Calix[4]arenes with Siloxanes Bridging Opposite Rings

Paul F. Hudrlik,* Anne M. Hudrlik, Liping Zhang, Wondwossen D. Arasho, and Jaeeock Cho

Department of Chemistry, Howard University, Washington, District of Columbia 20059

phudrlik@howard.edu

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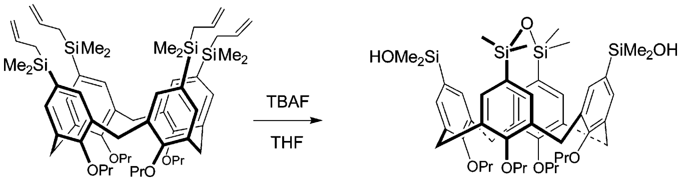

Several C-silylated (allyldimethylsilyl) calixarenes (**1**, **14**, and **18**) were treated with commercial TBAF in THF, giving the novel calixarenes **2**, **15**, and **19**, in which the opposite rings were bridged by a Si−O−Si siloxane group. Compound **19** and the derived phenol **20** (as well as the dibromocalixarene precursor **17**) were mixtures of cone and partial cone conformations according to NMR, while **2** and **15** (as well as **14** and the cone components of **17**, **19**, and **20**) were in flattened cone conformations.

Introduction

Calixarenes[1] have been widely studied as hosts and potential hosts for molecular recognition. Silylated calixarenes are of potential interest for molecular recognition of anions[2] because silicon can expand its coordination shell to become pentacoordinate or hexacoordinate, especially when bonded to electronegative atoms.[3]

We have recently developed a convenient procedure for the preparation of calix[4]arenes silylated on aromatic rings with Me_3Si, $PhMe_2Si$, Ph_2MeSi, and (allyl)Me_2Si groups.[4] We were particularly interested in the (allyl)Me_2Si group because it has the potential to be converted to a silicon group having a more electronegative atom such as F or O. We report here the first preparation of calixarenes substituted on the aromatic rings with silicon groups having an electronegative atom, including several calixarenes with a siloxane bridge linking opposite aromatic rings at the upper (wide) rim.[4a,5] Silylated calixarenes with electronegative substituents on the silicon are potentially useful in molecular recognition, and calixarenes bearing silanol or siloxane groups are potentially useful for the preparation of higher assemblages such as bis-calixarenes.

Results and Discussion

Tetrakis(allyldimethylsilyl)calixarene **1** was prepared from tetrabromocalixarene **13** by halogen−lithium exchange using *t*-BuLi followed by silylation with the supernatant from a mixture of (allyl)Me_2SiCl and Et_3N as described.[4] Allylsilanes and arylsilanes can both be cleaved by electrophilic or nucleophilic conditions, but we expected the allyl−silicon bond to be more labile. An allyldimethylarylsilane has been reported to yield a fluorodimethylarylsilane on treatment with TBAF in a mild procedure.[6] Using a modification of these conditions with

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* Corresponding author. Fax: (202) 806-5442.

[1] (a) Gutsche, C. D. Calixarenes. In *Monographs in Supramolecular Chemistry*; Stoddart, J. F., Ed.; The Royal Society of Chemistry: London, 1989. (b) Böhmer, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713−745. (c) Gutsche, C. D. Calixarenes Revisited. In *Monographs in Supramolecular Chemistry*; Stoddart, J. F., Ed.; The Royal Society of Chemistry: London, 1998. (d) Mandolini, L.; Ungaro, R., Eds. *Calixarenes in Action*; Imperial College Press: London, 2000. (e) Asfari, Z.; Böhmer, V.; Harrowfield, J.; Vicens, J. *Calixarenes 2001*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2001.

[2] Recognition of anions: (a) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486−516. (b) Matthews, S. E.; Beer, P. D. In ref 1e, pp 421−439.

[3] (a) Chuit, C.; Corriu, R. J. P.; Reyé, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371−1448. (b) Chuit, C.; Corriu, R. J. P.; Reye, C. In *Chemistry of Hypervalent Compounds*; Akiba, K., Ed.; Wiley-VCH: New York, 1999; pp 81−146. (c) Kira M.; Zhang, L. C. In *Chemistry of Hypervalent Compounds*; Akiba, K., Ed.; Wiley-VCH: New York, 1999; pp 147−169.

