

# Synthesis and Characterization of New Calixarenes from Bisphenol A

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The synthesis of bisphenol A-derived calixarenes has been studied by changing the protecting group of the phenol moiety and reaction conditions. Depending on the protecting groups, the corresponding calix[6,7,8]arenes are obtained in different ratios. For example, when mono-*p-tert*-butyldimethylsilyl-protected bisphenol A is treated with paraformaldehyde and a catalytic amount of aqueous KOH in refluxing *p*-xylene with a Dean-Stark water collector for 36 h, the corresponding calix[8]arene, calix[7]arene, and calix[6]arene are produced and separated in the ratio of about 3 : 2 : 1 and with overall 63% yield. The calixarenes are characterized by NMR spectroscopy and mass analysis. The X-ray crystal structure of the calix[8]arene shows a pleated loop conformation, stabilized by intramolecular hydrogen bonding between the inner phenolic hydroxy groups.

## Introduction

Calixarenes are cyclic oligonuclear phenolic compounds, which have been widely used as host molecules in the molecular recognition.<sup>1</sup> Typically, oligomers such as tetramers, hexamers, or octamers are most valuable frameworks for the construction of more complex structures. Thanks to the work of Gutsche, optimal conditions for the one-pot synthesis of these calixarenes from *p-tert*-butylphenol are established.<sup>2</sup> Structural modification of these calixarenes, specifically at the hydroxy or *tert*-butyl groups, has provided a variety of derivatives. Calixarenes having *p*-substituents other than *tert*-butyl have also been synthesized by oligomerization of the corresponding phenolic monomer. A considerable deviation in the product distribution, however, has been found depending on the *p*-substituent. When *p-tert*-pentylphenol is used as the starting material, the corresponding calix[4]arene is obtained in somewhat lower yields compared to the case of *p-tert*-butylphenol.<sup>3</sup> From 4-(phenylmethyl)phenol, the corresponding calix[5]arene is produced as the major product along with the hexamer and octamer.<sup>4</sup> From 4-adamantylphenol, the corresponding octamer is formed as the major product.<sup>5</sup> From *p*-cresol or *p*-ethylphenol, the corresponding calix[7]arene is obtained.<sup>6</sup> A low yield of calix[8]arene is obtained when *p*-phenylphenol is used.<sup>7</sup> The reason is not known that different product distribution results depending on the *p*-substituent of the starting phenol. We were intrigued with possible oligomeric calixarenes from mono-protected bisphenol A (4,4'-isopropylidenediphenol) derivatives. The monomer has a hybrid structure of *p-tert*-butylphenol and *p*-(phenylmethyl)phenol. The resulting calixarenes would be interesting since the two phenyl rings of bisphenol A constitute a tetrahedral dihedral angle and thus could provide hydrophobic aromatic walls suitable for the molecular recognition that involves cation- $\pi$  interactions.<sup>8,9</sup> A molecular model-

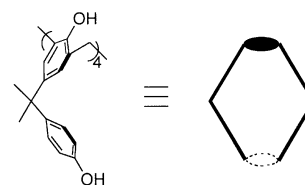


Figure 1

ing study using PM3 calculations suggested that the corresponding calix[4]arene have a pseudo-calixarene feature with a deep hydrophobic aromatic pocket to include tetramethylammonium cation (Fig. 1), while the aromatic rings of the calix[8]arene are somewhat flattened. Recently, Tung and Ji reported the synthesis and complexing properties of a calix[8]arene derived from bisphenol A. They obtained only the calix[8]arene starting from *p*-[1-(4-methoxyphenyl)-1-methylethyl]phenol and formaldehyde with potassium hydroxide in refluxing xylene.<sup>10</sup> We have examined several approaches to synthesize the cyclic tetramer of bisphenol A derivatives, the results of which are described herein.

