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ORIGINAL PAPER

Contribution to protonated tetraethyl *p-tert*-butylcalix[4]arene tetraacetate: stability and DFT calculated structure

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Abstract From extraction experiments in the two-phase water–nitrobenzene system and γ-activity measurements, the stability constant of protonated tetraethyl *p-tert*-butylcalix[4]arene tetraacetate in nitrobenzene saturated with water was determined. By using DFT calculations, the most probable structure of the tetraethyl *p-tert*-butylcalix[4]arene tetraacetate·H_3O^+ complex species was derived.

Keywords Calixarenes · Macrocycles · Protonation · DFT · Structure

Introduction

Calix[*n*]arenes are a well-known family of macrocyclic molecules with many potential applications in various branches of chemistry. Because of their one-pot preparation, easy derivatization and unique complexation abilities, calix[*n*]arenes are widely used as the building blocks for the constructions of more sophisticated molecular systems. Their unique 3D pre-organization makes them very attractive as the receptors for the complexation of cations, anions, and even neutral molecules. Calix[*n*]arenes find applications as selective binders and carriers, as analytical sensors, catalysts and model structures for biomimetic studies [1, 2]. In the field of host–guest chemistry, many studies have focused on the binding ability of calixarene derivatives with carbonyl groups at their lower rims toward metal ions, predominantly alkali and alkaline-earth, but also transition and heavy metal cations [3–11], and even toward H_3O^+ [12–17].

Recently, NMR evidence for protonated tetraethyl *p-tert*-butylcalix[4]arene tetraacetate has been reported [18]. In the present work, the stability constant of the mentioned cationic complex species (**1**·H_3O^+) (cf. Scheme 1) is evaluated in water-saturated nitrobenzene, and its DFT calculated structure is solved.

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Results and discussion

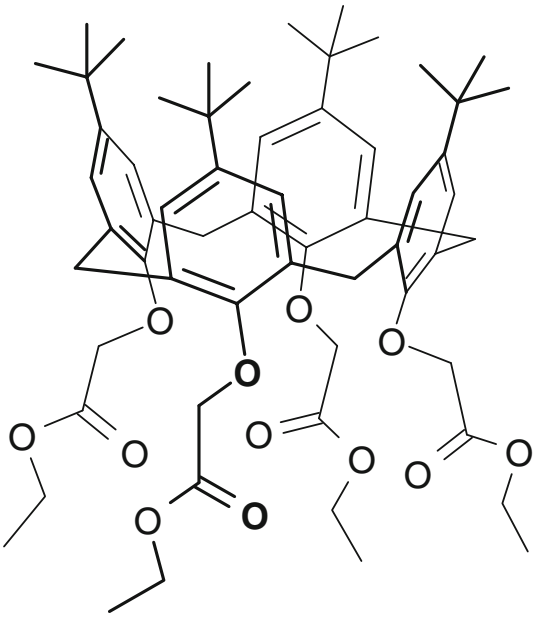
Extraction experiments

In terms of previous papers [19–21], the two-phase water–HCl/nitrobenzene–NaDCC–**1** (tetraethyl *p-tert*-butylcalix[4]arene tetraacetate) extraction system, chosen for determination of stability constant of the complex **1**·H_3O^+ in nitrobenzene saturated with water, can be characterized by the main chemical equilibrium (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.

$$H_3O^+(aq) + \mathbf{1}\cdot Na^+(nb) \rightleftarrows \mathbf{1}\cdot H_3O^+(nb) + Na^+(aq); K_{ex}(H_3O^+, \mathbf{1}\cdot Na^+) \quad (1)$$

$$K_{ex}(H_3O^+, \mathbf{1}\cdot Na^+) = \frac{[\mathbf{1}\cdot H_3O^+]_{nb}[Na^+]_{aq}}{[H_3O^+]_{aq}[\mathbf{1}\cdot Na^+]_{nb}} \quad (2)$$

It is necessary to emphasize that **1** is a considerably hydrophobic ligand, practically present in the nitrobenzene



Scheme 1

phase only, where this ligand forms—with H_3O^+ and Na^+—the very stable complexes $\mathbf{1}{\cdot}H_3O^+$ and $\mathbf{1}{\cdot}Na^+$.

