methylene resonance remains as a broadened singlet. The coalescence temperature for the upfield methylene resonances at −24 °C corresponds to a free energy barrier of 11.9 kcal/mol. In pyridine solution the coalescence temperature is lower than −70 °C and again demonstrates the importance of intramolecular hydrogen bonding in maintaining conformational rigidity in the calixarene series. A space-filling molecular model of **7** shows that a "flattened-cone" as well as a "flattened-1,3-alternate" form maximizes the intramolecular hydrogen bonding by establishing a cyclic array that includes all four of the OH groups, as illustrated in Figure 7. Of these two conformations the flattened-cone appears to be slightly less strained. The presence of three CH_2OCH_2 bridges in a calixarene system leads to still greater conformational flexibility. The ^1H NMR spectrum of *p-tert*-butylhexahomotrioxacalix[3]arene (**8**, R = *tert*-butyl) in $CDCl_3/CS_2$ solution shows no sign of restricted rotation at any temperature down to −90 °C, indicating that this compound is the most flexible of all of the ring systems investigated in the present study.

Conclusions. The conformational flexibility of calixarenes and oxacalixarenes carrying endo-annular hydroxyl groups is determined by the size of the macrocyclic ring which, in turn, influences the nature of the intramolecular hydrogen bonding.[27] To achieve the most effective intramolecular hydrogen bonding the calix[4]arenes, dihomooxacalix[4]arenes, and calix[5]arenes adopt a cone conformation; the tetrahomodioxacalix[4]arenes probably adopt a flattened-cone conformation; the calix[6]arenes are postulated to adopt a winged or hinged conformation; the calix[7]arenes are postulated to adopt a pseudo pleated-loop conformation; and the calix[8]arenes are thought to exist in a true pleated-loop conformation. Thus, as the ring size increases, the preferred conformation of the calixarenes becomes increasingly planar. Interconversion between the mirror image forms of a particular conformation takes place with varing degrees of ease; the value for the free energy of activation for inversion in nonpolar solvents decreases in the following order: calix[4]arenes = calix[8]arenes > calix[5]arenes = dihomooxacalix[4]arenes = calix[6]arenes > calix[7]arenes > tetrahomodioxacalix[4]arenes > hexahomotrioxacalix[3]arenes. In pyridine solution the intramolecular hydrogen bonding is disrupted, and the inversion barrier becomes primarily a function of ring size, viz. the value for the free energy of activation for inversion decreases in the following order: calix[4]arenes > calix[5]arenes > dihomooxacalix[4]arenes > calix[6]arenes > tetrahomodioxacalix[4]arenes > calix[8]arenes > hexahomotrioxacalix[3]arenes. The character of the para substituent appears to play no more than a minor role in determining the magnitude of the conformational inversion barrier in these compounds.

(27) Correlations between the free energy of activation for conformational inversion and the IR and NMR characteristics of the hydroxyl groups in the calixarenes are only approximate, as illustrated by the following data for the compounds in $CDCl_3$ or $CHCl_3$ solution.

	ν_{OH}, cm^{-1}	δ_{OH}	$\Delta G^{\ddagger}$, kcal/mol
calix[4]arenes	3160	10.2	15.7
calix[5]arenes	3280	8.0	13.2
calix[6]arenes	3150	10.5	13.3
calix[7]arenes	3155	10.3	12.3
calix[8]arenes	3230	9.6	15.7
dihomooxacalix[4]arenes	3300	9.0, 9.7	12.9
tetrahomodioxacalix[4]arenes	3370	9.0	11.9
hexahomotrioxacalix[3]arenes	3410	8.5	<9

Acknowledgment. We are indebted to the National Institutes of Health (Grant GM-23534) and to a Biomedical Science Support Grant for generous financial support of this work. We are indebted to Drs. Shou-I Chen, Balram Dhawan, Kwang H. No, Jeffery A. Levine, Lee-Gin Lin, Philip F. Pagoria, and P. K. Sujeeth for supplying most of the compounds used in this work.

Registry No. **1** (R = *tert*-butyl), 60705-62-6; **1** (R = hydrogen), 74568-07-3; **1** (R = phenyl), 60705-63-7; **1** (R = allyl), 81294-23-7; **1** (R = *tert*-octyl), 97998-54-4; **1** (R = *tert*-amyl), 77769-14-3; **1** (R = isopropyl), 97998-55-5; **1** (R = benzoyl), 97998-56-6; **1** (R = hydroxyethyl), 97998-57-7; **1** (R = dichloro, di-*tert*-butyl), 97998-59-9; **1** (R = bromo), 97998-58-8; **2** (R = *tert*-butyl), 68971-82-4; **2** (R = hydrogen), 82452-93-5; **2** (R = phenyl), 92887-20-2; **2** (R = *tert*-octyl), 98013-93-5; **2** (R = *tert*-amyl), 93503-77-6; **2** (R = isopropyl), 98013-94-6; **3** (R = *tert*-butyl), 78092-53-2; **3** (R = hydrogen), 96107-95-8; **3** (R = *tert*-octyl), 98013-95-7; **3** (R = allyl), 98013-96-8; **4** (R = *t*-Bu), 81475-22-1; **5** (R = *t*-Bu), 84161-29-5; **6** (R = *t*-Bu), 72251-68-4; **7** (R = *t*-Bu), 85097-23-0; **8** (R = *t*-Bu), 76543-12-9.