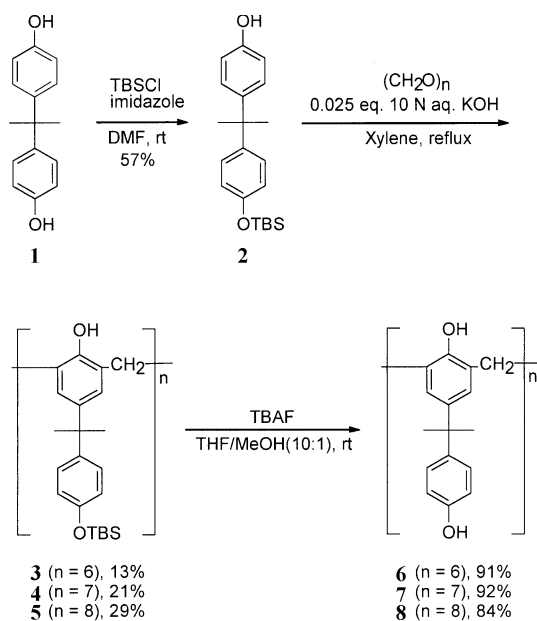
## Results and Discussion

We chose a silyl-protecting group for the mono-protection of bisphenol A. Thus, mono-protection of bisphenol A with *tert*-butyldimethylsilylchloride gave phenol **2** in 57% yield. Starting from phenol **2**, we studied the calixarene formation according to the procedures established for *p-tert*-butylcalixarenes.<sup>2</sup> A procedure for the tetramer was examined: A slurry of phenol **2** (500 mg, 1.46 mmol), formaldehyde (30 wt% solution in water, 157 mg, 1.83 mmol), and NaOH (2.6 mg, 0.066 mmol) in diphenyl ether was refluxed under nitrogen. A tar-like residue obtained after solvent removal, however, did not exhibit typical calixarene-type signals on NMR analysis. Also, under the conditions of the hexamer formation (500 mg, 1.46 mmol of phenol **2**; 102 mg, 3.18 mmol of paraformaldehyde; 28 mg, 0.50 mmol of KOH; 0.11 mL of

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water; 2 mL of *p*-xylene; reflux), again a tar-like material was mainly observed. However, a slight modification of the latter procedure (2.5 mol% of 10 N KOH solution; water collection by a Dean-Stark trap) produced a mixture of calixarenes. Three major products can be separated as homogeneous state ( $R_f = 0.73$ , 504 mg;  $R_f = 0.62$ , 234 mg;  $R_f = 0.59$ , 367 mg; in  $\text{CH}_2\text{Cl}_2/\text{hexanes}=1/1$  by volume) by column chromatography on silica gel (eluant: benzene/hexanes=35/75, by volume). Each product can be further purified by recrystallization for the structural identification. Analyses by  $^1\text{H}$  and  $^{13}\text{C}$  NMR suggested that they were calixarene oligomers. According to the MALDI-TOF mass spectra, they are assigned as the corresponding calix[8]arene, calix[6]arene, and calix[7]arene, respectively. Therefore, 13% of calix[6]arene **3**, 21% of calix[7]arene **4**, and 29% of calix[8]arene **5** are obtained under the reaction conditions, with overall 63% isolated yield. Since there has been little loss in the isolation process, the ratio is equal to the product distribution. The synthesis is amenable to a preparative scale, and 5.21 g (32% yield) of the calix[8]arene can be isolated, starting from 15.76 g of phenol **2** under the same conditions.<sup>11</sup>

It is of interest that other isomers such as the calix[6]arene and calix[7]arene are obtained in addition to the calix[8]arene. In our case, the protecting group and the reaction solvent are different from those of Tungs case. To find the effect of the protecting group on the product distribution, we changed to other protecting groups. Thus, bisphenol A was mono-protected as a tris(isopropyl)silyl ether or benzyl ether, which is more stable in basic conditions than the *tert*-butyldimethylsilyl group, and it was subjected to the conditions of tetramer formation. In each case, the corresponding calix[8]arene was the major product, but the product distribution was different from each other. In the case where bisphenol A is mono-protected as the tris(isopropyl)silyl ether, the calix[8]arene was isolated in 28% yield, along with unidentified oligomers.

