Isolation of All Four Conformations of *p-tert*-Butylcalix[5]arene Using Bridging Silyl Groups

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Treatment of *p-tert*-butylcalix[5]arene with $RMeSi(NMe_2)_2$ (R = Me, Ph) yields both di- and monosubstituted products: calix[5]$(RMeSi)_2(OH)$ (**1a**, R = Me; **1b**, R = Ph) and calix[5](RMeSi)$(OH)_3$ (**2a**, R = Me; **2b**, R = Ph). In all derivatives, the silicon atom bridges adjacent oxygens on the calix[5]arene. Isolation of the monosubstituted compounds requires careful control of stoichiometry using an excess of *p-tert*-butylcalix[5]arene. Variable-temperature NMR spectra of **2a** suggest that at least two different exchange processes are occurring; the high-temperature process appears to involve complete inversion of the calixarene with an activation energy of 64.4 (1.6) kJ/mol. These compounds are isolated and structurally characterized. The four solid-state structures closely approximate the four different ideal conformations of calix[5]arenes.

Because of their ease of synthesis, most calixarene research has focused on the even-numbered members of the family, particularly the calix[4]arenes, and to a lesser extent, the calix[6]- and calix[8]arenes.[1] Our work[2] has taken advantage of the constraint of the small cavity of the calix[4]arene to stabilize high-coordinate main-group element geometries and study their transformations within the cavity. However, in most cases, the cavity is too small to study the interaction of two atoms within the framework. To that end, we recently reported[3] the control of a phosphorus/metal interaction within the cavity of a calix[5]arene.[4] We believe that this cavity has the ideal balance between constraint and flexibility to study and control such interactions. Herein, we report insertion of one and two bridging silyl groups[5] into *p-tert*-butylcalix[5]arene in order to investigate the conformational effects of such bridging. We find that slight changes in the silyl group lead to large differences in solid-state conformation; in addition, we are able to measure the calix[5]arene inversion barrier in one of the derivatives.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of nitrogen in a Vacuum Atmospheres drybox or using standard Schlenk techniques, unless otherwise indicated. Solvents were dried using standard procedures and distilled under a nitrogen atmosphere and either used immediately or stored in the drybox prior to use. Glassware was oven-dried at 140 °C overnight prior to use. The reagents bis(dimethylamino)dimethylsilane and bis(dimethylamino)methylphenylsilane were obtained commercially and used without further purification. The *p-tert*-butylcalix[5]arene was synthesized by the literature procedure.[6] All ^1H NMR spectra were recorded on a Bruker AVANCE DRX-400 multinuclear NMR spectrometer resonating at 400.137 MHz. ^1H resonances were measured relative to residual proton solvent peaks and referenced to Me_4Si. Melting points were obtained in nitrogen-filled tubes on a Mel-Temp capillary apparatus and are uncorrected. Elemental analyses were obtained from Complete Analysis Laboratories, Inc. (E + R Microanalytical Division), Parsippany, NJ.

Synthesis of 1a. A stirred solution of *p-tert*-butylcalix[5]arene (0.812 g, 1.00 mmol) in toluene (40 mL) was treated dropwise with bis(dimethylamino)dimethylsilane (0.293 g, 2.00 mmol). The reaction mixture was stirred for 24 h, after which the volatiles were removed under vacuum. The residue was dissolved in hot chloroform (3 mL) and stored at −30 °C for 24 h. Filtration and vacuum-drying led to the product as air-stable colorless crystals (0.78 g, 85%). Mp: 249−51 °C. Anal. Calcd for $C_{59}H_{78}O_5Si_2$: C, 76.74; H, 8.51. Found: C, 76.50; H, 8.76. ^1H NMR ($CDCl_3$, ppm): −1.27 (s, 6H, CH_3), 0.19 (s, 6H, CH_3), 1.14 (s, 9H, *t*-Bu), 1.26 (s, 18H, *t*-Bu), 1.28 (s, 18H, *t*-Bu), 3.39 (d, 2H, $^2J_{HH}$ = 14.0 Hz, CH_2), 3.41 (d, 2H, $^2J_{HH}$ = 14.7 Hz, CH_2), 3.78 (s, 2H, CH_2), 4.11 (d, 2H, $^2J_{HH}$ = 14.7 Hz, CH_2), 4.16 (d, 2H, $^2J_{HH}$ = 14.0 Hz, CH_2), 5.66 (s, 1H, OH), 6.92 (s,

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(1) (a) *Calixarenes 2001*; Asfari, Z., Böhmer, V., Harrowfield, J., Vicens, J., Eds.; Kluwer: Dordrecht, 2001. (b) *Calixarenes in Action*; Mandolini, L, Ungaro, R., Eds.; Imperial College: London, 2000. (c) Gutsche, C. D. *Calixarenes Revisited*; Royal Society of Chemistry: Letchworth, 1998. (d) Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: Cambridge, 1989.

