NMR Spectroscopic and X-Ray Crystallographic Studies of Calix[4]arene·Ag^+ Complexes. Influence of Bound Ag^+ on C_{2v}–C_{2v} Interconversion in *cone*-Calix[4]arenes

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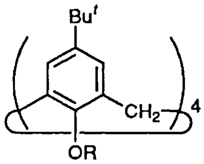
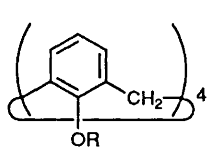
The Ag^+ complexes of conformationally immobilized tetra-*O*-propylcalix[4]arene with a cone or a partial-cone conformation (*cone*-**2**Pr^n or *partial-cone*-**2**Pr^n, respectively) have been successfully analysed by X-ray crystallography. In both complexes Ag^+ was bound to the upper rim cavity, sandwiched by the two *para* carbons in the distal phenyl units. The findings provide clear evidence for π-base participation. In particular, the basic calix[4]arene skeleton in *partial-cone*-**2**Pr^n·Ag^+ is almost the same as that in *partial-cone*-**2**Pr^n itself. This establishes that *partial-cone*-**2**R possesses two distal benzene rings ideally preorganized for Ag^+-binding. ^1H NMR spectroscopic studies for the Ag^+ complexes in solution indicated that Ag^+ is bound to the same site as that in the solid state. In conformationally mobile **2**Me, which exists in solution in equilibrium between *cone and partial-cone*, Ag^+ induced a shift of the equilibrium to *partial-cone* to form the *partial-cone*-**2**Me·Ag^+ complex. This is ascribed to the ideal preorganization in *partial-cone*-**2**R for the Ag^+-binding. These results are of great significance for an understanding of π-base participation in the metal-binding events and have important implications on the cation–π interaction in biological systems.

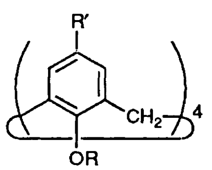
Calix[4]arenes provide 'soft' π-donor cavities composed of benzene rings as well as 'hard' oxygen cavities constructed on the lower rim.[1-3] Up to the present the metal-binding properties of the 'hard' oxygen cavities have been thoroughly studied.[1-9] In contrast, the studies on the binding properties of the 'soft' π-donor cavities have been very limited.[10-14] One representative example would be inclusion of trimethylammonium ions ($RNMe_3^+$) in the π-donor cavity of calix[4]arenes, the driving force of which is considered to be cation–π interactions.[10,11] Since interconversion among calix[4]arene conformers can be suppressed by the presence of *O*-substituents bulkier than the ethyl group,[15] one can isolate the four different conformers (*cone*, *partial-cone*, 1,2-*alternate* and 1,3-*alternate*). ^1H NMR spectroscopic studies have established that trimethylammonium ions are included only in *cone* conformers,[11] indicating that the preorganization of π-donors into an appropriate cavity shape is indispensable for effective inclusion. In the course of this study we unexpectedly found that Ag^+ is strongly bound to certain calix[4]arene conformers.[12,16] The ^1H NMR spectroscopic studies suggested that Ag^+ is bound to the π-basic cavity with the aid of the π-donor participation.[12,16] To obtain further insight into the π-donor participation in calix[4]arene·Ag^+ complexes we performed combined studies of ^1H NMR spectroscopy and X-ray crystallography. We have found that Ag^+ is bound to *cone* and *partial-cone* calix[4]arenes, in both cases interacting with the two distal benzene rings. Furthermore, it was shown that bound Ag^+ is effective in suppressing the rate of C_{2v}–C_{2v} interconversion in *cone* calix[4]arenes.



1Me; R = Me
1Pr^n; R = CH_2CH_2Me



2Me; R = Me
2Pr^n; R = CH_2CH_2Me
2Bu(2-Me); R = (*S*)-$CH_2CH(CH_3)CH_2Me$
2Dec^n; R = $(CH_2)_9Me$



3Pr^n; R = CH_2CH_2Me, R′ = CH_2OMe
4Pr^n; R = CH_2CH_2Me, R′ = CH_2Cl

Results and Discussion

Spectral Evidence for C_{2v}–C_{2v} *Interconversion*.—The name 'calixarene' originates from the Greek vase, 'calix crater'.[17] This naming is exactly suited to unmodified calix[*n*]arenes because they have a cup-like molecular shape stabilized by intramolecular hydrogen-bonding interactions among OH groups.[1,2,18] In contrast, this naming is not necessarily suitable for *O*-alkylated calix[*n*]arenes: in tetra-*O*-alkylated calix[4]arenes, for example, they can adopt not only a *cone* conformation but *partial-cone*, 1,2-*alternate* and 1,3-alternate conformations and the most stable conformation is *partial-cone*.[15,19] Computational studies predict that even tetra-*O*-alkylated *cone*-calix[4]arenes do not adopt regular C_{4v} symmetry but C_{2v} symmetry with a 'pinched' conformation.[20] In the ^1H NMR spectra, however, the four phenyl units all appear equivalent.[15,19] Hence, if the computational prediction is correct, it follows that the rate of C_{2v}–C_{2v} interconversion is faster than the NMR timescale. To the best of our knowledge, there exists no concrete spectral evidence that supports C_{2v} symmetry. The sole exceptional example is 5,11,17,23-tetracarboxy-25,26,27,28-tetraoctyloxycalix[4]arene: the ^1H NMR study shows that the C_2-symmetrical conformation with two non-equivalent