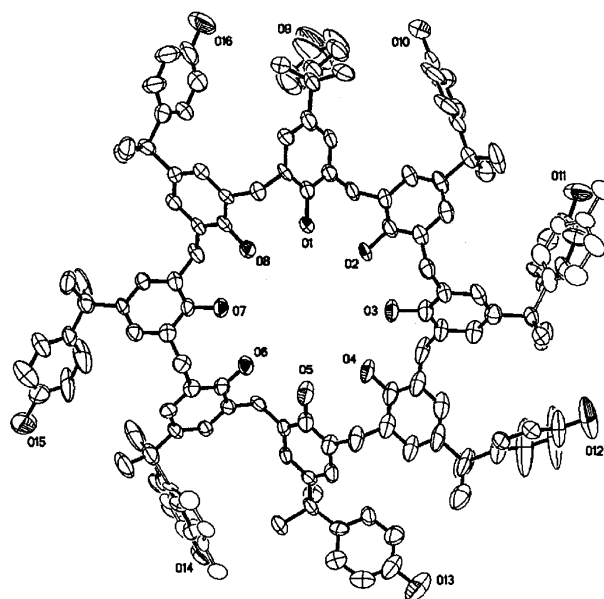


Scheme 1

The previous hexamer procedure again produced a mixture of calixarenes, but with a more complex pattern. Although we confirmed the isomer distribution depending on the protecting group, we could not obtain the desired calix[4]arenes of bisphenol A derivatives under various reaction conditions. Attempts at the formation of the desired calix[4]arenes through several stepwise approaches were also unsuccessful.

The silyl group of calixarenes **3-5** can be readily deprotected with tetrabutylammonium fluoride, giving calixarenes **6-8** in high yields. After a considerable effort, we could obtain single crystals by diffusing isopropyl ether into an acetone solution of calix[8]arene **8** in the presence of an equimolar amount of  $n\text{-Bu}_4\text{N}^+\text{BF}_4^-$ . The X-ray crystal structure of calixarene **8** adopts a pleated loop conformation, which is stabilized by intramolecular hydrogen bonding between the inner phenolic hydroxy groups.<sup>12</sup> Each of the adjacent O---O distance is within 2.60–2.78 Å, corresponding to O-H---O hydrogen bonding distances.<sup>13</sup> The distances between the quaternary carbons in the opposite positions range from 18.1–18.6 Å, showing a nano-scale structure. The distances between the inner phenolic oxygens in the opposite positions range from 6.8–7.2 Å: Solvent molecules in this hole are hardly observed. Acetone molecules reside between calixarene units, but ions such as  $n\text{-Bu}_4\text{N}^+$  or  $\text{BF}_4^-$  are absent in the structure.<sup>14</sup> Overall, the partial structure composed of the inner phenyl units is close to that of *p*-*tert*-butylcalix[8]arene.<sup>12</sup>

Particular stabilization of *p*-*tert*-butylcalix[8]arene through pleated hydrogen bonding is well analyzed by NMR coalescence temperature studies for a series of *p*-*tert*-butylcalix[9–20]arenes in a recent work of Gutsche and co-workers.<sup>15</sup> According to their study, only the calix[8]arene exhibits particular stability similar to that of *p*-*tert*-butylcalix[4]arene but its immediate neighbors calix[6, 7, and 9]arenes do not. Our attempts to grow single crystals of calixarenes **6** and

Figure 2. Crystal structure of calix[8]arene **8**.