(2) (a) Fan, M.; Shevchenko, I. V.; Voorhies, R. H.; Eckert, S. F.; Zhang, H.; Lattman, M. *Inorg. Chem.* **2000**, *39*, 4704. (b) Khasnis, D. V.; Burton, J. M.; McNeil, J. D.; Santini, C. J.; Zhang, H.; Lattman, M. *Inorg. Chem.* **1994**, *33*, 2657. (c) Khasnis, D. V.; Lattman, M.; Gutsche, D. *J. Am. Chem. Soc.* **1990**, *112*, 9422. (d) Khasnis, D. V.; Burton, J. M.; Lattman, M.; Zhang, H. *J. Chem. Soc., Chem. Commun.* **1991**, 562. (e) Shang, S.; Khasnis, D. V.; Burton, J. M.; Santini, C. J.; Fan, M.; Small, A. C.; Lattman, M. *Organometallics* **1994**, *13*, 5157. (f) Shang, S.; Khasnis, D. V.; Zhang, H.; Small, A. C.; Fan, M.; Lattman, M. *Inorg. Chem.* **1995**, *34*, 3610. (g) Shevchenko, I. V.; Zhang, H.; Lattman, M. *Inorg. Chem.* **1995**, *34*, 5405.

(3) Fan, M.; Zhang, H.; Lattman, M. *J. Chem. Soc., Chem. Commun.* **1998**, 99.

(4) For a recent review of calix[5]arene work, see: Notti, A.; Parisi, M. F.; Pappalardo, S. In ref 1a, Chapter 3.

(5) For some other silylated calixarenes see, for example: (a) Narumi, F.; Morohashi, N.; Matsumura, N.; Iki, N.; Kameyama, H.; Miyano, S. *Tetrahedron Lett.* **2002**, *43*, 621. (b) Hajek, F.; Graf, E.; Hosseini, M. W.; De Cian, A.; Fischer, J. *Tetrahedron Lett.* **1997**, *38*, 4555. (c) Neda, I.; Plinta, H.-J.; Sonnenburg, R.; Fischer, A.; Jones, P. G.; Schmutzler, R. *Chem. Ber.* **1995**, *128*, 267. (d) Gutsche, C. D.; Bauer, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 6059, and references therein.

(6) Stewart, D. R.; Gutsche, C. D. *Org. Prep. Proced. Int.* **1993**, *25*, 137.

10.1021/om020449w CCC: $22.00

Table 1. Crystal Data[a]

	1a	1b	2a	2b
formula	$(C_{59}H_{78}O_5Si_2)\cdot(CHCl_3)$	$(C_{69}H_{82}O_5Si_2)\cdot 2(CHCl_3)$	$(C_{57}H_{74}O_5Si)\cdot 2(C_7H_8)$	$(C_{62}H_{76}O_5Si)$
fw	1042.76	1286.26	1051.52	929.32
cryst syst	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a, Å	14.612(3)	11.627(1)	18.063(3)	14.622(3)
b, Å	15.595(2)	17.366(1)	14.530(2)	17.455(3)
c, Å	15.718(3)	18.580(2)	24.500(3)	21.173(3)
α, deg	93.24(1)	104.786(8)	90	90
β, deg	115.47(1)	91.756(7)	98.979(7)	91.58(1)
γ, deg	108.98(1)	105.536(8)	90	90
V, Å^3	2975.8(9)	3475.0(5)	6351(2)	5398(2)
Z	2	2	4	4
ρ_{cald}, g cm^{-1}	1.164	1.229	1.100	1.143
μ, mm^{-1}	0.239	0.329	0.085	0.091
T, K	228	228	228	228
R_1 [$I > 2\sigma(I)$][b]	0.060	0.073	0.088	0.120
wR_2 [all data][b]	0.171	0.225	0.216	0.335

[a] Graphite monochromatized Mo Kα radiation, $\lambda = 0.71073$ Å. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

2H, CH), 7.03 (d, 2H, $^4J_{HH} = 2.3$ Hz, CH), 7.10 (d, 2H, $^4J_{HH} = 2.3$ Hz, CH), 7.15 (overlapping, 4H, CH).