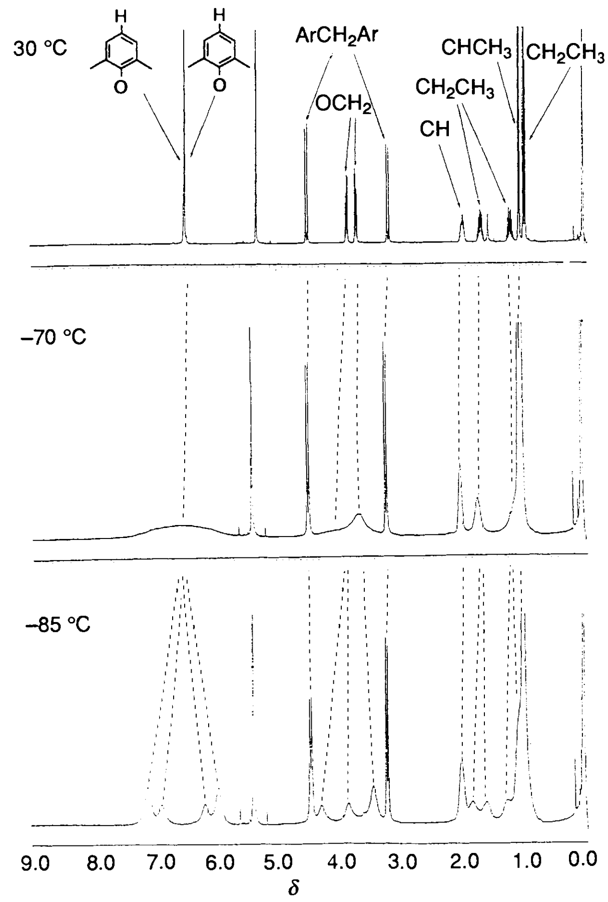


Fig. 1 ^{1}H NMR spectra of *cone*-2Bu(2-Me) in CD_2Cl_2: [*cone*-2Bu(2-Me)] = 1.0 × 10^{-2} mol dm^{-3}

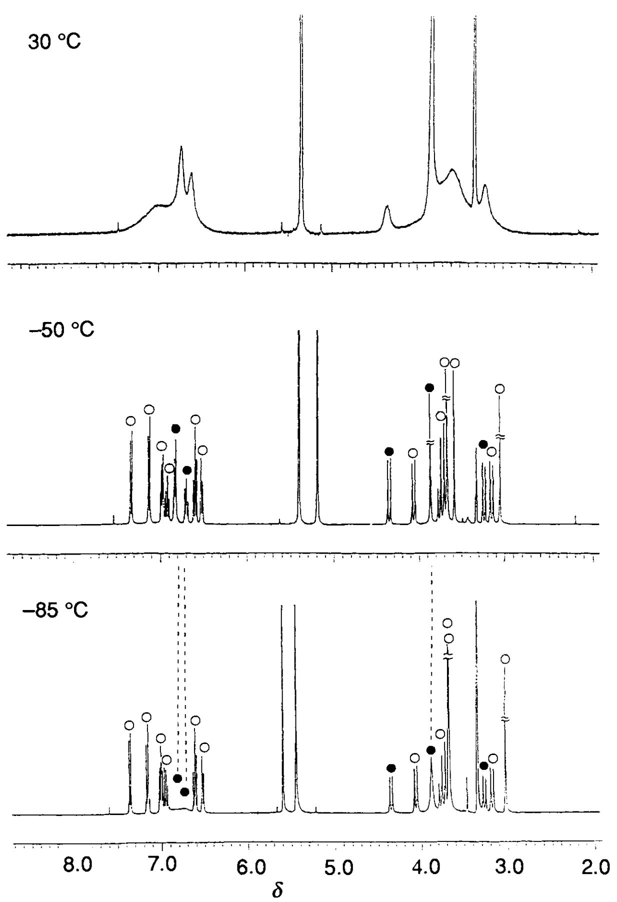


Fig. 2 ^{1}H NMR spectra of **2Me** in CD_2Cl_2:CD_3OD = 4:1 v/v: [**2Me**] = 1.0 × 10^{-2} mol dm^{-3}: ●, *cone*; ○, *partial-cone*

Table 1 Coalescence temperature (T_c) for C_{2v}–C_{2v} interconversion

	T_c/°C	
Calix[4]arene	in CD_2Cl_2	in CD_2Cl_2:CD_3OD = 4:1 v/v
cone-1Pr^n	n.o.[a]	n.o.[a]
cone-2Me	–85[c]	–85[c]
cone-2Pr^n	–85[c]	–85[c]
cone-2Bu(2-Me)	–70	–70
cone-2Dec^n	–50	ppt[b]
cone-3Pr^n	n.o.[a]	n.o.[a]

[a] The peak coalescence was not observed at –85 °C. [b] The precipitate was formed below –30 °C. At –30 °C the peaks were significantly broadened. [c] The peaks coalesced at this temperature.

phenyl units is observable even at 4 °C.[21] In this example, however, the C_{2v}–C_{2v} exchange rate is slow because of the intramolecular hydrogen bonds between the carboxylic acid groups.[21] It is not yet clear, therefore, if conventional tetra-*O*-alkylated *cone*-calix[4]arenes really adopt C_2 symmetry in solution.

To find unequivocal evidence for C_2 symmetry we measured the ^{1}H NMR spectra at room temperature to –85 °C. Fig. 1 shows the temperature-dependent ^{1}H NMR spectra of *cone*-2Bu(2-Me) with four (*S*)-2-methylbutyl groups. At 30 °C the signal for the OCH_2 protons appears as a pair of quartets. This splitting pattern is due to the vicinal coupling with C*H and the geminal coupling in OCH_2. With lowering of the temperature it is gradually broadened and eventually splits into three peaks with an integral intensity ratio of 2:1:1. The coalescence temperature (T_c) is –70 °C. Similarly, the signal for the ArH protons appears as a singlet (*m*-ArH and *p*-ArH are overlapped accidentally) at 30 °C whereas both *m*-ArH and *p*-ArH give two peaks at –85 °C, the integral intensity ratio being 2:1. The results clearly support the view that *cone*-2Bu(2-Me) has C_2 symmetry in which two of the distal phenyl units are upright while the other two distal phenyl units are flattened and they interconvert on the NMR timescale. The similar temperature dependence was observed for *cone*-2Dec^n. Presumably, the rate of C_{2v}–C_{2v} interconversion is suppressed by the steric crowding in *cone*-2Bu(2-Me) and by the interaction of the long Dec^n chains with solvent molecules in *cone*-2Dec^n. To the best of our knowledge, this is the first unequivocal evidence that tetra-*O*-alkylated *cone*-calix[4]arenes adopt C_2 symmetry.

