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Conformational and Complexational Properties of Distal Dialkyl Ester Derivatives of *p*-*tert*-Butylcalix[4]arene

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Complexation of primary alkylammonium ions by 1,3-distal calix[4]arene diesters was studied by NMR spectroscopy. The guest alkylammonium ions are found to bind mainly to the two ester moieties and are oriented outward with respect to the cone cavity of the host, forming *exo*-type complexes unlike the case of alkylammonium-calix[6]arene systems. Measurement of T_1 also revealed that the primary binding site is the two ester moieties and phenolic OH groups. The temperature dependence of the chemical shifts of phenolic OH protons in these diesters correlates with the basicity of the solvent moderately well and the temperature coefficients of their chemical shifts are found to significantly decrease upon complexation with propylammonium ion.

Introduction

Calix[4]arenes are popular and well-known building blocks in supramolecular chemistry.¹ When selectively functionalized either at the phenolic OH group in the lower rim and/or at the para position of the aromatic ring in the upper rim, they can provide versatile platforms, such as calixcrowns, calixquinones, calixspherands, etc., appropriate for complexation with various guests.²⁻⁴

Four conformational isomers are possible for calix[4]arenes: cone, partial cone, 1,2-alternate, and 1,3-alternate. Unmodified calix[4]arenes are known to adopt a cone conformation due to the stabilization by intramolecular hydrogen bonding interactions between phenolic OH groups but their structures are fluxional in the sense that they can undergo rapid inversional interconversion between two equivalent cone conformations. However, the rate of such interconversion can be made exceedingly slow by suitable derivatization at the phenolic OH groups so that the resulting derivative assumes a virtually rigid structure. Introduction of ester, keto, and amide groups into the lower rim of calix[4]arenes produces a series of new lipophilic cation receptors arranged to form a rigid cone conformation with remarkable complexing abilities toward small alkali metal cations, notably Na⁺ ion. Thus, preorganization of binding sites prior to complexation seems to play a very im-

portant role in determining the complexing abilities of calixarenes.¹

In this paper the conformational properties of 1,3-distal functionalized calix[4]arene, which is one of the most attractive frameworks for the development of functional ionophores, were studied from two perspectives. First, conformational behaviors of the diesters as well as their complexational properties toward several primary alkylammonium ions were investigated *via* measurement of chemical shifts and spin-lattice relaxation times (T_1) in solution state. Then, the effect of hydrogen bonding of OH groups on conformational stability was probed for the 1,3-distal modified calix[4]arenes 1-3 by means of ¹H NMR spectroscopic measurements in various solvents.

Results and Discussion

Conformational Stability. X-ray crystallography studies⁵ show that several 1,3-distal modified calix[4]arenes adopt a flat cone conformation. In this conformation the planes of two confronting benzene rings bearing alkylated OR groups become more parallel with the cone axis while the remaining two phenolic rings are tilted away from the same cone axis so that the two oxygen atoms in the OR groups get farther away from each other than in the normal cone conformation and, at the same time, the two OH

groups are pushed down toward the cavity. This arrangement enables the hydrogen bonding to be formed more easily between proximal hydroxyl (OH) and ether functional groups (OR). The variable temperature ^1H NMR spectral data of 1,3-distal modified calix[4]arenes (Figure 1) reveal that the ^1H NMR lines of the bridging ArCH_2Ar protons show no tendency to coalesce over the investigated temperature range. Monomethyl ester derivative of calix[4]arene **4**, in which stronger hydrogen bondings can be formed than in the diesters, also shows similar spectral patterns (Figure 1). These observations suggest that the conformational interconversion rates in the esters **1-4** are extremely slow on an NMR time scale, and hydrogen bondings and steric hindrances at their lower rim are considered to be responsible for such slow rates. The fact that without the hydrogen bonding effect the esters **1-4** could also take partial cone or 1,3-alternate conformation strongly suggests that hydrogen bondings prevent partial inversion of the unmodified unit. Along with this, the steric hindrance brought by the presence of ester moieties will surely prohibit total ring inversion as well.