7 failed, possibly due to their conformational flexibility. Instead, we obtained a layered packing structure of calix[8]arene **8**.<sup>16</sup>

### Conclusion

We have studied the synthesis of bisphenol A-derived calixarenes by changing the protecting groups of the phenol moiety and reaction conditions. Depending on the protecting group, the corresponding calix[6-8]arenes were obtained in different ratios. For example, starting from **2**, calix[6,7,8]arenes **6-8** were obtained in the ratio of about 3 : 2 : 1 and with overall 63% yield. These calixarenes were characterized by spectroscopic and mass analyses. Among these, the crystal structure of the calix[8]arene was obtained. The X-ray analysis shows a pleated loop conformation, stabilized by intramolecular hydrogen bonding between the inner phenolic hydroxy groups. The calix[8]arene has an extended structure, which would be useful as the starting framework for more extended molecules like dendrimers. In addition, if the calix[4]arene can be synthesized, it would lead to an interesting receptor molecule.

### Experimental Section

**General Methods.** <sup>1</sup>H NMR spectra are reported as follows: chemical shift in ppm from internal tetramethylsilane on the delta scale, multiplicity (s = singlet, d = doublet, br. s = broad singlet), integration, and coupling constant (in Hertz). MALDI-TOF mass analyses were performed by the Seoul branch of the Analytical Laboratory of Korea Basic Science Institute. Elemental analyses were performed by the Center for Biofunctional Molecules (CBM). Melting points are uncorrected ones. Chromatography means flash column chromatography which was carried out on Merck silica gel 60 (230-400 mesh). Analytical thin layer chromatography was carried out on Merck silica gel F<sub>254</sub> glass plates. All reactions were run under an atmosphere of argon.

**1-tert-Butyldimethylsilyloxy-4,4'-isopropylidenediphenol (2).** To a solution of bisphenol A (10.0 g, 44 mmol) in DMF (45 mL) was added imidazole (5.96 g, 88 mmol) and tert-butyldimethylsilyl chloride (7.26 g, 48 mmol) sequentially, and the mixture was stirred for 2 h at room temperature. The reaction mixture was quenched with water (100 mL) and subjected to extraction with diethyl ether (250 mL). The combined organic extracts were dried over anhydrous MgSO<sub>4</sub> and concentrated *in vacuo*. The crude residue was purified by chromatography (eluant: 10% ethyl acetate in hexanes) to afford the desired mono-silylated diphenol (8.60 g, 57%). *R<sub>f</sub>* = 0.34 (ethyl acetate/hexanes=1/4, v/v); mp 87-88 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.14 (d, *J* = 1.52, 2H), 7.11 (d, *J* = 1.52, 2H), 6.78 (d, *J* = 8.76, 2H), 6.75 (d, *J* = 8.76, 2H), 5.07 (s, 1H), 1.67 (s, 6H), 1.03 (s, 9H), 0.24 (s, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 153.7, 153.6, 144.1, 143.9, 128.4, 128.1, 119.7, 115.1, 42.1, 31.5, 26.1, 18.6, -4.0. The remaining mixture contained 1,1-bis(tert-butyldimethylsilyloxy)-4,4'-isopropylidenediphenol (5.40 g, 27%; *R<sub>f</sub>* = 0.92 in ethyl ace-

tate/hexanes=1/4) and starting bisphenol A (1.50 g, 15%; *R<sub>f</sub>* = 0.09 in ethyl acetate/hexanes=1/4).