Calixarenes. 14. The Conformational Properties of the Ethers and Esters of the Calix[6]arenes and the Calix[8]arenes

C. David Gutsche* and Lorenz J. Bauer

Contribution from the Department of Chemistry, Washington University, St. Louis, Missouri 63130. *Received February 14, 1985*

Abstract: Ethers and esters of calix[6]arenes and calix[8]arenes are obtainable from the parent calixarenes. We have studied their conformational behavior by means of ^1H NMR spectroscopy and have shown these compounds to be more flexible than the corresponding derivatives of the calix[4]arenes. Conformational freezing can be observed, nevertheless, particularly when the ether groups are large moieties such as trimethylsilyl. In the case of the trimethylsilyl ethers of the calix[6]arenes, conformational inversion appears to take place via a "para substituent through the annulus" route rather than the more usual "oxygen through the annulus" route.

Detailed studies of the conformational properties of the ethers and esters of the calix[4]arenes have been reported.[1,2] Because of the small annulus in the calix[4]arenes the replacement of the hydrogens of the hydroxyl function with anything larger than

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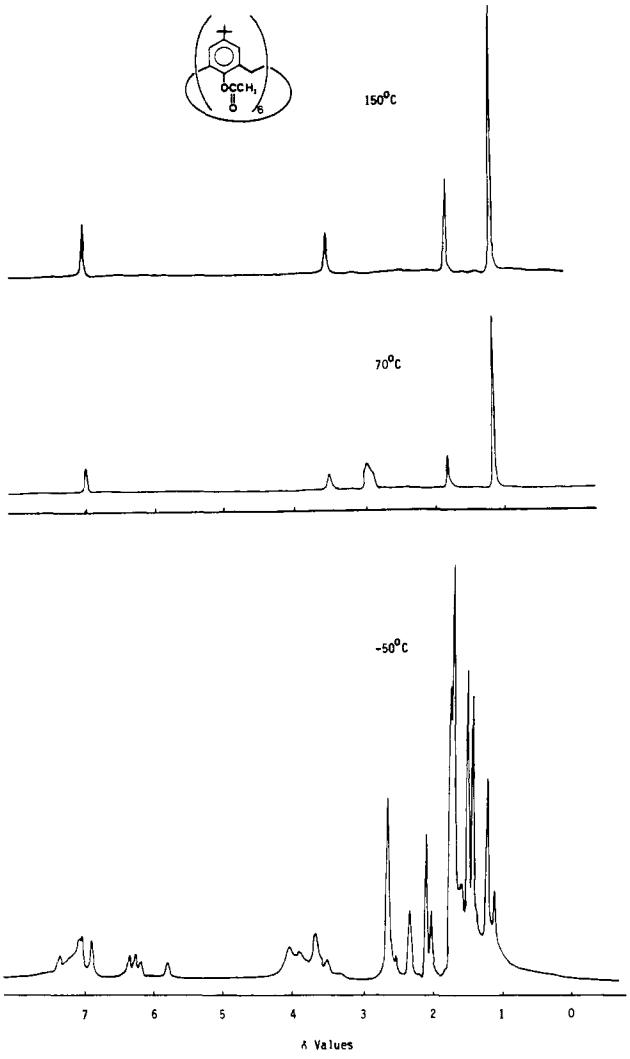


Figure 1. ^{1}H NMR spectra of the hexaacetate of *p-tert*-butylcalix[6]-arene at −50 °C in $CDCl_3$ and 70 and 150 °C in Me_2SO-d_6 solution.

methyl groups curtails the conformational flexibility at room temperature and freezes the molecule into one of four conformations (see Figure 1 of the preceding paper[3] for schematic representations of the "cone", "partial-cone", "1,2-alternate", and "1,3-alternate" conformations). The larger annuli in the calix-[6]arenes and calix[8]arenes, however, allow greater conformational flexibility, with the result that conformational freezing requires larger substituents and occurs at lower temperatures than in the calix[4]arenes. The purpose of the present work is to determine the temperatures at which conformational freezing occurs and to investigate the influence of substituents on the conformational properties of these larger calixarenes.

