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^{1}H and ^{7}Li NMR Study on the Complex Formation of Lithium Cations with Pyridinium Derivatives of Calix[4]arenes

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Complexation of lithium ions by three chromoionophoric calix[4]arenes has been studied by ^{1}H and ^{7}Li NMR spectroscopy. The signalling unit of the chromoionophores is the *N*-methylpyridinium(methyleneimino) group in conjugation with a phenolic group of the calixarene ring while the coordination spheres contain esteric (ethoxycarbonylmethoxy) or etheric (ethoxy, propoxy) units. ^{1}H NMR and NOESY measurements suggest the dominance of cone conformations of the calixarene rings with slight, solvent-dependent distortions. Complexation occurs only in the presence of a weak base. The interaction with lithium ions causes a broadening of both the ^{1}H and ^{7}Li NMR signals. Analysis of the chemical shifts in the three complexes indicates a different coordination environment for the lithium with the calixarene containing esteric groups from those having etheric groups. This explains the differences in the stabilities of the lithium complexes of the two types of calixarenes.

Keywords: Calix[4]arene; ^{1}H NMR; ^{7}Li NMR; Lithium ion; Complex

INTRODUCTION

The synthesis and the systematic spectroscopic studies of chromogenic/fluorogenic calixarenes supplied with various coordination spheres have attracted great interest in recent years. Calixarene ethers, esters and calixcrowns capable of binding alkali/alkali-earth metal ions selectively play important roles in developing new electrochemical and/or optical sensors (optodes) applicable in multi-ionic media, such as physiological liquids [1–5].

The structural changes in calixarene chromoionophores interacting with metal ions are most efficiently studied if UV–Vis absorption spectroscopic experiments are coupled with NMR spectroscopic measurements. Such combined studies have, however, been carried out only on a few chromogenic calixarenes reported in the literature, because the low solubilities of most of their complexes exclude the use of NMR methods. Many calixarenes are conformationally flexible, that is they exist as an equilibrium mixture of cone and partial cone conformers, interconverting to each other. As was shown by ^{1}H [6,7] and ^{13}C [8] experiments, the complexation of metal ions by such hosts is frequently associated with the shift of this equilibrium towards one of the conformers. The NMR spectra provide information on how much the introduction of the chromophore/fluorophore unit affects the complex-forming ability of the 'non-coloured' calixarene. Diamond and co-workers found that the coupling of anthracene units to the coordination sphere of a calixarene-tetraester hardly influences the selective complex formation with Ca^{2+} ions [9]. In other cases the stability of the complex is enhanced by 'cation–π' interactions between the metal ion and the π electron system of the chromophore group [8], or by electrostatic interaction between the metal ion and the deprotonated chromophore unit [10]. In a separate paper on a chromogenic calixarene, Diamond and colleagues established that the encapsulation of an ion did not lead to significant changes in the UV–Vis spectra but induced the deprotonation of the chromophore unit in reactions with weak bases, which is, in contrast, accompanied by a dramatic shift in the visible absorption [11]. Beside the binding site,

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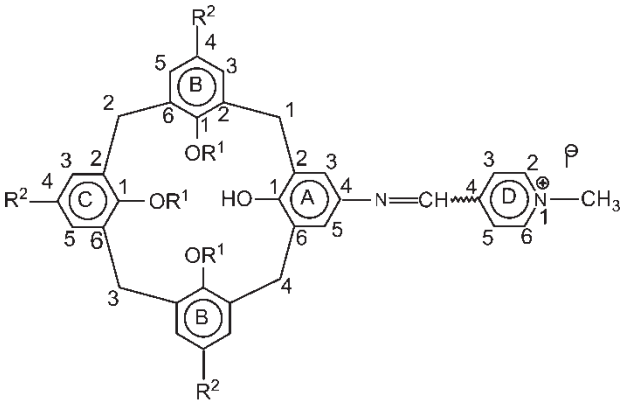

FIGURE 1 Structures of the calix[4]arenes studied.

the structural alteration of certain proton ionizable chromophore groups can be of great importance during complexation. In our laboratory the endo/exo quinoide tautomerism of the indophenol indicator units of some calix[4]arenes capped by di- and triamide bridges was studied by detailed NMR spectroscopy [12].

