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NMR Relaxation Time Studies of Ionophoric Calixarene Esters

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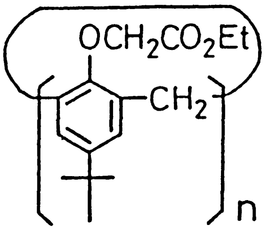
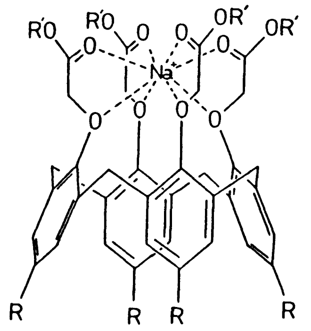
Relaxation times of ethoxycarbonylmethyl derivatives of p-t-butylcalix[n]arenes (n=4, 6, and 8) were estimated for the first time with ^{1}H NMR. It was shown that the benzene units feature a "seesaw" motion around the $ArCH_2Ar$ circle and the motion is suppressed by Na^+ serving as a template ion.

Calixarenes are cyclic oligomers made up of phenol units just as cyclodextrins are made up of glucose units. Although these two 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.[1-3] Thus, in order to understand the essential difference as host molecules between cyclodextrins and calixarenes, it is of great significance to assess the conformational properties characteristic of calixarene cavities. From a spectroscopic viewpoint, dynamic NMR studies and NMR relaxation time studies would provide useful information about the conformational properties. In contrast to a number of examples for dynamic NMR studies,[1-3] NMR relaxation time studies have been very limited. To the best of our knowledge, there exists only one precedent which deals with ^{1}H NMR relaxation times of t-butylamine complexed with calixarenes (but not those of calixarenes themselves).[4] In this communication, we report systematic studies on ^{1}H NMR relaxation times (T_1) of ionophoric calix[n]arene esters (**1**$_n$: n=4, 6, and 8). The main purpose of this study is to understand how the molecular motion of the calix[n]arenes changes upon inclusion of Na^+.



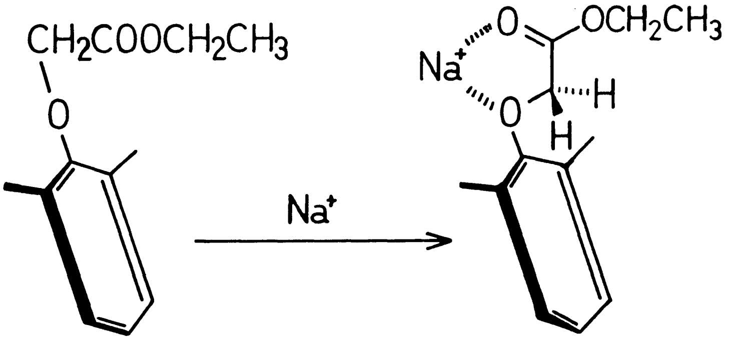
1$_n$



1$_4$-Na^+ Complex

The synthesis of $\mathbf{1}_n$ was described previously.[5)] The T_1 values of the proton resonances were obtained in THF-d_8 at 90 MHz and 36 °C under a nitrogen atmosphere by using the inversion recovery method.[6)]

It is known that $\mathbf{1}_n$ can bind Na^+ through interactions with two oxygens in the OCH_2CO moiety.[7,8)] In particular, $\mathbf{1}_4$ strongly encapsulates Na^+.[7,8)] The influence of added alkali picrates on chemical shifts of $\mathbf{1}_n$ is summarized in Table 1. $\mathbf{1}_4$ adopts a "cone" conformation and the oxygen-through-the-annulus rotation is sterically inhibited.[7)] Thus, it gives a pair of doublets for the $ArCH_2Ar$ protons. In $\mathbf{1}_6$ and $\mathbf{1}_8$, on the other hand, the rotation is still allowed, giving a sharp singlet for the $ArCH_2Ar$ protons. In $\mathbf{1}_4$, the δ values in the presence of Na^+ generally shift to lower magnetic fields, which is attributed to the electron-withdrawing nature of Na^+. There are two exceptions, however: (i) the OCH_2CO protons shift to the higher magnetic field by 0.21 ppm and (ii) the difference in δ between H_{exo} and H_{endo} becomes smaller (1.80 ppm in the absence of Na^+ to 0.98 ppm in the presence of Na^+). As illustrated below, the OCH_2CO protons are fixed on the benzene ring when the two oxygens coordinate to Na^+. Thus, these protons undergo the effect of the ring current which causes the up-field shift. The change (ii) implies that when $\mathbf{1}_4$ complexes Na^+, H_{exo} is less shielded whereas H_{endo} is more shielded. According to X-ray crystallographic studies by Arduini et al.,[9)] 25,26,27,28-tetrakis(N,N-diethylaminocarbonyl)methoxy-p-t-butylcalix[4]arene (which has the structure similar to $\mathbf{1}_4$) 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 the change (ii). In comparison to $\mathbf{1}_4$, the δ values for $\mathbf{1}_6$ and $\mathbf{1}_8$ were less affected by Na^+. In particular, the shifts observed for $\mathbf{1}_8$ were small. These results indicate that through complexation with Na^+, $\mathbf{1}_4$ undergoes the most distinct structural change and $\mathbf{1}_6$ next.



