

Extraction and DFT study on the complexation of H_3O^+ ion with tetrakis(2-ethoxyethoxy)-tetra-*p*-*tert*-butylcalix[4]arene

Emanuel Makrlík · Michal Čajan · Jan Budka · Petr Vaňura

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Abstract Extraction experiments in the two-phase water/nitrobenzene system and γ -activity measurements were used to determine the stability constant of protonated tetrakis(2-ethoxyethoxy)-tetra-*p*-*tert*-butylcalix[4]arene in nitrobenzene saturated with water. Density functional theory (DFT) calculations were applied to derive the most probable structure of the tetrakis(2-ethoxyethoxy)-tetra-*p*-*tert*-butylcalix[4]arene- H_3O^+ complex species.

Keywords Calixarenes · Macrocycles · Protonation · Extraction · Ab initio calculations · Complex structure

Introduction

The term “calixarene” was introduced by Gutsche and Muthukrishnan [1] to describe an homologous series of macrocyclic phenol–formaldehyde condensates whose constitution and structure had been the subject of much speculation during the preceding 30 years. Calixarene-based molecules have received intense attention in the last few decades. One of the most important features of these compounds is their diversity. Calixarenes find applications as selective binders and carriers, analytical sensors,

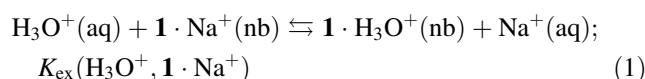
catalysts, and model structures for biomimetic studies [2, 3]. In the field of host–guest chemistry, many studies have focused on the binding ability of calixarene derivatives with carbonyl groups on their lower rims toward metal ions, predominantly alkali and alkaline earth, but also transition and heavy metal cations [4–12].

Recently, protonation of valinomycin, some calixarenes, and dibenzo-18-crown-6 has been investigated in detail [13–25]. In the current work, the experimental evidence for protonation of tetrakis(2-ethoxyethoxy)-tetra-*p*-*tert*-butylcalix[4]arene (**1**, Scheme 1) is described. Moreover, we apply quantum mechanical DFT calculations to predict the most probable structure of this protonated calix[4]arene compound (i.e., **1**· H_3O^+).

Results and discussion

Extraction experiments

Previous results [13, 14, 26–28] indicated that the two-phase water–HCl/nitrobenzene–NaDCC extraction system (see “Experimental”), chosen for determination of the stability constant of the **1**· H_3O^+ complex in water-saturated nitrobenzene, can be characterized by the main chemical equilibrium (Eq. 1) to which the equilibrium extraction constant (Eq. 2) corresponds; aq and nb denote the presence of the species in the aqueous and nitrobenzene phases, respectively.

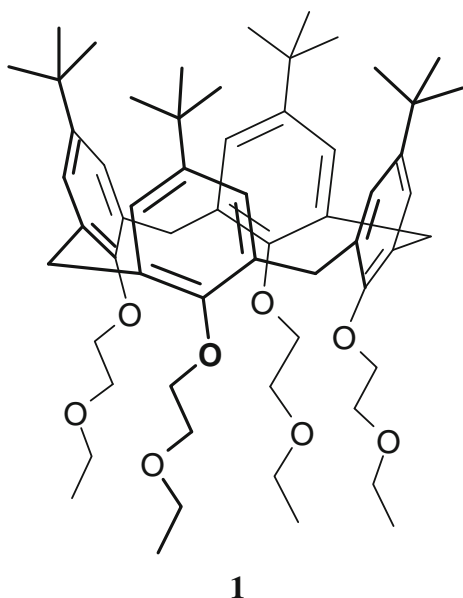


$$K_{\text{ex}}(\text{H}_3\text{O}^+, \mathbf{1} \cdot \text{Na}^+) = \frac{[\mathbf{1} \cdot \text{H}_3\text{O}^+]_{\text{nb}} [\text{Na}^+]_{\text{aq}}}{[\text{H}_3\text{O}^+]_{\text{aq}} [\mathbf{1} \cdot \text{Na}^+]_{\text{nb}}} \quad (2)$$