As part of our ongoing programme to synthesize chromoionophores for developing optical sensors, we have studied the optical properties of several calix[4]arenes with various chromophore groups: 2,4-dinitrophenylazo, pyridinium(methyleneimino) and indophenol. Among them, the variations in the UV–Vis absorption spectra of proton ionizable calix[4]arene triester **1** and triethers **2** and **3** comprising the *N*-methyl-pyridinium(methyleneimino) signalling group were studied in the presence of alkali metal salts [13]. This indicator group, described by Machado *et al.* [14], was introduced into the upper rim of the calix in conjugation with the phenolic moiety. We have found that ligands **1–3** (Fig. 1) exhibit distinct solvatochromism in various solvents and halochromism in the presence of alkali salts. The complex-forming abilities towards alkali cations were also studied and we found that compound **1** binds Li ion selectively and the reaction is accompanied by colouration [13,15].

In this paper, the complete structure elucidation of ligands **1–3** with respect to the conformation of the calix and the solvent-dependent isomerism of the signalling group are reported. Moreover, ^{1}H and ^{7}Li NMR data are provided for an explanation of the binding process of Li^+.

EXPERIMENTAL

The synthesis of hosts **1–3** was reported in our earlier paper [13]. ^{1}H and ^{7}Li NMR spectra were acquired on a Bruker DRX 500 Avance spectrometer at 500.13 and 194.34 MHz, respectively, at 300 K. ^{1}H NMR chemical shifts were determined relative to tetramethylsilane (TMS). ^{7}Li NMR chemical shifts were determined relative to external 1 M LiCl (in D_2O) without susceptibility correction. NOESY spectra were recorded in phase-sensitive mode with solvent peak suppression. Samples were degassed prior to relaxation time measurements by ultrasonic treatment (Tesla UC 002 BM 1). For the T_1 measurements inversion-recovery (IR) pulse sequences were applied. T_2 relaxation times of the ^{7}Li NMR signals were estimated first from the signal half-width, and then the inhomogeneity component of the T_2 relaxation was calculated from the T_2 value of a 7.2×10^{-3} M LiBr solution in acetonitrile, measured by the Carr–Purcell–Meiboom–McGill (CPMG) pulse sequence method. All other T_2 data were corrected by this magnetic field inhomogeneity contribution. The Bruker software package (WXIN-NMR 2.5) was used for acquisition and the relaxation time calculations.

RESULTS AND DISCUSSION

^{1}H NMR Spectra of Hosts 1–3

Solvent Effects

^{1}H NMR data of compounds **1–3** in $CDCl_3$ solution were reported previously [13]. Inorganic lithium salts are poorly soluble in chloroform, whereas their solubility is relatively high in acetone, acetonitrile and DMSO [16]. For cation complexation studies acetonitrile and DMSO are more suitable than acetone (or chloroform) because the metal-ion salts are likely to predominate in their ionic forms in these media. A different type of complexation reaction is expected to take place in acetone, where ion pairs rather than ions are the main species in solution. Finally, the spectra of host **1** were taken in all the above solvents, whereas those of **2** and **3** were measures in acetone only (Table I). As our UV–Vis spectroscopic studies [15] showed a strong complexation of Li^+ with high selectivity in acetone, most of the NMR measurements were carried out in this solvent. The chemical shifts obtained in various solvents are summarized in Table I.

