Monatsh Chem 139, 1353–1355 (2008)
DOI 10.1007/s00706-008-0938-9
Printed in The Netherlands

**Monatshefte für Chemie
Chemical Monthly**

DFT-calculated structure of protonated tetraphenyl *p-tert*-butylcalix[4]arene tetraketone

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Received 1 April 2008; Accepted 2 April 2008; Published online 9 June 2008

Abstract Using DFT calculations, two of the most probable structures (A, B) of the tetraphenyl *p-tert*-butylcalix[4]arene tetraketone $\cdot H_3O^+$ cationic complex species were derived. The hydroxonium ion H_3O^+, placed in the coordination cavity formed by the calix[4]arene lower-rim groups, is bound by strong hydrogen bonds to the phenoxy oxygen atoms of the calix[4]arene ligand (structures A, B) and also to one carbonyl oxygen (structure B).

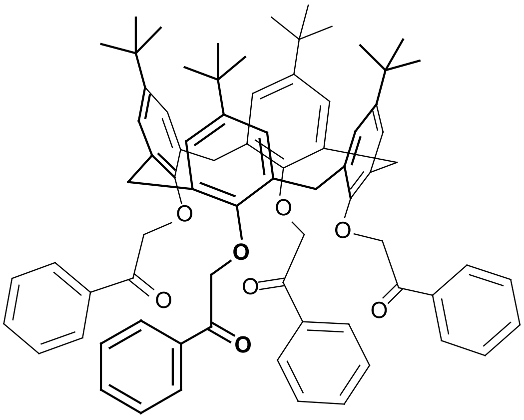
Keywords Calixarenes; Macrocycles; Protonation; DFT; Structure.

Introduction

Calixarene-based molecules have received intense attention in the last decades. One of the most important features of these compounds is their diversity. Calixarenes 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, especially alkali and alkaline-earth, but also transition and heavy metal cations [3–11].

Recently, the interactions of the H_3O^+ ion with some calix[4]arenes have been investigated [12–16]. Moreover, the solvent extraction of some univalent cations into nitrobenzene by using dicarbollylcobaltate anion [17] and tetraphenyl *p-tert*-butylcalix[4]-arene tetraketone (**1**; *cf*. Scheme 1) has been reported [18]. Besides, the stability constants of the evidenced complexes in nitrobenzene saturated with water have been determined [18]. In the present work, applying quantum mechanical DFT calculations, the most probable structures of the $\mathbf{1} \cdot H_3O^+$ complex species are solved.



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Scheme 1

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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 [19]. The 6–31G(d) basis set was used and the optimizations were unconstrained. Although a 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 experiment with theory [20–22].

In the model calculations, we optimized the molecular geometry of the parent calix[4]arene 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 mentioned ligand **1** forms a *pinched cone* structure [2] with C_2 symmetry.

In Figs. 2 and 3, the structures A and B of the $\mathbf{1}\cdot H_3O^+$ complex obtained by the full DFT optimizations are illustrated together with the lengths of the corresponding hydrogen bonds. Compared to free ligand **1** (Fig. 1), the calix[4]arene part of the complex $\mathbf{1}\cdot H_3O^+$ is more open and very close to C_4 symmetry. The hydroxonium ion H_3O^+, placed in the coordination cavity formed by the calix[4]arene lower-rim groups, is bound by strong hydrogen bonds to the phenoxy oxygen atoms of **1** (structures A and B) and also to one carbonyl oxygen of **1** (structure B). Finally, the calculated binding energies corresponding to the structures A and B of the $\mathbf{1}\cdot H_3O^+$ complex under study are very similar: -423.0 and $-422.2\,\mathrm{kJ\,mol^{-1}}$.

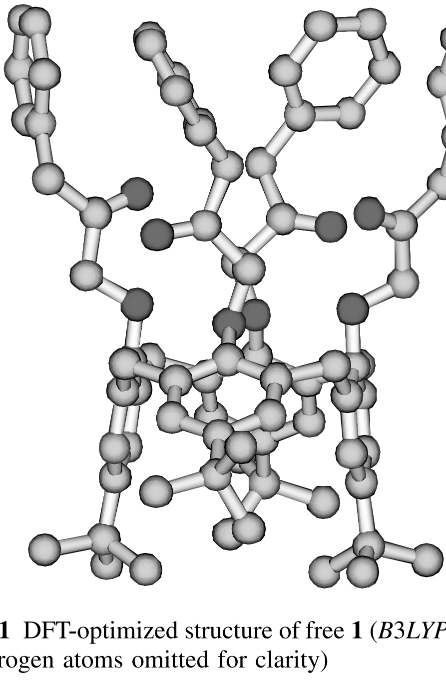

Fig. 1 DFT-optimized structure of free **1** (*B*3*LYP*/6–31G(d)) (hydrogen atoms omitted for clarity)