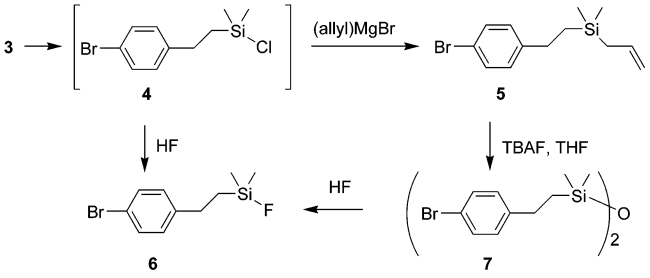
[4] (a) Hudrlik, P. F.; Hudrlik, A. M.; Arasho, W. D.; Zhang, L.; Cho, J. Abstracts, 60th Southwest Regional Meeting of the American Chemical Society, Fort Worth, TX, Sept 29 to Oct 5, 2004; American Chemical Society: Washington, DC, 2004. (b) Hudrlik, P. F.; Hudrlik, A. M.; Arasho, W. D.; Butcher, R. J., submitted.

[5] Calixarenes, which are silyl ethers having an O-Si-O bridge linking adjacent phenol rings at the narrow (lower) rim (from *p*-*t*-butylcalix[4]arene and Me_2SiCl_2), are known: Fan, M.; Zhang, H.; Lattman, M. *Organometallics* **1996**, *15*, 5216−5219. See also: Narumi, F.; Morohashi, N.; Matsumura, N.; Iki, N.; Kameyama, H.; Miyano, S. *Tetrahedron Lett.* **2002**, *43*, 621−625.

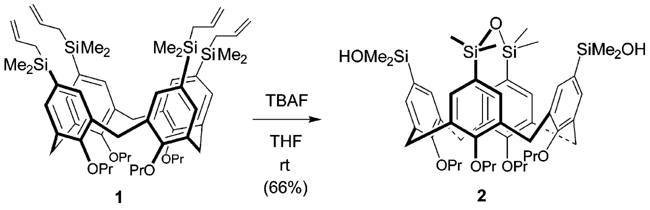
[6] Andrey, O.; Ducry, L.; Landais, Y.; Planchenault, D; Weber, V. *Tetrahedron* **1997**, *53*, 4339−4352.

10.1021/jo070661f CCC: $37.00

SCHEME 1



SCHEME 2

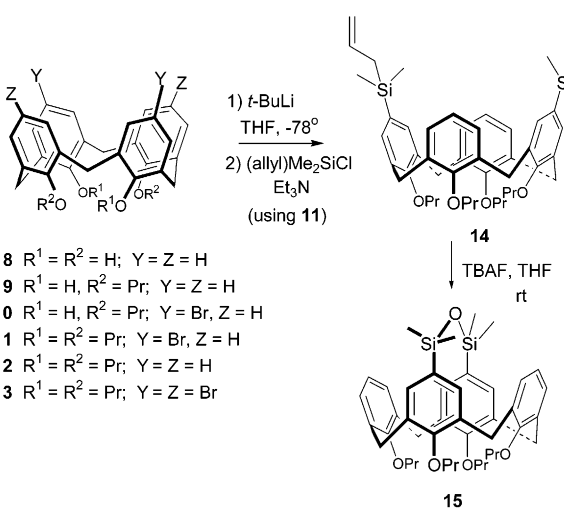


tetrakis(allyldimethylsilyl)calixarene **1** (TBAF, THF, room temperature (rt)) resulted in a compound which was not the expected fluorosilane. In particular, the expected coupling[7] of the CH_3Si with the F was not seen the ^{1}H NMR spectrum, and the MALDI-TOF mass spectrum did not agree with the expected molecular weight.