As is apparent from Table I, the structure of **1** is different in apolar (chloroform) and dipolar-aprotic solvents (acetone, acetonitrile, DMSO). In the first column of Table III (see later), the solvation shifts in acetone (with respect to chloroform) are presented. These data show that the chemical shifts of protons close to the nitrogen atom, such as the *N*-methyl and the D2,6-H protons, are dramatically displaced (from 2.85 to 4.29–4.66 ppm, and from 7.93 to 8.33–8.60 ppm). This indicates a reduction in

TABLE I ^{1}H NMR chemical shifts of ligands **1**–**3** in different solvents at 300 K

Signal	**1** $CDCl_3$ [4]	**1** Acetone-d_6	**1** CD_3CN	**1** DMSO-d_6	**2** Acetone-d_6	**3** Acetone-d_6
A3-H, A5-H	7.27	7.45	7.37	7.43	7.54	7.55
B3-H, B5-H	6.81*, 7.06*	6.73, 6.69	6.81*, 6.80*	6.71*, 6.78*	6.80*, 6.72*	6.79* 6.71*
B4-H/B4-*t*-Bu	6.78	6.55	6.66	6.60	0.89	0.90
B–OCH_2	5.01, 4.57	4.76, 4.57	4.71, 4.50	4.68, 4.57	3.90–4.02	3.77
B–$COOCH_2$	4.34	4.30	4.27	4.23	–	–
B–CH_3	1.37	1.34	1.32	1.29	1.55	1.16
C3-H, C5-H	7.07*	7.16	7.17	7.17	7.28	7.28
C4-H/C4-*t*-Bu	6.77	6.88	6.90	6.86	1.33	1.33
C–OCH_2	4.89	5.11	5.06	4.96	4.03	3.86
C–$COOCH_2$	4.20	4.16	4.14	4.09	–	–
C–CH_3	1.30	1.26	1.24	1.20	1.74	1.00
D2,6-H	7.93	9.19	8.64	9.03	9.23	9.23
D3,5-H	8.29	8.60	8.33	8.42	8.61	8.61
CH =	8.97	9.10	8.84	8.98	9.18	9.20
N–CH_3	2.85	4.66	4.29	4.36	4.66	4.67
AB–CH_2	4.44, 3.48	4.48, 3.47	4.40, 3.47	4.30, 3.47	4.35, 3.45	4.36, 3.45
BC–CH_2	4.90, 3.38	4.99, 3.36	4.85, 3.37	4.77, 3.34	4.42, 3.28	4.43, 3.28
OH	7.53	†	†	†	†	†

* Alternative assignment. † Separate OH signals could not be observed because of traces of water in these solvents and the chemical exchange.

the shielding effect and an increase in the positive polarization at the nitrogen atom.

Z/E Isomerism

When the chromogenic *N*-methylpyridinium moiety is attached to the calix[4]arene through an imino group, the molecule no longer has any symmetry plane due to *Z/E* isomerism. This means that some hydrogen atom-pairs (for example A3-H and A5-H, C3-H and C5-H, B4-H and B′4-H) are not isochronous and their signals should be separately observed in the ^{1}H NMR spectrum. However, the *Z/E* interconversions of some imines (enamines) have low energy barriers [17] resulting in fast exchanges on the NMR time scale, therefore only one set of signals appear in the spectra, even at 500 MHz. The *Z/E* isomers have a mirror image relationship (without an energy difference) and the chiral character of the molecules is indicated by the non-equivalence of the geminal protons (B–OCH_2).

NOESY Experiments

To support the signal assignments homonuclear NOESY spectroscopy was used. The most significant NOESY cross-peaks of compound **1** are summarized in Table II. A number of cross-peaks were observed between the CH_2 bridge protons and the aromatic protons and even between protons attached to different aromatic rings. For example, the signals of D2,6-H and D3,5-H protons could be assigned unambiguously, because the former gives a cross-peak with the *N*-methyl signal, while the latter gives one with the vinyl-proton signal. In the same way, the AB–CH_2 and BC–CH_2 signals could also be differentiated, because the former gives a cross-peak with the A2,6-H signal, while the latter gives one with the C2,6-H signal. Furthermore, it was possible to differentiate and assign the B-3H and B-5H signals (and certainly the B′3-H and B′5-H signals as well), as protons B3-H show steric proximity with the AB–CH_2 methylene protons, while protons B5-H do the same with the BC–CH_2 methylene protons. The methylene bridge protons are in steric proximity not only with their geminal counterparts and the aromatic protons but also with the protons of the O-substituent (B–OCH_2 and C–OCH_2). A partial homonuclear NOESY spectrum of **1** recorded in acetone is shown in Fig. 2.