**5,11,17,23,29,35,41,47-Octakis{[2-(4-tert-butyldimethylsilyloxy)phenyl]-propan-2-yl}-49,50,51,52,53,54,55,56-octahydroxycalix[8]arene (5).** A slurry of 1-tert-butyldimethylsilyloxy-4,4-isopropylidenediphenol **2** (1.71 g, 5.00 mmol), paraformaldehyde (255 mg, 8.50 mmol) and 10 *N* aqueous KOH solution (13 μL, 0.125 mmol) in xylene (10 mL), equipped with a Dean-Stark water collector, was refluxed with efficient stirring for 36 h. The reaction mixture was cooled and concentrated *in vacuo*. The crude residue was purified by chromatography (eluant: 35% benzene in hexanes) to afford calix[6]arene **3** (234 mg, 13%), calix[7]arene **4** (367 mg, 21%), and calix[8]arene **5** (504 mg, 29%). Calix[8]arene **5**: *R<sub>f</sub>* = 0.73 (CH<sub>2</sub>Cl<sub>2</sub>/hexanes=1/1, v/v). mp 254-255 °C (dec). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 9.61 (s, 8H), 7.07 (d, *J* = 8.60, 16H), 6.91 (s, 16H), 6.74 (d, *J* = 8.60, 16H), 4.33 (d, *J* = 13.33, 8H), 3.38 (d, *J* = 13.33, 8H), 1.57 (s, 48H), 1.03 (s, 72H), 0.24 (s, 48H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 153.7, 147.0, 145.2, 143.5, 129.0, 128.1, 127.3, 119.7, 42.1, 32.6, 31.7, 31.4, 26.1, 18.6, -3.9. MALDI-TOF MS: *m/z* obsd, 2858 (100%) [*M* + Na<sup>+</sup>]; calcd for C<sub>176</sub>H<sub>240</sub>O<sub>16</sub>Si<sub>8</sub> + Na<sup>+</sup>, 2860. Anal. calcd for C<sub>176</sub>H<sub>240</sub>O<sub>16</sub>Si<sub>8</sub>: C, 74.52; H, 8.53. Found: C, 74.56; H, 8.84.

Calix[6]arene **3**: *R<sub>f</sub>* = 0.62 (CH<sub>2</sub>Cl<sub>2</sub>/hexanes=1/1, v/v). mp 245-246 °C (dec). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 10.53 (br. s, 6H), 7.05 (d, *J* = 8.58, 12H), 6.90 (s, 12H), 6.73 (d, *J* = 8.58, 12H), 4.12 (br. s, 6H), 3.38 (br. s, 6H), 1.57 (s, 36H), 1.00 (s, 54H), 0.21 (s, 36H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 153.7, 144.7, 143.8, 128.8, 128.2, 127.4, 126.3, 119.6, 42.2, 33.2, 31.5, 26.1, 18.6, -3.9. MALDI-TOF MS: *m/z* obsd, 2149 (100%) [*M* + Na<sup>+</sup>]; calcd for C<sub>132</sub>H<sub>180</sub>O<sub>12</sub>Si<sub>6</sub> + Na<sup>+</sup>, 2150. Anal. calcd for C<sub>132</sub>H<sub>180</sub>O<sub>12</sub>Si<sub>6</sub>: C, 74.52; H, 8.53. Found: C, 74.98; H, 8.85.

Calix[7]arene **4**: *R<sub>f</sub>* = 0.59 (CH<sub>2</sub>Cl<sub>2</sub>/hexanes=1/1, v/v); mp 194-195 °C (dec). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 10.31 (s, 7H), 7.07 (d, *J* = 8.47, 14H), 6.91 (s, 14H), 6.74 (d, *J* = 8.47, 14H), 4.12 (br. s, 7H), 3.50 (br. s, 7H), 1.58 (s, 42H), 1.01 (s, 63H), 0.22 (s, 42H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 153.7, 147.6, 144.8, 143.7, 128.8, 128.2, 127.9, 119.6, 42.2, 33.1, 31.6, 26.2, 18.6, -3.9. MALDI-TOF MS: *m/z* obsd, 2505 (100%) [*M* + Na<sup>+</sup>]; calcd for C<sub>154</sub>H<sub>210</sub>O<sub>14</sub>Si<sub>7</sub> + Na<sup>+</sup>, 2505. Anal. calcd for C<sub>154</sub>H<sub>210</sub>O<sub>14</sub>Si<sub>7</sub>: C, 74.52; H, 8.53. Found: C, 74.51; H 8.75.