To study a simpler model compound, we prepared the allylsilane **5** (from hydrosilylation of 4-bromostyrene (**3**) with $ClMe_2SiH$ followed by treatment with the allyl Grignard) and subjected it to the previous conditions (TBAF, THF, rt) (Scheme 1). The product did not go through the GC under conditions used for **5**, suggesting that it had a high molecular weight. It was assigned the siloxane structure **7** from the MALDI-TOF mass spectrum and NMR spectra. Treatment of siloxane **7** with aqueous HF[8] in *i*-PrOH led to fluorosilane **6**. The ^{1}H NMR spectrum of **6** showed the J_{HF} coupling of CH_3Si to be 7 Hz, and the ^{13}C NMR spectrum showed J_{CF} couplings of 13.9 and 14.8 Hz. For confirmation, fluorosilane **6** was prepared by hydrosilylation of 4-bromostyrene with $ClMe_2SiH$ followed by treatment with aqueous HF.[8] The siloxane most likely arose via small amounts of water, which are present in commercially available solutions of TBAF. (In ref 6, the authors did not report a CH_3-F coupling in the ^{1}H NMR spectrum of the product from the previously mentioned reaction, and we suspect that their product was a silanol or a siloxane, not the fluorosilane.) Perusal of the literature led to another example of the conversion of an allylsilane to a silanol using TBAF (without added water).[9]

The product from the reaction of **1** with TBAF was assigned as the silanol/siloxane structure **2** (Scheme 2) based on its IR and NMR (^{1}H, ^{13}C, DEPT) spectra and MALDI-TOF MS. The IR spectrum indicated the presence of a hydroxyl group. The ^{1}H NMR spectrum, which included two large singlets at δ 0.49 and 0.01 of equal integration (assigned to the $SiCH_3$ groups), is consistent with the symmetry of the 1,3-bridged siloxane in **2** and not with that of the corresponding 1,2-bridged siloxane.

SCHEME 3



8 $R^1 = R^2 = H$; Y = Z = H
9 $R^1 = H$, $R^2 = Pr$; Y = Z = H
10 $R^1 = H$, $R^2 = Pr$; Y = Br, Z = H
11 $R^1 = R^2 = Pr$; Y = Br, Z = H
12 $R^1 = R^2 = Pr$; Y = Z = H
13 $R^1 = R^2 = Pr$; Y = Z = Br

(The ^{1}H NMR spectrum of **2** was consistent with a flattened cone structure as discussed below.) The MALDI-TOF MS showed a major peak at 893.4 $[\mathbf{2} + Na]^+$ and a smaller peak at 870.4 $[\mathbf{2}]^+$. A very small peak at 1745.7 in the MALDI-TOF MS, which corresponds to $[(2 \times \mathbf{2}) - H_2O + Na]$, is of particular interest as it suggests the possibility of a small amount of bis-calixarene formed by two molecules of **2** with the formation of another siloxane bond. No higher mass peaks were observed up to *m/z* 6000.

Calixarenes having silanol/siloxane substituents are not only potentially useful in molecular recognition but also for the formation of bis and higher calixarenes. We therefore investigated the generality of these reactions with a few more examples. To prepare a simpler calixarene, we chose bis-(allyldimethylsilyl)calixarene **14** as a substrate (Scheme 3).

The first attempt to prepare the precursor dibromocalixarene **11** involved selective alkylation to give a (dialkoxy)(dihydroxy)-calixarene, selective introduction of Br on the phenol rings, and then alkylation of the remaining hydroxyls. Selective electrophilic substitutions at phenols in the presence of phenol ethers have been frequently used in calixarene chemistry,[10] and we have used this procedure for the bromination of a calixarene dimethyl ether.[4] Treatment of tetrahydroxycalixarene **8** with K_2CO_3/CH_3CN[10] and *n*-PrI gave the dipropyl ether **9**[11] in 64% yield. Calixarene **9** was treated with NBS in MEK[12] to prepare dibromocalixarene **10**. However, the product **10**[13] contained an impurity (by ^{1}H NMR and MALDI-TOF MS), believed to be 10−20% of a monobromocalixarene. Compound **10** was not very soluble and was difficult to purify, so the product mixture was treated with NaH and PrI in DMF to convert **10** to the desired tetrapropyl ether precursor, dibromocalixarene **11**. Calixarene **11** was more soluble, but a successful purification (chromatography, recrystallization) was not achieved.