Ethers and Esters of Calix[6]arene. The temperature-dependent ^{1}H NMR spectrum of the hexamethyl ether of *p-tert*-butylcalix[6]arene (**2**) shows a pattern of sharp singlets down to −60 °C, indicating that **2** is conformationally mobile even at this low temperature. The hexaacetyl derivative (**6**), however, shows a broadened resonance for the methylene protons at room temperature which sharpens to a singlet at 150 °C and resolved into a complex multiplet at −50 °C, as shown in Figure 1. It is estimated that the coalescence temperature is near 25 °C, corresponding to a free energy barrier to conformational inversion

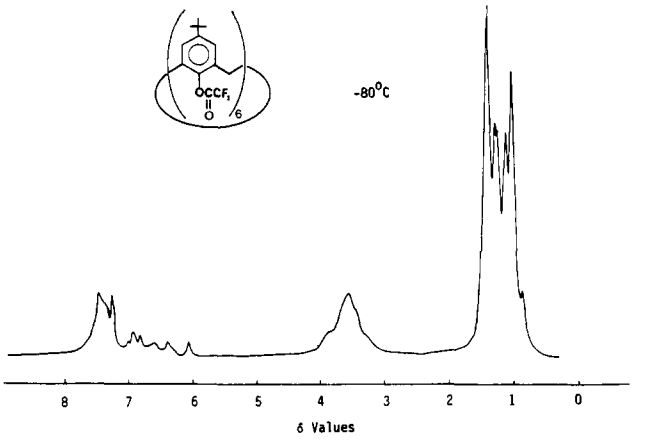


Figure 2. ^{1}H NMR spectrum of the hexakis(trifluoroacetate) of *p-tert*-butylcalix[6]arene at −80 °C in $CDCl_3$ solution.

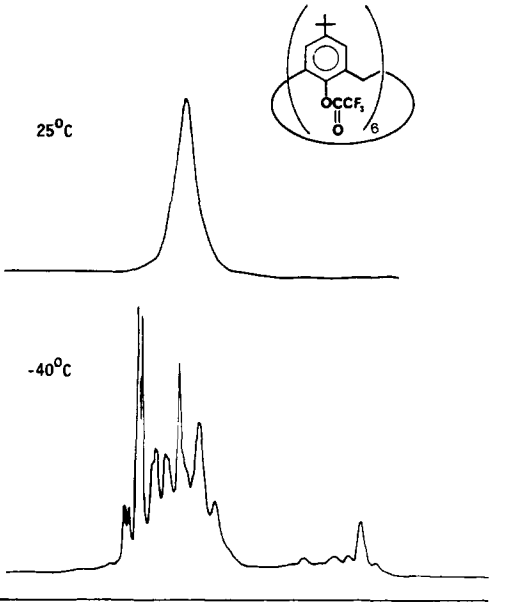
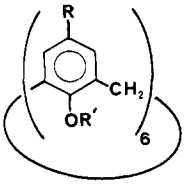
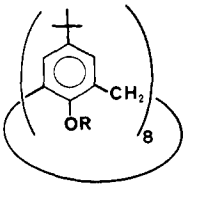


Figure 3. ^{19}F NMR spectra of the hexakis(trifluoroacetate) of *p-tert*-butylcalix[6]arene at 25 °C and at −40 °C in $CDCl_3$ solution.

of about 14 kcal/mol. In the hope of gaining insight into the low-temperature conformation, the hexakis(trifluoroacetyl) derivative (**7**) was studied. As shown in Figure 2, its ^{1}H NMR spectrum contains eight lines in the *tert*-butyl region and quite complex patterns in the methylene and aromatic regions. Since





compd	R	R′	compd	R
1	H	$SiMe_3$	10	CH_3
2	*tert*-butyl	CH_3	11	$CH_2C_6H_5$
3	*tert*-butyl	$CH_2C_6H_5$	12	$SiMe_3$
4	*tert*-butyl	$SiMe_3$	13	$COCH_3$
5	*tert*-butyl	$CH_2CH_2OCH_3$		
6	*tert*-butyl	$COCH_3$		
7	*tert*-butyl	$COCF_3$		
8	*tert*-octyl	$SiMe_3$		
9	$CH_2CH{=}CH_2$	$SiMe_3$		

the compound contains only six aromatic rings and six *tert*-butyl groups, it is probable that it freezes out as a mixture of conformers, a conclusion that is supported by the ^{19}F NMR spectrum, shown

(1) Bocchi, V.; Foina, D.; Pochini, A.; Ungaro, R. *Tetrahedron* **1982**, *38*, 373.
(2) Gutsche, C. D.; Dhawan, B.; Levine, J. A.; No, K. H.; Bauer, L. J. *Tetrahedron* **1983**, *39*. 409.
(3) Gutsche, C. D.; Bauer, L. J. *J. Am. Chem. Soc.*, preceding paper in this issue.

