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Contribution to the Protonation of a Calix[4]arene: DFT Calculated Structure of Protonated *p-tert*-Butylcalix[4]arenetetrakis(*N*,*N*-diethylacetamide)

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Summary. By using DFT calculations, the most probable structure of the *p-tert*-butylcalix[4]arenetetrakis(*N*,*N*-diethylacetamide) $\cdot$ H_3O^+ complex species was derived. In this complex, the hydroxonium ion H_3O^+ is predominantly bound by strong hydrogen bonds to three phenoxy oxygens of the ligand and partly to the remaining phenoxy oxygen atom by two somewhat weaker hydrogen bonds. Besides, the H_3O^+ cation is also bound to two carbonyl oxygens of the mentioned ligand by further two weaker hydrogen bonds.

Keywords. Calixarenes; Macrocycles; Protonation; DFT; Structure.

Introduction

Calixarene-based molecules have received intense attention in the last years. One of the most important features of these compounds is their diversity. Calixarenes find applications as selective binders and carriers, as analytical sensors, as 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 derivates with carbonyl groups at their lower rims toward metal ions, especially alkali and alkaline-earth, but also transition and heavy metal cations [3–11].

Recently, experimental evidence for the *p-tert*-butylcalix[4]arenetetrakis(*N*,*N*-diethylacetamide) $\cdot$ H_3O^+ ($\mathbf{1} \cdot H_3O^+$) complex species has been advanced [12]. In the present work, applying DFT calculations, the most probable structure of this cationic complex was derived.

Results and Discussion

The quantum mechanical calculations were carried out at the density functional level of theory (DFT, *B*3*LYP* functional) using the Gaussian 03 suite of programs [13]. The 6 – 31G(d) basis set was used and the optimization was unconstrained. In the model calculations, we optimized 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 a C_2 symmetry.

In Fig. 2, the lowest-energy-level structure obtained by optimization of the $\mathbf{1} \cdot H_3O^+$ complex 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 complex $\mathbf{1} \cdot H_3O^+$ is distorted so that its structure is very close to the C_4 symmetry. In this context it is necessary to emphasize that the hydroxonium ion H_3O^+, placed

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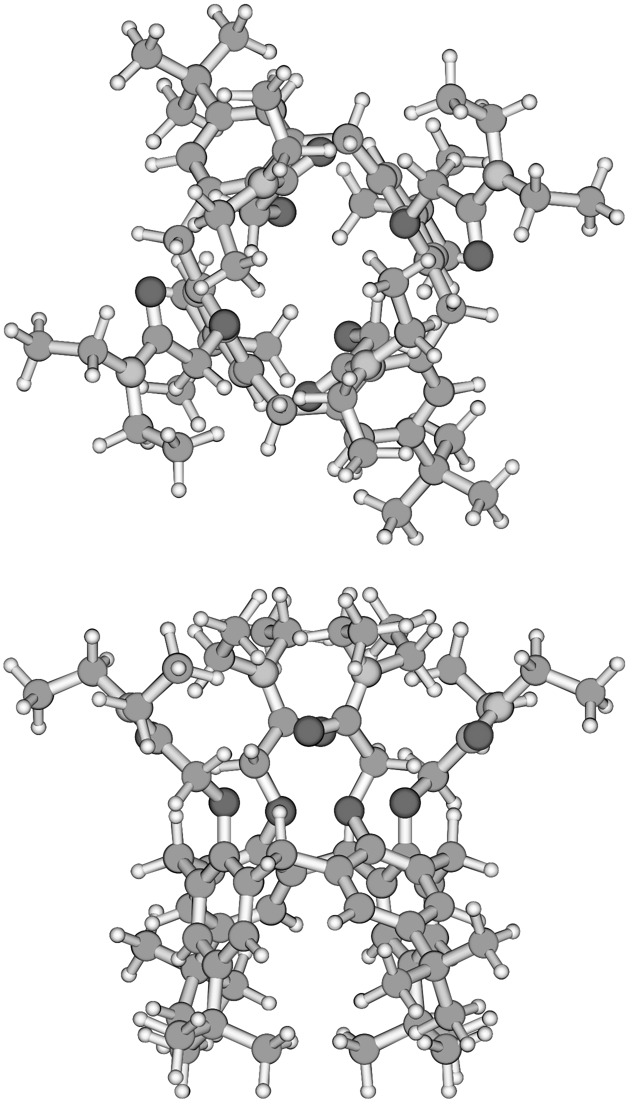

Fig. 1. Two projections of the DFT optimized structure of free **1** ($B3LYP$ – 31G(d))

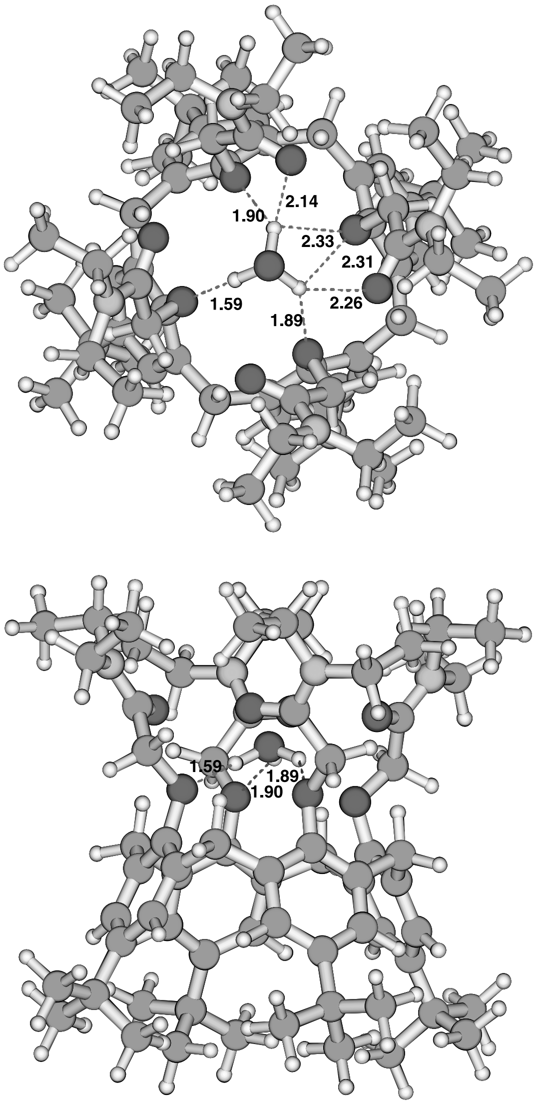

Fig. 2. Two projections of the DFT optimized structure of the $\mathbf{1} \cdot H_3O^+$ complex ($B3LYP/6-31G(d)$).

in the calixarene cage, is predominantly bound by strong hydrogen bonds to three phenoxy oxygen atoms of **1** (1.59–1.90 Å) and partly to the remaining phenoxy oxygen by two somewhat weaker hydrogen bonds as manifested by longer $O \cdots H$ distances (2.31, 2.33 Å). Besides, the considered H_3O^+ cation is also bound to two carbonyl oxygen atoms of the mentioned ligand by further two weaker hydrogen bonds (2.14, 2.26 Å).

Finally, the calculated stabilization energy of the complex $\mathbf{1} \cdot H_3O^+$ is 445.2 kJ mol^{-1}, which confirms the very high stability of this complex species [12].

In conclusion, it is possible to assume that many other calixarene compounds can form – naturally, under suitable conditions – the complex calixarene structures involving the cation H_3O^+.

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