E. Makrlík (✉)
Faculty of Applied Sciences, University of West Bohemia,
Pilsen, Czech Republic
e-mail: makrlík@centrum.cz

M. Čajan
Department of Inorganic Chemistry, Faculty of Sciences,
Palacký University, Olomouc, Czech Republic

J. Budka · P. Vaňura
Institute of Chemical Technology, Prague, Czech Republic



Scheme 1

It is necessary to emphasize that **1** is a considerably hydrophobic ligand, essentially present in the nitrobenzene phase only, where this ligand forms—with H_3O^+ and Na^+ —the relatively stable complexes $\mathbf{1}\cdot\text{H}_3\text{O}^+$ and $\mathbf{1}\cdot\text{Na}^+$.

Taking into account the conditions of electroneutrality in the organic and aqueous phases of the system under study, the mass balances of H_3O^+ and Na^+ ions at equal volumes of the nitrobenzene and aqueous phases, as well as the measured equilibrium distribution ratio of sodium, $D_{\text{Na}} = [\mathbf{1}\cdot\text{Na}^+]_{\text{nb}}/[\text{Na}^+]_{\text{aq}}$, combined with Eq. 2, we get the final expression for the above-mentioned extraction constant (Eq. 3); $C_{\text{HCl}}^{\text{in, aq}}$ is the initial concentration of HCl in the aqueous phase and $C_{\text{NaDCC}}^{\text{in, nb}}$ denotes the initial concentration of NaDCC in the organic phase of the system under consideration.

$$K_{\text{ex}}(\text{H}_3\text{O}^+, \mathbf{1}\cdot\text{Na}^+) = \frac{1}{D_{\text{Na}}(1 + D_{\text{Na}})} \frac{C_{\text{NaDCC}}^{\text{in, nb}}}{C_{\text{HCl}}^{\text{in, aq}} - C_{\text{NaDCC}}^{\text{in, nb}}} \quad (3)$$

From the extraction experiments and γ -activity measurements using Eq. 3, the following value of the constant $K_{\text{ex}}(\text{H}_3\text{O}^+, \mathbf{1}\cdot\text{Na}^+)$ was evaluated as $\log K_{\text{ex}}(\text{H}_3\text{O}^+, \mathbf{1}\cdot\text{Na}^+) = -0.8 \pm 0.1$. Furthermore, with respect to Refs. [13, 14, 26–28], for the exchange extraction constant $K_{\text{ex}}(\text{H}_3\text{O}^+, \text{Na}^+)$ corresponding to the equilibrium $\text{H}_3\text{O}^+(\text{aq}) + \text{Na}^+(\text{nb}) \rightleftharpoons \text{H}_3\text{O}^+(\text{nb}) + \text{Na}^+(\text{aq})$ and for the extraction constant $K_{\text{ex}}(\text{H}_3\text{O}^+, \mathbf{1}\cdot\text{Na}^+)$ defined above, as well as for the stability constants of the complexes $\mathbf{1}\cdot\text{Na}^+$ and $\mathbf{1}\cdot\text{H}_3\text{O}^+$ in nitrobenzene saturated with water, denoted by $\beta_{\text{nb}}(\mathbf{1}\cdot\text{Na}^+)$ and $\beta_{\text{nb}}(\mathbf{1}\cdot\text{H}_3\text{O}^+)$, one obtains Eq. 4.

$$\begin{aligned} \log \beta_{\text{nb}}(\mathbf{1}\cdot\text{H}_3\text{O}^+) &= \log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Na}^+) \\ &+ \log K_{\text{ex}}(\text{H}_3\text{O}^+, \mathbf{1}\cdot\text{Na}^+) \\ &- \log K_{\text{ex}}(\text{H}_3\text{O}^+, \text{Na}^+) \end{aligned} \quad (4)$$