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(7) For example, $PhSiMe_2F$: Fujita, M.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 5405−5415.

(8) (a) Eaborn, C. *J. Chem. Soc.* **1952**, 2846−2849. (b) Mutahi, M.; Nittoli, T.; Guo, L.; Sieburth, S. M. *J. Am. Chem. Soc.* **2002**, *124*, 7363−7375.

(9) Magar, S. S.; Desai, R. C.; Fuchs, P. L. *J. Org. Chem.* **1992**, *57*, 5360−5369.

(10) van Loon, J.-D.; Arduini, A.; Coppi, L.; Verboom, W.; Pochini, A.; Ungaro, R.; Harkema, S.; Reinhoudt, D. N. *J. Org. Chem.* **1990**, *55*, 5639−5646.

(11) Casnati, A.; Pochini, A.; Ungaro, R.; Ugozzoli, F.; Arnaud, F.; Fanni, S.; Schwing, M. J.; Egberink, R. J. M.; de Jong, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 2767−2777.

(12) Conner, M.; Janout, V.; Regen, S. L. *J. Org. Chem.* **1992**, *57*, 3744−3746.

(13) Conversions of **9** to **10** have been reported: (a) Gagnon, J.; Vézina, M.; Drouin, M.; Harvey, P. D. *Can. J. Chem.* **2001**, *79*, 1439−1446. (b) Dondoni, A.; Ghiglione, C.; Marra, A.; Scoponi, M. *J. Org. Chem.* **1998**, *63*, 9535−9539. Problems with this conversion have also been reported (ref 14).

The dibromocalixarene **11** was successfully prepared from tetrabromocalixarene **13** by the selective halogen−metal exchange reaction of Larsen and Jørgensen.[14] [Calixarene **13** was prepared from **8** by complete propylation (NaH, PrBr, DMF),[15] giving **12** in 74% yield, followed by bromination (NBS, MEK, reflux),[12,16] giving **13**[14] in 88% yield.] A selective bromine−lithium exchange[14] was accomplished by the treatment of **13** with 2−3 equiv of *n*-BuLi in THF at −78 °C for 15 min, followed by quenching with dry methanol, giving dibromocalixarene **11**[14] in 82% yield.

Silylation was accomplished by our procedure:[4] treatment of **11** with *t*-BuLi followed by the supernatant from a mixture of (allyl)$\mathrm{Me_2SiCl}$ and $\mathrm{Et_3N}$ giving the bis(allyldimethylsilyl)calixarene **14** in 67% yield.

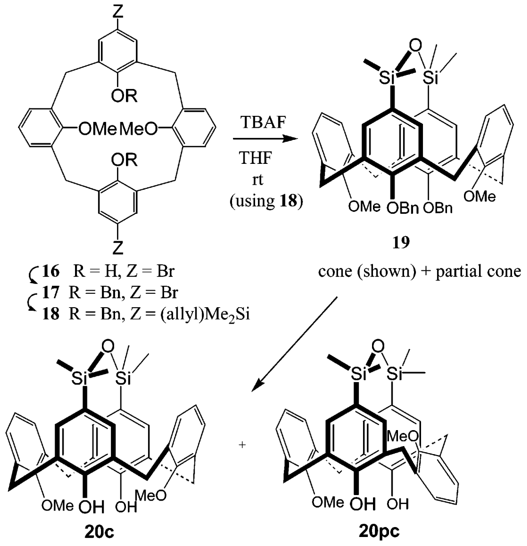
The reaction of **14** with TBAF in THF was similar to that of **1**, giving siloxane **15** in 60−74% yields. A similar reaction using DMF (undistilled) in place of THF gave a 50% yield of **15**. The calixarenes were characterized by IR, NMR (^{1}H, ^{13}C, DEPT), and MALDI-TOF spectra.