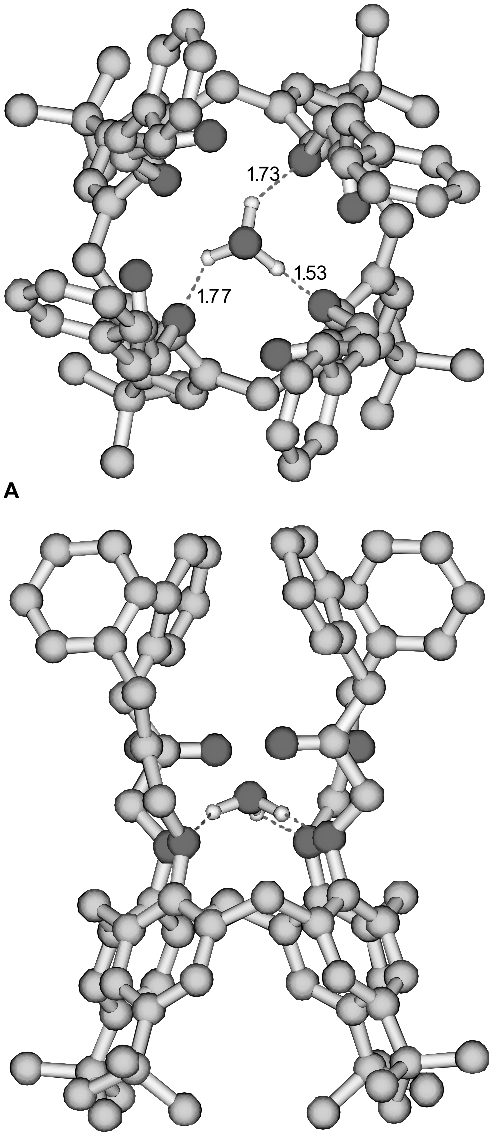

Fig. 2 Two projections of the DFT-optimized structure of the $\mathbf{1}\cdot H_3O^+$ complex (*B*3*LYP*/6–31G(d)) – structure A. H-bond lengths of H_3O^+ to phenoxy oxygens of **1**: 1.77, 1.73, and 1.53 Å (hydrogen atoms omitted for clarity except those of H_3O^+)

In conclusiuon, it should be noted that the structures A and B of the $\mathbf{1}\cdot H_3O^+$ complex are apparently in a dynamic equilibrium. Besides, from this point of view, the experimentally determined value of the stability constant of $\mathbf{1}\cdot H_3O^+$ in nitrobenzene saturated with water at 25°C corresponding to the equilibrium $\mathbf{1}(\mathrm{nb}) + H_3O^+(\mathrm{nb}) \leftrightarrow \mathbf{1}\cdot H_3O^+(\mathrm{nb})$, log β_{nb} $(\mathbf{1}\cdot H_3O^+) = 9.6$ [18], can be obviously considered as a certain "average" stability constant of the two DFT-calculated structures.

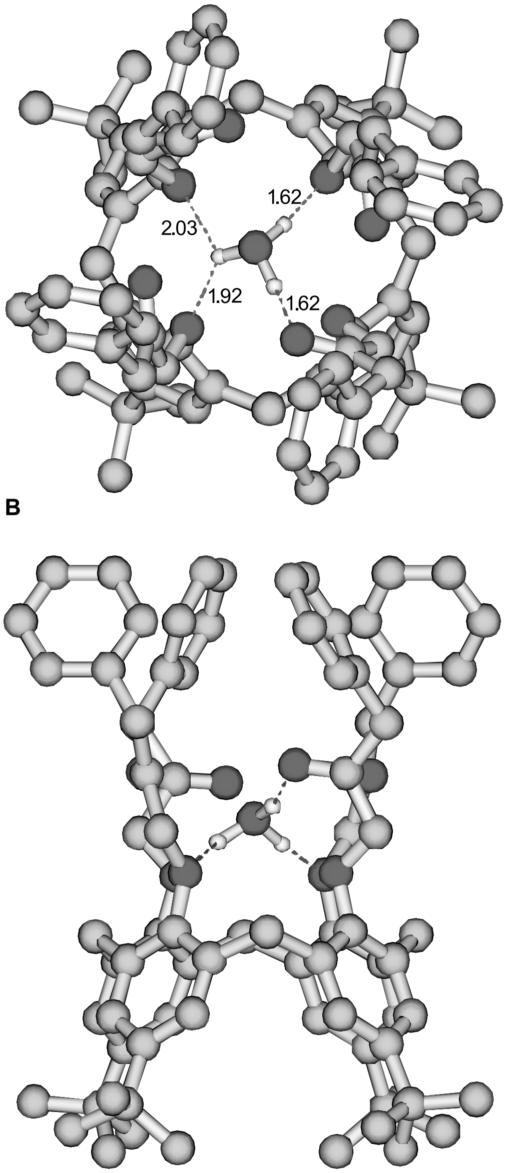

Fig. 3 Two projections of the DFT-optimized structure of the $\mathbf{1} \cdot H_3O^+$ complex ($B3LYP/6\text{–}31G(d)$) – structure B. H-bond length of H_3O^+ to phenoxy oxygens of **1**: 1.92, 2.03, and 1.62 Å; H-bond length of H_3O^+ to carbonyl oxygen of **1**: 1.62 Å (hydrogen atoms omitted for clarity except those of H_3O^+)

Acknowledgement

The present work was supported by the Academy of Sciences of the Czech Republic, Project T 400500402, and the Czech Ministry of Education, Youth and Sports, Projects MSM 4977751303 and MSM 6046137307.

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