^1H and ^{13}C Nuclear Magnetic Resonance Relaxation-time Studies of Ionophoric Calixarene Esters†

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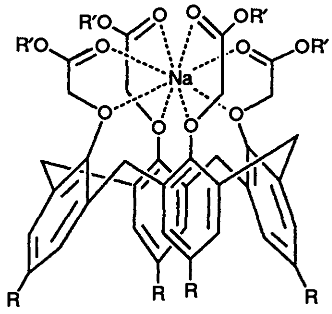
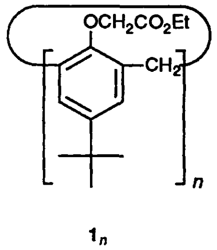
^1H and ^{13}C NMR relaxation times (T_1) of ethoxycarbonylmethyl derivatives of *p*-t-butylcalix[*n*]arenes have been determined at 90 MHz and 36 °C in [$^2H_8$]THF. It was found that these calixarenes feature a 'seesaw motion' around the $ArCH_2Ar$ linkage as a central support and that this molecular motion is largely suppressed through complexation with Na^+.

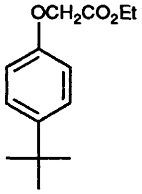
Calixarenes are cyclic oligomers made up of phenol units just as cyclodextrins are made up of glucose units. Although these two classes of oligomeric macrocycles have a similar cavity-shaped architecture, there exists a basic difference: the cyclodextrin cavity is conformationally fixed, whereas the conformational freedom still remains in the calixarene cavity.[1–6] In order to understand the essential difference between cyclodextrins and calixarenes as host molecules, it is of great significance to assess the conformational properties characteristic of calixarene cavities. Among NMR spectroscopic methods, dynamic NMR studies and NMR relaxation-time studies would provide useful information about the conformational properties. Dynamic NMR studies have frequently been used to estimate the rate of ring inversion.[1–4,7,8] In contrast, NMR relaxation-time studies have been very limited. To the best of our knowledge, there exists only one precedent, which deals with ^1H NMR relaxation times of t-butylamine complexed with calixarenes (but not those of calixarenes themselves).[9] In this paper, we report systematic studies on ^1H and ^{13}C NMR relaxation times (T_1) of ionophoric calix[*n*]arene esters (**1**$_n$; n = 4, 6 and 8). The main purpose of this study was to understand how the molecular segments composing the calixarene cavity change upon inclusion of Na^+. 4-(Ethoxycarbonylmethoxy)-t-butylbenzene **2** and 4-(ethoxycarbonylmethoxy)-3,5-dimethyl-t-butylbenzene **3** were used as reference compounds.



1$_4$-Na^+ Complex



1$_n$



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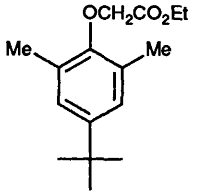

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Experimental

The synthesis of compounds **1**$_n$ was described previously.[10]

T$_1$ *Measurements.*—The T_1-values were obtained in perdeuteriotetrahydrofuran([$^2H_8$]THF) at 36 °C under nitrogen by using an inversion recovery method.[11,12] The apparatus used here was a Hitachi R-90H spectrometer (90.0 MHz for protons and 22.6 MHz for carbons). NMR samples (0.5 cm^3 of [$^2H_8$]THF solution) were prepared in 5 mm o.d. tubes, which were sealed under vacuum after degassing by five freeze–pump–thaw cycles. All glassware was washed with 0.01 mol dm^{-3} ethylenediaminetetraacetic acid (EDTA) solution to remove paramagnetic impurities.

Fig. 1 shows typical results for the inversion recovery method in ^{13}C NMR spectroscopy. The ^{13}C nucleus used here is carbon i in **1**$_4$ (*o*-position in the phenyl ring: for the assignment, see Results and Discussion section). It can be seen from Fig. 1 that the signal strength is inverted between 2.5 and 5 s, indicating the T_1-value for carbon i to be *ca.* 4 s. A plot of ln $\Delta H (= H_0 - H)$ *vs.* interval time is shown in Fig. 2 where H_0 is the signal strength at 50 s and H is that at t s. The slope ($= -T_1^{-1}$) was computed by the least-squares method: we thus obtained a value for T_1 of 4.29 s for carbon i. The treatment described above was repeated at least four times for each carbon. The T_1-values for such carbons that show strong peak intensity and the chemical shift fully separated from others are reproducible within the 10% relative standard deviation: the carbons are carbons b, d and f–j. On the other hand, when the peak was weak or overlapped by other peaks, the reproducibility was inferior: the relative standard deviations are 15% for carbons a and c, 25% for carbon e, and 20% for carbon k.

