9204 *J. Phys. Chem. A* **1999,** *103,* 9204−9210

Conformational Dynamics of 5,11,17,23-Tetra-*p*-*tert*-butyl-25,27-di(*N*,*N*-diethylaminocarbonyl)methoxy-26,28-dimethoxycalix[4]arene and Its Kinetics and Mechanisms of the Cesium Cation Complexation in Solution Studied by ^{1}H, ^{13}C, and ^{133}Cs NMR Spectroscopy

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Received: December 11, 1998; In Final Form: September 6, 1999

The conformational exchange of 5,11,17,23-tetra-*p*-*tert*-butyl-25,27-di(*N*,*N*-diethylaminocarbonyl)methoxy-26,28-dimethoxycalix[4]arene (**1**) and the complexation of the cesium cation by **1** in a binary mixture of deuterated acetonitrile and chloroform were studied by ^{1}H, ^{13}C, and ^{133}Cs NMR spectroscopy. The conformational interconversions of **1** were studied by ^{1}H 2D EXSY NMR. The partial cone (pc) ↔ cone (c) and the pc ↔ pc self-interconversion of **1** are characterized by $\Delta H^* = 70 \pm 10$ kJ/mol and $\Delta H^* = 64 \pm 10$ kJ/mol, respectively. The 1:1 complexes between the cesium cation and the c and pc conformer of **1** are described. The exchange between solvated Cs$^+$ and the cone complex follows a purely dissociative mechanism, characterized by $\Delta H^* = 89 \pm 2$ kJ/mol and $\Delta S^* = 71 \pm 4$ J/(mol K).

Introduction

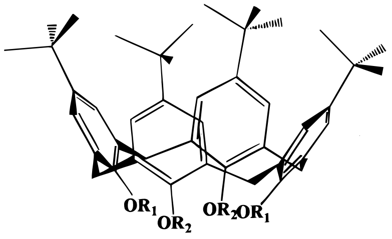
Calixarenes, synthetic, macrocyclic oligomers obtained through the base-catalyzed condensation of phenol and formaldehyde,[1] are used as building blocks in supramolecular chemistry due to their versatile recognition properties toward cations, anions, and neutral molecules.[2−5] The selectivity of the recognition properties can be varied through modifications at the phenolic oxygens (lower rim).[6−17]

The tetramer, calix[4]arene, can adopt four different conformations designated as cone, partial cone, 1,2 alternate, and 1,3 alternate depending on the relative orientations of the phenolic and para sites.[18] All these conformers have distinct ^{1}H and ^{13}C NMR spectra. Small substituents at the lower rim, i.e., methyl or ethyl groups, allow the phenyl units to flip through the annulus of the calixarene and the conformational exchange between the different conformers can be studied by NMR spectroscopy.[19−21] Acetamide, ester, and ketone substituents display a high affinity toward alkali metal cations.[14−17,22] The complexation properties depend on the donor groups and the conformation of the calixarene.[23−28]

Recently, the conformational interconversions of the flexible tetramethoxycalix[4]arene (**4**) were studied in solution, in deuterated chloroform, and in a binary mixture of deuterated chloroform and deuterated acetonitrile.[19] Studies of the kinetics and mechanisms of complexation of **4** by the sodium [28] and cesium [27] cation followed this work. While the sodium cation forms 1:1 complexes with **4** fixed in the cone conformation,[28] the cesium cation forms two types of 1:1 complexes, with the partial cone and the 1,3 alternate conformer of **4**, with a thermodynamic preference for the partial cone complex, which, however, is kinetically more labile.[27] (Scheme 1)

The complexation of the sodium and cesium cations by conformationally rigid calix[4]arene ester[29] (**5**) and acetamide (**3**)[30] derivatives was also studied in the same solvent. The two calix[4]arenes (**3**, **5**) are fixed in the cone conformation before and after complexation. Other stoichiometries, 2:1 calixarene:Na^{+} [29] and 1:2 calixarene:Cs^{+},[30] were shown to coexist in equilibrium with the 1:1 complexes. It has been shown that, in this solvent system, the cesium triiodide ion pair is dissociated, at least to a very large extent.[27]

SCHEME 1



	R$_1$	R$_2$
1	CH$_3$	CH$_2$CON(CH$_2$CH$_3$)$_2$
2	CH$_3$	H
3	CH$_2$CON(CH$_2$CH$_3$)$_2$	CH$_2$CON(CH$_2$CH$_3$)$_2$
4	CH$_3$	CH$_3$
5	CH$_2$COCH$_2$CH$_3$	CH$_2$COCH$_2$CH$_3$

In this work, 5,11,17,23-tetra-*tert*-butyl-25,27-di(*N*,*N*-diethylaminocarbonyl)methoxy-26,28-dimethoxycalix[4]arene (**1**), shown in Scheme 1, was synthesized. This calixarene has intermediate properties between **3** and **4**, combining the high ionophoricity of the acetamide groups with the flexibility provided by lower rim methoxy substituents.

The structure of **1** and of its complexes with Cs^{+}, the conformational interconversions of **1**, and the kinetics and mechanism of its cesium cation complexation were studied by ^{1}H, ^{13}C, and ^{133}Cs NMR spectroscopy in binary mixtures of deuterated chloroform and deuterated acetonitrile. It is shown that the cone, partial cone and 1,3 alternate conformers of **1** (Scheme 2) are present in this solvent system. Cs^{+} selectively recognizes the cone and partial cone conformers of **1** and the Cs^{+} exchange between the cone complex and the solvated Cs^{+} follows a purely dissociative mechanism.