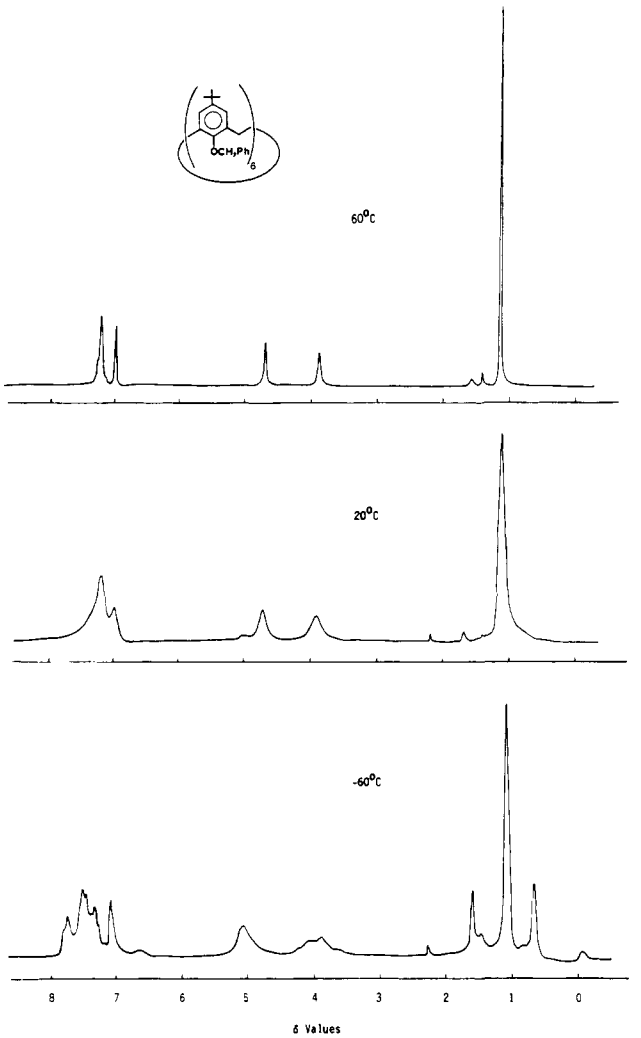


Figure 4. ^{1}H NMR spectra of the hexabenzyl ether of *p-tert*-butylcalix[6]arene at 60, 20, and −60 °C in $CDCl_3$ solution.

in Figure 3, which contains eight lines arising from the fluorine atoms of the trifluoroacetoxy group.

The hexabenzyl ether of *p-tert*-butylcalix[6]arene (**3**) shows a broader room-temperature peak for the methylene protons than does the acetate (**6**), suggesting that **3** is somewhat less flexible. As shown in Figure 4, the spectrum of **3** at −60 °C contains three well-resolved peaks in a 1:2:1 ratio arising from the *tert*-butyl protons, a broad peak arising from the benzyl methylene protons, and a complex envelope of peaks arising from the calixarene methylene protons. This pattern suggests that the compound has frozen out as a mixture of conformations. The ^{1}H NMR spectrum of the hexakis(trimethylsilyl) ether (**4**) is well resolved at room temperature, indicating that this derivative is considerably less conformationally flexible than the methyl ether, the benzyl ether, or the acetate. As shown in Figure 5, the spectrum of **4** contains two peaks in a 2:1 ratio arising from the trimethylsilyl protons at δ 0.67 and −0.28, two peaks in a 1:2 ratio arising from the *tert*-butyl protons at δ 1.01 and 1.38, a pair of doublets arising from eight of the methylene protons centered at δ 3.16 and 4.06, a singlet arising from four of the methylene protons at δ 3.77, and a pair of peaks in a 2:1 ratio arising from the aromatic protons at δ 7.11 and 6.67. This pattern is commensurate with the "up–out–up–down–out–down" conformation that has been established by X-ray crystallography of the hexakis(2-methoxyethyl) ether of *p-tert*-butylcalix[6]arene (**5**)[4] and the hexamethyl ether of *p*-allylcalix[6]arene (**4**).[5] As the temperature is increased above