Several NMR studies concerning the conformational analysis of the calix[4]arene skeleton have been reported [6,18–21]. Cone conformations can be

TABLE II Significant NOESY cross-peaks in the spectra of **1** (acetone-d_3 solution, 300 K)

Signal 1	Signal 2	NOE intensity (%)*
BC–CH_2	BC–CH_2(gem)	100
AB–CH_2	AB–CH_2(gem)	92.3
N–CH_3	D2,6-H	19.4
CH =	A3,5-H	19.05
A3,5-H	AB–CH_2	24.3
BC–CH_2–	C3,5-H	29.2
BC–CH_2	B5-H	16.0
AB–CH_2	B3-H	14.7
A3,5-H	B3-H	9.9
C3,5-H	C4-H	28.7
C3,5-H	B5-H	14.9
B3,5-H	B4-H	42.1
C–OCH_2	BC–CH_2	21.9
B–OCH_2	BC–CH_2	14.9
B–OCH_2	B–OCH_2(gem)	67.5
AB–CH_2	B–OCH_2	13.9
B–CH_3	B–OCH_2	32.2
C–CH_3	C–OCH_2	37.5

* The largest cross-peaks were observed between the signals of geminal BC–CH_2 protons. The volume integrals of these cross-peaks were considered as 100%. All other volume integrals were determined relative to this value.