Complexation with Primary Alkylammonium Ions.

It is well known that the hexaester derivatives derived from calix[6]arenes have a good ionophoric ability toward both alkali metal (especially Cs^+ or K^+) and primary alkylammonium cations, in contrast to the tetraester derivatives based on calix[4]arenes which, having preorganized rigid cone conformations, do not display remarkable complexing ability toward the primary alkylammonium ions.¹ This difference may be thought to arise from the difference in the size of available space around the binding sites (ester and phenol ether moiety in the lower rim) as well as the ring size of the host itself (tetramer or hexamer).

The ^1H NMR spectra of 1,3-distal modified calix[4]arenes **1-3** and their complexes with propylammonium picrate (shown in Figure 2) consist of sharp and very well resolved lines. The chemical shifts of free hosts are consistent with the flat cone conformation. That is, the ^1H NMR spectrum of bridging ArCH_2Ar protons consists of a pair of doublets with a coupling constant $J \approx 13$ Hz. The separation between these doublets ($\Delta\delta$) is 1.1 ppm which is small compared to the case of tetraesters ($\Delta\delta \approx 1.5$ ppm) and the hydroxyl proton line appears at around 7 ppm. The ^1H NMR lines of phenolic OH protons in organic compounds generally appear at 4-5 ppm⁷ and that of the unmodified calix[4]arene (forming strong hydrogen bonding) appears at 10-11 ppm,⁸ which leads us to the conclusion that the phenolic OH protons in diesters **1-3** are involved in the formation of hydrogen bondings although not as intensively as in the case of unmodified calix[4]arene and monoester **4**.

The changes in the ^1H chemical shifts of the calixarenes upon complex formation with primary alkylammonium ions provide information that can help us elucidate the structures of the complexes formed. The chemical shifts of free hosts and their complexes in CDCl_3 are presented in Table 1. We see that the chemical shift of the phenolic protons is shifted upfield by as much as 0.9 ppm and those of the two bridging methylene protons are brought closer to each other (from $\Delta\delta \approx 1.1$ ppm to $\Delta\delta \approx 0.85$ ppm) upon complexation with propylammonium picrate. This means that the conformations of diester-primary alkylammonium complexes assume a more flattened cone form than the free diesters. This fact is also supported by the increase in the chemical shift differences between the two types of protons of *p*-tert-butyl groups and between the two types of aromatic protons, each in alkylated and phenolic units. On the other hand, it can be