Using the value $\log K_{\text{ex}}(\text{H}_3\text{O}^+, \text{Na}^+) = 0.3$ inferred from Ref. [29], the constant $\log K_{\text{ex}}(\text{H}_3\text{O}^+, \mathbf{1}\cdot\text{Na}^+)$ given above, $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Na}^+) = 5.6 \pm 0.1$ [30], and applying Eq. 4, we obtain the stability constant of the $\mathbf{1}\cdot\text{H}_3\text{O}^+$ complex in water-saturated nitrobenzene at 25 °C as $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{H}_3\text{O}^+) = 4.5 \pm 0.2$. This means that in the mentioned medium the stability constant of the considered cationic complex species $\mathbf{1}\cdot\text{H}_3\text{O}^+$ is somewhat lower than that of the $\mathbf{1}\cdot\text{Na}^+$ complex.

Quantum mechanical calculations

The quantum mechanical calculations were carried out at the density functional level of theory (DFT, B3LYP functional) using the Gaussian 03 suite of programs [31]. The cc-pVDZ basis set was used and the optimizations were unconstrained. Although a possible influence of a polar solvent on the detailed structures of **1** and the $\mathbf{1}\cdot\text{H}_3\text{O}^+$ complex species could be imagined, our quantum chemical calculations, performed in an analogous way, showed very good agreement of experiment with theory [32–37].

In the model calculations, we optimized the molecular geometries of the parent calixarene ligand **1** and its complex with H_3O^+ . The optimized structure of **1** is shown in Fig. 1, from which it follows that one pair of opposite aromatic rings is almost parallel, while the remaining two rings are pushed away. The respective structure of **1**, also called a pinched cone structure [3], thus has nearly planar symmetry, not C_4 .

In Fig. 2, the lowest-energy structure obtained by the optimization of the $\mathbf{1}\cdot\text{H}_3\text{O}^+$ complex is illustrated together with the lengths of the corresponding hydrogen bonds (in Å). Compared to the free ligand **1** (Fig. 1), the calixarene part of the considered complex is cone-like, and its structure is much closer to C_4 symmetry. At this point it is necessary to emphasize that the hydroxonium cation H_3O^+ is bound by three strong hydrogen bonds to three phenoxy oxygen atoms (1.61, 1.47, and 1.57 Å) and by two somewhat weaker hydrogen bonds to the remaining phenoxy oxygen of **1** (2.46 and 2.41 Å), as depicted in Fig. 2.

Finally, the calculated stabilization energy of the complex $\mathbf{1}\cdot\text{H}_3\text{O}^+$ is $-347.4 \text{ kJ mol}^{-1}$, which confirms the relatively high stability of this cationic complex species.

In conclusion, it should be noted that the stability constants of protonated *p*-*tert*-butylcalix[4]arene tetraacetic acid (**2**), tetraethyl *p*-*tert*-butylcalix[4]arene tetraacetate (**3**), tetramethyl *p*-*tert*-butylcalix[4]arene tetraketone (**4**), tetraphenyl *p*-*tert*-butylcalix[4]arene tetraketone (**5**), *p*-*tert*-butylcalix[4]arene-tetrakis(*N,N*-dimethylacetamide) (**6**),