As summarized in Table 1, on the other hand, the essential peaks in *cone*-2Pr^n coalesced at –85 °C. Because of the measurement limitation of the NMR apparatus we could not obtain the data below –85 °C, so one must regard T_c as being below –85 °C. The coalescence of the peaks ascertains, however, that *cone*-2Pr^n also adopts C_2 symmetry. Neither peak broadening nor peak coalescence was observed for *cone*-1Pr^n and *cone*-3Pr^n which have Bu^t and CH_2OMe, respectively, at the *para* positions. This means that their T_c values (if they exist) are lower than that for *cone*-2Pr^n having H at the *para* positions.

The temperature dependence of conformationally mobile **2Me** is more complicated but more interesting (Fig. 2). It is known that interconversion among four conformers (*cone*, *partial-cone*, 1,2-*alternate* and 1,3-*alternate*) becomes slower than the NMR timescale at –30 °C and the separated peaks can be assigned to each conformer.[15,19] When the solution temperature was further lowered, only the peaks assignable to *cone*-**2Me** were broadened and coalesced at –85 °C. This implies that among the four conformers only *cone*-**2Me** retains

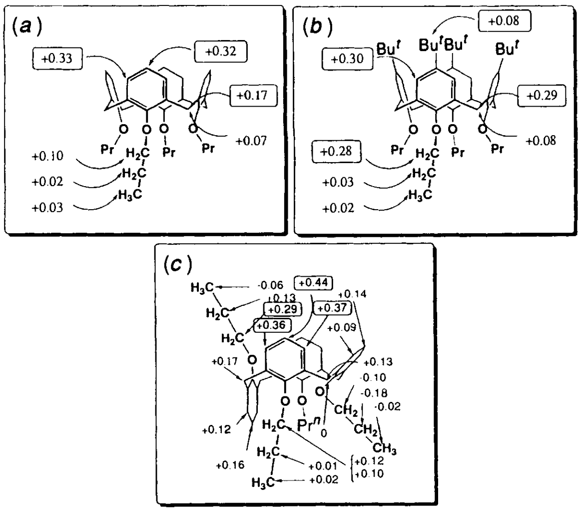


Fig. 3 Chemical shift changes induced by Ag^+ addition in $CDCl_3$:CD_3OD = 4:1 v/v at 25 °C: (calix[4]arene) = 1.0×10^{-2} mol dm^{-3}, [$AgCF_3SO_3$] = 1.0×10^{-1} mol dm^{-3}; + denotes the down-field shift and – denotes the up-field shift

Table 2 Coalescence temperature (T_c) for C_{2v}–C_{2v} interconversion in the presence of Ag^+ in CD_2Cl_2:CD_3OD = 4:1 (v/v)[a]

Complex	T_c/°C
cone-1Pr^n·Ag^+	n.o.[b]
cone-2Pr^n·Ag^+	−60
cone-2Bu(2-Me)·Ag^+	−50
cone-2Dec^n·Ag^+	−40[c]

[a] CD_3OD was used to dissolve $AgCF_3SO_3$: [$AgCF_3SO_3$] = 1.0×10^{-1} mol dm^{-3}, [calix[4]arene] = 1.0×10^{-2} mol dm^{-3}. [b] The peak coalescence was not observed at −85 °C. [c] The complex was partially precipitated at −40 °C.

additional molecular motion, the rate of which crosses the NMR timescale at around −85 °C. It is reasonable to ascribe this motion to C_{2v}–C_{2v} interconversion in the *cone* conformer.

Complexation with Ag^+ *and its Influence on the* T_c *of* C_{2v}–C_{2v} *Interconversion*.—We previously reported that *cone*-2Me can bind Li^+ and Na^+ to the lower rim cavity composed of four oxygens.[16-22] In contrast, such a metal-binding ability was not observed for *cone*-2Pr^n.[12] The difference is related either to the steric crowding or to the apolar environment generated by four Pr^n groups. We here noticed that the ^1H NMR spectra of *cone*-1Pr^n and *cone*-2Pr^n change significantly on addition of Ag^+. This suggests that Ag^+ is bound to somewhere other than the crowded, apolar lower rim cavity. Fig. 3 shows the chemical shift change at room temperature induced by Ag^+ addition. In *cone*-2Pr^n a large down-field shift is observed for *m*-H and *p*-H whereas the shift of the OCH_2 protons is relatively small. The result supports the view that Ag^+ resides in the π-basic upper rim cavity but not in the oxygenic lower rim cavity. In *cone*-1Pr^n, on the other hand, the bulky Bu^t groups obstruct the interaction between Ag^+ and the *para* positions. Under such limited conditions Ag^+ is included deep into the cavity, interacting mainly with the *meta* positions, avoiding the steric crowding of the Bu^t groups. This deep binding mode makes the downfield shift of the OCH_2 protons and the *exo* proton in $ArCH_2Ar$ larger than those in *cone*-2Pr^n.