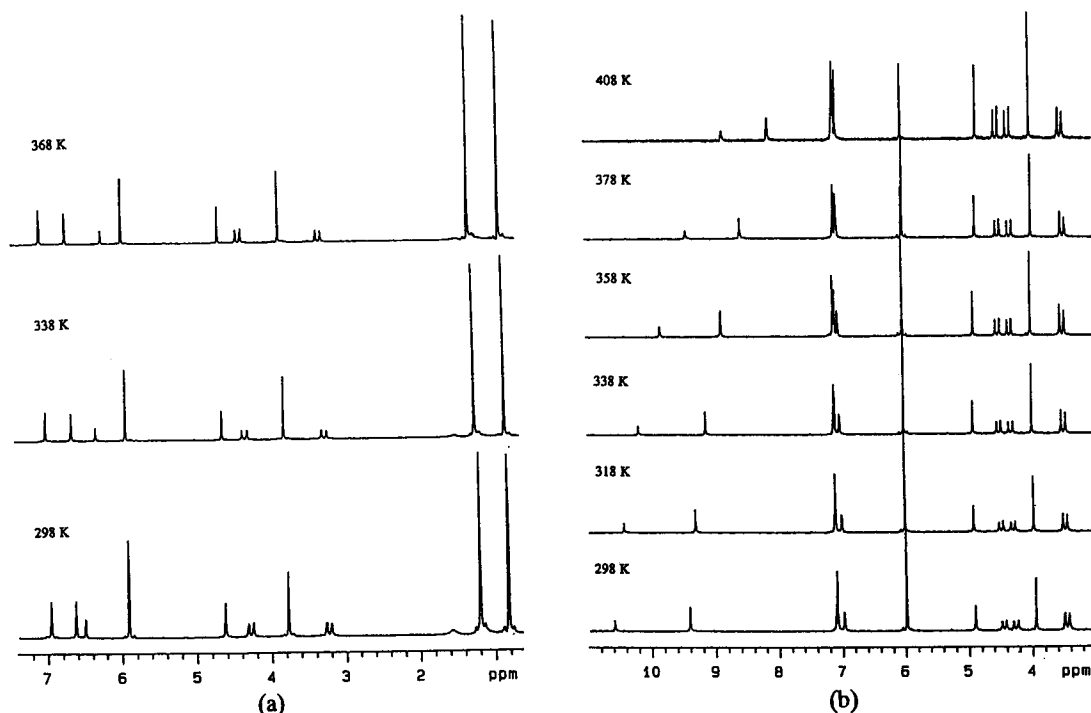


Figure 1. Temperature varied ^1H NMR spectra of (a) calix[4]arene 1,3-distal dimethyl ester **1** and (b) calix[4]arene monomethyl ester **4** in $\text{C}_2\text{D}_2\text{Cl}_4$, 200 MHz.

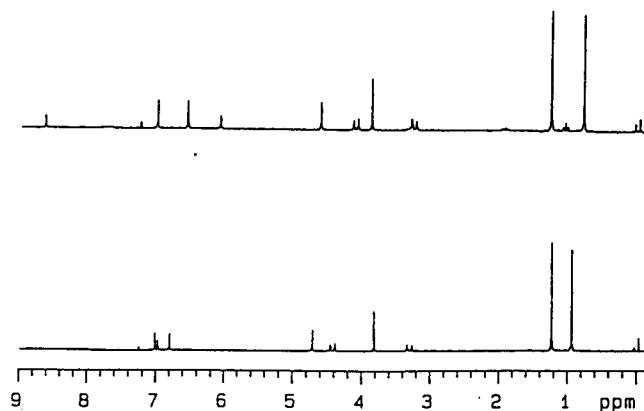


Figure 2. ^1H NMR spectra of free calix[4]arene 1,3-distal diester **1** (lower) and its complex (upper) with propylammonium picrate in CDCl_3 at 298 K. A pair of doublets around 4 ppm corresponds to the bridging methylene protons.

seen that the chemical shifts of the guest propylammonium ions scarcely change upon complexation with diesters (Figure 2). In the case of hexaesters derived from calix[6]arenes, a dramatic complexation-induced upfield shift is observed for proton resonances of alkylammonium guest ions, which indicates that the guest is held tightly deep in the aromatic cavity of calixarene and comes under the strong influence of the ring current of the phenyl groups by forming *endo*-type complexes.⁹ Hence, it is reasonable that propylammonium ions bound to diesters are oriented outward with respect to the cone cavity, forming *exo*-type complexes. Bulkier alkylammonium ions exhibit a similar trend but found to form less strong complex than propylammonium guest. The 2D-COSY/NOESY spectra of dimethyl ester complexed with propylammonium ion, as shown in Figures 3 and 4, enable us to distinguish readily between the two aromatic proton lines and between the two *p-tert*-butyl proton lines.

The association constant for complexation of dimethyl ester **1** with propylammonium picrate ion in $\text{THF-}d_8$ was determined by the ^1H NMR titration method. While maintaining a constant concentration of the host, we observed the individual ^1H chemical shifts of diester **1** as a function of the concentration ratio $[\text{Guest}]/[\text{Host}]$. From the plots of δ_{obs} versus $[\text{Guest}]/[\text{Host}]$ one can estimate the association constant (K_a) for this system (shown in Figure 5). The result indicates that the dimethyl ester **1** can also form complexes with primary alkylammonium guests, although it shows much poorer affinity toward propylammonium ion compared with hexaester derivatives of calix[6]arenes.