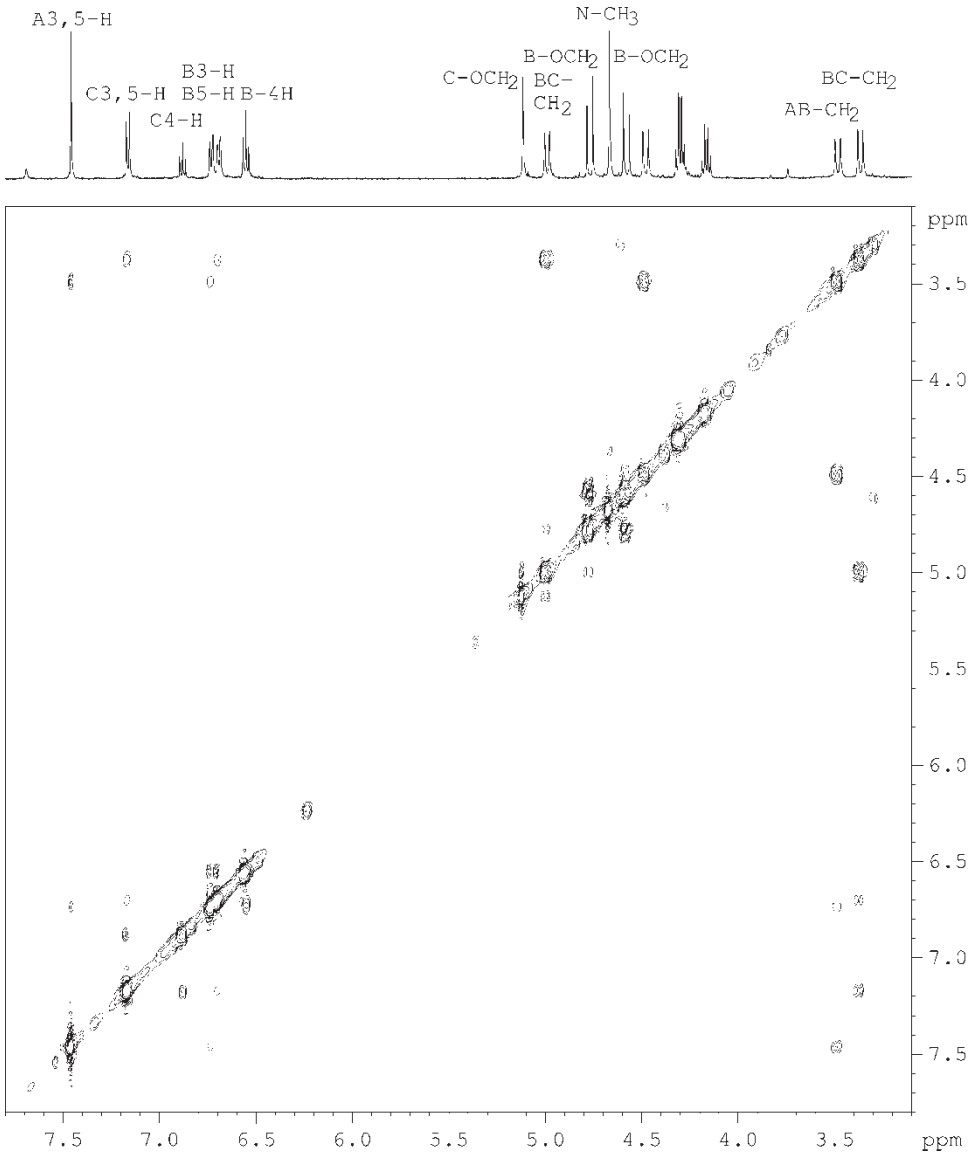

FIGURE 2 Part of the homonuclear NOESY spectrum of calixarene **1** recorded in acetone.

directly detected by NOESY experiments, as hydrogens in spatial proximity result in cross-peaks in the 2D NOE spectrum. Therefore, the cross-peaks of the A3,5-H protons with the B3-H signal and those of the C3,5-H protons with the B5-H signal (which appeared in both acetone and acetonitrile) together suggest the dominance of the cone conformation of ligand **1**. The characteristic pair of doublets of the $ArCH_2Ar$ protons also support this conclusion for **2** and **3**, where NOESY spectra were not recorded. However, distortion of the ideal cone conformation in the whole series is reflected by the differences of the $ArCH_2Ar_{ax/eq}$ protons and also those of the Ar3,5-H protons. The values $\Delta\delta$ $ArCH_2Ar_{ax/eq} \approx 0.9–1$ ppm and $\Delta\delta$ A,B-Ar3,5-H $\approx 0.5–0.7$ ppm indicate that the B rings are nearly parallel, whereas the A rings are more parallel, the C rings are less flattened. The extent of conformational distortion depends partially on the solvent and is larger with hosts **2** and **3** due to the steric requirements of the *p-tert*-butyl groups.

Complexation of the Lithium Ion

As mentioned earlier, the complexation studies were carried out in acetone, in which LiBr has high solubility (1.93 M at 20°C [16]) allowing variation of the salt concentration over a wide range. For the visible spectroscopic studies, fairly diluted ligand solutions (5×10^{-5} M) were used, but for the NMR investigations higher ligand concentrations (7×10^{-4} M) were used because of the different sensitivities of the two methods. The measurements were performed in acetone solutions saturated with ligand **1**, containing triethylamine (TEA) in 400-fold molar excess and LiBr in 1.5-fold, 3-fold,

TABLE III ^{1}H NMR shifts of ligands **1**–**3** upon solvation and binding with LiBr at 300 K