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, $D_{Na} = [\mathbf{1}{\cdot}Na^+]_{nb}/[Na^+]_{aq}$, combined with (2), we get the final expression for the mentioned extraction constant [Eq. (3)]; $C_{HCl}^{in,aq}$ is the initial concentration of HCl in the aqueous phase and $C_{NaDCC}^{in,nb}$ denotes the initial concentration of NaDCC in the organic phase of the system under consideration.

$$K_{ex}(H_3O^+, \mathbf{1} \cdot Na^+) = \frac{1}{D_{Na}} \frac{C_{NaDCC}^{in,nb}}{(1 + D_{Na})\, C_{HCl}^{in,aq} - C_{NaDCC}^{in,nb}} \quad (3)$$

From the extraction experiments and γ-activity measurements by using (3), the following value of the constant $K_{ex}(H_3O^+, \mathbf{1}{\cdot}Na^+)$ was evaluated as $\log K_{ex}(H_3O^+, \mathbf{1}{\cdot}Na^+) = -1.3 \pm 0.1$. Moreover, with respect to [21–23], for the exchange extraction constant $K_{ex}(H_3O^+, Na^+)$ corresponding to the equilibrium $H_3O^+(aq) + Na^+(nb) \rightleftarrows H_3O^+(nb) + Na^+(aq)$ and for the extraction constant K_{ex} $(H_3O^+, \mathbf{1}{\cdot}Na^+)$ defined above, as well as for the stability constants of the complexes $\mathbf{1}{\cdot}Na^+$ and $\mathbf{1}{\cdot}H_3O^+$ in nitrobenzene saturated with water, denoted by $\beta_{nb}(\mathbf{1}{\cdot}Na^+)$ and $\beta_{nb}(\mathbf{1}{\cdot}H_3O^+)$, one gets (4).

$$\log \beta_{nb}(\mathbf{1} \cdot H_3O^+) = \log \beta_{nb}(\mathbf{1} \cdot Na^+) + \log K_{ex}(H_3O^+, \mathbf{1} \cdot Na^+) - \log K_{ex}(H_3O^+, Na^+) \quad (4)$$

Using the value $\log K_{ex}$ $(H_3O^+, Na^+) = 0.3$ inferred from [19], the constant $\log K_{ex}(H_3O^+, \mathbf{1}{\cdot}Na^+)$ given above as well as $\log \beta_{nb}(\mathbf{1}{\cdot}Na^+) = 9.2 \pm 0.1$ [24], and applying (4), we obtain the stability constant of the $\mathbf{1}{\cdot}H_3O^+$ complex in water saturated nitrobenzene at 25 °C as $\log \beta_{nb}(\mathbf{1}{\cdot}H_3O^+) = 7.6 \pm 0.2$. In this context it should be noted that Kudo et al. [25] determined the stability constant of the complex dicyclohexyl-18-crown-6·H_3O^+ in nitrobenzene saturated with water employing an ion-transfer polarographic method as $\log \beta_{nb} = 7.76 \pm 0.08$. This means that the stability constants of $\mathbf{1}{\cdot}H_3O^+$ and the dicyclohexyl-18-crown-6·H_3O^+ cationic species in the mentioned medium are comparable.

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 [26]. The 6-31G(d) basis set was used and the optimizations were unconstrained. Although possible influence of a polar solvent on the detailed structures of **1** and $\mathbf{1}{\cdot}H_3O^+$ could be imagined, our quantum calculations in similar cases, performed in an analogous way, showed very good agreement of the experiment with theory [27, 28].

In the model calculations, we optimized the molecular geometry of the parent calixarene ligand **1** and its complex with H_3O^+. The optimized structure of **1** is shown in Fig. 1. From this figure it follows that the most stable conformation of the calixarene ligand **1** forms a pinched cone structure [2] with C_2 symmetry.