Diester-diquinone **5** exhibited somewhat different complexation behavior. The ^1H NMR spectra of the complex and the free diquinone are presented in Figure 6. In this diquinone system, upon complexation with propylammonium ion, the chemical shifts of guest protons as well as the aromatic and quinone protons in the host show little changes as in the case of diester; however, those of the two bridging methylene protons are found to have larger separation between them which increased from $\Delta\delta=0.62$ ppm for the free host to $\Delta\delta=1.25$ ppm for the complex. These results indicate that in this case, too, the propylammonium guest ion

Table 1. ^1H NMR chemical shifts of free hosts and their complexes in CDCl_3 at 298 K (0.03 M solution, ppm)*

H'	1	1+PAP	1+tBAP	1+BzAP	2	2+PAP	3	3+PAP
a	6.98	6.10	6.52	6.72	7.04	6.13	7.10	6.02
b	7.02	7.01	7.02	7.02	7.02	7.01	7.02	7.01
b'	6.81	6.57	6.72	6.75	6.81	6.57	6.78	6.53
c	1.26	1.29	1.27	1.27	1.26	1.29	1.27	1.29
c'	0.97	0.81	0.90	0.93	0.97	0.81	0.95	0.79
d	4.44	4.13	4.32	4.34	4.45	4.14	4.44	4.11
e	3.32	3.28	3.31	3.31	3.32	3.27	3.30	3.25
f	4.74	4.64	4.71	4.69	4.72	4.62	4.58	4.50
g	3.84	3.90	3.85	3.84	4.45	4.35	1.54	1.56
h					1.34	1.36		

*All complex solutions are prepared by addition of excess guest molecules (insoluble in CDCl_3) to free host solution (0.03 M), and removing the undissolved guest after enough mixing and/or complexation time (more than 1 day). PAP(propyl ammonium picrate), tBAP(*t*-butyl ammonium picrate), and BnAP(benzyl ammonium picrate).

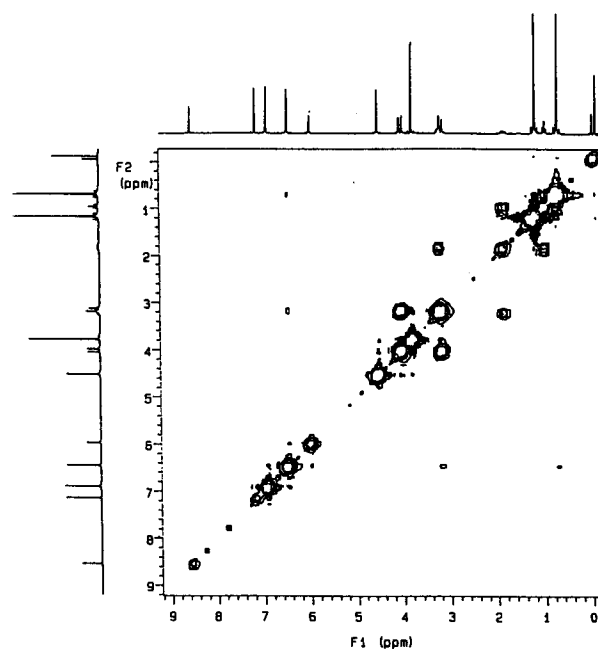


Figure 3. 2D-COSY spectrum of calix[4]arene 1,3-distal methyl ester complex with propylammonium picrate in CDCl_3 at 298 K (obtained at 200 MHz).

binds to the similar binding site as it does in diesters. In the diester-diquinone system, however, the two carbonyl oxygens of quinone moiety may also be involved in the complexation process.

