

# Cyclic Li<sup>+</sup>-Bonded System with Large Li<sup>+</sup> Polarizability Due to Collective Li<sup>+</sup> Motion in Calixarenes: an FT-IR Study

Bogumil Brzezinski,<sup>†</sup> Franz Bartl,<sup>‡</sup> and Georg Zundel<sup>\*,§</sup>

Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60780 Poznań, Poland,  
Institute of Medical Physics and Biophysics, Universitätsklinikum Charite, Humboldt University Berlin,  
Ziegelstrasse 5/9, D-10098 Berlin, and Institute of Physical Chemistry, University of Munich,  
Theresienstrasse 41, D-80333 Munich, Germany

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Li<sup>+</sup> complexes of OH deprotonated calix[4]arene, calix[6]arene, and calix[8]arene were prepared. The spectra of these complexes show that with Li<sup>+</sup> ions the complex formation is complete. In the 1:4, 1:6, and 1:8 complexes, respectively, the Li<sup>+</sup> ions are localized in their Li<sup>+</sup> bonds since only a broad band was found in the FT-IR spectra. In the case of the corresponding 1:3, 1:5, and 1:7 complexes far-IR continua are observed in the region 380–150 cm<sup>-1</sup>. These continua demonstrate that these Li<sup>+</sup>-bonded systems show large Li<sup>+</sup> polarizability due to collective Li<sup>+</sup> motion. This Li<sup>+</sup> polarizability increases with the size of the Li<sup>+</sup>-bonded systems.

## 1. Introduction

In the last few years calixarenes have become very popular compounds in supramolecular chemistry since their OH groups can be selectively functionalized.<sup>1,2</sup> These compounds build very stable complexes with various metal ions.<sup>3,4</sup>

Recently, we removed one proton from calixarenes with strong bases, such as 1-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) or with the much more stronger base phosphazene (P<sub>2</sub>Et). In the monoanions of the studied calixarenes, cyclic hydrogen-bonded chains were present. These systems show large proton polarizability<sup>5,6</sup> due to collective proton fluctuation.<sup>7</sup> The polarizabilities were indicated by intense continua in the IR spectra, beginning at about 3000 cm<sup>-1</sup> and extending toward smaller wavenumbers.<sup>5,6</sup>

In the last years we studied various systems with Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and Be<sup>2+</sup> bonds. With these bonds the cations connect two groups, as does the proton in the hydrogen bonds. We have demonstrated that also these bonds show large cation polarizabilities due to cation fluctuation in double-minimum potentials or broad flat potential wells.<sup>8,9</sup> Furthermore, we studied Li<sup>+</sup> and Na<sup>+</sup> monosalts of crown ethers. Also the motion of these cations in cyclic multi minima potentials cause cation polarizabilities, as indicated by continua in the FAR infrared spectra.<sup>10</sup>

In this paper we studied cyclic Li<sup>+</sup>-bonded systems in calixarenes.

## 2. Experimental Section

The calix[4]arene, calix[6]arene, calix[8]arene, and the strong base P<sub>2</sub>Et were purchased from Aldrich and Fluka, respectively. The calixarenes were purified by crystallization from water, whereas the P<sub>2</sub>Et base was used without any purification. The deprotonation of the calixarenes was performed by addition of stoichiometric amounts of P<sub>2</sub>Et (related to the OH protons) to the well-suspended calixarenes in acetonitrile. The concentration of the calixarenes was 0.02 mol dm<sup>-3</sup>.

The Li<sup>+</sup> complexes were prepared by mixing a solution of the corresponding fully deprotonated calixarenes and LiClO<sub>4</sub>, both in acetonitrile. In the case of the fully substituted

calixarenes, the stoichiometry of the fully deprotonated calixarenes to Li<sup>+</sup> cations was 1:4, 1:6, and 1:8, respectively (Scheme 2), and in the case of the not fully substituted calixarenes it was 1:3, 1:5, and 1:7, respectively (Scheme 3).

For comparison, also P<sub>2</sub>Et and its 1:1 complex with HAuCl<sub>4</sub> were studied. These complexes were prepared by addition of the pure base to an ethanol solution of HAuCl<sub>4</sub>. The solvent was evaporated under reduced pressure at room temperature. The residue was dissolved in acetonitrile. The concentration of this solution was 0.02 mol dm<sup>-3</sup>.