Synthesis of 1b. A stirred solution of *p*-*tert*-butylcalix[5]arene (0.812 g, 1.00 mmol) in toluene (30 mL) was treated dropwise with bis(dimethylamino)methylphenylsilane (0.417 g, 2.00 mmol). The mixture was stirred for 24 h. The solution was concentrated to approximately 3 mL and the pale yellow solution allowed to further concentrate slowly under nitrogen for 2 days. Filtration, followed by thorough washing with hexane (10 mL) and vacuum-drying, yielded the product as air-stable colorless crystals (0.74 g, 71%). Mp: 296 °C (dec). Anal. Calcd for $C_{69}H_{82}O_5Si_2$: C, 79.11; H, 7.89. Found: C, 78.70; H, 7.94. Crystals suitable for X-ray analysis were obtained by recrystallization from chloroform. ^{1}H NMR ($CDCl_3$, ppm): 0.91 (br s, 6H, CH_3), 1.08 (s, 18H, *t*-Bu), 1.14 (s, 18H, *t*-Bu), 1.37 (s, 9H, *t*-Bu), 3.23 (d, 2H, $^2J_{HH} = 15.2$ Hz, CH_2), 3.46 (d, 2H, $^2J_{HH} = 14.6$ Hz, CH_2), 3.50 (d, 1H, $^2J_{HH} = 15.1$ Hz, CH_2), 4.20 (d, 2H, $^2J_{HH} = 15.2$ Hz, CH_2), 4.55 (d, 1H, $^2J_{HH} = 14.6$ Hz, CH_2), 4.88 (d, 1H, $^2J_{HH} = 15.1$ Hz, CH_2), 5.35 (s, 1H, OH), 6.79 (d, 2H, $^4J_{HH} = 2.4$ Hz, CH), 6.82 (d, 2H, $^4J_{HH} = 2.4$ Hz, CH), 6.97 (d, 2H, $^4J_{HH} = 2.4$ Hz, CH), 6.99 (d, 2H, $^4J_{HH} = 2.0$ Hz, CH), 7.25 (s, 2H, CH), 7.27−7.38 (comp m, 6H, CH), 7.52−7.55 (comp m, 4H, CH).

Synthesis of 2a. A stirred solution of *p*-*tert*-butylcalix[5]arene (2.43 g, 3.00 mmol) in toluene (30 mL) was treated dropwise with bis(dimethylamino)dimethylsilane (0.154 g, 1.05 mmol). The reaction mixture was stirred for 24 h and filtered to remove a small amount of precipitate. The volatiles were removed under vacuum and the residue stirred twice with hexane (50 mL for 24 h each) to remove the excess *p*-*tert*-butylcalix[5]arene. The resulting solid was filtered and pumped dry to yield the product as an air-stable white powder (0.91 g, 100% based on bis(dimethylamino)dimethylsilane). Mp: 206−8 °C (dec). Anal. Calcd for $C_{57}H_{74}O_5Si$: C, 78.94; H, 8.60. Found: C, 78.73; H, 8.49. Crystals suitable for X-ray analysis were grown by dissolving the product in hot toluene and leaving the solution under a stream of nitrogen. ^{1}H NMR ($CDCl_3$, ppm): −1.94 (br s, 3H, CH_3), −0.20 (br s, 3H, CH_3), 1.11 (s, 18H, *t*-Bu), 1.26 (s, 9H, *t*-Bu), 1.29 (s, 18H, *t*-Bu), 3.35 (br pseudo-t, 3H, CH_2), 3.79 (br pseudo-d, 4H, CH_2), 4.15 (br pseudo-d, 3H, CH_2), 5.5 (br, 3H, OH), 6.94 (d, 2H, $^4J_{HH} = 2.2$ Hz, CH), 7.08 (d, 2H, $^4J_{HH} = 2.2$ Hz, CH), 7.15 (d, 2H, $^4J_{HH} = 2.3$ Hz, CH), 7.20, 7.21 (overlapping, 4H, CH).

Synthesis of 2b. A stirred solution of *p*-*tert*-butylcalix[5]arene (2.432 g, 3.00 mmol) in toluene (40 mL) was treated with bis(dimethylamino)methylphenylsilane (0.219 g, 1.05 mmol). The mixture was stirred for 24 h. The volatiles were removed under vacuum, and the residue was stirred twice with hexane (50 mL for 24 h each) to remove the excess *p*-*tert*-butylcalix[5]arene The resulting solid was filtered and pumped dry to yield the product as an air-stable white powder (0.96 g, 100% based on bis(dimethylamino)methylphenylsilane). Mp: 258−60 °C (dec). Anal. Calcd for $C_{62}H_{76}O_5Si$: C, 80.13; H, 8.24. Found: C, 79.78; H, 8.35. Crystals suitable for X-ray analysis were obtained by dissolving the sample in hot toluene followed by slow evaporation of the solution. ^{1}H NMR ($CDCl_3$, ppm): −0.35 (br s, 3H, CH_3), 1.16 (s, 18H, *t*-Bu), 1.21 (s, 9H, *t*-Bu), 1.25 (s, 18H, *t*-Bu), 3.32 (d, 1H, $^2J_{HH} = 14.1$ Hz, CH_2), 3.66 (d, 2H, $^2J_{HH} = 14.6$ Hz, CH_2), 3.71 (d, 2H, $^2J_{HH} = 14.3$ Hz, CH_2), 3.78 (d, 2H, $^2J_{HH} = 14.3$ Hz, CH_2), 4.24 (d, 1H, $^2J_{HH} = 14.1$ Hz, CH_2), 4.33 (d, 2H, $^2J_{HH} = 14.6$ Hz, CH_2), 6.66 (br s, 3H, OH), 7.06 (d, 2H, $^4J_{HH} = 2.3$ Hz, CH), 7.10 (s, 2H, CH), 7.11−7.12 (overlapping, 4H, CH), 7.27 (d, 2H, $^4J_{HH} = 2.3$ Hz, CH), 7.34−7.44 (comp m, 3H, CH), 7.68−7.71 (comp m, 2H, CH).