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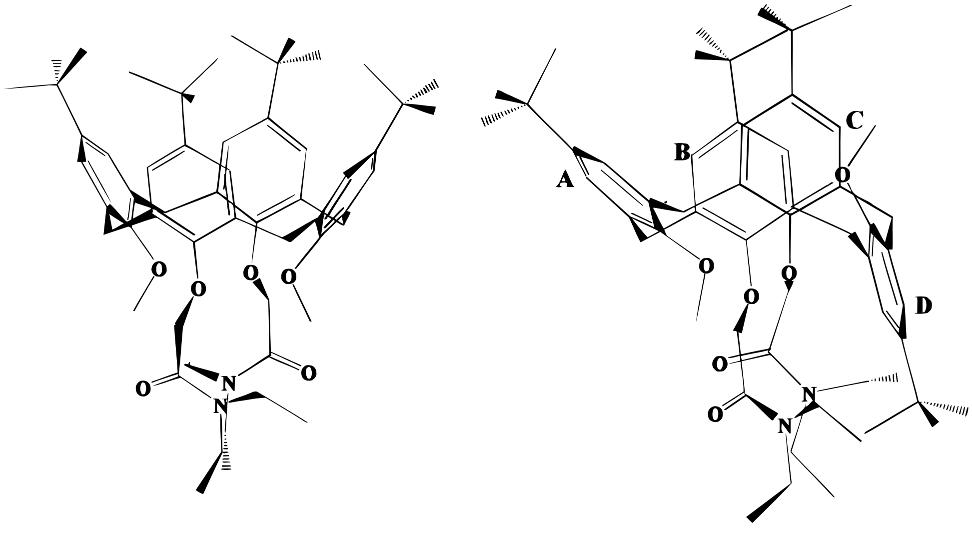
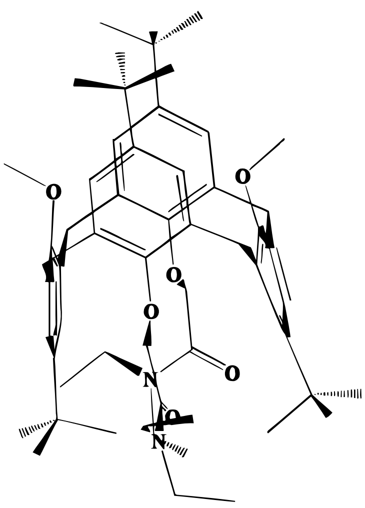
SCHEME 2



cone **partial cone**



1,3 alternate

Experimental Section

Chemicals and Solutions. 5,11,17,23-Tetra-*tert*-butyl-25,27-di(*N*,*N*-diethylaminocarbonyl)methoxy-26,28-dimethoxycalix[4]arene (**1**) was synthesized from the tetrahydroxyderivative (Aldrich 99%) in two steps. First, 5,11,17,23-tetrabutyl-25,27-dimethoxycalix[4]arene (**2**) was synthesized as described by No et al.[31] In the second step, 0.15 g of NaH (60% in oil) was added to 1 g (1.48 mmol) of **2**, suspended in 50 mL of anhydrous THF and 10 mL of dry DMF, followed by the addition of 0.8 g of α-chloro-*N*,*N*-diethylacetamide and refluxed for 3 h under an Ar atmosphere. The reaction mixture was then worked up with a procedure similar to the one described by Arduini et al.[12] in the case of the reported synthesis of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(*N*,*N*-diethylaminocarbonyl)methoxycalix[4]arene (**3**). This procedure yields 0.6 g of **1**.

Elemental Analysis. Analysis calculated for $C_{58}H_{82}N_2O_6$: C (77.12), H(9.15), N (3.1), found C (76.91), H (9.22), N (3.11).

Free (1): ^1H NMR (1:1 $CDCl_3$ (7.24 ppm):CD_3CN, 255 K), cone conformer: 0.71 (s, 18, $C(CH_3)_3$), 0.85 (t, $J = 7$ Hz, 6, $NCH_2C\mathbf{H}_3$), 0.9 (t, $J = 7$ Hz, 6, $NCH_2C\mathbf{H}_3$), 0.99 (s, 18, $C(CH_3)_3$), 2.97 (d, $J = 15$ Hz, 4H, H_{eq}), 3.11 (q, $J = 7$ Hz, 4, $NC\mathbf{H}_2CH_3$), 3.17 (q, $J = 7$ Hz, 4, $NC\mathbf{H}_2CH_3$), 3.75 (s, 6, CH_3O), 4.12 (d, $J = 15$ Hz, 4H, H_{ax}), 4.14 (s, 4, OCH_2CO), 6.53 (s, 4, Ar), 6.89 (s, 4, Ar).

^{13}C NMR (1:1 $CDCl_3$ (77.8 ppm):CD_3CN, 255 K), cone conformer: 12.46, 13.9 ($NCH_2\mathbf{C}H_3$), 30.4, 31.05 ($C(\mathbf{C}H_3)_3$), 31.1 ($CH_{ax}H_{eq}$), 33.5, 34.03 ($\mathbf{C}(CH_3)_3$), 39.4, 40.18 ($N\mathbf{C}H_2CH_3$), 60.25 (CH_3O), 73.4 ($O\mathbf{C}H_2CO$), 125.2, 125,5 (ArH), 131.9, 134.6, 144.9, 145.7, 153.8, 154.8 (Ar), 166.9 (CO).