In order to shed more light on the nature of binding sites involved in the complexation of diesters by alkyl- and arylammonium ion the spin-lattice relaxation times (T_1) for protons in free hosts and their complexes were measured by the conventional inversion recovery method and the results are summarized in Table 2. The spin-lattice relaxation times of the protons of phenolic and alkyl ester moiety (OCH_2 , COO and COOR), which constitute the binding site, are found to decrease upon complexation but those of the other

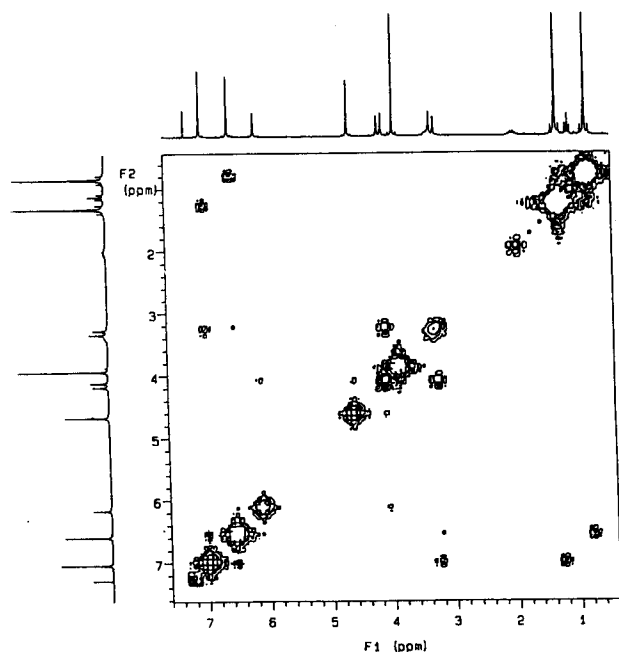


Figure 4. 2D-NOESY spectrum of calix[4]arene 1,3-distal methyl ester complex with propylammonium picrate in CDCl_3 at 298 K (obtained at 200 MHz).

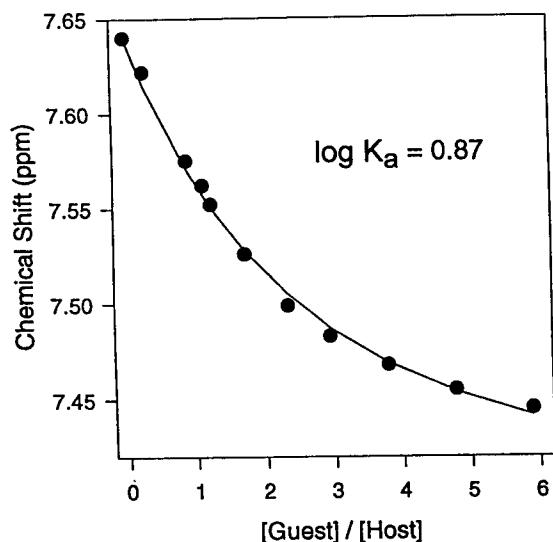


Figure 5. Plot of phenolic OH proton chemical shift versus ρ in calix[4]arene 1,3-distal dimethyl ester 1 and propylammonium picrate system in acetonitrile at 298 K.

protons remain invariant or are only slightly affected. This means that alkyl ester moiety and phenolic OH groups become less mobile upon complexation, which are well consistent with the conclusion obtained from the observation of chemical shift changes.

Hydrogen Bonding. The conformations of 1,3-distal modified calix[4]arenes (1,3-distal diether, dicyano, etc.) were studied using X-ray crystallography and NMR experiments by several groups,^{5,6} which revealed that these diesters 1-3 adopt flat cone conformations which allow for the facile formation of hydrogen bonding between the re-