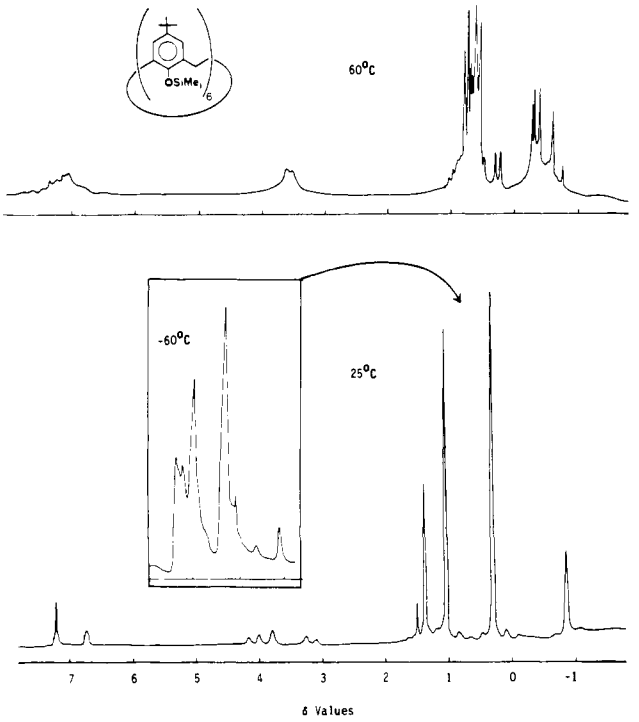


Figure 5. ^{1}H NMR spectra of the hexakis(trimethylsilyl) ether of *p-tert*-butylcalix[6]arene at 60, 25, and −60 °C in $CDCl_3$ solution.

room temperature the ^{1}H NMR spectrum of **4** becomes less well-resolved, passing through a coalescence point at 61 °C and then sharpening to a spectrum of singlet resonances at 100 °C. The free energy barrier for this conformational inversion is calculated to be 16.1 kcal/mol. As the temperature is lowered below room temperature the spectral pattern also becomes less well-resolved, but at −60 °C the trimethylsilyl and *p-tert*-butyl resonances sharpen into complex patterns, indicating that "rocking" motions with rather low inversion barriers are taking place in the molecule.

The barrier to conformational inversion for all of the parent calixarenes[3] as well as the methyl ether (**2**), benzyl ether (**3**), and acetate (**6**) of *p-tert*-butylcalix[6]arene is essentially independent of the character of the para substituent. This follows logically from the assumption that the inversion involves the passage of the oxygen end rather than the para substituent end of the aryl moieties through the annulus of the calixarene ring. In contrast, in the hexakis(trimethylsilyl) ethers of the calix[6]arenes, the para substituent does have an effect. As shown in Figure 6, the room-temperature ^{1}H NMR spectrum of the hexakis(trimethylsilyl) ether of calix[6]arene (**1**) is unresolved at room temperature and shows a coalescence point at −2 °C, corresponding to an inversion barrier of 12.6 kcal/mol. However, the ^{1}H NMR spectrum of the hexakis(trimethylsilyl) ether of *p-tert*-octylcalix[6]arene (**8**), as shown in Figure 7, shows a coalescence temperature of 78 °C, which corresponds to an inversion barrier of 17.0 kcal/mol. This is even a bit higher than the inversion barrier for the trimethylsilyl ether of *p-tert*-butylcalix[4]arene (**4**). Space-filling molecular models of the hexakis(trimethylsilyl) ethers of the calix[6]arenes show quite clearly that it is easier to rotate the para substituent end than the (trimethylsilyl)oxy end of the aryl moiety through the annulus when the para substituent is hydrogen. The models also suggest, although somewhat less emphatically, that this is true even when the para substituent is *p-tert*-butyl or *p-tert*-octyl. Therefore, it is postulated that when very large groups such as trimethylsilyl are attached to the oxygens of a calix[6]arene, the preferred pathway for conformational inversion involves rotation of the aryl rings in a direction that brings the para substituent end through the annulus of the calixarene.

Ethers and Esters of the Calix[8]arenes. The room-temperature ^{1}H NMR spectra of the octamethyl ether (**10**), the octabenzyl

(4) Ungaro, R.; Pochini, A.; Andreetti, G. D.; Domiano, P. *J. Inclusion Phenom.* **1984**, *2*, 000.
(5) Gutsche, C. D.; Lin, L. G. *J.*, unpublished results.