Single-Crystal X-ray Diffraction Studies. All crystals are colorless. Diffraction data were collected on a Bruker P4 diffractometer. The crystals used in the experiments were coated with mineral oil under a low-temperature nitrogen stream. Crystallographic data are summarized in Table 1. All structures were solved by direct methods and subsequent difference Fourier syntheses and refined by full-matrix least-squares methods against F^2 (SHELX97).[7] One solvent chloroform molecule was found in the crystal lattice of **1a**, while two were observed in **1b**. In **1a**, the chloroform is approximately in the space formed by three phenyls, as well as attached *tert*-butyls. In **1b**, one chloroform is approximately inside the calix[5]arene cavity while the other is outside. Two toluene molecules were found in the crystal lattice of **2a**. All solvent molecules, except for the chloroform inside the **1b** cavity, are positionally disordered. In addition, some (*tert*-butyl)methyl groups in each structure are disordered. This is most pronounced in **2b**, where 12 of the 15 methyl groups are disordered. The disordered atoms above were refined with occupancy and distance restraints. All non-hydrogen atoms, except for the disordered methyl C atoms in **2b**, were refined anisotropically, while H atoms were constrained with a riding model. Intramolecular hydrogen bonds were formed in **1a** and **1b**. The A···B distance of A−H···B for O(1)−H···O(5) in **1a** is 2.745(4) Å, while for O(1)−H(1)···O(2) in **1b** it is 3.112(4) Å. Intermolecular H bonds, formed between calix[5]arene molecules, were found in **2a** and **2b**. Selected bond distances and angles are listed in Table 2.

Results and Discussion

Synthesis. Insertion of two bridging silyl groups into *p*-*tert*-butylcalix[5]arene is straightforward using stoichiometric amounts of the calixarene and RMeSi-

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(7) Sheldrick, G. M. *SHELX97, Program for Crystal Structure Solution and Refinement*; Institut fur Anorgische Chemie: Göttingen, Germany, 1998.

Table 2. Selected Bond Lengths (Å) and Angles (deg)

1a		1b	
Si(1)−O(3)	1.647(3)	Si(1)−O(3)	1.641(3)
Si(1)−O(2)	1.647(4)	Si(1)−O(2)	1.649(3)
Si(1)−C(1)	1.825(6)	Si(1)−C(1)	1.831(4)
Si(1)−C(2)	1.827(6)	Si(1)−C(71)	1.859(4)
Si(2)−O(4)	1.642(3)	Si(2)−O(5)	1.641(3)
Si(2)−O(5)	1.650(3)	Si(2)−O(4)	1.660(3)
Si(2)−C(4)	1.825(5)	Si(2)−C(2)	1.840(4)
Si(2)−C(3)	1.846(5)	Si(2)−C(81)	1.866(4)
O(3)−Si(1)−O(2)	112.01(19)	O(3)−Si(1)−O(2)	110.65(13)
O(3)−Si(1)−C(1)	110.9(2)	O(3)−Si(1)−C(1)	107.83(18)
O(2)−Si(1)−C(1)	110.3(2)	O(2)−Si(1)−C(1)	104.34(17)
O(3)−Si(1)−C(2)	105.7(2)	O(3)−Si(1)−C(71)	110.76(17)
O(2)−Si(1)−C(2)	104.8(3)	O(2)−Si(1)−C(71)	110.85(17)
C(1)−Si(1)−C(2)	112.9(3)	C(1)−Si(1)−C(71)	112.2(2)
O(4)−Si(2)−O(5)	110.44(17)	O(5)−Si(2)−O(4)	107.96(15)
O(4)−Si(2)−C(4)	111.6(2)	O(5)−Si(2)−C(2)	106.58(18)
O(5)−Si(2)−C(4)	103.3(2)	O(4)−Si(2)−C(2)	110.13(18)
O(4)−Si(2)−C(3)	107.9(2)	O(5)−Si(2)−C(81)	109.59(17)
O(5)−Si(2)−C(3)	110.8(2)	O(4)−Si(2)−C(81)	112.14(17)
C(4)−Si(2)−C(3)	112.9(3)	C(2)−Si(2)−C(81)	110.3(2)