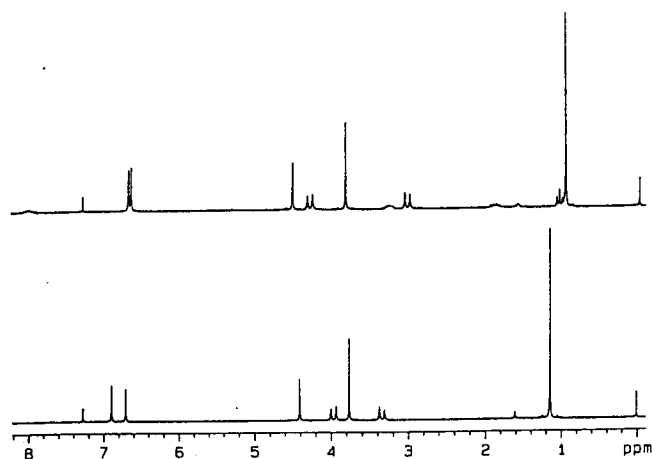


Figure 6. ^1H NMR spectra of free calix[4]diquinone 1,3-dimethyl diester 5 (lower) and its complex (upper) with propylammonium picrate in CDCl_3 at 298 K. A pair of doublets around 4 ppm corresponds to the bridging methylene protons.

Table 2. ^1H relaxation times (T_1) of free hosts and their complexes in CDCl_3 at 298 K (0.03 M solution, sec)*

H	1	1+PAP	1+tBAP	1+BzAP	2	2+PAP	3	3+PAP
a	0.77	0.71	0.78	0.71	0.72	0.62	0.67	0.64
b	0.68	0.67	0.69	0.66	0.65	0.62	0.62	0.60
b'	0.71	0.81	0.76	0.71	0.68	0.74	0.67	0.75
c	0.73	0.76	0.77	0.73	0.74	0.72	0.66	0.66
c'	0.73	0.76	0.77	0.72	0.74	0.72	0.66	0.68
d	0.23	0.20	0.22	0.22	0.22	0.19	0.21	0.18
e	0.22	0.19	0.20	0.20	0.20	0.18	0.20	0.17
f	0.60	0.42	0.48	0.53	0.54	0.38	0.46	0.33
g	1.27	0.95	1.12	1.13	1.53	1.01	0.70	0.54
h					1.81	1.49		

*Same condition as described in Table 1.

maintaining two OH protons and the oxygens of the ether functional groups. In general, temperature dependence of the ^1H NMR chemical shift has been recognized as a useful criterion for distinguishing "exposed (solvent interacting)" from "buried (intramolecular)" hydrogen bonding. The former usually exhibits a larger temperature coefficient than the latter.¹⁰ In the case of the phenolic OH protons of these diesters 1-3, however, the temperature coefficients are found to be larger than expected from the normal intramolecular hydrogen bonds often found in smaller molecules. It may be reasoned that ring fluctuations upon heating may be responsible for such unusually large temperature coefficients for these compounds. The temperature-varied chemical shifts of phenolic OH protons in diesters 1-3 and their temperature coefficients are presented in Figure 7. The OH protons in bulkier ester derivatives are found to appear at lower fields and exhibit smaller temperature coefficients.

The temperature-varied chemical shifts of the phenolic OH protons of diester 1 in several common organic solvents are shown in Figure 8. The solvent-induced resonance shift seems somewhat dependent on the presence of intramolecular hydrogen bonds and the basicity of the solvent. The chemical shift of the OH proton in pyridine solvent (which is the most basic among the employed solvents) ap-

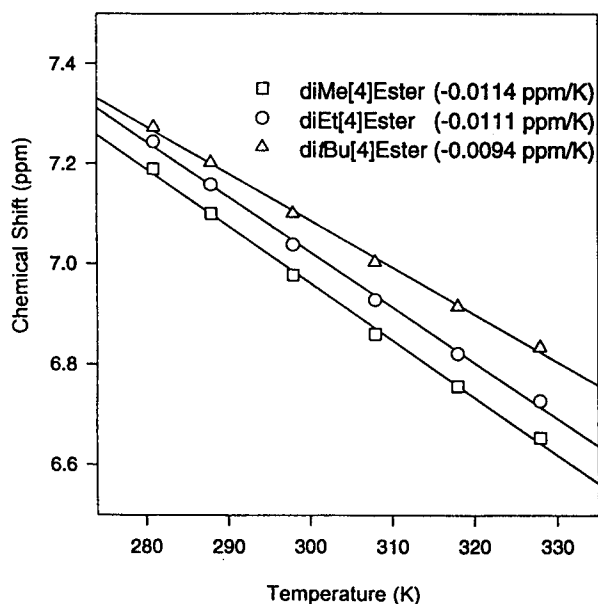


Figure 7. Temperature dependent chemical shifts of phenolic OH proton in calix[4]arene 1,3-distal diesters 1-3 and their temperature coefficients in CDCl_3 solvent.