Here, it is interesting to estimate whether Ag^+ bound to the π-basic upper rim cavity influences the rate of C_{2v}–C_{2v} interconversion (Table 2). We have already observed that in the presence of metal cations the ^1H NMR peaks are broadened not only by the intramolecular metal exchange but also by the intermolecular metal exchange (*i.e.*, complexation–decomplexation).[12] In order to avoid the line-broadening effect arising from the intermolecular Ag^+ exchange we added Ag^+ ([$AgCF_3SO_3$] = 1.0×10^{-1} mol dm^{-3}) in large excess over the calix[4]arene (1.0×10^{-2} mol dm^{-3}) and measured the ^1H NMR spectra at 30 to −85 °C. At 30 °C the proton signals of *cone*-2Pr^n·Ag^+ appear as if the four phenyl units are all equivalent (Fig. 4). With lowering of the solution temperature the peaks are broadened and coalesced at −60 °C. At −85 °C the ArH protons and the OCH_2 protons are split into a pair, two peaks for Ag^+-complexed phenyl units and two peaks for uncomplexed phenyl units. Since T_c for *cone*-2Pr^n is −85 °C (or lower than −85 °C: see Table 1), the result implies that bound Ag^+ suppresses the rate of C_{2v}–C_{2v} interconversion. As demonstrated later by the X-ray crystallographic studies, Ag^+ is sandwiched by the two distal phenyl units. Thus, the exchange process observed by ^1H NMR spectroscopy is shown as in Fig. 5: that is, C_{2v}–C_{2v} interconversion in the presence of Ag^+ accompanies the π-bond formation/scission reaction.

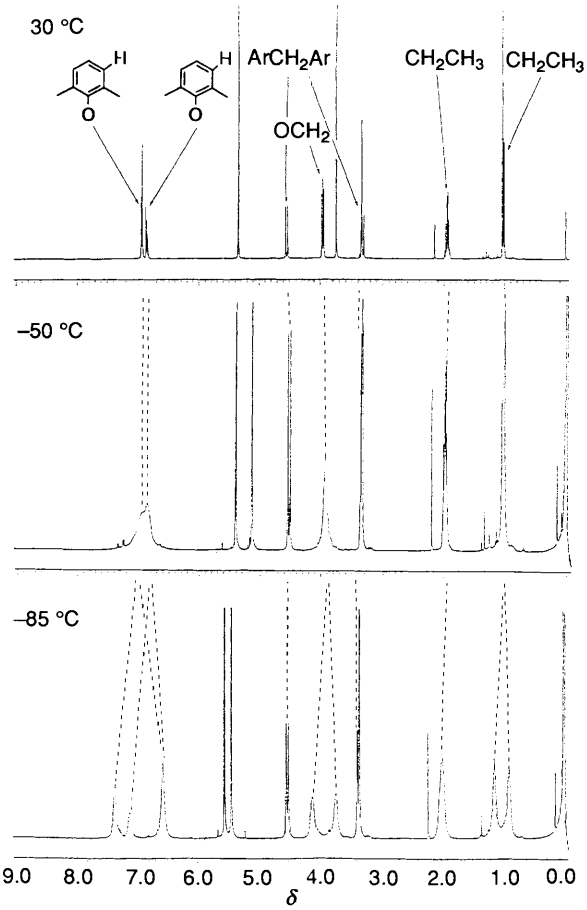


Fig. 4 ^1H NMR spectra of *cone*-2Pr^n·Ag^+ in CD_2Cl_2:CD_3OD = 4:1 v/v: [*cone*-2Pr^n] = 1.0×10^{-2} mol dm^{-3}, [$AgCF_3SO_3$] = 1.0×10^{-1} mol dm^{-3}

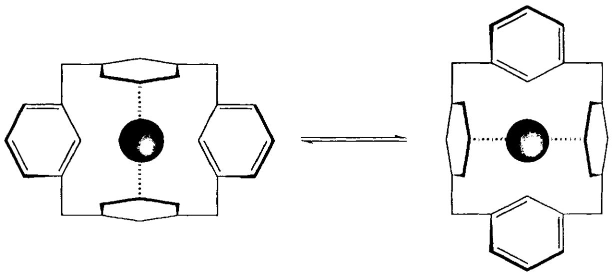


Fig. 5 C_{2v}–C_{2v} interconversion in cone-calix[4]arene·Ag^+ complexes which accompanies the π-bond formation/scission

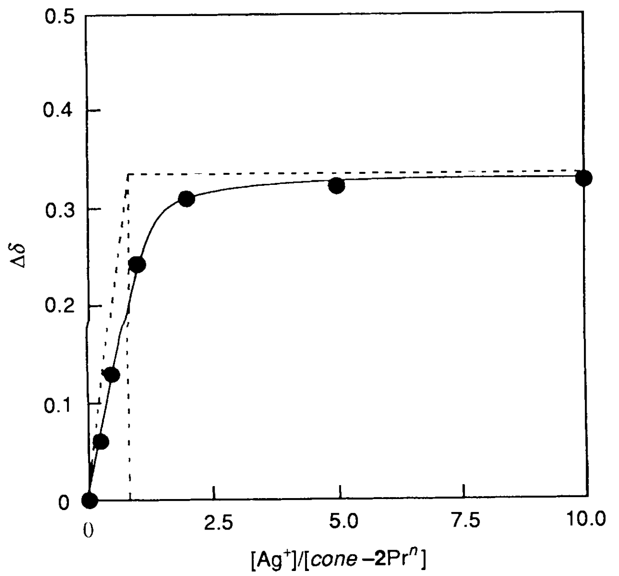


Fig. 6 Plot of $\Delta\delta$ *vs.* [Ag$^+$]/[*cone*-**2**Pr^n]: 25 °C, $CDCl_3$: CD_3OD = 4:1 v/v. In this plot δ for *p*-H was monitored

A similar T_c increase was also observed for *cone*-**2**Bu(2-Me) and *cone*-**2**Dec^n (Table 2). However, peak coalescence was not observed for *cone*-**1**Pr^n even in the presence of an excess of Ag$^+$. The interaction with Ag$^+$ may be weak because of the bulky Bu^t groups. In conformationally mobile **2**Me *partial-cone* was the sole conformer recognizable as the Ag$^+$ complex. This means that the *partial-cone* can form a more stable π-complex than the *cone*. This problem will be discussed again later in relation to the X-ray analysis of the Ag$^+$ complexes. In the *cone*-**2**Bu(2-Me)·Ag$^+$ complex the peak separation arising from C_{2v}–C_{2v} interconversion occurs clearly at −85 °C. One can thus estimate the interconversion rate at T_c (= −50 °C):[23] k = 465 s^{-1} and $\Delta G^\ddagger$ = 10.4 kcal mol^{-1}. Since the $\Delta G^\ddagger$ values for *cone*–*cone* interconversion are 14.3–16.4 kcal mol^{-1},[24] the wobble motion for C_{2v}–C_{2v} conversion can take place much more easily than the ring inversion motion.