2a		2b	
Si−O(2)	1.644(6)	Si−O(2)	1.637(8)
Si−O(1)	1.678(6)	Si−O(1)	1.661(8)
Si−C(1)	1.825(9)	Si−C(1)	1.796(11)
Si−C(2)	1.861(9)	Si−C(71)	1.860(11)
O(2)−Si−O(1)	109.0(3)	O(2)−Si−O(1)	111.4(4)
O(2)−Si−C(1)	103.6(4)	O(2)−Si−C(1)	112.0(5)
O(1)−Si−C(1)	107.0(4)	O(1)−Si−C(1)	109.0(5)
O(2)−Si−C(2)	111.2(4)	O(2)−Si−C(71)	101.9(5)
O(1)−Si−C(2)	108.6(4)	O(1)−Si−C(71)	103.3(5)
C(1)−Si−C(2)	117.1(4)	C(1)−Si−C(71)	118.8(6)

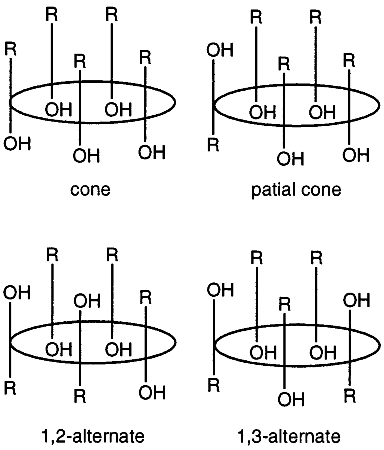
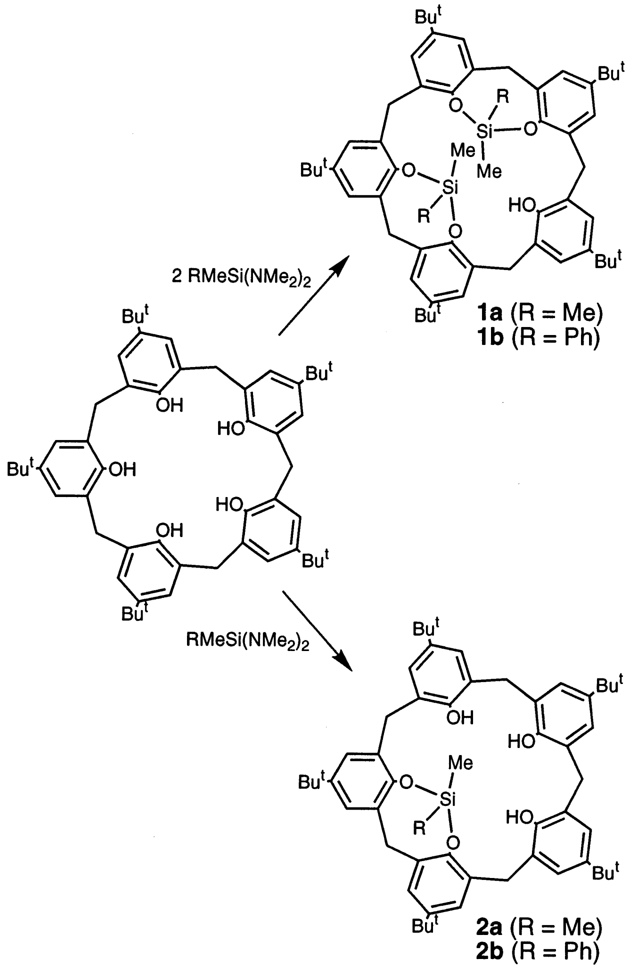


Figure 1. Idealized conformations of calix[5]arenes.

Scheme 1



$(NMe_2)_2$ (R = Me, Ph) according to Scheme 1. Insertion of a single bridging silyl group is more difficult to control and requires the use of excess calixarene. We find that the best molar ratio of silane to calixarene is 0.35:1 for this reaction. With this ratio, no disubstitution occurs, and the excess calix[5]arene is easily removed by washing with hexane. Increasing the amount of silane leads to some disubstitution, and separation of the mono- and disubstituted species is very difficult. Attempts to insert a bulkier bridging silyl group were unsuccessful. Treatment of *p*-*tert*-butylcalix[5]arene with either $Ph_2Si(NMe_2)_2$ or Ph_2SiCl_2 led to complex mixtures whether the reactions were carried out at room temperature or in refluxing toluene. In addition, significant amounts of unreacted calixarene were present.

NMR Spectra. The ^{1}H NMR spectra of these compounds are consistent with the formulations in Scheme 1 and, in some cases, give detailed information as to their specific conformations. There are four idealized conformations of calix[5]arenes:[8,9] the cone, partial cone, 1,2-alternate, and 1,3-alternate. These are illustrated in the "stick" diagrams in Figure 1. In fact, these are the same conformations that exist for the more common calix[4]arenes. For derivatives **1a** and **1b**, all peaks in the NMR spectra are sharp. There are three singlets for the *tert*-butyl groups in a 2:2:1 ratio. Two peaks are observed for the $SiMe_2$ unit in **1a**; this is consistent with what has been observed before in $SiMe_2$-substituted calix[4]arenes:[10] the two methyl groups are nonequivalent due to the three-dimensional geometry of the calixarene. In fact, one of these resonances appears at a very low chemical shift, δ −1.3. This suggests that this group lies "above" one (or more) of the aromatic rings. The methylene region of **1b** shows the expected six doublets (geminal coupling due to nonequivalent

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(8) See ref 1c, Chapter 4.