^1H NMR (1:1 $CDCl_3$ (7.24 ppm):CD_3CN, 255 K), partial cone conformer: 0.78 (s, 18, $C(CH_3)_3$), 1.01 (s, 9, $C(CH_3)_3$), 1.07 (s, 9, $C(CH_3)_3$), 2.22 (s, 3, CH_3O), 2.76 (d, $J = 13$ Hz, 2H, H_{eq}), 2,88 (s, 3, CH_3O), 3.02 (s, 4, OCH_2CO), 3.43 (d, $J = 13$ Hz, 2H, H_{ax}), 3.58 (d, $J = 13$ Hz, 2H, H_{eq}), 4.42 (d, $J = 13$ Hz, 2H, H_{eq}), 6.32 (s, 2, Ar), 6.67 (s, 2, Ar), 6.81 (s, 2, Ar), 7.03 (s, 2, Ar).

^{13}C NMR (1:1 $CDCl_3$ (77.8 ppm):CD_3CN, 255 K), partial cone conformer: 12.53, 14.01 ($NCH_2\mathbf{C}H_3$), 30.19, 31.14, ($C(\mathbf{C}H_3)_3$), 33.43, 33.7, ($\mathbf{C}(CH_3)_3$), 37.25, 39.6 ($NCH_2\mathbf{C}H_3$), 57.8, 60.01 (CH_3O), 71.6 ($O\mathbf{C}H_2CO$), 124.7, 126.1, 127.4,

(ArH), 131.7, 132.2, 132.6, 135.2, 143.1, 143.9, 154.2, 154.9 (Ar), 167 (CO).

*(Cs^+,**1**) complex: ^1H NMR (1:1 $CDCl_3$ (7.24 ppm):CD_3CN, 255 K):* 0.8 (t, $J = 7$ Hz, 6, $NCH_2C\mathbf{H}_3$), 0.88 (t, $J = 7$ Hz, 6, $NCH_2C\mathbf{H}_3$), 0.97 (s, 18, $C(CH_3)_3$), 1.0 (s, 18, $C(CH_3)_3$), 2.83 (q, $J = 7$ Hz, 4, $NC\mathbf{H}_2CH_3$), 3.01 (q, $J = 7$ Hz, 4, $NC\mathbf{H}_2CH_3$), 3.13 (s, 6, CH_3O), 3.36 (d, $J = 15$ Hz, 4H, H_{eq}), 3.48 (d, $J = 15$ Hz, 4H, H_{ax}), 4.17 (s, 4, OCH_2CO), 6.78 (s, 4, Ar), 6.93 (s, 4, Ar).

*(Cs^+,**1**) complex: ^{13}C NMR (1:1 $CDCl_3$ (77.8 ppm):CD_3CN, 255 K):* 12.56, 13.73 ($NCH_2\mathbf{C}H_3$), 30.85, 31.01 ($C(\mathbf{C}H_3)_3$), 33.62, 33.88 ($\mathbf{C}(CH_3)_3$), 36.67 ($CH_{ax}H_{eq}$), 39.79, 40.56 ($N\mathbf{C}H_2CH_3$), 57.13 (CH_3O), 70.38 ($O\mathbf{C}H_2CO$), 127.78, 127.94 (ArH), 132.56, 136.03, 145.15, 145.2, 149.3, 156.3 (Ar), 166.06 (CO).

Cesium triiodide (Johnson Matthey 99%) was used as cesium cation source. CsI_3 was dried under vacuum overnight prior to use.

All measurements were made in a binary mixture of deuterated chloroform and deuterated acetonitrile. Deuterated acetonitrile (99.8%) was purchased from either Aldrich or Cambridge Isotope Laboratories, and deuterated chloroform (99.8%) was purchased from Cambridge Isotope Laboratories. The solvents were dried over 4 Å molecular sieves before use.

NMR Measurements. The ^1H, ^{13}C, and ^{133}Cs NMR spectra were recorded on a Bruker AMX-500 NMR spectrometer at 500.14, 125.77, and 65.59 MHz, respectively. The ^1H and ^{13}C NMR spectra are referenced to chloroform (7.24 and 77.8 ppm, respectively) and the ^{133}Cs spectra to 10 mM CsCl in 20% D_2O (0 ppm at 300 K). The error on the temperature is estimated to be 0.5 K.

^{133}Cs NMR Spectra. The parameters were chosen to obtain quantitative spectra. A relaxation delay of 0.5−2 s, a 90° pulse of 14 μs, an acquisition time of 0.02−1 s, and a sweep width of 20 kHz were used, and 64−24*K* scans were accumulated per spectrum.

^1H 2D-EXSY Spectroscopy. A standard NOESY pulse sequence was used for these experiments.[32−34] A relaxation delay of 4.5 s, a 90° pulse of 3.1 μs, sweep width 7 kHz, acquisition time 0.07 s, 16 scans of 1024 points by 256 slices with a total measuring time of $5^1/_2$−7 h per spectrum. The spectra for the complexed and free calixarene were respectively recorded at 255, 274, and 292 K and 246, 255, 274, and 283 K. At each temperature a series of 4 or 5 2D-EXSY spectra were recorded. Mixing times (τ_m) varied between 10 ms and 1.25 s.