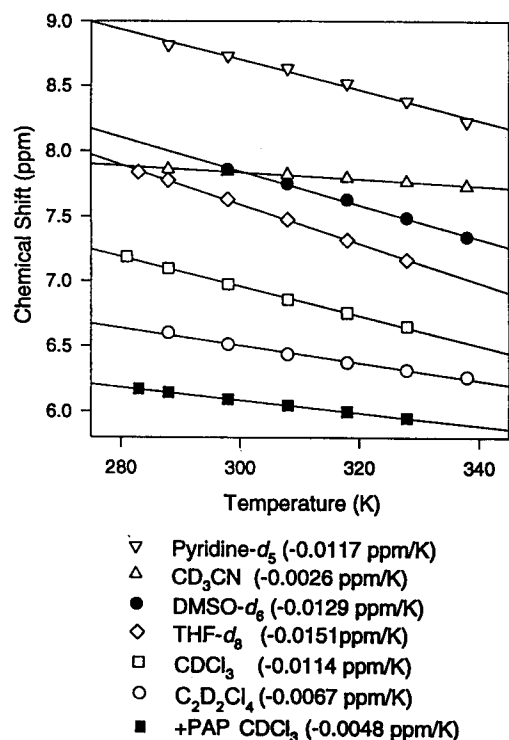


Figure 8. Temperature dependent chemical shifts of phenolic OH proton in calix[4]arene 1,3-distal dimethyl ester 1 in various solvents and their temperature coefficients.

appears at the lowest field because of the extra deshielding due to the pairing of pyridine-N: \cdots HO.¹⁰ It is found that the temperature dependency of the changes in chemical shift of phenolic OH proton for the diester is significantly reduced upon complexation with propylammonium ion, suggesting that the conformation of the complex assumes a relatively rigid cone form compared with the free host.

Experimental

Preparation of Calix[4]arene Based Hosts.

Monomethyl ester **4**¹¹ and calix[4]-diquinone **5**^{4b} were prepared according to the published procedures. 1,3-Distal functionalized calix[4]arene **1-3** were also prepared following a slightly modified known procedure.¹² A mixture of *p*-tert-butylcalix[4]arene (1 mmol), K_2CO_3 (2 mmol), and alkylating agent (2 mmol) in dry THF was refluxed under N_2 for 18-24 h. After evaporation of the solvent, the residue was extracted with CH_2Cl_2 . Purification was achieved by column chromatography followed by recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ solution to obtain a pure di-functionalized calix[4]arene in good yield (70-95%).

NMR Measurements. All the deuterated solvents for the experiment, CDCl_3 , $\text{C}_2\text{D}_2\text{Cl}_4$, and $\text{THF-}d_8$, etc., were purchased from Aldrich and/or Sigma Chemical Co. and used without further purification. Each sample for relaxation time determination 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.

^1H NMR spectra were obtained on a Varian VXR-200S spectrometer operating at 200 MHz. (Unless otherwise specified, measurements were run at 298 K and CDCl_3 was used as solvent.) All the peaks were identified by means of COSY and NOESY experiments. Chemical shift values were quoted in parts per million (ppm) downfield from TMS employed as an internal reference. The spin-lattice (longitudinal) relaxation times (T_1) for protons were measured in CDCl_3 by the inversion recovery method using at least 16 different delays between π and $\pi/2$ pulses. The time delay for next acquisition after one transient was set to be more than 10 times of the longest T_1 value of interest. Each T_1 value was estimated with the aid of exponential fitting program in VNMR software equipped in the Varian NMR system. They ranged from 0.2 to 1 sec for protons. The chemical shifts of protons in hosts were observed as a function of ρ , the concentration ratio of guest to host to determine the association constant. The concentration of propylammonium picrate was varied from 0 to 0.20 M with a fixed host concentration of 0.04 M in $\text{THF-}d_8$, so that the ρ varied from 0 to 5.