Determination of Association Constants (K_{ass}).—In ^{1}H NMR spectra (400 MHz; CD_2Cl_2–CD_3OD = 4:1 v/v) at room temperature *cone*-**2**Pr^n·Ag$^+$ and *partial-cone*-**2**Pr^n·Ag$^+$ did not give the signals for the complexes separated from those for free *cone*-**2**Pr^n and *partial-cone*-**2**Pr^n but simply induced a change in the chemical shift. This indicates that the rate of Ag$^+$ complexation/decomplexation is faster than the NMR time-scale. We thus determined the K_{ass} from plots of $\Delta\delta$ *vs.* [Ag$^+$] where the calix[4]arene concentration (1.0 × 10^{-2} mol dm^{-3}) was maintained constant while the Ag$^+$ concentration (0 to 1.0 × 10^{-1} mol dm^{-3}) was varied. A typical plot is shown in Fig. 6. It is clearly seen from Fig. 6 that a 1:1 complex is formed with Ag$^+$. The log K_{ass} values determined by non-linear least-squares computation[25] are 2.66 for *cone*-**1**Pr^n·Ag$^+$, 2.96 for *cone*-**2**Pr^n·Ag$^+$ and 3.28 for *partial-cone*-**2**Pr^n·Ag$^+$. The results indicate that as expected from the conformational isomerism data for **2**Me·Ag$^+$, *partial-cone*-**2**Pr^n gives a K_{ass} value greater than that of *cone*-**2**Pr^n. On the other hand, K_{ass} for *cone*-**1**Pr^n·Ag$^+$ is smaller than that for *cone*-**2**Pr^n·Ag$^+$ but the difference is small. The result implies that although the upper rim of *cone*-**1**Pr^n is crowded with four Bu^t groups, Ag$^+$ can still find a binding-site which is not hampered by this steric crowding.

X-Ray Crystallographic Studies.—The ultimate evidence for π-base participation in the binding of Ag$^+$ to calix[4]arenes was obtained from the X-ray crystallographic data. Single crystals of *cone*-**2**Pr^n·$AgCF_3SO_3$ and *partial-cone*-**2**Pr^n·$AgCF_3SO_3$ were prepared by recrystallization from acetone. We also attempted to grow a single crystal of 1,3-*alternate*-**2**Pr^n·$AgCF_3SO_3$ but it afforded only a powder. The *cone* and *partial-cone* crystals were successfully analysed by X-ray diffraction. The crystal data for *cone*-**2**Pr^n·$AgCF_3SO_3$ and *partial-cone*-**2**Pr^n·$AgCF_3SO_3$ are summarized in Table 3. The positional parameters, bond lengths and bond angles for *cone*-**2**Pr^n·$AgCF_3SO_3$ and *partial-cone*-**2**Pr^n·$AgCF_3SO_3$* have been deposited at the Cambridge Crystallographic Data Centre. Corresponding ORTEP drawings are illustrated in Figs. 7 and 8. The distances from Ag$^+$ to four *para* carbons and four oxygens are summarized in Table 4.

Examination of these drawings raises a number of intriguing points which are characteristic of calix[4]arene·Ag$^+$ complexes. In *cone*-**2**Pr^n·$AgCF_3SO_3$ (Fig. 7), the Ag$^+$ ion is included in the π-basic benzene cavity at the upper rim but not in the oxygen cavity at the lower rim. The four benzene rings are arranged in C_2 symmetry, the two distal benzene rings being flattened and the residual two benzene rings standing upright. The Ag$^+$ ion is sandwiched by the *para* carbons in the upright benzene rings. This is the first novel example of inclusion of metal cations in the calix[*n*]arene cavity.[26] The distances between the *para* carbons and Ag$^+$ are 2.39 Å [for C(4)–Ag$^+$] and 2.40 Å [for C(18)–Ag$^+$]. The distances are shorter than the sum of the half-width of the benzene π-electron cloud and the ionic radius of Ag$^+$ (2.86 Å) and comparable to or slightly shorter than those reported for π-prismands and deltaphanes.[27–29] On the other hand, the distances between the oxygen atoms and Ag$^+$ are 4.12 Å [for O(2)–Ag$^+$] and 4.28 Å [for O(4)–Ag$^+$]. The distances are much longer than the sum of the oxygen atomic radius and the Ag$^+$ radius (2.78 Å). These results allow us to conclude that Ag$^+$ ion is included in the *cone*-calix[4]arene cavity only with the aid of a cation–π interaction.

In *partial-cone*-**2**Pr^n·Ag$^+$ (Fig.8), the Ag$^+$ ion is sandwiched by the two *para* carbons in the distal benzene rings. The distances between the *para* carbons and Ag$^+$ are 2.40 Å [for C(4)–Ag$^+$] and 2.41 Å [for C(18)–Ag$^+$]. These values are comparable to those observed for *cone*-**2**Pr^n·Ag$^+$. On the other hand, the distance from Ag$^+$ to the *para* carbon in the phenyl unit distal to the inverted phenyl unit is 5.63 Å. This value is too large for the π-donor participation. The distance from Ag$^+$ to the phenolic oxygen in the inverted phenyl unit is 2.94 Å. This value is comparable to the sum of the ionic radius of Ag$^+$ and O (2.78 Å). However, the distances to the other oxygens (4.24–5.15 Å) are all too long to consider electrostatic interactions. These X-ray data clearly establish that the Ag$^+$ is trapped in the upper rim of *partial-cone*-**2**Pr^n through a cation–π interaction with two benzene rings and an electrostatic interaction with one phenolic oxygen.