T_1. The longitudinal relaxation time (T_1) was determined by the inversion−recovery method, and 10 delay times between 10 ms and 6.5 s were used. The T_1 of the free and complexed aromatic protons varied between 880 and 1100 ms.

Data Treatment. *1D ^{133}Cs Spectra.* The line widths, intensities, and chemical shifts were determined by fitting each peak with a Lorentzian line shape. The integrals were calculated using these intensities and line widths. The kinetic analysis of these spectra was done by a complete band shape analysis using the DNMR5 software.[35]

^1H 2D-EXSY Spectra. The 2D spectra were symmetrized and all peaks integrated using standard Bruker software. The rate constants were determined by a matrix method, described in the literature.[36,37]

$$R = -\ln(A)/\tau_m \qquad (1)$$

where A contains the intensities of the peaks in the EXSY spectrum, weighted by their relative populations p_j, $A_{ij} = I_{ij}(\tau_m)/p_j$, and τ_m is the mixing time. The off-diagonal elements of R are made of the rate constants, k_{ij}, with $k_{ij}p_i = k_{ji}p_j$.

The rate constants are averaged over at least four measurements with different mixing times. The error is given as the standard deviation of these measurements.

With this approach all rate constants can be determined on one spectrum. Integration of all peaks gives a square matrix of the intensities I. These intensities are divided by the population of each site, which is determined by integration on the 1D spectrum at the same temperature. This gives the matrix $\mathbf{A}$. Finally, the calculation of the logarithm of matrix $\mathbf{A}$ followed by the division of each of its elements by τ_m gives the matrix $\mathbf{R}$, whose off-diagonal elements are the rate constants for the exchange between the various sites. Even if all rate constants could be obtained from one EXSY spectrum, at least four EXSY spectra were measured at all the temperatures of this study, with different τ_m values.

Results and Discussion

1 was synthesized from 5,11,17,23-tetrabutyl-25,27-dimethoxycalix[4]arene (**2**) using NaH as base. The use of Na^+ as counterion selectively produces the cone conformer of calix[4]arenes, since Na^+ has the highest affinity toward the cone conformer in the complex formation.[23,38−40] The bulkiness of the acetamide group does not allow the flipping of the lower rim acetamide-substituted phenolic units through the annulus of the calix[4]arene;[1,12] thus only the cone (c), partial cone (pc) and the 1,3 alternate (1,3alt) conformer of **1**, shown in Scheme 2, can be formed through conformational interconversions involving the cone conformer.

The aromatic region of the ^1H 1D and 2D EXSY NMR spectra of 32.1 mM **1** in a binary mixture of deuterated chloroform and deuterated acetonitrile at 255 K is shown in Figure 1. Figure 1 confirms the formation of three different conformers in equilibrium. Two peaks of equal intensity at 6.53 and 6.89 ppm characterize the major species, assigned to the cone conformer. The partial cone conformer is characterized by four peaks of equal integrals at 6.32, 6.67, 6.81, and 7.03 ppm and the 1,3 alternate conformer by two peaks at 6.62 and 6.61 ppm. The peaks at 6.32 and 6.67 ppm can be attributed to the acetamido-bearing phenyl rings, since at low temperature, the expected meta coupling can be observed (Figure 1; B and C protons in Scheme 2). At higher temperatures, the four peaks have the same line width, controlled by the exchange. The four ^1H signals of the partial cone conformation can then be assigned, since, on the basis of the diamagnetic anisotropy of the phenyl rings, B is expected to resonate at higher field than C, and A at higher field than D.[45] Accordingly, the assignment is 6.32 (B), 6.67 (C), 6.81 (A), and 7.03 (D). Similarly, the two signals of the cone conformation at 6.53 and 6.89 ppm can be attributed, respectively, to the acetamido- and methoxy-bearing phenyl rings.

The cone conformer is further described by two doublets at 2.97 and 4.12 ppm in the methylene−methoxy region and two *tert*-butyl peaks at 0.71 and 0.99 ppm. The partial cone conformer is described by two pairs of doublets in the methylenic region at 2.76, 3.43, 3.58, and 4.42 ppm and three peaks in the *tert*-butyl region at 0.78, 1.01, and 1.07 ppm, with a 2:1:1 intensity ratio. These data unambiguously confirm the presence of the cone and partial cone conformers as major and minor species in a binary mixture of acetonitrile and chloroform. The two small peaks of equal intensity in the aromatic region at 6.62 and 6.61 ppm are tentatively assigned to the 1,3 alternate conformer of **1**.

The relative distribution between the cone, partial cone, and the 1,3 alternate conformer is respectively 70%, 29%, and 1%