A cell with Si windows and a wedge-shaped layer were used to avoid interferences (mean layer thickness 0.176 mm). The IR spectra were taken with a FT-IR spectrophotometer IFS 113v from Bruker, using a DTGS detector in the MIR region (125 scans, resolution 1 cm<sup>-1</sup>) and a helium-cooled bolometer in the far-IR region (125 scans, resolution 1 cm<sup>-1</sup>). All solvents were stored over a 3 Å molecular sieve. All preparations and transfers of solutions were carried out in a carefully dried glovebox under nitrogen atmosphere.

## 3. Results and Discussion

The structure of the calixarenes and of the P<sub>2</sub>Et base is shown in Scheme 1. The spectrum of the protonated P<sub>2</sub>Et in acetonitrile was already shown in ref 7. In this spectrum the NH<sup>+</sup> stretching vibration is found at 3343 cm<sup>-1</sup>. The spectra of the 1:4, 1:6, and 1:8 mixtures of the corresponding calixarenes (calix[4]arene, calix[6]arene, and calix[8]arene) with the P<sub>2</sub>Et base are shown in the region of the NH<sup>+</sup> stretching vibration in Figure 1. For comparison, the spectrum of protonated P<sub>2</sub>Et is also given. The integration of these bands in the region 3450–3250 cm<sup>-1</sup> gives the following integrated intensities: 12.51 for the protonated P<sub>2</sub>Et, and 12.37, 18.70, and 24.84, respectively, for the corresponding mixtures of the calixarenes with P<sub>2</sub>Et. Thus, the calixarenes are always completely deprotonated.

**3.1. Fully Li<sup>+</sup>-Substituted Calixarenes.** Figure 2 shows that the fully substituted calixarenes cause one broad band in the region 370–270 cm<sup>-1</sup>. The ion motion band of the pure acetonitrile solution of LiClO<sub>4</sub>, observed at 405 cm<sup>-1</sup><sup>8</sup> has completely vanished, indicating a complete complex formation.

The Li<sup>+</sup> ions are localized in the Li<sup>+</sup> bonds, and no collective Li<sup>+</sup> fluctuation takes place since this broad band is observed instead of a continuum. This band is caused by the vibration of the Li<sup>+</sup> ions in the Li<sup>+</sup> bonds present in the calixarenes (Scheme 2). The intensity of this broad band increases in the

\* To whom correspondence should be addressed. Mailing address: Prof. Dr. Georg Zundel, Bruno-Walter-Strasse 2, A-5020 Salzburg, Austria.

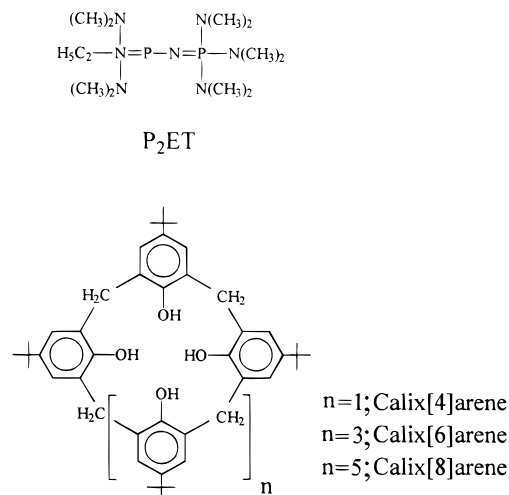
<sup>†</sup> Adam Mickiewicz University.

<sup>‡</sup> Humboldt University Berlin.

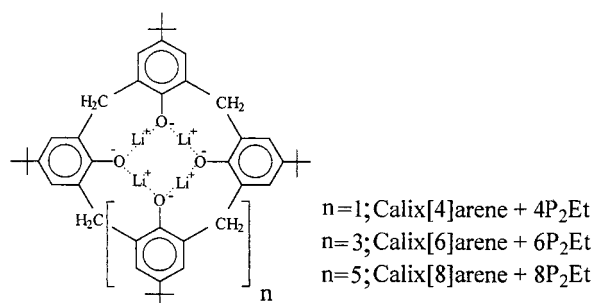
<sup>§</sup> University of Munich.