The T_1-values for protons showed good reproducibility (within the 10% relative standard deviation) except for protons b and e: their signals overlapped and the reproducibility was inferior (within only 15% relative standard deviation).

Further details of the measurement method were described previously.[12] The chemical shifts recorded in Tables 1 and 3 were those obtained on a 90 MHz NMR spectrometer. When the peaks overlapped, the assignment was effected with the aid of a 400 MHz NMR spectrometer.

Results and Discussion

^1H *NMR Relaxation Times.*—The chemical shifts and relaxation times of protons in species **1**$_n$ are summarized in

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† Preliminary communication: see ref. 19.

Table 1 Chemical shifts (δ) of protons in calixarenes 1_n, their Na$^+$ complexes and reference compounds[a]

	δ							
Proton	1_4	1^4·Na$^+$	1_6	1_6·Na$^+$	1_8	1_8·Na$^+$	**2**	**3**
a	1.26	1.36	1.20	1.00	0.97	0.98	1.21	1.27
b	4.17	4.36	4.16	3.97	3.94	3.97	4.16	4.18
c	4.78	4.57	4.49	4.20	4.12	4.22	4.55	4.34
d	1.09	1.16	1.02	1.12	1.13	1.13	1.27	1.12
e(*exo*)	3.14	3.42						
			4.05	4.06	4.08	4.05	(6.75)[c]	2.52[d]
e(*endo*)	4.94	4.40						
f	6.81	7.23	7.03	7.00	7.01	7.02	7.25	6.99
Picrate[b]		8.63		8.69		8.73		

[a] 36 °C, [$^2H_8$]THF, internal standard SiMe$_4$, [1_n] 0.10 mol dm^{-3}, [alkali picrate] 0.12 mol dm^{-3}. Under these conditions, species 1_n totally exist as their Na$^+$ complexes.[10] [b] δ 8.74 in the absence of calixarenes. [c] ArH at *o*-position to the ester side-chain. [d] 2,6-Dimethyl groups.

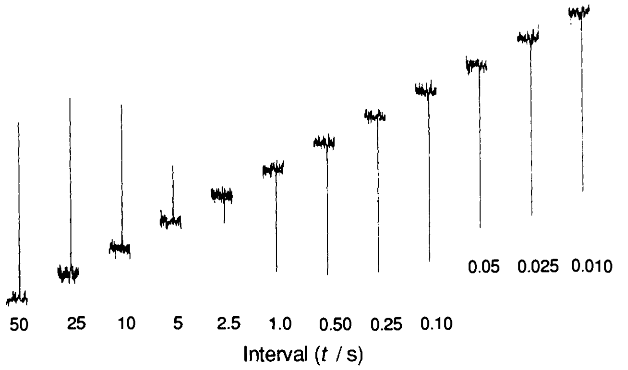


Fig. 1 Peak height of carbon i as a function of the interval time (90 MHz; [$^2H_8$]THF; 36 °C)

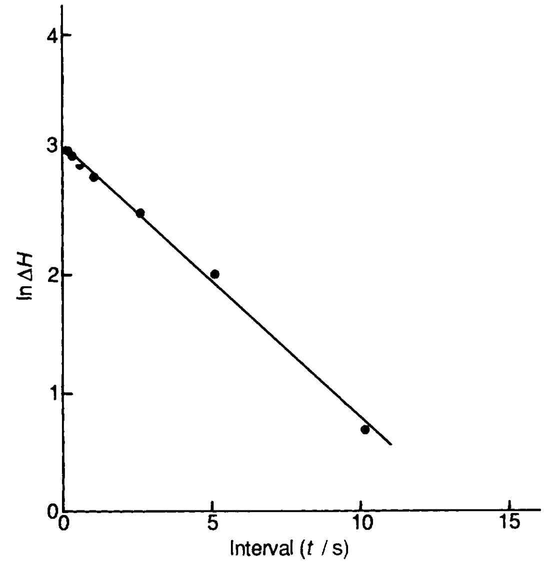
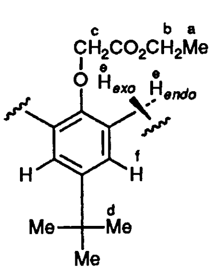


Fig. 2 Plot of ln Δ*H* *vs.* interval time. The data in Fig. 1 are used.