**5,11,17,23,29,35,41,47-Octakis[2-(4-hydroxyphenyl)propan-2-yl]-49,50,51,52,53,54,55,56-octahydroxycalix[8]arene (8).** To a solution of calix[8]arene **5** (300 mg, 0.106 mmol) in methanol (0.4 mL) and THF (4 mL), was added *n*-Bu<sub>4</sub>N<sup>+</sup>F<sup>-</sup>·4H<sub>2</sub>O (209 mg, 1.27 mmol), and the resulting solution was stirred for 10 h at room temperature. The mixture was quenched with 1 *N* HCl solution and subjected to extraction with ethyl acetate. The combined organic extracts were washed with brine, dried over anhydrous MgSO<sub>4</sub>, and concentrated *in vacuo*. The crude residue was purified by chromatography (60% ethyl acetate in hexanes) to afford the desired desilylated calix[8]arene **8** (171 mg, 84%). *R<sub>f</sub>* = 0.57 (ethyl acetate/hexanes=1/4, v/v). mp 292-293 °C (dec). <sup>1</sup>H

NMR (300 MHz, acetone- $d_6$ )  $\delta$  9.53 (br. s, 8H), 8.09 (s, 8H), 6.99 (br. s, 32H), 6.71 (d,  $J = 9.09$ , 16H), 3.81 (br. s, 16H), 1.52 (s, 48H).  $^{13}\text{C}$  NMR (75 MHz, acetone- $d_6$ )  $\delta$  155.5, 146.9, 145.3, 141.7, 128.8, 128.0, 127.2, 115.1, 41.7, 31.8, 31.0. Anal. calcd for  $\text{C}_{128}\text{H}_{128}\text{O}_{16} \cdot 5\text{H}_2\text{O}$ : C, 76.39; H, 6.93. Found: C, 76.15; H, 7.07.

**5,11,17,23,29,35-Hexakis[2-(4-hydroxyphenyl)propan-2-yl]-37,38,39,40,41,42-hexahydroxycalix[6]arene (6)**. Similarly **6** was obtained from **3** in 91% yield (143 mg scale).  $R_f = 0.28$  (ethyl acetate/hexanes=3/2, v/v). mp 257-258 °C (dec).  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ )  $\delta$  10.08 (br. s, 6H), 8.11 (s, 6H), 7.01 (d,  $J = 8.25$ , 12H), 6.99 (s, 12H), 6.71 (d,  $J = 8.25$ , 12H), 3.80 (br. s, 12H), 1.52 (s, 36H).  $^{13}\text{C}$  NMR (75 MHz, acetone- $d_6$ )  $\delta$  155.8, 147.9, 144.8, 141.9, 128.0, 127.9, 127.3, 115.0, 41.7, 32.4, 31.0. Anal. calcd for  $\text{C}_{96}\text{H}_{96}\text{O}_{12} \cdot \text{H}_2\text{O}$ : C, 76.19; H, 6.94. Found: C, 76.52; H, 6.96.

**5,11,17,23,29,35,41-Heptakis[2-(4-hydroxyphenyl)propan-2-yl]-43,44,45,46,47,48,49-heptahydroxycalix[7]arene (7)**. Similarly **7** was obtained from **4** in 92% yield (124 mg scale).  $R_f = 0.23$  (ethyl acetate/hexanes=3/2, v/v). mp 165-166 °C.  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ )  $\delta$  9.78 (br. s, 7H), 8.11 (s, 7H), 7.00 (d,  $J = 7.95$ , 14H), 6.95 (s, 14H), 6.72 (d,  $J = 7.95$ , 14H), 3.73 (br. s, 14H), 1.49 (s, 42H).  $^{13}\text{C}$  NMR (75 MHz, acetone- $d_6$ )  $\delta$  155.4, 147.6, 144.8, 141.8, 128.0, 127.7, 127.6, 115.0, 41.7, 32.1, 30.2. Anal. calcd for  $\text{C}_{112}\text{H}_{112}\text{O}_{14} \cdot 5\text{H}_2\text{O}$ : C, 75.90; H, 6.95. Found: C, 75.96; H, 7.25.

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