

An NMR Study on Complexation of *p*-*tert*-Butylcalix[6]arene Ester Derivatives with Ethylammonium Picrate

Sangdoon Ahn, Suk-Kyu Chang,[†] Taehoon Kim,[†] and Jo Woong Lee*
 Department of Chemistry, Seoul National University, Seoul 151-742, Korea
[†]Department of Chemistry, Chung-Ang University, Seoul 156-756, Korea

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Complexation of *p*-*tert*-butylcalix[6]arene ester derivatives with ethylammonium ion was investigated *via* measurement of their proton relaxation times and chemical shifts in CDCl₃. The results suggest that the *endo*-type complexes are formed and the overall rotation of these complexes is more rapid than that of the corresponding free hosts.

Studies of conformational interconversions in calixarenes are of recent interest because the solution structure and conformational characteristics of calixarene-based host systems greatly affect their (molecular) recognition of small organic molecules as well as ionic guests.^{1,2} Although spin-lattice relaxation time measurement is a very informative and powerful technique that can be utilized for this purpose, its applications have been limited to studying a few calixarenes or guest ions only.^{3,4} In this communication we report the solution dynamic properties inferred from the analysis of proton chemical shifts and relaxation times for the complexes formed between various calix[6]arene ester derivatives (1-4) and ethylammonium picrate.

The ester derivatives (1-4) were prepared following the reported standard procedures.⁵ Each sample was placed in a 5 mm o.d. NMR tube and sealed under vacuum after degassing by repeating the freeze-pump-thaw cycle at least five times.

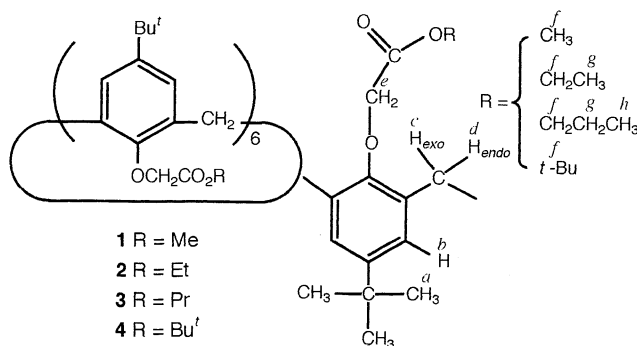
Observed proton chemical shifts for the free ester derivatives (1-4) and the corresponding complexed forms in CDCl₃ are summarized in Table 1. ¹H NMR spectrum of 3 is not so well

Table 1 Observed proton chemical shifts of hosts, guest(G) and their complexes^a

	Chemical Shifts, δ (ppm)							
	1	1+G	2	2+G	3 [#]	3+G	4 ^{##}	4+G
<i>a</i>	1.15	1.08	0.97	1.09	0.94	1.09	0.97	1.08
<i>b</i>	7.11	6.91	6.95	6.90	6.93	6.90	7.07	6.89
<i>c</i>	4.00	3.46	4.06	3.46	4.10	3.47	<i>b</i>	3.43
<i>d</i>	4.00	4.43	4.06	4.45	4.10	4.46	<i>b</i>	4.49
<i>e</i>	4.23	4.59	4.53	4.57	4.59	4.59	4.56	4.48
<i>f</i>	3.38	3.80	4.18	4.24	4.14	4.12	1.14	1.50
<i>g</i>			1.24	1.31	1.68	1.71		
<i>h</i>					0.94	0.97		
NH ₃ ⁺	7.92*	5.78		5.81		5.85		6.42
CH ₂	3.12*	0.13		0.14		0.15		0.33
CH ₃	1.35*	-1.28		-1.29		-1.27		-1.36
Pic	8.77*	8.79		8.79		8.83		8.78

^a 50 and 60 mM solutions of hosts and guest in CDCl₃ at 298 K, 200 MHz. *Chemical shifts of free guest in THF-d₈ at 298 K, due to insolubility in CDCl₃. [#]Chemical shifts at 323K, too broad for correct assignment at 298 K. ^{##}Coalesced peaks in C₂D₂Cl₄ at 368 K, show multiplets characteristic of 1,2,3-alternate conformation at room temperature. ^b Too broad to determine the chemical shifts.

resolved to allow the precise assignment of each resonance line while that of 4 shows relatively well resolved multiplet peaks originating from the well-known 1,2,3-alternate conformation at room temperature.⁶ Upon complexation with ethylammonium picrate, methylene resonances (ArCH₂Ar) of all the investigated hosts are split into two doublets ($J \sim 15$ Hz), indicating that the complexes formed have cone conformation. Furthermore, the δ values for ¹H in these complexes are all but identical, which means that they have similar structures in solution. Also noteworthy is the dramatic complexation-induced upfield shift for proton resonances of ethyl group in guest. Upon complexation, the methyl and methylene protons of ethylammonium guest undergo upfield shift by 2.6 and 2.9 ppm, respectively, which may indicate that the guest is held deeply and tightly in the aromatic cavity of calixarene, thus forming *endo*-type complex. The interaction of calixarene derivatives with the primary alkylammonium ion may be assumed due mainly to the complexation through a tripodal arrangement of N⁺-H...O=C (host) hydrogen bonds and R-NH₃⁺...O=C (host) charge dipole interaction.⁷ Due to this type of primary interaction in the complex, the ethylammonium guest has two possible orientations to assume, either head-up or head-down with respect to



the cone cavity. The large upfield shifts observed are thought to arise from the so-called CH- π interaction⁸ and indicate that the ethyl group side of the guest is embedded in the cavity and subject to the ring current of phenyl groups. The *endo* type complexation may be caused predominantly by this interaction. The formation of similar type complexes is also observed with other primary alkylammonium guests such as *n*-propyl and butylammonium picrates.