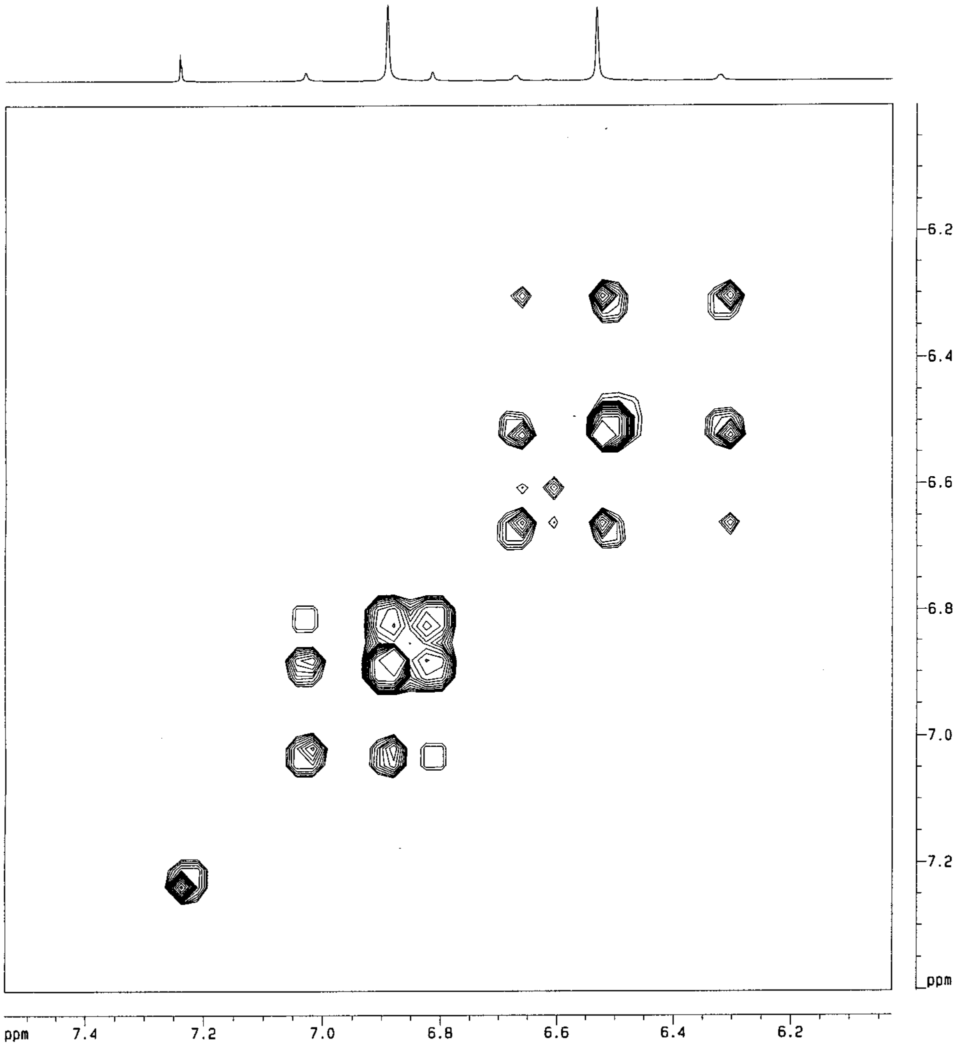


Figure 1. Aromatic region of the 1D ^{1}H and 2D ^{1}H EXSY NMR spectra of 32.1 mM **1** at 255 K.

at 255 K. This distribution between the different conformers reflects the thermodynamic stability of the different conformers, since the relative distribution did not change over a period of 2 months, excluding the possibility of a kinetically controlled product distribution. Further, the relative populations of the three conformers are invariant with temperature within the error limits, in agreement with a conformational process characterized by a very small entropic variation.

Figure 1 shows the appearance of two sets of cross peaks between the partial cone and the cone conformers, respectively, for the acetamido (6.32 and 6.67 ppm) and the methoxy (6.81 and 7.03 ppm) bearing phenyls.

It was possible to study the conformational interconversion between the partial cone and cone and the self-interconversion of the partial cone conformer, involving the thermodynamically favored cone conformer, by ^{1}H 2D-EXSY between 246 and 283 K. The rate constants were obtained from the aromatic region of the spectrum as described in the Experimental Section, using eq 1. Only the signals of the acetamido bearing phenyl rings at 6.32, 6.53, and 6.67 ppm were used since these signals do not overlap (see Figure 1). At 255 K the rate constants for the pc ↔ c conformational exchange and the pc ↔ pc self-interconversion are respectively 1.3 ± 0.2 and 0.55 ± 0.1. As expected, the rate of the pc ↔ pc self-interconversion is similar to the rate of the pc ↔ c interconversion, since it proceeds through the cone conformer. This is observed at every temperature studied. The activation enthalpies for the pc ↔ c and the pc ↔ pc self-interconversion are respectively $\Delta H^* = 70 \pm 10$ kJ/mol and $\Delta H^* = 64 \pm 10$ kJ/mol (Figure 7). These parameters are similar for the two processes, since the rate-determining step is the same in both processes. In the case of the tetramethoxy derivative (**4**), in the same solvent, the enthalpy of activation for the pc ↔ c interconversion process was found to be comparable, $\Delta H^* = 56 \pm 2$ kJ/mol,[19] but, as expected on the basis of the steric constraints, slightly smaller. Given the small range of temperatures (37 K; see Figure 7) for which these kinetic results could be obtained, the errors on the entropies of activation preclude their useful determination.