Siloxanes **2** and **15**, as well as their precursor allylsilanes **1** and **14**, were fixed in the cone (or flattened cone) conformation because the method used to introduce the Pr groups on the narrow rim has been shown to give calix[4]arenes fixed in the cone conformation when (four) Pr or larger groups are used.[17] We decided to prepare a more flexible calixarene by using benzyl ethers that could later be converted to the hydroxy compounds. Dibromo dimethyl ether **16**[10] was prepared (94% crude yield) from the corresponding unbrominated compound by treatment with NBS in MEK,[12,18] then converted to the corresponding dibenzyl ether **17** using NaH, BnBr, and DMF (77% yield). Treatment of **17** with *t*-BuLi followed by silylation using the supernatant from a mixture of (allyl)$\mathrm{Me_2SiCl}$ and $\mathrm{Et_3N}$ gave the desired bis(allyldimethylsilyl)calixarene **18**[4] (67% yield).

Treatment of **18** with TBAF in THF resulted in siloxane **19** in 78−90% yields (Scheme 4). Siloxane **19** was crystalline and showed one spot on TLC. However, the ^{1}H NMR spectrum indicated that it was a mixture of cone and partial cone conformers as discussed below. Precursor dibromide **17** had similar characteristics. By contrast, the silane **18** was an oil, showed one spot on TLC, and had an ^{1}H NMR spectrum that showed broad peaks in all regions, suggesting that it existed as a mixture of equilibrating conformations (on the ^{1}H NMR time scale) at room temperature.

Removal of the benzyl groups from siloxane **19** using $\mathrm{H_2}$ in the presence of 10% Pd/C afforded dihydroxycalixarene **20** as a mixture of cone and partial cone conformational isomers (which showed two spots on TLC). These conformers were separated by chromatography giving cone calixarene **20c** in 26−35% yields and partial cone calixarene **20pc** in 30−40% yields. The cone form **20c** contained a small amount of an impurity, believed to be the desilylated compound (by NMR and MALDI-TOF MS). We were surprised that **20** was formed as a mixture of conformational isomers. Usually the hydrogen bonding favors the cone. Perhaps the siloxane bridge raises the barrier to conformational change. (Heating the NMR sample of **20pc** ($\mathrm{CDCl_3}$ solution) at 60 °C for 3 days did not change the ^{1}H NMR spectrum.)

SCHEME 4



The assignment of **20pc** as a partial cone (PC) structure was made using NMR (^{1}H, ^{13}C, DEPT, HMQC). The precursor benzyl ether **19** was assigned as a mixture of cone and partial cone (samples of two different ratios were available, aiding in the peak assignment). The precursor dibromocalixarene **17** displayed a similar ^{1}H NMR spectrum to that of **19** and was similarly assigned as a cone and partial cone. Some of the pertinent NMR data for **17**, **19**, **20pc**, and **20c** are summarized in Table A in the Supporting Information. The assignments are based on the following data.

(1) The appearance of $\mathrm{ArCH_2Ar}$ in the ^{1}H NMR spectra[19,20] [inner and outer pair of doublets (**20pc**) and inner singlet and outer pair of doublets (**17**, **19**), with ^{13}C correlations to ca. δ 35 (C between anti Ar groups[20,21]) and ca. δ 30 (C between syn Ar groups[20,21]] is consistent with partial cone but does not completely rule out the 1,2-alternate conformation[19,20] (for **17**) (which, however, is not a commonly observed conformation[22]).

(2) Two separate OMe signals, one at high field (δ 2.9−3.2), are seen in the ^{1}H NMR spectra of the compounds assigned partial cone conformations (**20pc** and the partial cone components of **17** and **19**). The assignments were confirmed by HMQC correlation with ^{13}C δ 59−60 ($\mathrm{CH_3}$ by DEPT). High field OMe groups have previously been assigned in partial cone calixarenes and were suggested to be pointing into the cavity.[22−24] (The partial cone structure drawn for **20pc** shows the methoxy from

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[14] Larsen, M.; Jørgensen, M. *J. Org. Chem.* **1996**, *61*, 6651−6655.

[15] Arduini, A.; Casnati, A. Calixarenes. In *Macrocycle Synthesis: A Practical Approach*; Parker, D., Ed.; Oxford University Press: New York, 1996; pp 145−173.

[16] Gutsche, C. D.; Pagoria, P. F. *J. Org. Chem.* **1985**, *50*, 5795−5802.