(9) Detailed studies have shown that these four idealized conformations are insufficient to completely describe conformations of calix[5]arenes because of increased mobility relative to calix[4]arenes. See: (a) Stewart, D. R.; Krawiec, M.; Kashyap, R. P.; Watson, W. H.; Gutsche, C. D. *J. Am. Chem. Soc.* **1995**, *117*, 586. (b) Harada, T.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2231. (c) Thondorf, I.; Brenn, J. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2293. For simplicity, we prefer to use the descriptions in Figure 1 as approximations to the conformations actually observed.

(10) Fan, M.; Zhang, H.; Lattman, M. *Organometallics* **1996**, *15*, 5216. The chemical shifts for the SiMe resonances are solvent-dependent, varying by as much as about 1 ppm.

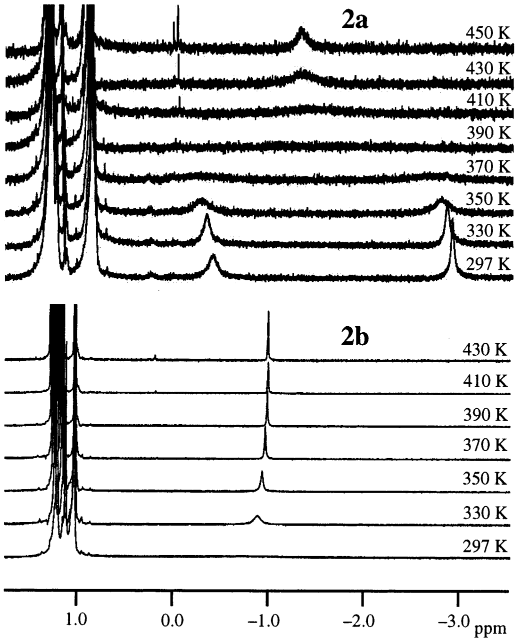

Figure 2. High-temperature NMR spectra of **2a** and **2b** in dmso-d_6.

methylene hydrogens), with two of the doublets being half the intensity of the others. Overall, the spectrum is consistent with a C_s geometry for **1b**. However, the methylene region of **1a** is very unusual, showing two doublets centered around δ 3.4, two doublets around δ 4.2, and a singlet (integrating to two hydrogens) at δ 3.8. This means that the two hydrogens on the methylene group opposite the free hydroxyl group are equivalent. The only geometry consistent with this spectrum has this methylene carbon and the free hydroxyl oxygen residing on the same C_2 axis. This is borne out in the X-ray structure (see below).

The NMR spectra of **2a** and **2b** are more difficult to interpret, since some of the peaks are broad. For **2b**, the peaks are sharp in the *tert*-butyl and methylene regions, and the splitting patterns are similar to **1b**, consistent with overall C_s symmetry. However, the SiMe resonance is quite broad. For **2a**, both the methylene and SiMe peaks are broad. The fact that the peaks in the disilyl derivatives are sharper than those in the monosilyl species is not surprising, since the latter should be much more flexible in solution due to rotation of the free phenolic groups through the annulus. In an effort to gain insight into the solution structures of **2**, we obtained variable-temperature NMR spectra over the range 180−300 K (in CD_2Cl_2) and 300−450 K (in DMSO-d_6). The low-temperature spectra are difficult to interpret and suggest that two, or more, conformations are present. These conformations may be due not only to rotation of the free phenolic groups but perhaps also to different conformations of the eight-membered silicon-containing ring (see X-ray structures below). Nothing more will be said of the low-temperature spectra. The high-temperature spectra are more easily interpreted, and the spectra in the region $\delta = -3.5$ to 2.0 are reproduced in Figure 2. For **2a**, the two SiMe resonances[10] coalesce into a single peak as the temperature is raised. In addition, all geminal coupling of the methylene hydrogens disappears. This suggests that the molecule is inverting due not only to rotation of the free phenolic groups but also to rotation of the $SiMe_2$ group through the annulus. This contrasts to the spectra of **2b**, where a simple sharpening of the SiMe peak occurs, implying that the steric bulk of the phenyl substituent prevents the SiMePh group from rotating through the annulus. For **2a**, the activation energy, E_a,[11,12] for the inversion is found to be 64.4 (1.6) kJ/mol. Comparison with literature values is not straightforward, since only free energies of activation for inversion at the coalescence temperature, $\Delta G_c^‡$, are reported. For **2a**, $\Delta G_c^‡ =$ 71(2) kJ/mol. This can be compared to the $\Delta G_c^‡$ value of 55 kJ/mol for the starting material *p-tert*-butylcalix[5]arene.[13] However, a better comparison might be with the 1,2-dimethyl-substituted *p-tert*-butylcalix[5]arene ($\Delta G_c^‡ = 42$ kJ/mol),[9a] since both have three free phenolic groups. (The reduced barrier in the dimethylated analogue compared to the parent is attributed to the loss of intramolecular hydrogen bonding which is not compensated for by the steric bulk of the methyl groups.)[9a,14] Thus, the replacement of two methyl groups with a bridging $SiMe_2$ increases $\Delta G_c^‡$ by about 70%.