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Magnetic Property of Oxide with the Perovskite Structure, $A_2\text{Fe(III)BO}_6$ ($A=\text{Ca, Sr, Ba}$ and $B=\text{Sb, Bi}$)

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In the course of magnetic study on several perovskite-type oxides, $A_2\text{Fe(III)BO}_6$ ($A=\text{Ca, Sr, Ba}$, and $B=\text{Sb, Bi}$), we have observed a strong irreversibility in their dc-magnetizations. When the structural data and the Mössbauer spectra are considered, such an irreversibility is to be associated with some competitions between the nearest-neighbors (*nn*) and the next-nearest-neighbors (*nnn*) in their magnetic sublattices. Particularly, the Mössbauer spectra indicate that $\text{Sr}_2\text{FeBiO}_6$ of cubic perovskite-structure is apparently well ordered crystalline compound. Nonetheless this antiferromagnet shows a magnetic property which resembles that of a spin-glass. The strong history dependence is observed below 91 K and the irreversible magnetic behavior is also observed from the measurement of hysteresis loops at 10 K after zero-field-cooled (*zfc*) and field-cooled (*fc*) processes. Considering the *nn* and the *nnn* superexchanges of almost same order in ordered perovskite, it is proposed that there exists a competition and cancellation of antiferromagnetic and ferromagnetic superexchange between the nearest-neighbors and the next-nearest-neighbors, thus introducing a certain degree of frustration.

Introduction

Low-temperature antiferromagnetism is often observed in many compounds having the general formula $A_2\text{Fe(III)BO}_6$ where *A* and *B* are diamagnetic cations.¹ When there is a large difference in size between Fe^{3+} and B^{5+} , the materials adopt a perovskite-related structure with an alternate ordering of the cations B^{5+} and Fe^{3+} on the octahedral sites.² The magnetic Fe^{3+} ions ($3d^5: {}^6A_{1g}$) thus form a face-centered array in a cubic unit cell having $a_0 \approx 8 \text{ \AA}$, that is $2a_p$ where a_p is the cell parameter of the primitive perovskite unit cell.

Several years ago, we reported the synthesis of $\text{Sr}_2\text{FeBiO}_6$ and $\text{Ba}_2\text{FeBiO}_6$ under the high oxygen pressure.^{3,4} The strong superstructure lines in powder X-ray diffraction pattern of $\text{Sr}_2\text{FeBiO}_6$ showed an ordered perovskite with a double unit cell parameter. The weak extra reflections in $\text{Ba}_2\text{FeBiO}_6$ also lead to an indexation with a pseudocubic unit cell parameter. The inverse of zero-field-cooled magnetic susceptibilities of both compounds in the high-tem-

perature range obeyed typical Curie-Weiss law

$$\chi = C / (T - \theta)$$

with Curie paramagnetic constant $C \approx 4.6 \text{ emu.K/mol}$ implying a spin value of $S=5/2$ as expected for high-spin Fe^{3+} . Quite largely negative Curie temperature indicated predominant antiferromagnetic exchange interactions between the Fe moments. However, a marked deviation from the linearity below about 200 K was observed in both two compounds. Nevertheless the ^{57}Fe Mössbauer spectra of $\text{Sr}_2\text{FeBiO}_6$ at 80 K showed a superposition of a magnetic hyperfine sextuplet and a paramagnetic singlet, which was explained to result from slow relaxation process in long-range superexchange. Such experimental results of magnetic susceptibility and the Mössbauer effect allowed us to conclude that the antiferromagnetic long-range ordering is induced below 91 K with $\text{Sr}_2\text{FeBiO}_6$.

In view of the magnetic study of these compounds our main interest has been focussed on a strong deviation of