Complex Formation. Figure 2 shows the ^{133}Cs NMR spectra of variable amounts of **1**, in the presence of 30.1 mM of CsI_3, in a binary mixture of deuterated acetonitrile and deuterated chloroform at 238 K. In the absence of **1**, the resonance of solvated Cs^+ at 52 ppm is observed. Upon addition of **1**, two new signals at −19.5 and −72 ppm superimpose on the spectra of solvated Cs^+, and the peak of solvated Cs^+ disappears when an excess of **1** is added ([**1**]/[CsI_3] > 1). The two new peaks at −19.5 and −72 ppm are assigned to complexes formed between the cesium cation and different conformers of **1**. Figure 3 shows the methylene and methoxy region of the ^{1}H NMR spectrum of variable amounts of **1** in the presence (3a−e) and absence (3f) of 30.1 mM CsI_3. The $OC\mathbf{H}_2CO$ signal at 4.16, the two bridging methylene doublets at 3.49 and 3.37, the OCH_3 at 3.14, and the two amidomethylene quartets at 3.03 and 2.85 ppm unambiguously demonstrate that a complex is formed between

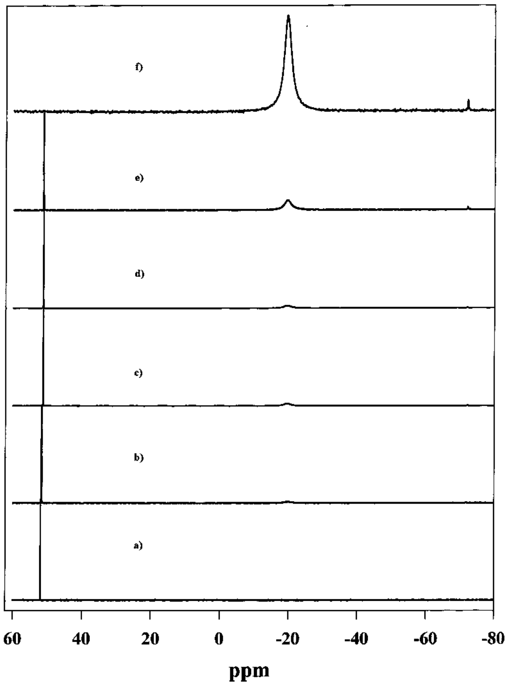


Figure 2. ^{133}Cs NMR spectra of 30.1 mM CsI_3 in the absence (a) and presence (b−f) of (b) 7.3, (c) 14.25, (d) 21.17, (e) 29.61, and (f) 47.32 mM **1** at 238 K.

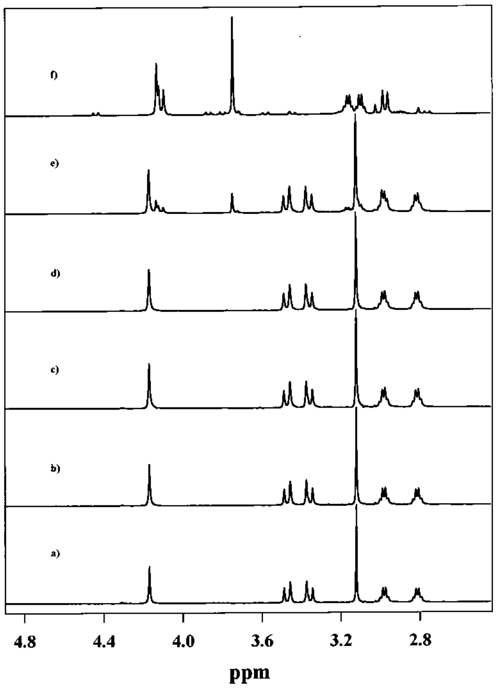


Figure 3. ^{1}H NMR spectra of various amounts of **1** in the presence (a−e) and absence (f) of 30.1 mM CsI_3 (b−f) at 238 K: (a) 7.3, (b) 14.25, (c) 21.17, (d) 29.61, (e) 47.32, and (f) 32.1 mM.

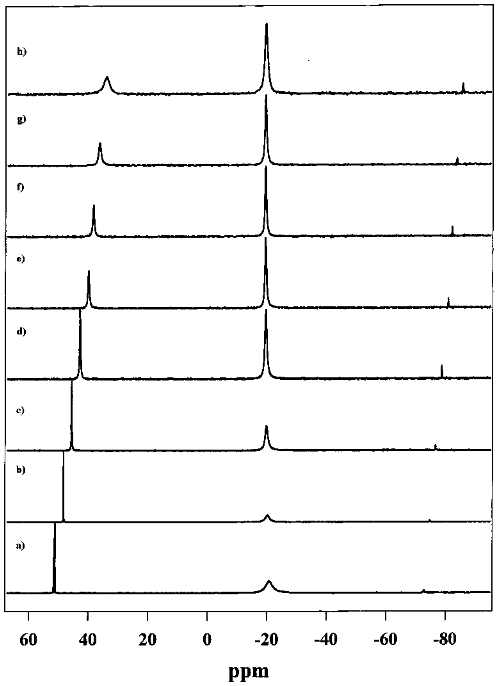


Figure 4. ^{133}Cs NMR spectra of 47.7 mM CsI_3 and 33.98 mM **1** at various temperatures: (a) 238, (b) 250, (c) 265, (d) 278, (e) 292, (f) 300, (g) 314, and (h) 328 K.

the cesium cation and the cone conformer of **1**. The *tert*-butyl region of the spectrum, where peaks at 0.83, 1.03, and 1.14 ppm in a 2:1:1 intensity ratio can be observed, gives the best indications for the partial cone conformer complex (figure is given in Supporting Information). Consequently, the minor species observed on the ^{133}Cs NMR spectrum (Figure 2) can be assigned to a complex formed between the Cs$^+$ and the partial cone conformer of **1**. Further, it has been shown recently that the Cs$^+$ cation has a higher affinity toward the partial cone conformer than toward the 1,3 alternate conformer.[27] According to the integrals of ^{133}Cs and ^{1}H NMR spectra, 1.5−2.5% of the Cs$^+$ is bound in the minor species. The small amounts of the partial cone complex present, and the spreading of these intensities over a larger number of peaks, compared to the cone conformer, prevent the detection of this complex in the other parts of the ^{1}H NMR spectra.