Tables 1 and 2, respectively. The protons are lettered as shown below.



As recorded in Table 1, 1_4 shows a pair of doublets for the ArC*H*$_2$Ar protons and this split pattern was not affected by the measurement temperature. This indicates that species 1_4 adopts a cone conformation and the oxygen-through-the-annulus rotation is inhibited by the CH$_2$CO$_2$Et groups. On the other hand, species 1_6 and 1_8 show a sharp singlet for the ArC*H*$_2$Ar protons. This indicates that the rotation is still allowed in these large calixarene rings.

The δ-values for protons a, b and c shift to higher magnetic field on going from 1_4 to 1_8 and the δ-values for species 1_4 are comparable to those for compounds **2** and **3**. In contrast, the δ-values for aromatic proton f shift to lower magnetic field on going from 1_4 to 1_8 and the δ-values for species 1_6 and 1_8 are comparable to those of compounds **2** and **3**. As mentioned above, species 1_4 adopts a cone conformation and is conformationally immobile. Thus, the EtO$_2$CCH$_2$ moiety in species 1_4 cannot be affected by the ring current of the benzene moiety whereas proton f is always affected by the ring current. This is why protons a, b and c in species 1_4 are 'normal' (*i.e.*, comparable to reference compounds) whereas the δ-value for proton f unusually shifts to higher magnetic field. In species 1_6 and 1_8 the oxygen-through-the-annulus rotation of the phenyl units is still allowed. Thus, not only the δ-values for protons a, b and c but also that for proton f shift to higher magnetic field (although to a smaller extent).

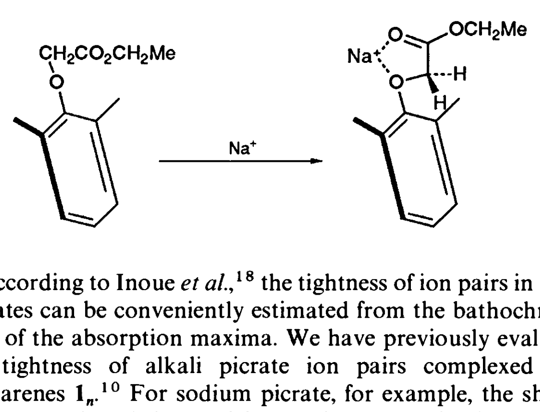
It is known that calixarenes 1_n can bind Na$^+$ through interactions with two oxygens in the OCH$_2$CO moiety.[10,13–16] The association constants (*K*) in THF are estimated to be $\log K = 3.95$ for 1_4, 3.15 for 1_6 and 2.61 for 1_8.[10] Hence, we consider that compounds 1_n exist totally as Na$^+$ complexes under the measurement conditions (see footnote *a* to Table 1). The large association constant observed for species 1_4 is rationalized in terms of the fitness between the ionophoric cavity and the ionic size of Na$^+$. In addition, the structure preorganized to the cone conformation may also be important. In species 1_4, the δ-values in the presence of Na$^+$ generally shift to lower magnetic field, which effect is attributed to the electron-withdrawing nature of Na$^+$. There are two exceptions, however: (i) the OCH$_2$CO protons shift to higher magnetic field by 0.21 ppm and (ii) the difference in δ-values between H_{exo} and H_{endo} becomes smaller (1.80 ppm in the absence of Na$^+$; 0.98 ppm in the presence of Na$^+$). As illustrated below, the OCH$_2$CO protons are forced to be located on the benzene ring when the two oxygens co-ordinate to Na$^+$. Thus, these protons undergo a ring current effect which causes the upfield shift. Change (ii) implies that when species 1_4 complexes with Na$^+$, H_{exo} is less shielded whereas H_{endo} is more shielded. According to X-ray crystallographic studies by Arduini *et al.*,[17]

Table 2 Relaxation times (T_1) of protons in calixarenes $\mathbf{1}_n$, their Na^+ complexes, and reference compounds[a]