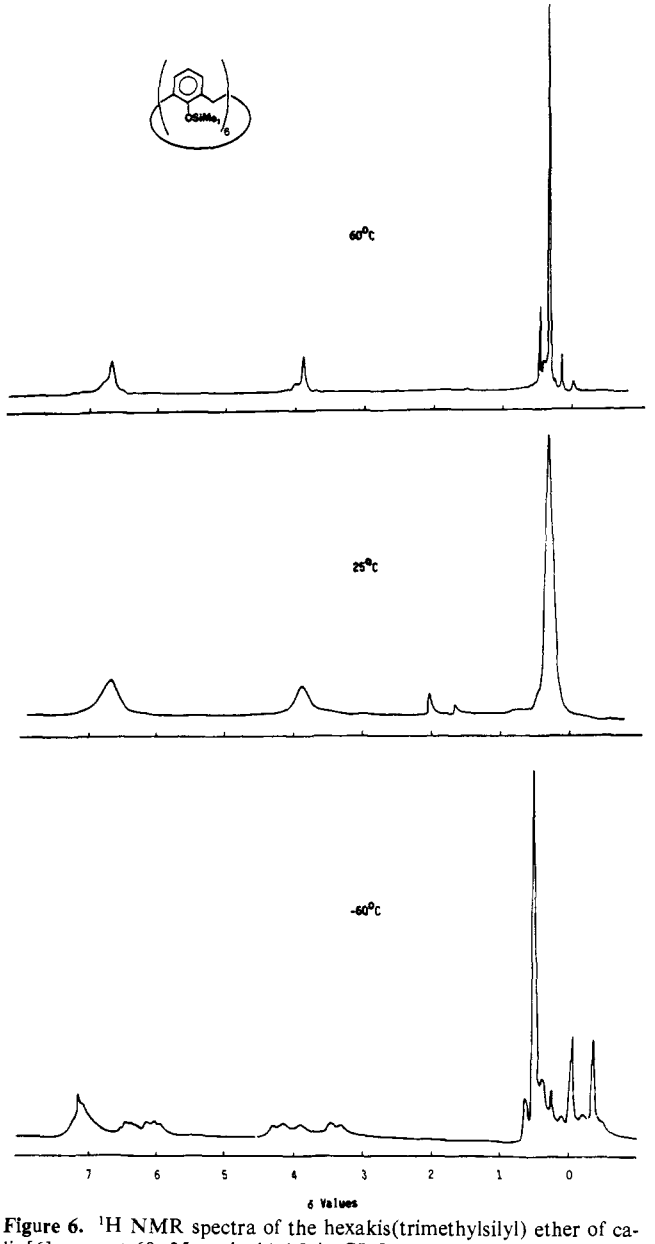


Figure 6. ^{1}H NMR spectra of the hexakis(trimethylsilyl) ether of calix[6]arene at 60, 25, and −11 °C in $CDCl_3$ solution.

ether (**11**), the octakis(trimethylsilyl) ether (**12**), and the octaacetate (**13**) of *p-tert*-butylcalix[8]arene all show singlets for the methylene resonances, slightly broadened in the case of the benzyl and trimethylsilyl ethers. The spectrum of the methyl ether shows no broadening of the methylene resonances down to −90 °C, while those of the benzyl ether and the acetate resolve into more complex patterns at about −70 °C. In contrast, the spectrum of the trimethylsilyl ether at −50 °C, as shown in Figure 8, contains a well-resolved pattern of six lines at δ 4.27, 4.13, 3.98, 3.77, 3.48, and 3.19 arising from the methylene protons. The coalescence temperature occurs at −5 °C, corresponding to an inversion barrier of 13.2 kcal/mol. Whether the conformational inversion pathway in this compound involves rotation of the (trimethylsilyl)oxy end or the *tert*-butyl end of the aryl moieties, or both, is uncertain.

Conclusions. Large groups attached to the oxygen atoms of the calixarenes increase the barrier to conformational inversion in the calix[6]arenes as well as the calix[8]arenes, although to a lesser extent than in the calix[4]arenes where conformations can be frozen at room temperature or higher. Conformational inversion via the "oxygen through the annulus" route can be curtailed by sufficiently large groups such as trimethylsilyl attached to the oxygen atoms, and the "para substituent through the annulus" route becomes the preferred one.