	1 Solvation	**1** $CDCl_3$	**1** Acetone-d_6	**1** Acetonitrile-d_3	**2** Acetone-d_6	**3** Acetone-d_6
A3,5-H	0.18	0.07	0.1	0.1	−0.03	−0.04
B3,5-H	−0.08, −0.37	0.24	0.29; 0.11	0.24; 0.22	0.37, 0.19	0.37, 0.22
B4-H	−0.23	0.18	0.12	0.13		
B–OCH_2	−0.25; 0.00	0.30; −0.22	0.42; −0.09	0.27; −0.09	*ca* 0.2	0.24
B–$COOCH_2$	0.04			−0.05		
B–CH_3	−0.03	−0.06	−0.02	−0.05	0.06	TEA
C3,5-H	0.09	0.21	0.24	0.17	0.11	0.12
C4-H	0.11	0.34	0.19	0.17		
C–OCH_2	0.22	0.14	−0.05	−0.13	0.66	0.65
C–$COOCH_2$	−0.04		0.29	0.24		
C–CH_3	−0.04	0.11	0.18	0.14	−0.39	TEA
D2,6-H	1.27	−0.21	−0.49	−0.31	−0.56	−0.60
D3,5-H	0.31	−0.22	−0.41	−0.30	−0.56	−0.55
CH =	0.13	−0.71	−0.23	−0.32	−0.65	−0.69
N–CH_3	1.81	1.41	−0.29	−0.17	−0.32	−0.32
AB–CH_2	0.04; −0.01		−0.19; −0.02	−0.21; −0.23		
BC–CH_2	0.09; −0.02		0.09; −0.07	0.03; 0.06		

4.5-fold, 6.9-fold, 8.4-fold and 11.5-fold excess. Our UV–Vis studies proved that ligand **1** in acetone did not form a complex with the Li-salt, unless a significant excess of a weak base, such as TEA, was present. The addition of lithium ions alone in 10-fold excess, or of TEA alone in 100-fold excess, did not result in any change in the ^{1}H NMR spectra. By contrast, the above solutions containing both compounds showed clear signs of complex formation, including the visible colour change. Regrettably, the most characteristic change in the NMR spectrum was line broadening, which prevented us from studying the complexation shifts of the individual protons. This phenomenon can arise either from a slow exchange process between the complexed and uncomplexed ligand or from some slow conformational or tautomeric transformation in the complex formed. A further explanation for the line broadening can be the formation of dimers or higher oligomers [22].

In DMSO-d_6 solution, compound **1** behaved differently. The NMR spectra did not show any change referring to complexation even in the presence of Li-salt and TEA in large excess. Presumably the binding of lithium is severely restricted by the strong solvating power of DMSO, which can coordinate cations via the sulfoxide oxygen donor atoms.

In chloroform, the solubility of LiBr is very low, so that adding Li salt solution to the chloroform-*d* solution of compound **1** in controlled quantities could not be achieved. However, interaction with Li^+ could also be shown in this solvent. A 100-fold excess of TEA did not cause any change in the NMR spectrum, but adding a small crystal of LiBr to the solution resulted in the appearance of a new set of signals with intensities increasing in time. Unfortunately, some line broadening also took place, but the new set of signals may be due to the association of the Li-salt with **1**.

The complexation experiment in acetonitrile-d_3 solvent gave very similar results to those with acetone-d_6, although the signal broadening was negligible. In the presence of Li^+ excess only one set of signals appeared that could be assigned to the complex formed. The complexation shifts were similar to the data measured in acetone, and the conformation is similar to that of the free ligand. Unfortunately, the large excess of TEA meant that NOESY measurements of reasonable quality could not be achieved.

The results of the binding studies are collected in Table III. The first column shows the solvation shifts of **1** when the solvent was changed from the apolar chloroform to the dipolar-aprotic acetone. Columns 2–4 show the chemical shift differences of the ligands in the simultaneous presence of Li^+ ions and TEA and the values are referred to the chemical shifts in the same solvent. The solvent plays an important role in the binding process. The change of positive polarization at the nitrogen atom is observable even in chloroform solution, as the second column of Table III shows. This is indicated by the negative complexation shifts at the indicator moiety ($\Delta\delta$D2,6-H, $\Delta\delta$D3,5-H, $\Delta\delta$ CH═ and $\Delta\delta$ NCH_3) in every case. Therefore, the data in the other columns correspond to a combined effect of the complex formation and of the solvent-induced polarization rearrangement in ligand **1**.