	T_1/s							
Proton	$\mathbf{1}_4$	$\mathbf{1}_4 \cdot Na^+$	$\mathbf{1}_6$	$\mathbf{1}_6 \cdot Na^+$	$\mathbf{1}_8$	$\mathbf{1}_8 \cdot Na^+$	**2**	**3**
a	2.51	0.50	1.44	0.64	0.78	0.74	4.12	5.67
b	1.17	*b*	0.75	*b*	0.43	0.38	4.30	5.25
c	0.36	0.23	0.20	0.13	0.16	0.14	2.43	4.12
d	0.73	0.54	0.64	0.56	0.48	0.49	2.23	2.71
e	0.17	0.15[c]	0.19	*b*	0.12	0.09	(4.06)[d]	3.70
f	0.67	0.31	0.41	0.35	0.37	0.32	4.01	5.02
Picrate[e]		6.75		7.82		9.78		

[a] Measurement conditions are given in footnote *a* to Table 1. [b] The T_1-value could not be determined because of the overlap of signals from H^b and H^e. [c] The T_1 for H_{exo}. The peaks for H_{endo} overlapped with those for H^b. [d] The T_1 for ArH at *o*-position to the ester side-chain. [e] T_1 9.15 s in the absence of calixarenes.

25,26,27,28-tetrakis-(*N,N*-diethylaminocarbonyl)methoxy-*p*-t-butylcalix[4]arene (which has a structure similar to that of species $\mathbf{1}_4$) adopts C_{2v} symmetry whereas its Na^+ complex adopts C_{4v} symmetry. This change from lower symmetry to higher symmetry induces the shift of the $ArCH_2Ar$ protons leading to change (ii). In calix[4]arenes with C_{2v} symmetry two confronting phenol units are more or less coplanar while the other two confronting phenol units are parallel to each other.[17] This 'flattening' effect in the absence of Na^+ causes the rotation of the $ArCH_2Ar$ linkage so that H_{endo} is placed in the plane of the aromatic rings while H_{exo} is placed above the aromatic rings. It is known that $\Delta\delta$ between H_{exo} and H_{endo} in calix[4]arenes serves as a measure of the 'flattening': $\Delta\delta$ is generally ~0.9 ppm for a system in the cone conformation and in the 'flattened' conformation, $\Delta\delta$ is significantly decreased.[3] The $\Delta\delta$-value for species $\mathbf{1}_4$ (1.8 ppm) is twice that for the typical cone conformation. This means that phenol units in species $\mathbf{1}_4$ are more parallel because of steric crowding among the ester groups on the narrow, lower rim. The decrease of $\Delta\delta$-values upon binding to Na^+ implies the occurrence of 'flattening' of four phenol units which interact with Na^+. In comparison to species $\mathbf{1}_4$, the δ-values for calixarenes $\mathbf{1}_6$ and $\mathbf{1}_8$ were less affected by Na^+. In particular, the shifts observed for species $\mathbf{1}_8$ were relatively small. These results indicate that, through complexation with Na^+, species $\mathbf{1}_4$ experiences the most distinct structural change and $\mathbf{1}_6$ less change. On the other hand, the NMR spectra for model compounds **2** and **3** were scarcely changed by the addition of Na^+.

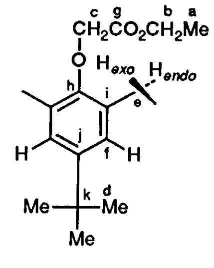


According to Inoue *et al.*,[18] the tightness of ion pairs in alkali picrates can be conveniently estimated from the bathochromic shift of the absorption maxima. We have previously evaluated the tightness of alkali picrate ion pairs complexed with calixarenes $\mathbf{1}_n$.[10] For sodium picrate, for example, the shift to longer wavelength induced by species $\mathbf{1}_n$ was in the order of $\mathbf{1}_4 > \mathbf{1}_6 > \mathbf{1}_8$. In particular, the shift (31 nm) induced by species $\mathbf{1}_4$ is as large as that induced by cryptand 222, indicating that sodium picrate encapsulated in species $\mathbf{1}_4$ is strongly solvent separated. As shown in Table 1, the δ-value for picrate ions shifts to higher magnetic field in the order $\mathbf{1}_4 > \mathbf{1}_6 > \mathbf{1}_8$. This indicates that the tightness of the ion pairs can be detected by the ^1H NMR chemical shift: the more solvent-separated the picrate, the larger the upfield shift.