The ^{133}Cs NMR line width of the cone complex is 165 Hz at 238 K. This line width is much larger than that for the complex between the cesium cation and the cone conformer of *p-tert*-butylcalix[4]arene-tetraacetamide (12 Hz).[30] This clearly shows the reduced symmetry of the binding site composed of 4 phenolic and 2 carbonyl oxygens compared to a binding site made of 4 phenolic and 4 carbonyl oxygens. The lower symmetry of the cesium complex with the cone conformer of **1** creates an asymmetric electronic distribution around the quadrupolar cation, and increases the electric field gradient and consequently the line width.

This is confirmed by the temperature variation of the line width of the cone complex. At low temperature, the line width decreases with increasing temperature which is due to quadrupolar relaxation (see Figure 4), whereas at higher temperatures, the signals of the solvated cesium cation and of the cone complex broaden in parallel, obeying an exchange model (see Figure 5). Conformational changes can be ruled out, since in the corresponding ^{1}H NMR spectra the chemical shifts and coupling constants do not change with increasing temperature and only the peaks of the cone complex are observed. Further, it has been shown[46] that, in the absence of an exchange, the ^{133}Cs NMR relaxation is dominated by quadrupolar relaxation, even in the case of water.

Figure 4 shows the temperature dependence of the ^{133}Cs NMR spectra of a 47.7 mM CsI_3 and 33.87 mM **1**. The line width of the cone complex goes through a minimum at ∼300 K. The line width of the partial cone complex is not exchange broadened in the temperature range studied. Above 300 K the first-order rate constants for the cesium cation exchange between the cone complex and solvated Cs$^+$ could be determined using the DNMR5 software.[35] The experimental and calculated spectra

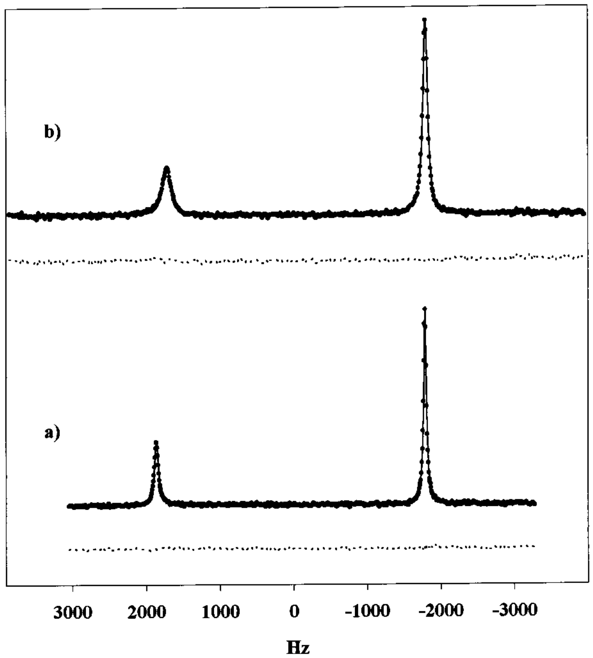


Figure 5. ^{133}Cs NMR spectra of 30.91 mM CsI_3 and 14.25 mM showing the measured spectrum, the DNMR5 fit (solid line), and the difference (dotted line): (a) 314 K, $k_{diss} = 93 \pm 1 = 2$ s^{-1} and (b) 328 K, $k_{diss} = 180 \pm 5$ s^{-1}.

SCHEME 3

a) $$A \underset{k_B}{\overset{k_A}{\rightleftharpoons}} B$$

b) $$C + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (C,M)$$

c) $$(C,M) + M^* \overset{k_2}{\rightleftharpoons} (C,M^*) + M$$

at 314 and 328 K are shown in Figure 5. The dissociation rate constants are 93 ± 2 and 180 ± 5 s^{-1} at 314 and 328 K, respectively.

These rate constants are only meaningful when the corresponding mechanism of exchange is known. Two limiting mechanistic hypotheses, a dissociative exchange (Scheme 3b) and an associative exchange mechanism (Scheme 3c) will be considered. k_A is related to k_{-1} and k_2 by eq 2.[41,42]

$$k_A = k_{-1}[(M,C)^+]/[M^+] + k_2[(M,C)^+] \qquad (2)$$

To determine the exchange mechanism a concentration study at constant $[\mathbf{1}]/[CsI_3] = 0.71$ and 5.26 mM $\le CsI_3] \le$ 47.7 mM was done at 330 K. A plot of $k_A/[(M,C)^+]$ as a function of 1/[M] is shown in Figure 6. $k_A/[(M,C)^+]$ is proportional to 1/[M] and the line extrapolates to zero within the precision of the measurement, giving $k_{-1} = 220 \pm 10$ s^{-1}. This shows the absence of a significant contribution of the associative exchange mechanism to the observed exchange between the solvated Cs$^+$ and the (**1**, Cs$^+$) cone complex.