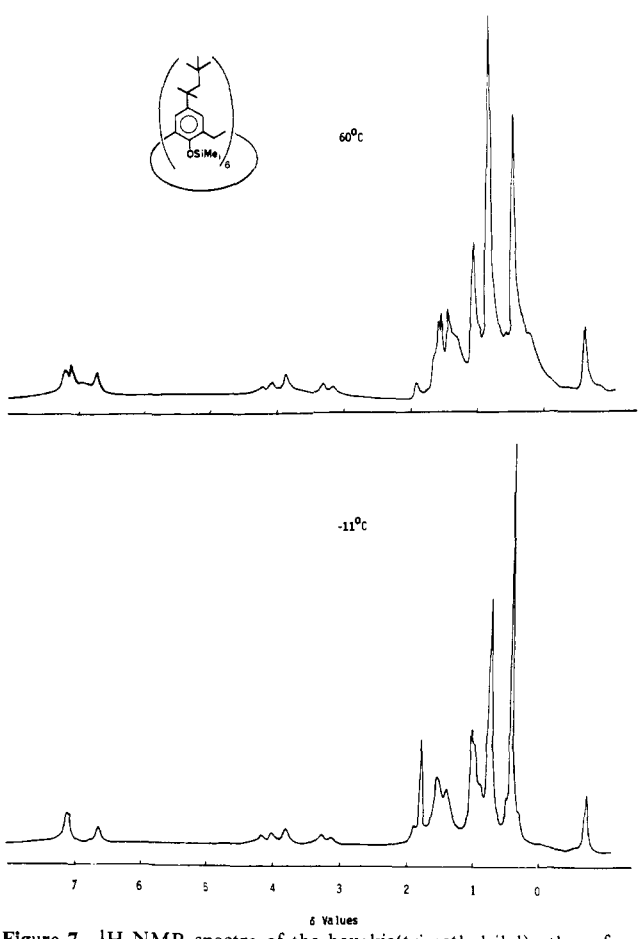


Figure 7. ^{1}H NMR spectra of the hexakis(trimethylsilyl) ether of *p*-(1,1,3,3-tetramethylbutyl)calix[6]arene at 60 and −11 °C in $CDCl_3$ solution.

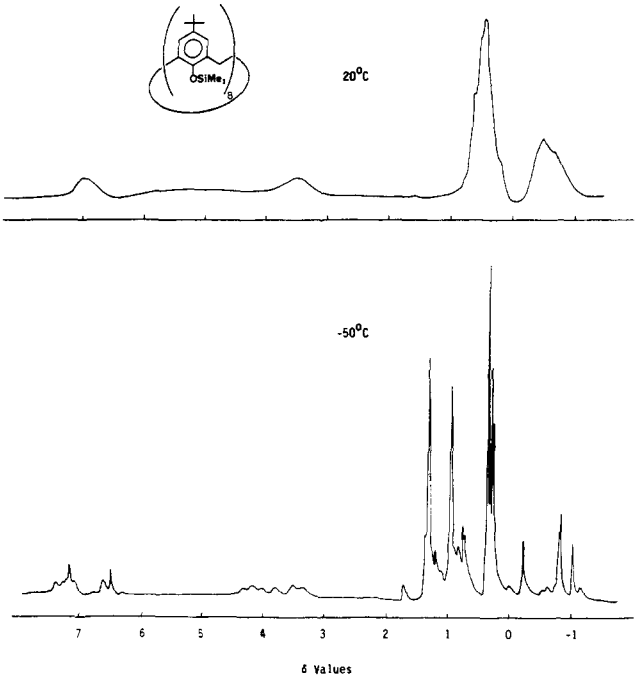


Figure 8. ^{1}H NMR spectra of the octakis(trimethylsilyl) ether of *p-tert*-butylcalix[8]arene at 20 and −50 °C in $CDCl_3$ solution.

Experimental Section

5,11,17,23,29,35-Hexa-*tert*-butyl-37,38,39,40,41,42-hexakis(trifluoroacetoxy)calix[6]arene (7). A 1.0-g sample of *p-tert*-butylcalix[6]arene was dissolved in 50 mL of pyridine at room temperature and treated with 2 mL of trifluoroacetic anhydride. The mixture was refluxed

for 2 h and then poured into ice. The red solid that was obtained was dissolved in acetone and filtered, the acetone was evaporated, and the residue was dried and recrystallized from $CHCl_3$ to give 1.34 g (84%) of colorless crystals: mp above 410 °C; IR (KBr) 1770 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 6.75 (s, 2, ArH), 3.6 (s, 2, $ArCH_2Ar$), 1.25 (s, 9, $C(CH_3)_3$. Anal. Calcd for $C_{78}H_{78}O_{12}F_{18}$: C, 60.45; H, 5.08. Found: C, 59.92; H, 5.34.

5,11,17,23,29,35-Hexakis(1,1,3,3-tetramethylbutyl)-37,38,39,40,41,42-hexakis[(trimethylsilyl)oxy]calix[6]arene (8). A slurry of 1.0 g of *p-tert*-octylcalix[8]arene, 6 mL of *N,O*-bis[(trimethylsilyl)-oxy]acetamide, and 50 mL of acetonitrile was refluxed 4 h. The precipitate was collected and recrsytallized from $CHCl_3$ to give 0.81 g (60%) of a white powder: mp 324–327 °C; ^1H NMR (toluene-d_8) δ 6.66 (s, 2, ArH), 3.70 (br s, 2, $ArCH_2$), 1.67 (s, 2, $ArC(CH_3)_2CH_2C(CH_3)_3$), 1.29 (s, 6, $ArC(CH_3)_2CH_2C(CH_3)_3$, 0.71 (s, 9, $ArC(CH_3)_2CH_2C(CH_3)_3$), 0.02 (s, 9, $Si(CH_3)_3$). Anal. Calcd for $C_{108}H_{180}O_6Si_6$: C, 73.47; H, 10.20. Found: C, 74.03; H, 9.93.