In Fig. 2, the lowest-energy-level structure obtained by the optimization of the $\mathbf{1}{\cdot}H_3O^+$ complex from four initial arrangements of H_3O^+ and the calixarene ligand **1** is illustrated together with the lengths of the corresponding hydrogen bonds (in Å). Compared to free ligand **1** (Fig. 1), the calixarene part of the considered complex is more cone-like and its structure is much closer to C_4 symmetry (Fig. 2). The hydroxonium ion H_3O^+, placed in the coordination cavity formed by the calixarene lower-rim groups, is bound by strong hydrogen bonds to three phenoxy oxygen atoms of **1** (1.76, 1.57, and 1.74 Å). This fact confirms our experimental results published recently [18].

Experimental

Cesium dicarbollylcobaltate (CsDCC) was supplied by Katchem, Řež, Czech Republic. A nitrobenzene solution of HDCC [29] was prepared from CsDCC by the procedure described in [30]. 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. Compound **1** (cf. Scheme 1), called also sodium ionophore

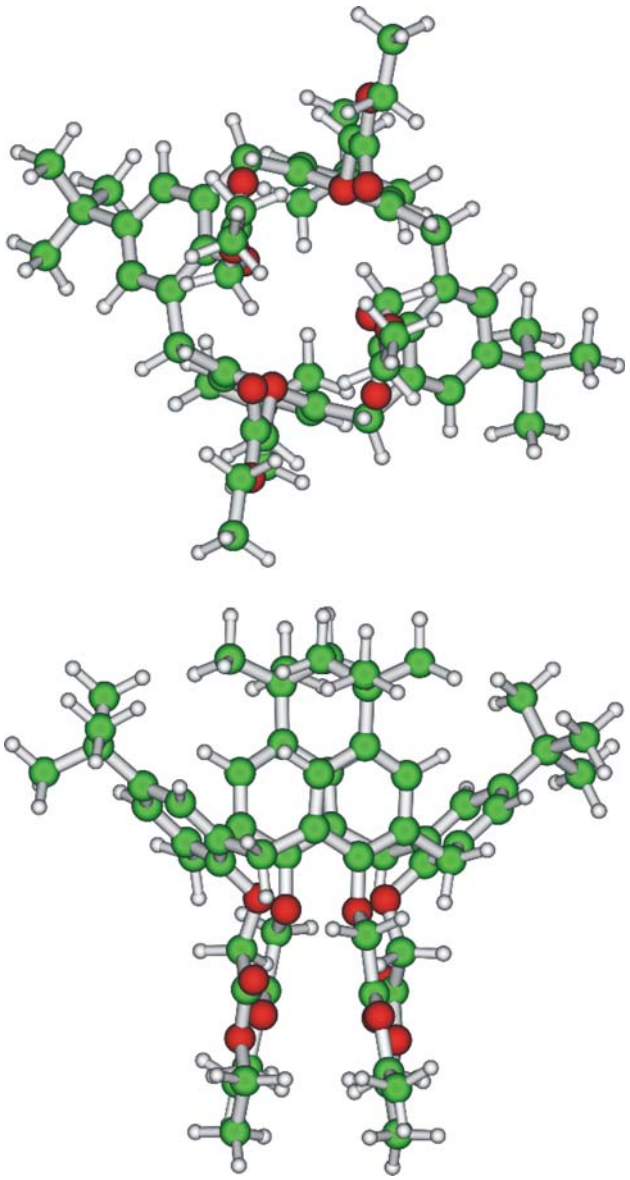


Fig. 1 Two projections of the DFT optimized structure of free **1** [B3LYP/6-31G(d)]