In Table 5 we compare the dihedral angles between each phenyl units and the mean plane of the four $ArCH_2Ar$ methylene units obtained by the present X-ray crystallographic studies with those estimated for **2**Me conformers by computational (MM3) studies.[20b] Although it is more reasonable to use X-ray crystallographic data for **2**Me or **2**Pr^n conformers for comparison,[20a,30] concrete data for the dihedral angles are not available to us. Since the basic calix[4]arene skeletons for each conformer are very similar to each other,[15,20,30] we used computational data which are now in our hands.[20b] In *cone*-**2**Pr^n·Ag$^+$ the two flattened phenyl units (dihedral angle, θ = 38.2 and 36.6°) are more flattened than those in *cone*-**2**Me (θ = 44.5°) whereas the two upright phenyl units (θ =

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* The X-ray analysis of *partial-cone*-**2**Pr^n·$AgCF_3SO_3$ has been reported in part previously.[12]

Table 3 Summary of data collection, structure solution and refinement details

	cone-2Pr^n·AgCF$_3$SO$_3$	*partial-cone*-2Pr^n·AgCF$_3$SO$_3$
Crystal data		
Empirical formula	$C_{41}H_{48}AgF_3O_7S$	$C_{41}H_{48}AgF_3O_7S$
M	849.76	849.76
Colour, habit	Colourless, prism	Colourless, prism
Crystal size/mm	0.20 × 0.20 × 0.20	0.45 × 0.4 × 0.3
Crystal system	Monoclinic	Monoclinic
a/Å	18.714(1)	17.902(2)
b/Å	13.4398(8)	13.485(1)
c/Å	16.4402(8)	16.592(2)
β/°	102.991(4)	99.942(8)
V/Å^3	4030.9(4)	3945.8(7)
Space group	$P2_1/n$	$P2_1/n$
Z	4	4
d_{calc}/g cm^{-3}	1.400	1.430
μ/cm^{-1}	50.6	51.7
Data collection		
Diffractometer	Enraf–Nonius CAD4 Fr 586	Enraf–Nonius CAD4 Fr 586
Radiation	Cu-Kα (λ = 1.541 84 Å)	Cu-Kα (λ = 1.541 84 Å)
T/°C	22	25
Scan mode	ω–2θ	ω–2θ
θ range/°	2–65	2–65
Refl. measured	7081	6973
Unique refl.	6567	6152
Refl. used	4312[a]	4408[a]
Structure solution and refinement		
R	0.0672	0.093
R_w	0.0995	0.127
Max. residual peak/e Å^{-3}	0.707	1.04

[a] $I_o > 3\sigma(I_o)$.