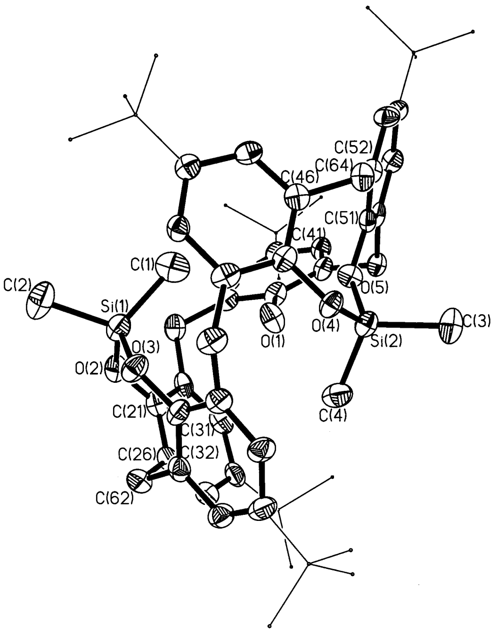

Figure 3. Molecular structure of **1a**. Ellipsoids shown at 40% probability. Hydrogen atoms are omitted for clarity. Some atom numbers are omitted for clarity. Atom numbering is consistent with other structures.

Solid-State Structures. The X-ray structures of **1a**, **1b**, **2a**, and **2b** are shown in Figures 3−6, respectively, and selected bond distances and angles are tabulated in Table 2. Remarkably, these four structures closely approximate the four different conformations shown in Figure 1: 1,2-alternate (**1a**), cone (**1b**), partial cone (**2a**), and 1,3-alternate (**2b**). To compare the solid-state

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(11) (a) Gasparro, F. P.; Kolodny, N. H. *J. Chem Ed.* **1977**, *54*, 258. (b) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.

(12) E_a was determined by a plot of the SiMe resonances at coalescence and above, since the peaks before coalescence have an unknown broadening component from the low-temperature exchange involving rotation of the free phenolic groups through the annulus (see text). The distance between the individual SiMe resonances remained constant at 1000 Hz over the temperature range 297−330 K; this value was used for the peak separation at “no exchange”.

(13) Gutsche, C. D.; Bauer, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 6052.

(14) Van Gelder, J. M.; Aleksiuk, O.; Biali, S. E. *J. Org. Chem.* **1996**, *61*, 8419.

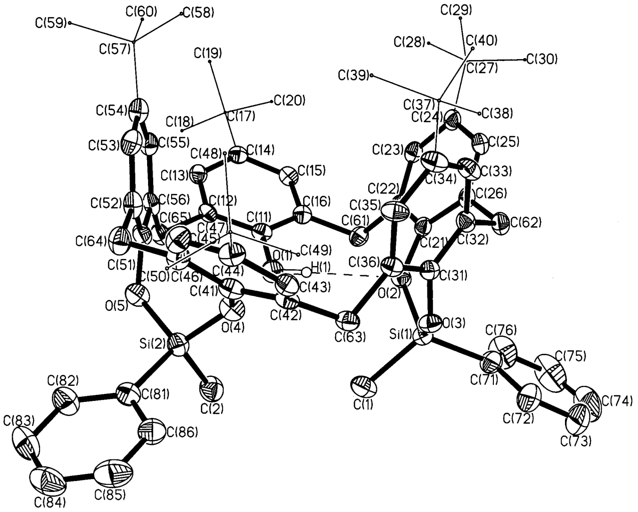

Figure 4. Molecular structure of **1b**. Ellipsoids are shown at 40% probability. Hydrogen atoms are omitted for clarity.

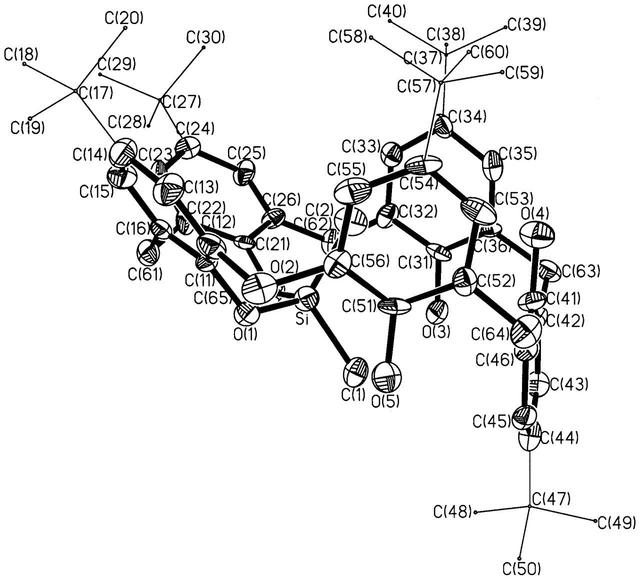

Figure 5. Molecular structure of **2a**. Ellipsoids are shown at 40% probability. Hydrogen atoms are omitted for clarity.

geometries to those observed in solution, several features of the X-ray structures will be discussed: eight-membered ring conformations containing the silicon, overall symmetry, and nonbonded (silicon-) methyl ring distances.