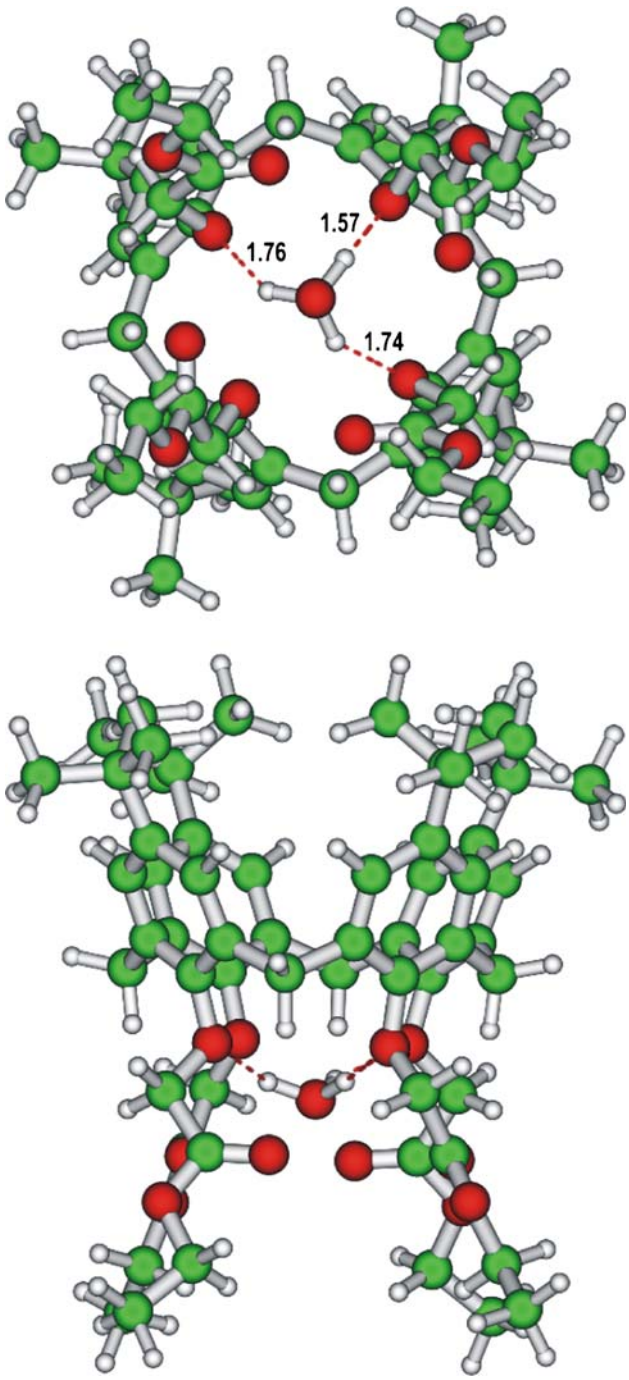


Fig. 2 Two projections of the DFT optimized structure of the $\mathbf{1}{\cdot}H_3O^+$ complex [B3LYP/6-31G(d)]

X, was purchased from Fluka, Buchs, Switzerland. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclide $^{22}Na^+$ (DuPont, Belgium) was of standard radiochemical purity.

The extraction experiments were carried out in 10-cm^3 glass test-tubes covered with polyethylene stoppers: 2 cm^3 of an aqueous solution of HCl of a concentration in the range from 1×10^{-3} to 1×10^{-2} *M* and microamounts of $^{22}Na^+$ were added to 2 cm^3 of a nitrobenzene solution of **1** and NaDCC, whose initial concentrations varied also from 1×10^{-3} to 1×10^{-2} *M* (in all experiments, the initial concentration of **1** in nitrobenzene, $C_1^{in,nb}$, was equal to the initial concentration of NaDCC in this medium, $C_{NaDCC}^{in,nb}$). The test tubes filled with the solutions were shaken for 24 h at 25 ± 1 °C, using a laboratory shaker. Then the phases were separated by centrifugation. Afterwards, 1-cm^3 samples were taken from each phase and their γ-activities were measured using a well-type NaI(Tl) scintillation detector connected to a γ-analyzer NK 350 (Gamma, Budapest, Hungary). The equilibrium distribution ratio of sodium,

D_{Na}, was determined as the ratio of the measured radioactivities of $^{22}Na^{+}$ in the nitrobenzene and aqueous samples.

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