The most significant changes in the chemical shifts can be observed at the B–OCH_2 protons, where one proton is shifted upfield, while the other moves downfield. This means that the chemical non-equivalence of these protons increases and the lower rim is affected by the complexation. The spectra also provide evidence that

the chiral character of the ligand is retained in the complex formed.

According to our UV–Vis spectroscopic measurements, homologues **2** and **3** have lower equilibrium constants with Li^+ than compound **1** [15,23]. Therefore, when ligands **2** and **3** were treated with a 3.2-fold excess of LiBr in the presence of a 500-fold TEA excess, the spectrum displayed a set of minor signals only, referring to complexation. The individual complexation shifts for compounds **2** and **3** are very close and they show similarity to those of ligand **1**. The lower rim is affected by the complexation in both cases too, as indicated by the $\Delta\delta$ values at the $B-OCH_2$ signals.

The reactions between metal salts and calixarene ionophores in various non-aqueous media, with regard to the thermodynamic parameters, were reviewed by de Namor *et al.* [24]. They pointed out that care has to be taken to distinguish the complexation of the metal ion

$$M^+(s) + L(s) \rightarrow ML^+(s) \quad (1)$$

from the process involving ion pairs

$$M^+X^-(s) + L(s) \rightarrow ML^+X^-(s) \quad (2)$$

where $M^+(s)$, M^+X^- (s) and L(s) denote the metal ion, the salt and the ligand, respectively, all in the solvated state. In polar solvents, such as acetonitrile, reaction (1) is undoubtedly the dominant process. In solvents with low dielectric constant, such as chloroform and to some extent acetone, reaction (2) is preferred.

As mentioned before, our calixarenes do not react directly with metal salts, only in the presence of TEA, which is not complexed by our hosts but facilitates the dissociation of the phenolic OH group. Instead of reactions (1) and (2), therefore, the process may be interpreted in terms of reaction (3) [15]:

$$M^+Br^- + LOH + Et_3N \rightarrow [M^+LO - H\cdots NEt_3]Br^- \rightarrow M^+LO^- + Et_3N{\cdot}HBr \quad (3)$$

where LOH denotes a calixarene composed of a phenolic hydroxy group.

It should be noted that the thermodynamic parameters for our systems cannot be calculated solely from the NMR spectroscopic results. Their determination would also require the values for the degree of dissociation of the amine salt $Et_3N{\cdot}HBr$ in various solvents. Although the quantitative treatment of the binding process is not possible at this point, an equilibrium involving an ion pair (which may contain Et_3N) and an ionic complex can be assumed, which depends on the solvent polarity. The former may be the dominant species in chloroform and the latter in acetonitrile. The medium polarity of acetone suggests the simultaneous occurrence of both species.

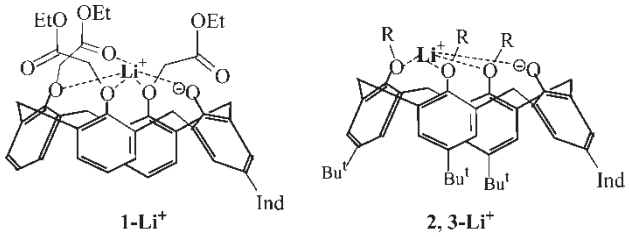

FIGURE 3 The probable structures of the lithium complexes of **1**–**3** (Ind denotes the chromogenic indicator group).