37,38,39,40,41,42-Hexakis[(trimethylsilyl)oxy]calix[6]arene (1) was prepared in the manner described above to yield 55% of the product as colorless crystals after recrystallization from $CHCl_3$/MeOH: mp 284–286 °C; ^1H NMR (toluene-d_8) δ 7.35 (t, 1, ArH), 6.95 (d, 2, ArH), 3.70 (s, 2, $ArCH_2Ar$), 0.02 (s, 9, $Si(CH_3)_3$). Anal. Calcd for $C_{60}H_{84}O_6Si_6$: C, 65.93; H, 7.69. Found: C, 67.58; H, 8.10.

Acknowledgment. We are indebted to the National Institutes of Health (Grant GM-23534) for generous financial support of this work and to Drs. Shou-I Chen, Balram Dhawan, and Lee-Gin Lin for supplying several of the compounds used in this work.

Calixarenes. 15. The Formation of Complexes of Calixarenes with Neutral Organic Molecules in Solution

Lorenz J. Bauer and C. David Gutsche*

Contribution from the Department of Chemistry, Washington University, St. Louis, Missouri 63130. *Received February 14, 1985*

Abstract: A study of the interaction, in solution, between calixarenes (as putative host molecules) and a variety of potential guest molecules is reported. By employing the aromatic solvent induced shift (ASIS) values of ^1H NMR resonances of the calixarenes in toluene solution (chloroform as the reference solvent), evidence is adduced for the formation of complexes between certain calix[4]arenes and toluene. The data indicate that the extent of complexation depends on the para substituent of the calixarene; e.g., *p-tert*-butyl- and *p-tert*-amylcalix[4]arene appear to form tighter complexes with toluene than *p*-hydro- and *p-tert*-octylcalix[4]arenes. This correlates with X-ray crystallographic observations on these compounds. Aliphatic amines are shown to interact quite strongly with calix[4]arenes in polar solvents (acetone and acetonitrile), forming complexes that are thought to involve proton transfer from calixarene to amine to produce a calixarene anion and an ammonium cation, followed by ion pairing. Chemical shift and relaxation time (T_1) data, along with measurements of the changes in the free energies of activation for conformational inversion of the calixarenes in the presence of various amines, provide evidence that these are endo-calix complexes.

The calixarenes,[1] which are macrocyclic compounds containing cavities of molecular-sized dimensions, are interesting because of their potential as enzyme mimics. The first step in a faithful enzyme mimic process involves the formation of a complex between the mimic and the substrate, followed then by chemical alteration of the substrate. The present study is concerned with the extent to which calixarenes interact with other molecules to form complexes in solution.

Many of the calixarenes form complexes in the solid state, this property having been observed even before the basic structures of the calixarenes were established. For example, *p-tert*-butylcalix[4]arene (**2**) forms complexes with chloroform,[2] benzene,[3] toluene,[4] xylene,[3] and anisole;[3] *p-tert*-butylcalix[5]arene (**7**) forms complexes with isopropyl alcohol[5] and acetone;[3] *p-tert*-butylcalix[6]arene (**8**) forms a complex containing chloroform and methanol;[2] *p-tert*-butylcalix[7]arene forms a complex containing methanol;[6] and *p-tert*-butylcalix[8]arene (**9**) forms a complex with chloroform.[2] The tenacity with which the guest (substrate) compound[7] is held by the calixarene varies widely among the calixarenes. Whereas the cyclic octamer loses the guest molecule chloroform upon standing a few minutes at room temperature and atmospheric pressure, the cyclic tetramer and cyclic hexamer retain solvent even after many hours of drying under high vacuum at high temperature. The endo calix character of the complexes formed by the cyclic tetramers has been established by the X-ray crystallographic studies of Andreetti et al.[4] which show, for example, that the *p-tert*-butylcalix[4]arene–toluene complex contains the toluene well-imbedded in the center of the calix. The pertinent question in comtemplating the utility of calixarenes as enzyme mimics, however, is whether analogous complexes exist *in solution*. To date, there has been little or no information bearing on this question.

A variety of macrocyclic compounds have been shown to form complexes in solution, including the cyclodextrins,[8] crown ethers,[9] cryptands,[9] and cyclophanes.[11] In many instances where strong

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(3) Coruzzi, M.; Andreetti, G. D.; Bocchi, V.; Pochini, A.; Ungaro, R. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1133.

(4) Andreetti, G. D.; Ungaro, R.; Pochini, A. *J. Chem. Soc., Chem. Commun.* **1979**, 1005.

(5) Ninagawa, A.; Matsuda, H. *Makromol. Chem. Rapid Commun.* **1982**, *3*, 65.

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