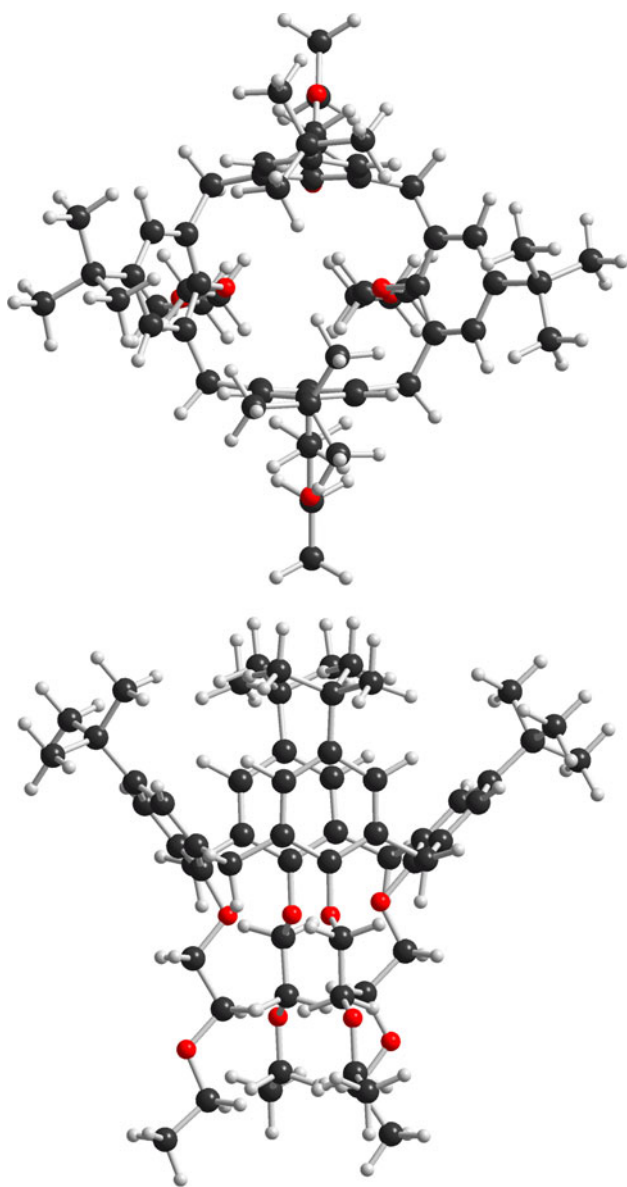


Fig. 1 Two projections of the DFT-optimized structure of free **1** [B3LYP/cc-pVDZ]