To gain further insight into the solution structure of the present host-guest system the spin-lattice relaxation times for protons in the ethylammonium guest, free hosts, and their complexes were measured by the inversion recovery method and are summarized in Table 2. That the observed relaxation times for various complexes are close to one another is also consistent with the conclusion inferred previously from the behavior of

Table 2. Proton relaxation times of hosts, guest(G) and their complexes^a

H	Relaxation times, T_1 (sec)					
	1	1+G	2	2+G	3+G	4+G
a	0.58	0.63	0.53	0.60	0.55	0.60
b	0.50	0.56	0.47	0.55	0.52	0.52
c	0.15	0.16	0.14	0.15	0.14	0.15
d	0.15	0.15	0.14	0.15	0.14	0.17
e	0.22	0.27	0.23	0.27	0.25	0.28
f	0.53*	0.66*	0.63	0.80	0.75	0.47
g			1.11	1.23	1.03	
h					1.36	
NH ₃ ⁺	1.16**	0.24		0.29	0.28	0.27
CH ₂	2.76**	0.55		0.60	0.57	0.49
CH ₃	3.45**	0.85		0.89	0.74	0.79

^a Observed under the same conditions as in Table 1. T_1 data for free **3** and **4** are unreliable. * Determined from initial slope calculation due to nonexponentiality of its relaxation curve. ** T_1 data for free guest in THF-d₃ (instead of CDCl₃) at 298 K due to the solubility problem.

chemical shifts data that the ethylammonium complexes formed have similar structural properties. As was expected, the T_1 's for the protons in ethylammonium guest were found to markedly decrease upon complexation with calixarene based ester hosts. In general one may expect that mobility of the guest will decrease upon complexation, thus decreasing T_1 for its protons. In contrast to this, however, the relaxation times for protons in the hosts were found to increase by ca. 10 to 20 % upon complexation, which is conflicting with the observation made by Shinkai *et al.* Earlier, Shinkai *et al.* observed that the relaxation times of most protons in **2** decreased upon complexation with Na⁺ ion as guest (in THF).⁴ They also observed that the ArCH₂Ar methylene protons of **2** remained as a singlet which may be attributed to the fact that in THF solution the conformational interconversions are still taking place very fast on the NMR time scale since the guest Na⁺ is only loosely bound to the host. Observations for our host-guest system, however, are completely contrary to those by Shinkai *et al.* As was previously mentioned, the ArCH₂Ar methylene protons are found well resolved into a pair of doublets in our case, indicating that the complex formed in CDCl₃ is more stable than **2**-Na⁺ complex in THF and that the former assumes relatively rigid cone conformation upon complexation. The coalescence temperature for these proton doublets in the **2**-ethylammonium picrate complex was found to be above 400 K (in C₂D₂Cl₄), which also suggests relatively deep and tight binding of ethylammonium guest into the calixarene cavity. One may expect that the molecular size of such tightly bound complexes will be in general smaller than that of the corresponding free host molecules.

The difference in the behavior of T_1 upon complexation for the above two cases may be explained in terms of overall molecular rotations of the resulting complexes. That is, the longer T_1 means the shorter correlation time for overall tumbling motions and faster tumbling rate of the complexes. With all other conditions remaining invariant, faster tumbling rate may be attributed to the smaller effective radius of the

complex according to the Debye theory.⁹ This means that loosely bound **2**-Na⁺ complex will have larger effective radius than the free host while for tightly bound host-ethylammonium picrate complexes the opposite is true. This inference is consistent with our previous conclusion that upon complexation the complex with cone conformation, which has relatively smaller effective radius compared to the original host molecule, can be formed. Relative reduction in effective molecular radii could be calculated from the observed increase of relaxation times by making use of the Debye relation assuming the isotropic overall molecular tumbling. It turned out that the effective radii shrank by about 2 ~ 2.5% upon complex formation in our case. Of course, the conformational inversions may be frozen upon complex formation but this can hardly affect the observed spin-lattice relaxation times because these motions ($\tau > 10^{-5}$ sec) are supposed to be too slow to make any significant contributions to T_1 which is in general affected only by much faster molecular motions ($\tau \sim 10^{-7-12}$ sec). Preliminary measurement of ¹³C relaxation times also revealed that the T_1 's generally increase upon complexation. Further investigations including the relaxation time measurements with other related hosts and guests are now under way in our laboratory and will be published later.

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