Calculations have shown[15] that only the boat-chair (BC) and twisted boat (TB) conformations are stable minima for the 12*H*-dibenzo[*d*,*g*][1,3,2]dioxasilocin ring (i.e., the eight-membered ring incorporating the silicon in these structures), with a slight preference for the former (less than 10 kJ/mol). The silicon-containing eight-membered rings in **2a** and **2b** adopt the BC conformation. In **1a**, the Si(1) ring adopts this arrangement, while the Si(2) ring exhibits a TB form. Both silicon rings are in the TB conformation in **1b**. In fact, the rings in **1b** are twisted in "opposite" directions, which minimizes the repulsions between the two methyl groups. Even so, the distance between C(1) and C(2) is quite short, 3.54 Å. The reasons for the two different conformations in **1a** are less obvious and could be due to either intramolecular or crystal-packing forces. Interconversion between the BC and TB forms, as well as between two equivalent TB conformations (i.e., the two rings in **1b**), is a low-energy process requiring less than 18 kJ/mol.[15] Thus, in solution, these should freely interconvert, leading to overall C_2 symmetry for **1a** and C_s symmetry for **1b**. Although there is no crystallographically imposed symmetry plane, both **2a** and **2b** should have C_s symmetry in solution.

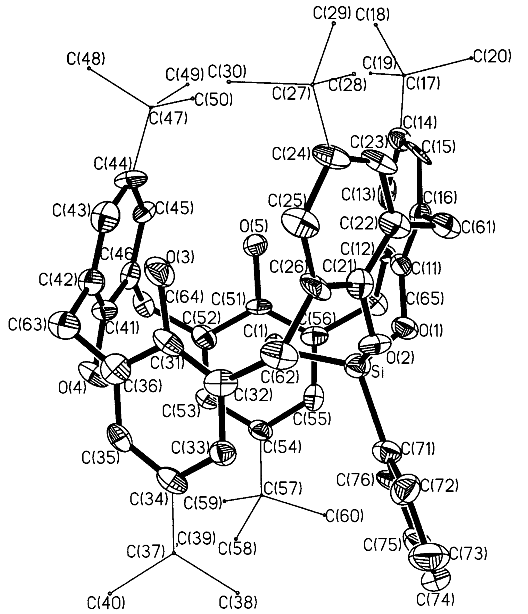

Figure 6. Molecular structure of **2b**. Ellipsoids are shown at 40% probability. Hydrogen atoms are omitted for clarity.

The solid-state structures are entirely consistent with the upfield chemical shifts for some of the methyl resonances. In **1a**, the distances between C(1) and the closest aromatic ring carbons are 3.5−3.9 Å [six carbons numbered C(41) through C(46)]; this range is 3.5−3.8 Å between C(4) and C(31)−C(36). The ring current effect on these methyl groups leads to the upfield chemical shift at δ −1.27. C(2) and C(3) have no such close contacts, and their methyl resonance appears at a more normal δ 0.19 value. In **2a**, each methyl group has close contacts with the rings: 3.8−3.9 Å between C(1) and C(41)−C(46); 3.6−3.9 Å between C(2) and C(31)−C(36); and 3.6−4.3 Å between C(2) and C(51)−C(56). In this case, both methyl resonances appear at negative chemical shifts, δ −0.20 and −1.94 ($CDCl_3$). Finally, in **2b**, the distances between C(1) and C(31)−C(36) and C(51)−C(56) are 3.5−3.9 and 3.5−4.3 Å, respectively, leading to an upfield chemical shift, δ −0.35 ($CDCl_3$).

The fact that these four closely related calix[5]arene derivatives exhibit such conformational diversity in the solid state clearly demonstrates how flexible the calix[5]arene backbone is and that subtle changes can stabilize different conformations.

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[15] Burke, L. P.; DeBellis, A. D.; Fuhrer, H.; Meier, H.; Pastor, S. D.; Rihs, G.; Rist, G.; Rodebaugh, R. K.; Shum, S. P. *J. Am. Chem. Soc.* **1997**, *119*, 8313.

Supporting Information Available: Tables of data collection and refinement, atomic coordinates and equivalent isotropic displacement coordinates, anisotropic thermal parameters, bond distances, bond angles, and hydrogen atom coordinates, and unit-cell packing diagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

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