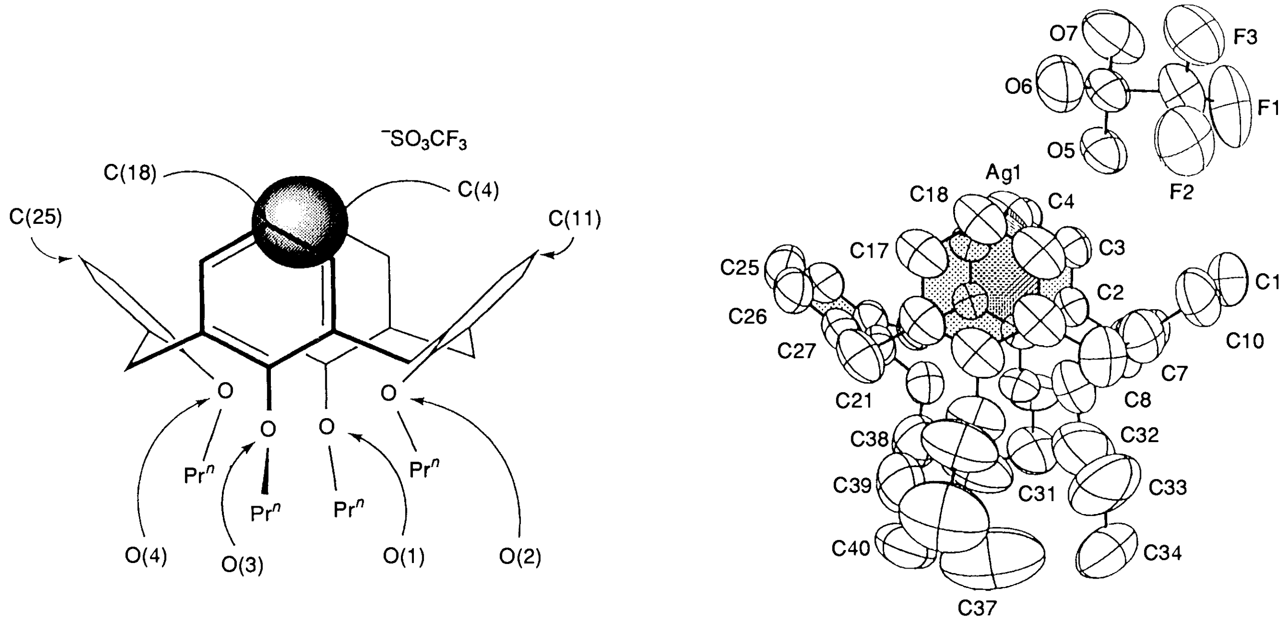


Fig. 7 X-Ray structure of the *cone*-2Pr^n·AgCF$_3$SO$_3$ complex

96.5 and 95.7°) stand up more than those in *cone*-**2**Me (θ = 88.3°). Since Ag$^+$ is sandwiched by the two standing phenyl units, the change implies that the *para* carbons in these phenyl units must get closer to interact with Ag$^+$. This inevitably induces flattening of the two residual phenyl units. In *partial-cone*-**2**Pr^n, in contrast, the θ values for the Ag$^+$ complex are surprisingly close to those for free *partial-cone*-**2**Pr^n. The differences are only 1.2–2.8°. This means that *partial-cone*-**2**Pr^n possesses an Ag$^+$ binding site composed of two phenyl units, the distance of which is perfectly adjusted to the size of Ag$^+$. As mentioned above, when Ag$^+$ is added to the conformationally mobile **2**Me in solution, the conformers are all isomerized to *partial-cone*-**2**Pr^n·Ag$^+$. Furthermore, K_{ass} for *partial-cone*-**2**Pr^n·Ag$^+$ is greater than *cone*-**2**Pr^n·Ag$^+$. The results can be rationalized such that *partial-cone*-**2**R·Ag$^+$ complexes are more stable than *cone*-**2**R·Ag$^+$ complexes because of *ideal preorganization* of the two distal phenyl units.

Conclusions

The original purpose of the present study was the X-ray analysis of **2**R·Ag$^+$ complexes. It was shown that both *cone*-**2**Pr^n and

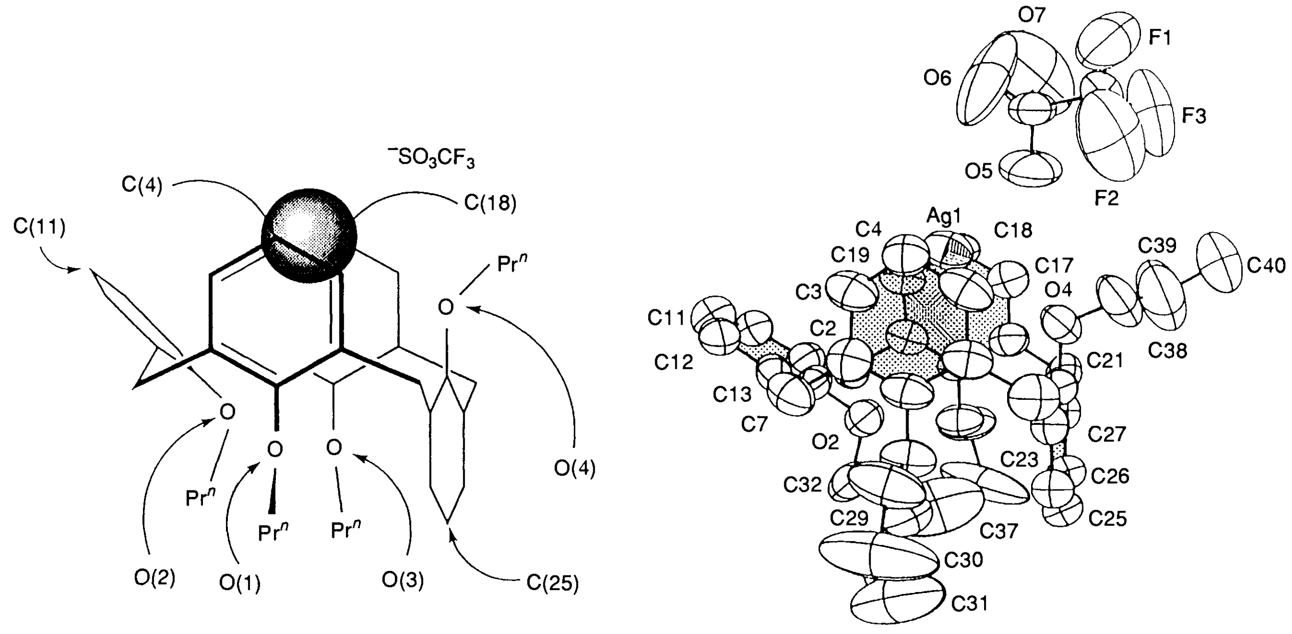


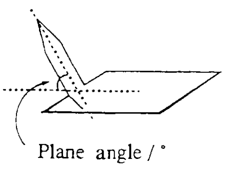
Fig. 8 X-Ray structure of the *partial-cone*-2Pr^n·AgCF$_3$SO$_3$ complex

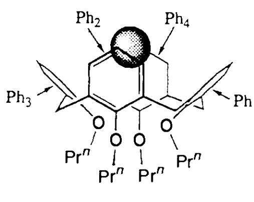
Table 4 Selected bond distances (Å)

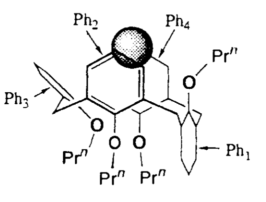
	cone-2Pr^n·AgCF$_3$SO$_3$	*partial-cone*-2Pr^n·AgCF$_3$SO$_3$
Ag–C(4)	2.39	2.40
Ag–C(11)	5.03	5.63
Ag–C(18)	2.40	2.41
Ag–C(25)	5.23	6.23
Ag–O(1)	5.12	5.15
Ag–O(2)	4.12	4.24
Ag–O(3)	5.12	5.12
Ag–O(4)	4.28	2.94