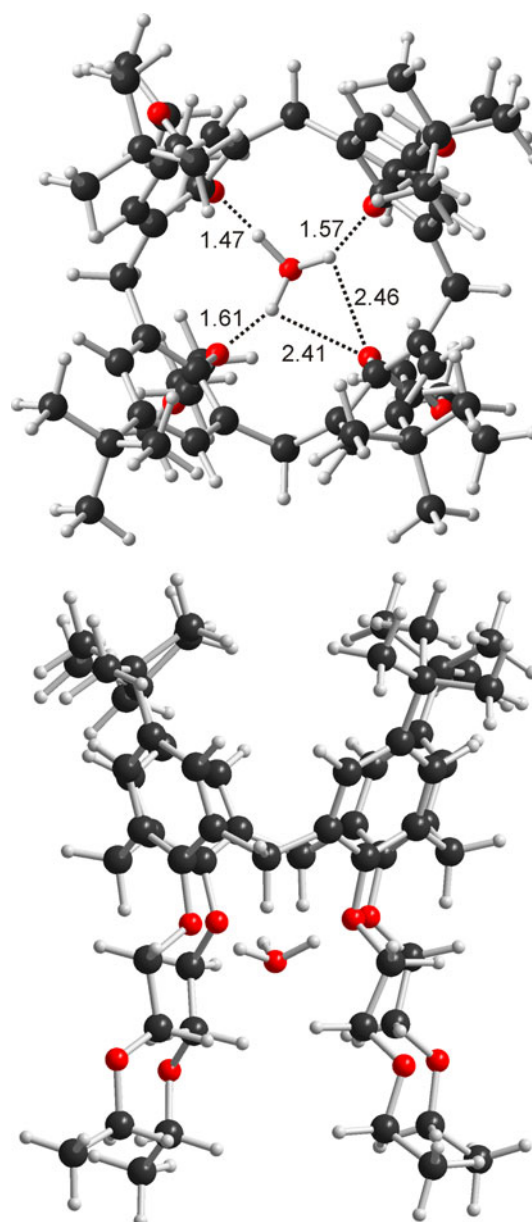


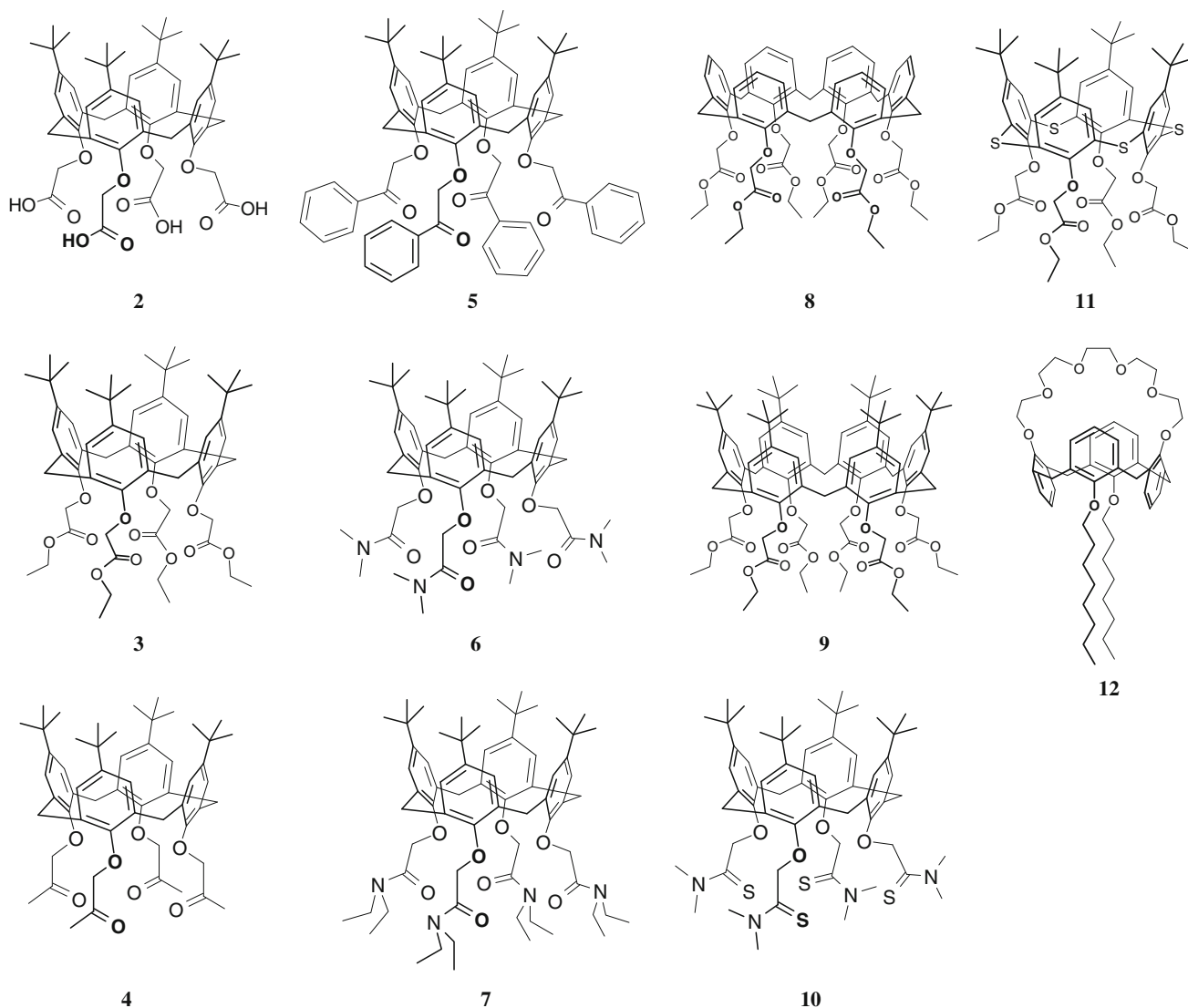
Fig. 2 Two projections of the DFT-optimized structure of the **1**·H₃O⁺ complex [B3LYP/cc-pVDZ]