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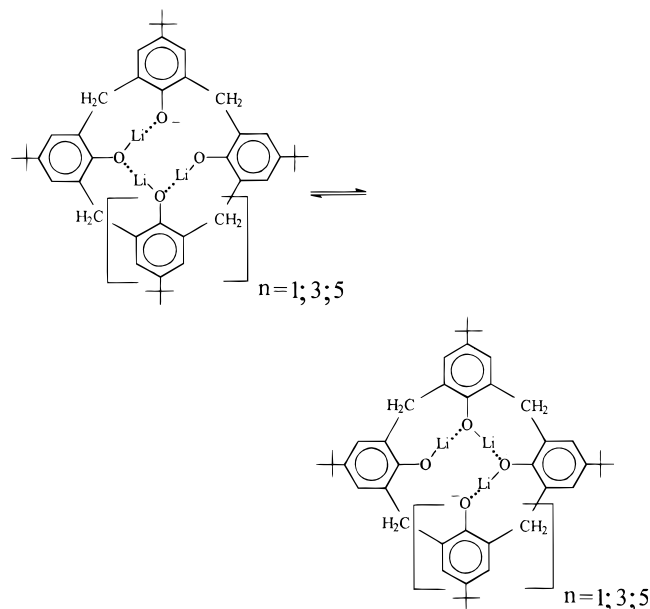
## SCHEME 1



## SCHEME 2: Fully Substituted Calixarenes



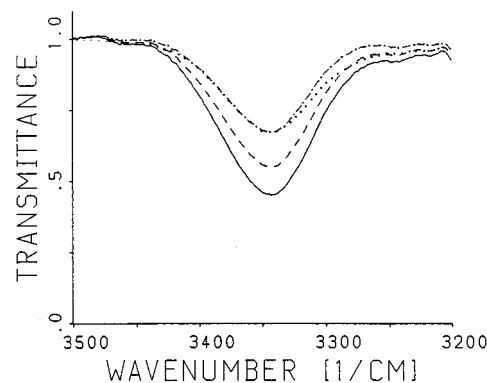
## SCHEME 3: Nonfully Substituted Calixarene



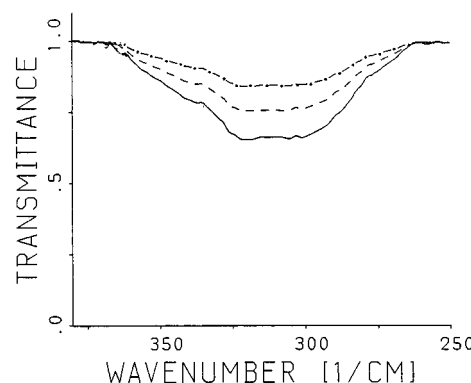
series of the calixarenes since the number of  $\text{Li}^+$  bonds increases. The spectra are identical if related to the same number of bonds. Hence, all bonds cause the same absorbance.

**3.2. Nonfully Substituted Calixarenes.** Corresponding to the hydrogen-bonded chains<sup>7</sup> the spectra of the fully deprotonated calixarenes mixed with 1:3, 1:5, and 1:7  $\text{Li}^+\text{ClO}_4$  molecules, respectively, are shown in Figure 3.

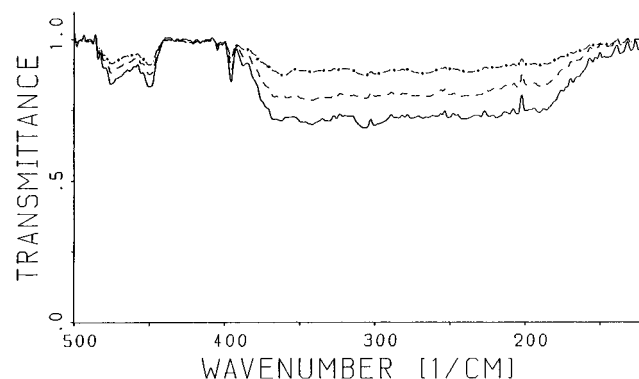
In all these spectra continua are observed in the region  $390\text{--}150\text{ cm}^{-1}$ . They indicate that these  $\text{Li}^+$ -bonded systems show large  $\text{Li}^+$  polarizability due to collective  $\text{Li}^+$  fluctuation, as shown in Scheme 3.