Table 5 Geometries of X-ray and MM3 optimized structures

	cone-2Pr^n·AgCF$_3$SO$_3$	*cone*-2Me	*partial-cone*-2Pr^n·AgCF$_3$SO$_3$	*partial-cone*-2Me
	X-Ray	MM3	X-Ray	MM3
Plane angle/°				
Ph$_1$	38.2	44.5	−91.2	−94.0
Ph$_2$	96.5	83.3	96.4	94.5
Ph$_3$	36.6	44.5	31.3	32.5
Ph$_4$	95.7	83.3	96.9	94.5







partial-cone-**2**Pr^n bind Ag^+ with the aid of cation–π interactions. In particular, the *cone*-**2**Pr^n·Ag^+ complex is the first example of inclusion of a metal cation in the calix[4]arene π-base cavity.[26] ^1H NMR spectroscopic data showed that in solution Ag^+ is also bound to the same site as that in the solid state. Furthermore, the finding that *partial-cone*-**2**R·Ag^+ complexes are particularly stable in solution is in good accord with the fact that, in the solid state, the two distal benzene rings in *partial-cone*-**2**Pr^n are perfectly preorganized for Ag^+-binding. These novel results were obtained because one can easily prepare the π-basic cavities with the different sizes and the different shapes from calix[4]arenes. We believe that the data obtained herein are indispensable for further comprehension of the nature of π-base participation and cation–π interactions in the metal binding processes which are increasingly considered to play important roles in biological systems such as acetylcholine receptors,[31] K^+ ion channels,[32] *etc.*

Experimental

Miscellaneous.—^1H NMR spectra were measured with a JEOL JNM-GSX-400 NMR spectrometer.

Materials.—Preparations of the following compounds have been described: *cone*-**1**Pr^n,[15] *partial-cone*-**1**Pr^n,[15] **2**Me,[15] *cone*-**2**Pr^n,[33] *partial-cone*-**2**Pr^n [34] and *cone*-**2**Bu(2-Me).[35]

25,26,27,28-*Tetradecyloxycalix*[4]*arene* (*cone*-**2**Dec^n).—Calix[4]arene-25,26,27,28-tetraol (0.50 g, 1.18 mmol) was dissolved in DMF (50 cm^3) and treated with oil-dispersed NaH (net 60%; 0.94 g, 23.6 mmol) at 5 °C under a nitrogen stream. After the addition of 1-bromodecane (10.42 g, 47.1 mmol), the reaction mixture was stirred at 5 °C for 5 h. Unchanged NaH was decomposed by the addition of methanol. The mixture was diluted with aqueous 1 mol dm^{-3} HCl and the solution was extracted with chloroform. The chloroform layer was separated, washed three times with water and dried over $MgSO_4$. The solution was evaporated to dryness and the residue was recrystallized from chloroform–methanol; m.p. 66.5–67.5 °C, yield 88%; ν_{max}(Nujol)/cm^{-1} no ν_{OH}; δ_H($CDCl_3$; 30 °C) 0.88 [3 H, t, $CH_3(CH_2)_7CH_2CH_2$], 1.18–1.36 [14 H, m, $CH_3(CH_2)_7CH_2CH_2$], 1.82–1.93 [2 H, m, $CH_3(CH_2)_7CH_2CH_2$], 3.14 and 4.44 (each 1 H, each d, $ArCH_2Ar$), 3.87 [2 H, t, $CH_3(CH_2)_7CH_2CH_2$], 6.47–6.60 (3 H, m, ArH) (Found: C, 82.95; H, 10.65. Calc. for $C_{68}H_{104}O_4$: C, 82.87; H, 10.64%).

5,11,17,23-*Tetrakis*(*methoxymethyl*)-25,26,27,28-*tetrapropoxycalix*[4]*arene* (*cone*-**3**Pr^n).—5,11,17,23-Tetrakis(chloromethyl)-25,26,27,28-tetrapropoxycalix[4]arene (*cone*-**4**Pr^n)[36] (0.40 g, 0.51 mmol) and oil-dispersed NaH (net 60%; 0.33 g, 8.14 mmol) were suspended in DMF (30 cm^3) and methanol (15 cm^3) under a nitrogen stream. The reaction mixture was heated at 60 °C for 24 h under a nitrogen stream. After cooling, unchanged NaH was decomposed by the addition of methanol. The mixture was diluted with aqueous 1 mol dm^{-3} HCl and extracted with chloroform. The chloroform layer was separated, washed three times with water and dried over $MgSO_4$. The solution was evaporated to dryness and the residue was subjected to a column chromatography separation (silica gel; chloroform); m.p. 137.0–139.0 °C, yield 61%; δ_H($CDCl_3$; 30 °C) 0.98 (3 H, t, $CH_3CH_2CH_2$), 1.82–1.99 (2 H, m, $CH_3CH_2CH_2$), 3.13 and 4.42 (each 1 H, each d, $ArCH_2Ar$), 3.32 (3 H, s, CH_3O), 3.82 (2 H, t, $CH_3CH_2CH_2$), 4.09 (2 H, s, $ArCH_2O$) and 6.61 (2 H, s, ArH) (Found: C, 74.95; H, 8.4. Calc. for $C_{48}H_{64}O_8$: C, 74.97; H, 8.39%).

X-Ray Crystal Structure Determination of cone-**2**Pr·$ArCF_3SO_3$ *and partial-cone*-**2**Pr·$AgCF_3SO_3$.—Colourless crystals were obtained by recrystallization from acetone. The crystal structures were determined by X-ray diffraction. Reflections were measured at 22 °C in the ω–2θ scan mode [$2 < \theta/\text{deg} < 65$], using Cu-Kα radiation (λ = 1.541 84 Å). The structures were solved by direct methods[37] and refined by the full-matrix least-squares methods. The *R* factors were R = 6.7% and R_w = 10.0% for *cone*-**2**Pr^n·$AgCF_3SO_3$ and R = 9.3% and R_w = 12.7% for *partial-cone*-**2**Pr^n·$AgCF_3SO_3$. All calculations were performed with MolEN.[38]

Determination of Association Constants (K_{ass}).—Association constants were determined by non-linear least-squares computation of $\Delta\delta$ *vs.* [Ag^+] plots. Details of the method have been described previously.[25]

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Paper 4/03440F
Received 7*th June* 1994
Accepted 27*th June* 1994