p-*tert*-butylcalix[4]arene-tetrakis(*N,N*-diethylacetamide) (**7**), hexaethyl calix[6]arene hexaacetate (**8**), hexaethyl *p*-*tert*-butylcalix[6]arene hexaacetate (**9**), *p*-*tert*-butylcalix[4]arene-tetrakis(*N,N*-dimethylthioacetamide) (**10**), tetraethyl *p*-*tert*-butyltetrathiocalix[4]arene tetraacetate (*cone*) (**11**), and 1,3-*alternate*-25,27-bis(1-octyloxy)calix[4]arene-crown-6 (**12**) (see Scheme 2) in nitrobenzene saturated with water at 25 °C are $\log \beta_{\text{nb}}(\mathbf{2}\cdot\text{H}_3\text{O}^+) = 2.1$ [24], $\log \beta_{\text{nb}}(\mathbf{3}\cdot\text{H}_3\text{O}^+) = 7.6$ [21], $\log \beta_{\text{nb}}(\mathbf{4}\cdot\text{H}_3\text{O}^+) = 9.7$ [20], $\log \beta_{\text{nb}}(\mathbf{5}\cdot\text{H}_3\text{O}^+) = 9.6$ [19], $\log \beta_{\text{nb}}(\mathbf{6}\cdot\text{H}_3\text{O}^+) = 10.9$ [22], $\log \beta_{\text{nb}}(\mathbf{7}\cdot\text{H}_3\text{O}^+) = 8.1$ [14], $\log \beta_{\text{nb}}(\mathbf{8}\cdot\text{H}_3\text{O}^+) = 4.8$ [16], $\log \beta_{\text{nb}}(\mathbf{9}\cdot\text{H}_3\text{O}^+) = 6.8$ [17], $\log \beta_{\text{nb}}(\mathbf{10}\cdot\text{H}_3\text{O}^+) = 5.5$ [23], $\log \beta_{\text{nb}}(\mathbf{11}\cdot\text{H}_3\text{O}^+) = 5.1$ [15], and $\log \beta_{\text{nb}}$

(**12**·H₃O⁺) = 6.3 [18]. Thus, in this nitrobenzene medium, the stability constants of the considered protonated calixarene ligands increase in the series of $\mathbf{2} < \mathbf{1} < \mathbf{8} < \mathbf{11} < \mathbf{10} < \mathbf{12} < \mathbf{9} < \mathbf{3} < \mathbf{7} < \mathbf{5} < \mathbf{4} < \mathbf{6}$.

Experimental

Compound **1** (Scheme 1) was prepared using the method described by Iwamoto et al. [38]. Cesium dicarbollylcolbaltate (CsDCC) was synthesized by means of the method published by Hawthorne et al. [39]. A nitrobenzene



Scheme 2

solution of hydrogen dicarbollylcobaltate (HDCC) [26] was prepared from CsDCC by the procedure described elsewhere [40]. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The equilibration of the nitrobenzene solution of HDCC with stoichiometric NaOH, which was dissolved in an aqueous solution of NaCl (0.2 M), yielded the corresponding NaDCC solution in nitrobenzene. The radionuclide $^{22}\text{Na}^+$ (DuPont, Belgium) was of standard radiochemical purity.

The extraction experiments were performed in 10 cm³ glass test tubes with polyethylene stoppers: 2 cm³ of an aqueous solution of HCl of a concentration in the range from 1×10^{-3} to 1×10^{-2} M and microamounts of $^{22}\text{Na}^+$ were added to 2 cm³ of a nitrobenzene solution of **1** and NaDCC, whose initial concentrations also varied from 1×10^{-3} to 1×10^{-2} M (in all experiments, the initial

concentration of **1** in nitrobenzene, $C_1^{\text{in,nb}}$, was equal to the initial concentration of NaDCC in this medium, $C_{\text{NaDCC}}^{\text{in,nb}}$). The test tubes filled with the solutions were shaken for 12 h at 25 ± 1 °C, using a laboratory shaker. Then the phases were separated by centrifugation. Afterwards, 1 cm³ samples were taken from each phase and their γ -activities were measured by using a well-type NaI(Tl) scintillation detector connected to a γ -analyzer NK 350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratios of sodium, D_{Na} , were determined as the ratios of the measured radioactivities of $^{22}\text{Na}^+$ in the nitrobenzene and aqueous samples.

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