The T_1-values for hydrogen nuclei were determined under the same conditions as given in Table 1. Examination of Table 2 reveals that T_1-values in the absence of Na^+ decrease in the order of $\mathbf{2} \approx \mathbf{3} > \mathbf{1}_4 > \mathbf{1}_6 > \mathbf{1}_8$. This implies that the T_1-value for ^1H relaxation is primarily governed by the molecular weight. We now focus our attention on comparison between species $\mathbf{1}_n$ and their Na^+ complexes. The T_1-values for most protons decrease when calixarenes $\mathbf{1}_n$ complexed Na^+, indicating that Na^+ acts as a template ion to suppress ring fluctuation. Basically, the change in T_1 is parallel to the change in δ: the most distinct T_1 decrease was observed for species $\mathbf{1}_4$ and the next for species $\mathbf{1}_6$, whereas the T_1-values for species $\mathbf{1}_8$ were scarcely changed. Among six different protons in calixarenes $\mathbf{1}_n$, the marked T_1 decrease was observed for methyl protons (proton a) in species $\mathbf{1}_4$ (ΔT_1 2.01 s) and $\mathbf{1}_6$ (ΔT_1 0.80 s). This change means that the molecular motion of the ester groups, which is possible in the absence of Na^+, is considerably frozen by complexation with Na^+. The T_1 decrease for the aromatic protons (proton f) is also noteworthy (ΔT_1 0.36 s for species $\mathbf{1}_4$). This suggests that the freezing effect occurring at the ester moieties through interactions with Na^+ is transmitted to the aromatic rings. On the other hand, the T_1-values for the $ArCH_2Ar$ protons (proton e), which serve as connectors of the aromatic rings, change to a smaller extent.

The foregoing results establish that, in calixarenes $\mathbf{1}_n$, terminal groups in an ethoxycarbonylmethoxy-*p*-t-butylbenzene unit move vigorously whereas the motion of the central $ArCH_2Ar$ moiety is rather suppressed. Na^+ ion acts as a template ion specifically to freeze the motion of these terminal groups. Thus, the ethoxycarbonylmethoxy-*p*-t-butylbenzene unit features a 'seesaw motion' around the $ArCH_2Ar$ moiety as a central support. We further tested the propriety of this hypothesis through relaxation-time studies by ^{13}C NMR spectroscopy.

^{13}C NMR Relaxation Times.—The ^{13}C NMR chemical shifts are summarized in Table 3. In the numbering system we assigned the same alphabetical letters to hydrogen-bonded carbons. To carbons not linked to hydrogen atom(s) we assigned new alphabetical letters.



^1H–^{13}C Two-dimensional NMR spectroscopy (400 MHz)

Table 3 Chemical shifts (δ) of carbons in calixarenes $\mathbf{1}_n$, their Na^+ complexes, and reference compounds[a]

	δ							
Carbon	$\mathbf{1}_4$	$\mathbf{1}_4 \cdot Na^+$	$\mathbf{1}_6$	$\mathbf{1}_6 \cdot Na^+$	$\mathbf{1}_8$	$\mathbf{1}_8 \cdot Na^+$	**2**	**3**
a	14.54	14.47	14.51	14.39	14.41	14.39	14.41	14.45
b	60.54	62.34	60.90	61.21	61.07	61.38	61.06	60.95
c	72.12	73.59	71.24	70.77	70.81	70.77	65.95	70.05
d	31.82	31.59	31.83	31.85	31.88	31.82	31.77	31.74
e	32.65	30.73	[b]	30.93	31.04	30.92		16.68[c]
f	125.91	126.70	127.07	126.64	126.46	126.67	114.75	126.26
g	170.47	172.10	169.46	169.11	168.87	169.48	168.88	168.97
h	154.16	150.91	153.90	153.93	154.05	153.79	156.87	154.46
i	134.38	135.28	133.61	133.64	133.65	133.62	126.52	130.21
j	154.35	148.70	146.61	146.96	146.87	147.11	144.22	146.95
k	34.42	34.82	34.61	34.85	34.85	34.87	34.53	34.56

[a] Measurement conditions are recorded in footnote *a* to Table 1. [b] The peak was not found probably because of the overlap with peak d. In the 400 MHz NMR spectrum this carbon appears at δ 32.04. [c] 2,6-Dimethyl groups.