[17] (a) Groenen, L. C.; Ruël, B. H. M.; Casnati, A.; Timmerman, P.; Verboom, W.; Harkema, S.; Pochini, A.; Ungaro, R.; Reinhoudt, D. N. *Tetrahedron Lett.* **1991**, *32*, 2675−2678. (b) Gutsche, C. D.; Reddy, P. A. *J. Org. Chem.* **1991**, *56*, 4783−4791.

[18] Shimizu, S.; Moriyama, A.; Kito, K.; Sasaki, Y. *J. Org. Chem.* **2003**, *68*, 2187−2194.

[19] Gutsche, C. D.; Dhawan, B.; Levine, J. A.; No, K. H.; Bauer, L. J. *Tetrahedron* **1983**, *39*, 409−426.

[20] Ungaro, R. Introduction. In *Calixarenes in Action*; Mandolini, L., Ungaro, R., Eds.; Imperial College Press: London, 2000; pp 1−10.

[21] Jaime, C.; de Mendoza, J.; Prados, P.; Nieto, P. M.; Sánchez, C. *J. Org. Chem.* **1991**, *56*, 3372−3376.

[22] Groenen, L. C.; van Loon, J.-D.; Verboom, W.; Harkema, S.; Casnati, A.; Ungaro, R.; Pochini, A.; Ugozzoli, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1991**, *113*, 2385−2392.

[23] Soi, A.; Bauer, W.; Mauser, H.; Moll, C.; Hampel, F.; Hirsch, A. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1471−1478.

[24] See also: Fischer, S.; Grootenhuis, P. D. J.; Groenen, L. C.; van Hoorn, W. P.; van Veggel, F. C. J. M.; Reinhoudt, D. N.; Karplus, M. *J. Am. Chem. Soc.* **1995**, *117*, 1611−1620.

TABLE 1. ^{1}H NMR Resonances (δ) of Calixarenes Assigned as Flattened Cones

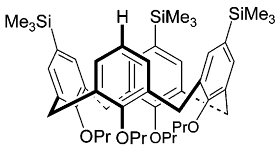
compd	Ar	Ar	OCH_2		$OCH_2\underline{CH_2}$		$OCH_2CH_2\underline{CH_3}$	
2	7.39 (s)	6.16 (s)	4.03 (m)	3.67 (t)	1.94	1.87	1.12 (t)	0.88 (t)
14	7.22 (s)	6.19 (t) 6.02 (d)	4.02 (m)	3.67 (t)	1.96	1.87	1.11 (t)	0.88 (t)
15	7.18 (d) 6.98 (t)	6.21 (s)	4.02 (m)	3.67 (t)	1.93	1.87	1.12 (t)	0.87 (t)
17	6.98 (t)	6.40 (s)	NA	NA	NA	NA	NA	NA
19	7.21 (d) 7.02 (t)	6.29 (s)	NA	NA	NA	NA	NA	NA
20c	7.22 (d) 7.06 (t)	6.18 (s)	NA	NA	NA	NA	NA	NA
21	7.27 7.24	6.25 (s) 6.15 (m)	4.05 (m)	3.71 (t) 3.68 (t)	2.03	1.90	1.10 (t) 1.09 (t)	0.91 (t)

the inverted ring in the cavity, but we have no evidence to support that over the structure with the other methoxy group in the cavity.[23]) High (or intermediate) field OMe groups have been assigned in 1,2- and 1,3-alternate calixarenes as well.[22,24] However, the fact that the ^{1}H NMR of **17** showed two very different OMe signals (for the partial cone component, in addition to a single OMe peak for the cone component) is consistent with the partial cone rather than the 1,2-alternate since symmetry considerations suggest that only one OMe signal should be observed for the undistorted 1,2-alternate structure.[25] (The ^{13}C NMR also shows separate OMe signals.)

(3) The OCH_2Ph signals in the ^{1}H NMR spectra for **17** and **19** appear as a singlet for the cone and as a pair of doublets for the partial cone, indicating diastereotopic protons.

(4) The aromatic regions of the ^{1}H NMR spectra for **17** and **19** (and **20pc** where applicable) include high field singlets (2 H for the partial cone and 4 H for the cone, assigned to substituted rings), a triplet (2 H for the cone, assigned to para hydrogens), and two triplets (1 H each of the partial cone, assigned to meta hydrogens of unsubstituted rings).