Nevertheless, the NMR data do allow us to envisage the coordination environment of the lithium ion in hosts **1**–**3**. Thus, in host **1** the cation probably resides in the vicinity of the $B-OCH_2$ groups using their donor oxygen atoms (complexation shifts $\Delta\delta$ $B-OCH_2 \approx 0.3-0.4$ and $\Delta\delta$ $AB-CH_2 \approx -0.2$ ppm) and the ester carbonyl group of the C ring (complexation shifts $\Delta\delta$ $C-COOCH_2 \approx 0.29$ ppm) for coordination (the $B-COOCH_2$ groups do not show noticeable shifts). The complex is stabilized by the phenolate function of the chromophore via ionic interaction (Fig. 3). The structure of the lithium complex of hosts **2** and **3** is assumed to be different. Here the cation is probably located near to the $C-OCH_2$ group ($\Delta\delta$ $C-OCH_2 \approx 0.6$ ppm) but the other two phenoxy groups are also involved in the binding ($\Delta\delta$ B, $C-OCH_2 \approx 0.2$ ppm). In this structure the Li^+ ion is bound in a rather remote position from the phenolate moiety, which leads to weaker ionic interaction resulting in lower complex stabilities.

^{7}Li Spectra of the Li^+-1 Supramolecular Systems

The ^{7}Li isotope with spin 3/2 is a readily detected nucleus (relative sensitivity is 0.27 with respect to ^{1}H); thus ^{7}Li NMR spectroscopy is also an efficient tool for studying the complexation process. However, these experiments require a different approach. Significant complexation of the Li^+ ions can be attained by the addition of the ligands in a considerable excess, which cannot be achieved in the concentration range suitable for NMR experiments, because of the limited solubility of our ligands. Therefore, in our experiments the estimated ratio of the uncomplexed Li^+ varied from 100% to 15% (calculated from the stability constant and the concentration).

The chemical shift of the uncomplexed ^{7}Li signal is primarily determined by the quality of the solvent (which effects the dissociation of the Li-salt applied and the solvation of the ions). By our measurements, in various dipolar-aprotic solvents (acetone-d_6, DMSO-d_6, acetonitrile-d_3), relatively sharp signals ($\Delta 1/2$ 0.4–0.6 Hz) were observed. The concentration,

TABLE IV T_1 and T_2 relaxation times of the ^{7}Li signal and the chemical shifts in different solutions at 300 K

Solvent	Li concentration (M)	Ratio of uncomplexed Li (%)	δ (ppm)	T_1 (s)	T_2 (s)
Acetone-d_6	7.9×10^{-4}	100	1.07	4.21	0.34
Acetone-d_6	8.1×10^{-4}	15	1.15	0.083	0.034
CD_3CN	7.14×10^{-3}	100	−2.19	7.57	1.60
CD_3CN	2.8×10^{-4}	90	−2.00	0.24	0.017

as well as the presence of TEA, also has some impact on the chemical shift.

The sharp ^{7}Li signal in the presence of various amounts of **1** and excess TEA shows a slight upfield shift and significant line broadening. No individual complexed and uncomplexed ^{7}Li signal could be observed, which could be connected with the chemical exchange between the two species. T_1 and T_2 relaxation times were measured and the most significant ^{7}Li NMR data are collected in Table IV. As can be seen from these data, both T_1 and T_2 relaxation times are significantly smaller when ligand **1** is present and the lithium is partly complexed. The change in T_2 relaxation times is connected with the rate process. However, there is another possible explanation for the line-broadening phenomenon. In the complex formed, the Li^+ ion is arranged in an asymmetric environment, where the charge distribution is different from that of the solvated state. The ^{7}Li isotope, having 3/2 spin and a quadrupole moment, gives sharp signals only in a symmetric environment [25]. ^{23}Na signals exhibit similar effects when Na^+ ions are complexed by calixarene or cyclen derivatives [24–27]. However, other workers [28,29] proved by line-shape analysis at different temperatures that the broadening of the ^{23}Na signals also can be caused by a further equilibrium, where a 2:1 calixarene:Na^+ complex takes place. The low boiling point of the solvent, however, does not allow the measurements to be made over a sufficiently wide range of temperatures.

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