Table 4 Relaxation times (T_1) of carbons in calixarenes $\mathbf{1}_n$, their Na^+ complex, and reference compounds[a]

	T_1/s							
Carbon	$\mathbf{1}_4$	$\mathbf{1}_4 \cdot Na^+$	$\mathbf{1}_6$	$\mathbf{1}_6 \cdot Na^+$	$\mathbf{1}_8$	$\mathbf{1}_8 \cdot Na^+$	**2**	**3**
a	3.09	2.77	2.63	1.73	2.30	1.89	4.95	6.49
b	1.69	0.91	1.25	0.94	0.71	1.10	5.46	4.46
c	0.86	0.35	0.59	0.35	0.27	0.20	2.21	2.71
d	1.21	0.78	0.73	0.79	0.55	0.57	1.64	1.72
e	[b]	3.23	[c]	0.05	0.25	0.19		7.54[d]
f	0.36	0.29	0.20	0.71	0.20	0.26	3.78	2.94
g	11.87	4.88	7.03	4.10	4.69	3.49	23.12	25.92
h	9.74	1.69	7.77	4.15	4.55	4.62	15.30	20.60
i	4.29	1.41	3.02	2.55	1.85	2.61	3.63	20.47
j	8.25	1.26	4.43	3.70	3.34	2.97	23.84	23.83
k	11.81	5.02	7.86	8.07	6.23	6.24	21.26	25.66

[a] Measurement conditions are recorded in footnote *a* to Table 1. [b] The T_1-value could not be determined because of the serious overlap with peaks d and k. [c] The peak was not found probably because of the overlap with peak d. [d] 2.6-Dimethyl groups.

was used for assignment of ^{13}C NMR peaks. Thus, carbons a–f bearing hydrogen(s) can be easily assigned. Among the remaining carbons g–k, carbon k can be readily distinguished from other carbons because it appears in the aliphatic region ($\delta \sim 30$). The peak which appears at the lowest magnetic field is assignable to carbonyl carbon g. Now, three carbons, h, i and j, remain. Among them, carbon h, linked to an ethereal oxygen, should appear at lower magnetic field ($\delta \sim 155$). Discrimination between carbons i and j was very difficult. We thus measured the gated decoupling spectrum of species $\mathbf{1}_6$: the peak at δ 134 changed into a triplet ($J = 6$ Hz) whereas that at δ 147 remained a singlet. Thus, the former peak is assigned to carbon i next to the CH_2 group and the latter peak is assigned to carbon j.

The T_1-values for carbon nuclei are summarized in Table 4. It can be seen from Table 4 that the T_1-values for hydrogen-bonded carbons a–f are much smaller than those for non-hydrogen-bonded carbons g–k. This reveals that the T_1-value is primarily governed by dipole–dipole relaxation. Also important is the molecular-weight effect: T_1-values decrease in the order of $\mathbf{2} \approx \mathbf{3} > \mathbf{1}_4 > \mathbf{1}_6 > \mathbf{1}_8$. Again, the most distinct T_1 difference between species $\mathbf{1}_n$ and $\mathbf{1}_n \cdot Na^+$ complex is seen for species $\mathbf{1}_4$. When compound $\mathbf{1}_4$ forms a complex with Na^+, the T_1-values for all carbons are decreased. This means that the molecular motion of species $\mathbf{1}_4$ is efficiently frozen through complexation with Na^+. A T_1 decrease of greater than 4 s is observed for carbons g, h, j and k. These are all non-hydrogen-bonded carbons which are not subject to dipole–dipole relaxation with hydrogen atom(s). This suggests that the T_1-values for this class of carbons are mainly governed by spin–rotation relaxation. The benzene moiety in species $\mathbf{1}_4$ consists of carbons f and h–j. Except for hydrogen-bonded carbon f, the T_1-values are greatly decreased but the T_1 change for carbon i is relatively smaller than that for other carbons. This indicates that the 'seesaw motion' postulated on the basis of the T_1-measurements of ^1H relaxation really exists and that the motion is considerably suppressed by complexation with Na^+. A similar situation is seen for the $EtOCOCH_2$ moiety: carbons a–c have protons on them, so that the T_1-values change to a smaller extent. In contrast, the T_1-value for carbon g which has no proton on it undergoes the template effect of Na^+: the T_1-value is decreased by 6.99 s. This indicates that the molecular motion of the $EtOCOCH_2$ moiety is also suppressed through interactions with Na^+.

In conclusion, the present paper demonstrates the first systematic research on T_1 relaxation times of calixarenes. It is clear that the molecular motion of the calixarene skeleton is efficiently frozen through complexation with metal cations.

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