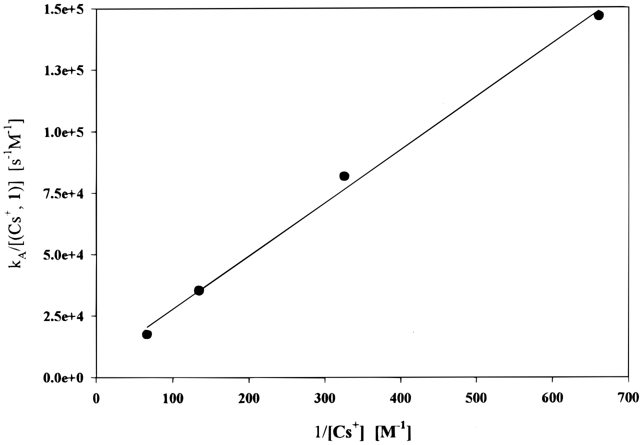


Figure 6. $k_A/[(M,C)^+]$ as a function of $1/[M^+]$ (see eq 2) at 330 K with the ratio calixarene/cesium $[1]/[CsI_3] = 0.71$.

TABLE 1: Rate Constants (s^{-1}) for the Different Exchange Processes at 255 K

partial cone → cone	partial cone → partial cone	cone complex → free cone	cone complex → free partial cone
1.3 ± 0.2[a]	0.55 ± 0.09[a]	0.019 ± 0.004[b]	0.020 ± 0.004[b]

[a] 31.1 mM **1**. [b] 47.7 mM **1** and 30.1 mM CsI_3.

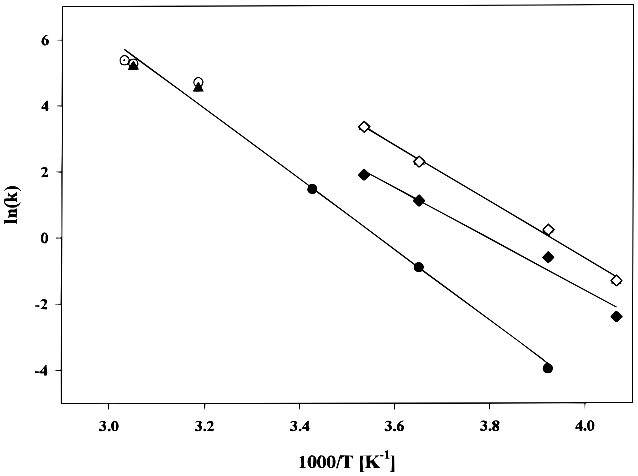


Figure 7. Eyring plot of the pseudo-first-order dissociation rate constants determined by a complete band shape analysis of the ^{133}Cs NMR spectra (○, 30.91 mM CsI_3, 14.25 mM 1, and ▲, 47.7mM CsI_3 and 33.98 mM **1**), ^{1}H 2D-EXSY NMR spectra (●, 30.1 mM CsI_3 and 47.32 mM **1**) and $k_A/[(M,C)^+]$ as a function of $1/[M^+]$ (⊙). Eyring plots of the partial cone−cone (◇) and partial cone−partial cone (◆) interconversions of 32.1 mM **1**.

Between 255 and 292 K the exchange between the free and complexed **1** could be studied by ^{1}H 2D EXSY NMR spectroscopy. The rate constants for the different exchange processes were derived from the aromatic part of the spectrum. At 274 and 292 K, only the exchange between the cone conformer of **1** and its complex with Cs$^+$ could be observed. At 255 K the exchange between the partial cone and the cone conformer as well as the exchange between the partial cone conformer and the cone complex could also be observed. The rate constants for the exchange between the cone complex and the cone and partial cone conformer of **1** are respectively 0.019 ± 0.004 and 0.020 ± 0.004 s^{-1}. The results obtained at 255 K are summarized in Table 1. These data further confirm the high affinity of the cesium cation toward the cone conformer compared to the partial cone or 1,3alternate conformer of **1**.

This dissociation of the (Cs$^+$,**1**) cone complex is characterized by $\Delta H^* = 89 \pm 2$ kJ/mol and $\Delta S^* = 71 \pm 4$ J/(mol K) (Figure 7). These values are larger than the activation parameters, $\Delta H^* = 67 \pm 2$ kJ/mol and $\Delta S^* = 40 \pm 3$ J/(mol K), for the dissociation of the (Cs$^+$,**3**) cone complex.[30] These data are similar to the activation parameters for the dissociation of the Cs$^+$ inclusion complexes with cryptand C222 and C222B in organic solvents obtained by Popov et al.,[43,44] suggesting that solvent molecules are excluded from the (Cs^+, **1**) cone complex. For comparison, the values of the activation parameters for the dissociation of the (Cs^+, **4**) partial cone complex are $\Delta H^* = 47 \pm 2$ kJ/mol and $\Delta S^* = -32 \pm 6$ J/(mol K). This result supports the view that in this latter case, the coordination sphere of the Cs^+ comprises at least a solvent molecule, making the dissociation process enthalpically more favorable.

Acknowledgment. The Natural Science and Engineering Research Council of Canada (NSERC) is gratefully acknowledged for a research grant and the Schweizerische Nationalfonds zur Förderung der Wissenschaftlichen Forschung for a postdoctoral fellowship to U.C.M. Dr. Glenn A. Facey is thanked for his help in recording the NMR spectra.

Supporting Information Available: Figure 3A giving the *tert*-butyl region of the proton NMR spectrum corresponding to Figure 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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