Calixarenes **2**, **14**, **15**, and **20c** have ^{1}H NMR spectra characteristic of flattened (or pinched) cone structures, in which two of the aryl groups are closer together (pinched) and nearly parallel, and the other two are splayed outward.[23,26] Tetra-O-alkylated calix[4]arenes in the cone conformation usually have ^{1}H NMR spectra expected for a symmetrical cone, believed to be due to fast equilibration in solution between flattened cone conformations.[26a−d] The flattened cone has been observed in the ^{1}H NMR in cases in which a particular flattened cone conformation is favored. The characteristic signals are a portion of the aromatic signals at high field (δ 6−6.2), assigned to the parallel rings,[27] and, for those calix[4]arenes having four OPr (or OCH_2-R) groups, two sets of OPr signals of equal intensity.[28] Jørgensen and co-workers have noted that a chemical shift difference of about 0.4 ppm for the OCH_2 groups shows that one flattened cone conformer (in a rapid exchange situation) is clearly favored (assuming minimal effects from substituents in the 5 and 17 positions).[26f,g]



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Pertinent ^{1}H NMR data are summarized in Table 1. The analogous NMR resonances of the tris(trimethylsilyl)calixarene **21**, prepared earlier in this laboratory,[29] are included in Table 1. For **2**, **15**, and **20c**, the parallel rings are expected to be those connected by the siloxane bridge, and for **14**, those having the least bulky groups (H) in the *p*-positions, and these expectations are supported by the aromatic chemical shifts and couplings. The separation of the OCH_2 signals of **14** (0.35 ppm) is very similar to those of the bridged calixarenes **2** and **15** (0.35−0.36 ppm). For the cone and partial cone mixtures, **17** and **19**, the cone component appeared to be in a flattened conformation, and the cone aromatic signals that were assigned are included in Table 1.

We were initially surprised to see that the cone component of **17** appeared to adopt a flattened structure. A high field aromatic singlet of 4 H indicated that the parallel aromatic rings were those with Br as the *p*-substituent. By contrast, dibromocalixarene **11** having propyl groups on the oxygens has an ^{1}H NMR spectrum expected for a symmetrical cone. Usually, the flattened cone conformation appears to be established by substituents on the upper rim, but in this case, the conformation appears to be determined by the bulky benzyloxy groups on the lower rim.

Summary. Several novel calix[4]arenes (**2**, **15**, and **19**, as well as the derived **20c** and **20pc**) bridged on the upper rim by siloxane groups were prepared via allyldimethylsilyl calixarenes and commercial TBAF in THF. From a tetrakis silyl compound (**1**), 1,3-siloxane (**2**) was obtained rather than 1,2-siloxane, as assigned by ^{1}H NMR. Calixarene **19** and its dibromo precursor **17**, which have two diametrically situated benzyl ethers and two methyl ethers on the lower rim, were shown to be mixtures of partial cone and cone conformations by NMR, especially ^{1}H NMR and HMQC. (The derived **20pc** was also a partial cone.) The bridged calixarenes **2**, **15**, and **20c**; calixarene **14**; and the

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[25] For NMR spectra of 1,2-alternate calixarenes, see ref 22.

[26] (a) Grootenhuis, P. D. J.; Kollman, P. A.; Groenen, L. C.; Reinhoudt, D. N.; van Hummel, G. J.; Ugozzoli, F.; Andreetti, G. D. *J. Am. Chem. Soc.* **1990**, *112*, 4165−4176. (b) Conner, M.; Janout, V.; Regen, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 9670−9671. (c) Arduini, A.; Fabbi, M.; Mantovani, M.; Mirone, L.; Pochini, A.; Secchi, A.; Ungaro, R. *J. Org. Chem.* **1995**, *60*, 1454−1457. (d) Scheerder, J.; Vreekamp, R. H.; Engbersen, J. F. J.; Verboom, W.; van Duynhoven, J. P. M.; Reinhoudt, D. N. *J. Org. Chem.* **1996**, *61*, 3476−3481. (e) Jørgensen, M.; Larsen, M.; Sommer-Larsen, P.; Petersen, W. B.; Eggert, H. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2851−2855. (f) Larsen, M.; Krebs, F. C.; Harrit, N.; Jørgensen, M. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1749−1757. (g) Jørgensen, M.; Krebs, F. C. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1929−1934. (h) Dondoni, A.; Kleban, M.; Hu, X.; Marra, A.; Banks, H. D. *J. Org. Chem.* **2002**, *67*, 4722−4733.