**Figure 1.** 1 FT-IR spectra of acetonitrile solutions of (···) 1:1 complex of  $\text{P}_2\text{Et}$  with  $\text{HAuCl}_4$ , (— · —) 1:4 mixture of calix[4]arene with  $\text{P}_2\text{Et}$ , (— — —) 1:6 mixture of calix[6]arene with  $\text{P}_2\text{Et}$ , and (—) 1:8 mixture of calix[8]arene with  $\text{P}_2\text{Et}$ .



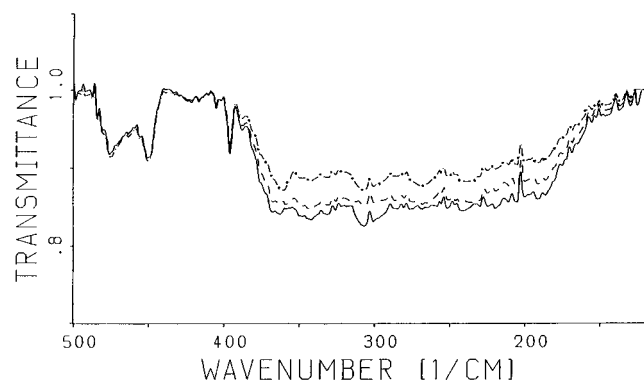
**Figure 2.** FT-IR spectra of acetonitrile solutions of fully deprotonated calixarenes with  $\text{LiClO}_4$ : (— · —) 1:4 mixture of calix[4]arene, (— — —) 1:6 mixture calix[6]arene, and (—) 1:8 mixture of calix[8]arene.



**Figure 3.** FT-IR spectra of acetonitrile solutions of fully deprotonated calixarenes with  $\text{LiClO}_4$ : (— · —) 1:3 mixture of calix[4]arene, (— — —) 1:5 mixture of calix[6]arene, and (—) 1:7 mixture of calix[8]arene.

The intensity of these continua increases within the series of these compounds, i.e., with increasing ring. The reason of this intensity increase is the increasing number of  $\text{Li}^+$  bonds and/or increasing size of the  $\text{Li}^+$ -bonded systems.

To clarify which is the true reason, we calculated the spectra related to the same number of  $\text{Li}^+$  ions. These calculated spectra are shown in Figure 4. This figure demonstrates that not only the concentration of the  $\text{Li}^+$  bonds but also the increase of the size of the  $\text{Li}^+$ -bonded systems determines the intensity of the continuum. With increasing size of the ring, the intensity of the continuum and the  $\text{Li}^+$  polarizability increase due to collective  $\text{Li}^+$  motion. This is particularly true going from calix[4]arene to calix[6]arene. Thus, the number of  $\text{Li}^+$  bonds and the size of the  $\text{Li}^+$ -bonded system determine the  $\text{Li}^+$  polarizability. The resulting increase of the polarizability with



**Figure 4.** The same spectra as in Figure 3 but related to the same Li<sup>+</sup> bond concentration.

increasing size of the systems is analogous to the respective ones of the hydrogen-bonded systems.<sup>7</sup>

#### 4. Conclusions

With P<sub>2</sub>Et the calixarenes can be completely deprotonated with regard to their OH groups. The deprotonated calixarenes form with Li<sup>+</sup> ions fully and nonfully substituted salts. In the case of the fully substituted salts, the Li<sup>+</sup> ions are localized in the four, six, or eight Li<sup>+</sup> bonds, respectively. In the nonfully substituted calixarenes, the Li<sup>+</sup>-bonded systems show large Li<sup>+</sup> polarizability due to collective Li<sup>+</sup> fluctuation. This polariz-

ability increases with the concentration of Li<sup>+</sup> bonds, but especially also with the size of Li<sup>+</sup>-bonded systems. These results are comparable with those obtained earlier with hydrogen-bonded systems in calixarenes.

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