We previously evaluated the tightness of alkali picrate ion pairs from the shift of the absorption maxima.[8)] For sodium picrate, for example, the shift to longer wavelengths induced by $\mathbf{1}_n$ was in the order of $\mathbf{1}_4 > \mathbf{1}_6 > \mathbf{1}_8$. In particular, the shift induced by $\mathbf{1}_4$ is as large as that induced by cryptand 222, indicating that sodium picrate encapsulated in $\mathbf{1}_4$ is strongly solvent-separated. As shown in Table 1, the δ value for picrate ion shifts to higher magnetic fields in the order of $\mathbf{1}_4 > \mathbf{1}_6 > \mathbf{1}_8 \approx$ no $\mathbf{1}_n$. This indicates that the tightness of the ion pairs can be detected by the ^1H NMR chemical shift: the more solvent-separated, the larger up-field shift.

Table 1. Chemical shifts (δ) of **1**$_n$ and their Na^+ complexes[a)]

Proton	δ/ppm					
	1$_4$	**1**$_4$-Na^+	**1**$_6$	**1**$_6$-Na^+	**1**$_8$	**1**$_8$-Na^+
a	1.26	1.36	1.20	1.00	0.97	0.98
b	4.17	4.36	4.16	3.97	3.94	3.97
c	4.78	4.57	4.49	4.20	4.12	4.22
d	1.09	1.16	1.02	1.12	1.13	1.13
e(exo)	3.14	3.42				
			4.05	4.06	4.08	4.05
e(endo)	4.94	4.40				
f	6.81	7.23	7.03	7.00	7.01	7.02
Picrate[b)]	-	8.63	-	8.69	-	8.73

a) 36 °C, THF-d_8, internal standard TMS, [**1**$_n$] = 0.10 mol dm^{-3}, [alkali picrate] = 0.12 mol dm^{-3}. Under these conditions, **1**$_n$'s totally exist as Na^+ complexes.[5)]

b) δ = 8.74 ppm in the absence of calixarenes.

Table 2. Relaxation times (T_1) of **1**$_n$ and their Na^+ complexes[a)]

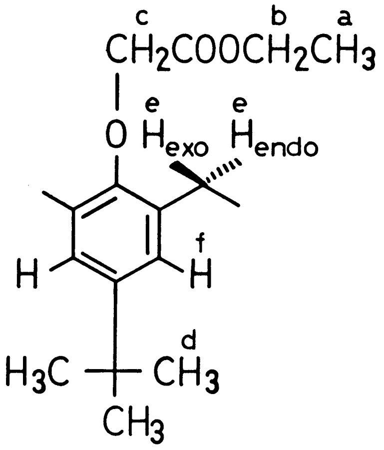
Proton	T_1/s					
	1$_4$	**1**$_4$-Na^+	**1**$_6$	**1**$_6$+Na^+	**1**$_8$	**1**$_8$+Na^+
a	2.51	0.50	1.44	0.64	0.78	0.74
b	1.17	b)	0.75	b)	0.43	0.38
c	0.36	0.23	0.20	0.13	0.16	0.14
d	0.73	0.54	0.64	0.56	0.48	0.49
e	0.17	0.15[c)]	0.19	b)	0.12	0.09
f	0.67	0.31	0.41	0.35	0.37	0.32
Picrate[d)]	-	6.75	-	7.82	-	9.78

a) Measurement conditions are recorded in footnote a) in Table 1.

b) T_1 could not be determined because of the overlap of H^b and H^e.

c) T_1 for H_{exo}. The peaks for H_{endo} overlapped with those for H^b.

d) T_1 = 9.15 s in the absence of calixarenes.



The T_1 values obtained under the same conditions as Table 1 are summarized in Table 2. The T_1 values for most protons decreased when $\mathbf{1}_n$ complexed Na^+, indicating that Na^+ acts as a template ion to suppress the ring fluctuation. Basically, the change in T_1 is parallel to the change in δ: the most distinct T_1 decrease was observed for $\mathbf{1}_4$ and next for $\mathbf{1}_6$, whereas the T_1 values for $\mathbf{1}_8$ scarcely changed. Among six different protons in 1_n, the marked T_1 decrease was observed for methyl protons (proton a) in $\mathbf{1}_4$ (ΔT_1 2.01 s) and $\mathbf{1}_6$ (ΔT_1 0.80 s). This change means that the molecular motion of ester groups, which is possible in the absence of Na^+, is considerably frozen by complexation with Na^+. The T_1 decrease in aromatic protons (proton f) is also noteworthy (ΔT_1 0.36 s for $\mathbf{1}_4$ and 0.06 s for $\mathbf{1}_6$). This suggests that the freezing effect induced at the ester moieties 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 aromatic rings, changed to a smaller extent.

The foregoing results establish that in $\mathbf{1}_n$, the terminal groups in an ethoxycarbonylmethoxy-p-t-butylbenzene unit move vigorously whereas the molecular motion of the central $ArCH_2Ar$ is rather suppressed. Na^+ ion acts as a template ion to specifically freeze the molecular motion of these terminal groups. Thus, the ethoxycarbonylmethoxy-p-t-butylbenzene unit features a "*seesaw motion*" around the $ArCH_2Ar$ as a central support. This is a novel image for ionophoric calix[n]arenes obtained by the T_1 measurements.

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