[27] Position of aromatic resonances in flattened cone calixarenes is discussed in: Goldmann, H.; Vogt, W.; Paulus, E.; Böhmer, V. *J. Am. Chem. Soc.* **1988**, *110*, 6811−6817.

[28] For examples, see ref 26b−h.

[29] Hudrlik, P. F.; Arasho, W. D.; Hudrlik, A. M. *J. Org. Chem.* **2007**, *72*.

cone component of the mixtures **17** and **19** were assigned the flattened cone conformation by ^{1}H NMR.

Experimental Section

5,17-Bis(1,3-dimethylsiloxano)-11,23-bis(hydroxydimethylsilyl)-25,26,27,28-tetrakis(1-propyloxy)calix[4]arene (2). To a solution of 0.092 g (0.093 mmol) of the allylcalixarene **1**^{4} in 4.0 mL of THF was added 1.0 mL of TBAF (1.0 M in THF, 1.0 mmol), and the mixture was stirred for 8 h at rt. Brine (3 mL) was added, and the mixture was transferred to a separatory funnel using 5 mL of ether. The organic layer was dried ($MgSO_4$) and concentrated to give an oil. TLC (4:1 petroleum ether/ethyl acetate) showed three spots with R_f values of 0.45, 0.56, and 0.75. The crude product was chromatographed (4:1 petroleum ether/CH_2Cl_2), giving 0.054 g (66% yield) of **2** as a glassy solid: mp 81−83 °C; $R_f = 0.56$ (4:1 petroleum ether/ethyl acetate); ^{1}H NMR δ 7.39 (s, 4 H, Ar), 6.16 (s, 4 H, Ar), 4.45 (d, $J = 13.4$ Hz, 4 H, Ar$\underline{CH_2}$Ar), 4.03 (m, 4 H, OPr), 3.67 (t, $J = 6.6$ Hz, 4 H, OPr), 3.17 (d, $J = 13.5$ Hz, 4 H, Ar$\underline{CH_2}$Ar), 1.94, 1.87 (appears as two overlapping sextets, 10 H, reduces to 8 H in presence of D_2O, OPr, SiOH), 1.12 (t, $J = 7.4$ Hz, 6 H, OPr), 0.88 (t, $J = 7.4$ Hz, 6 H, OPr), 0.49 (s, 12 H, SiMe), 0.01 (s, 12 H, SiMe); ^{13}C NMR δ 159.7 (C), 156.3 (C), 137.0 (C), 134.0 (CH), 132.5 (CH), 132.4 (C), 131.6 (C), 131.2 (C), 76.7 (CH_2), 76.5 (CH_2), 30.8 (CH_2), 23.6 (CH_2), 23.1 (CH_2), 10.9 (CH_3), 9.8 (CH_3), 0.4 (CH_3), −0.6 (CH_3); IR ($CHCl_3$) 3234, 2961, 1585, 1465, 1386, 1253, 1124, 1064, 1007, 968, 821 cm^{-1}; MALDI-TOF MS showed four peaks: m/z 870.6 (medium, **2**, M$^+$, calcd 870.4), 893.4 (large, $[M + Na]^+$, calcd 893.4), 967.5 (small, $[M + Na + THF]^+$ would be 965.5), and 1745.7 (small, $[(2 \times M) - H_2O + Na]^+$, calcd 1745.8). No higher mass peaks were observed up to m/z 6000.

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Supporting Information Available: Synthesis procedures for **5**−**7**, **14**, **15**, **17**, **19**, **20c**, and **20pc**; copies of ^{1}H and ^{13}C NMR spectra for the preceding compounds and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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