous DMF was slowly added (for 1 h) at room temperature. After 2 h at room temperature the reaction mixture was heated at 90 °C for 16 h. The DMF was removed under reduced pressure, and 50 mL of water was added. After dichloromethane extraction and concentration, flash chromatography (dichloromethane/EtOAc, 99:1 then 98:2) afforded **7** (0.398 g, 31%) as a yellow solid. An analytical sample was obtained by recrystallization in a mixture of EtOH/$CHCl_3$. Mp: 264 °C (decomp). IR ($CHCl_3$): ν 1546, 1481, 1372, 1167 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.87 (s, 27H), 1.34 (s, 27H), 2.40 (s, 9H), 2.88−3.05 (m, 6H), 3.06 (d, J = 14.1 Hz, 6H), 3.89−4.10 (m, 12H), 4.11−4.20 (m, 6H), 4.37 (d, J = 14.1 Hz, 6H), 6.88 (s, 6H), 7.20 (s, 6H), 7.22−7.50 (m, 9H), 8.27 (d, J = 7.8 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 28.73, 31.08, 31.76, 34.22, 34.37, 48.67, 49.10, 54.69, 61.20, 73.48, 115.4, 123.8, 124.0, 127.7, 131.3, 132.4, 133.1, 133.3, 133.6, 133.9, 146.3, 146.5, 147.8, 150.0, 154.5. Anal. Calcd for $C_{99}H_{123}N_7O_{18}S_3$, H_2O: C, 65.58; H, 6.95; N, 5.41. Found: C, 65.82; H, 7.18; N, 5.88.

X_6Me_3tren 8. Na_2CO_3 (0.604 g, 5.70 mmol) was added to a solution of **7** (0.641 g, 0.357 mmol) in 30 mL of anhydrous DMF at room temperature. The reaction mixture was vigorously stirred, and thiophenol (0.293 mL, 2.85 mmol) was added, leading to a greenish coloration. After 24 h at 50 °C, the DMF was removed under reduced pressure and 50 mL of an aqueous solution of NaOH (1 M) was added. After dichloromethane extraction and concentration, the resulting residue was dissolved in 3 mL of dichloromethane, and 5 mL of acetonitrile was added. The resulting precipitate was isolated by suction filtration and washed twice with acetonitrile giving **8** (0.330 g, 75%) as a white solid. Mp: 251−252 °C (decomp). IR ($CHCl_3$): ν 3660 to 3110, 1480 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.06 (s, 27H), 1.08 (s, 27H), 2.58 (m, 6H), 2.82 (m, 6H), 2.92 (m, 6H), 3.05 (s, 9H), 3.41 (d, J = 14.9 Hz, 6H), 3.92 (m, 6H), 4.49 (d, J = 14.9 Hz, 6H), 6.93 (s, 6H), 7.04 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 30.08, 31.44, 31.49, 34.17, 34.24, 48.80, 49.79, 55.25, 61.00, 73.54, 125.6, 126.2, 133.2, 133.4, 145.7, 145.9, 152.4, 154.2. Anal. Calcd for $C_{81}H_{114}N_4O_6$, 2.5 H_2O, 0.5 CH_3CN: C, 75.45; H, 9.30; N, 4.83. Found: C, 75.34; H, 9.17; N, 4.78.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of compounds **2**, **5**, and **6** and ^{13}C NMR spectra of compounds **7** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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