Short communication

Theoretical Study on the Protonation of Cucurbit[7]uril

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Abstract

By using quantum mechanical DFT calculations, the most probable structures of the cucurbit[7]uril·H_3O^+ and cucurbit[7]uril·$(H_3O^+)_2$ cationic complex species were derived. In these two complexes having a plane symmetry, each of the considered H_3O^+ cations is bound by relatively strong hydrogen bonds to the corresponding carbonyl oxygens of the parent cucurbit[7]uril macrocycle.

Keywords: Cucurbit[7]uril; protonation; H_3O^+ cation; DFT calculations; complex structures

1. Introduction

Cucurbit[*n*]urils are macrocyclic compounds consisting of *n* glycoluril units connected by 2*n* methylene bridges. The shape of the macrocycle resembles a hollow barrel with a hydrophobic interior and partially negative charged rims of carbonyls on both sides of the macrocycle. This structure makes the macrocycles suitable to bind organic guests bearing one or more positive charges in their structures.[1–14]

Recently, protonation of valinomycin, some calix[4]arenes, dibenzo-18-crown-6, a hexaarylbenzene-based receptor and cucurbit[6]uril has been investigated in

detail.[15–28] However, up to now, the structures of the protonated cucurbit[7]uril species (abbrev. **1**; see Scheme 1) have not been solved. Therefore, in the current work, the most probable structures of the **1**·H_3O^+ and **1**·$(H_3O^+)_2$ cationic complexes are derived by quantum mechanical DFT calculations. It is obvious that these structures may be an important contribution to the theoretical study of the cucurbit[7]uril macrocyclic receptor.

2. Results and Discussion

The quantum mechanical calculations were carried out at the density functional level of theory (DFT, B3LYP functional)[29,30] using the Gaussian 03 suite of programs.[31] The 6-31G(d) basis set was used and the optimizations were unconstrained. In order to increase the numerical accuracy and to reduce oscillations during the molecular geometry optimization, two-electron integrals and their derivatives were calculated by using the pruned (99,590) integration grid, having 99 radial shells and 590 angular points per shell, which was requested by means of the Gaussian 03 keyword "Inf=UltraFine".

Although a possible influence of a polar solvent on the detailed structures of **1**, **1** · H_3O^+ and **1** · $(H_3O^+)_2$ could
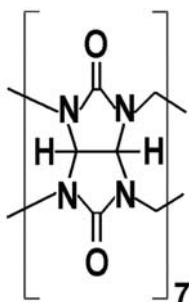
Scheme 1. Structural formula of cucurbit[7]uril (abbrev. **1**).

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be imagined, our quantum mechanical calculations in similar cases, performed in an analogous way, showed very good agreement of experiment with theory.[32–41]

In the model calculations, we optimized the molecular geometries of the parent macrocycle **1** and its complex species with H_3O^+. The optimized structure of the free macrocyclic receptor **1** with C_7 symmetry is illustrated in Figure 1.
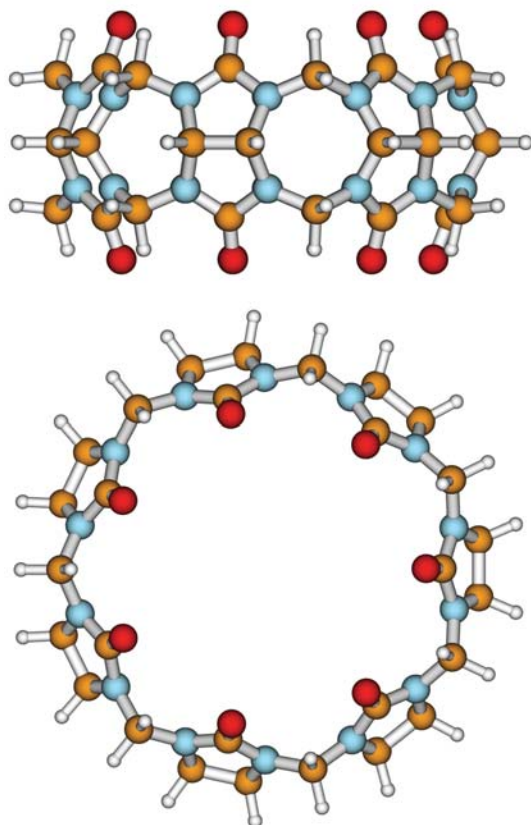

Figure 1. Two projections of the DFT optimized structure of free macrocycle **1** [B3LYP/6-31G(d)].

In Figure 2, the structure obtained by the full DFT optimization of the **1**·H_3O^+ complex having a plane symmetry is depicted, together with the lengths of the corresponding bonds (in Å; 1Å = 0.1 nm). As follows from this figure, the complexation with the H_3O^+ cation changes the overall shape of the parent macrocycle **1**. In the resulting **1**·H_3O^+ cationic complex species, which is most energetically favoured, the "central" cation H_3O^+ is bound by three relatively strong hydrogen bonds to the three corresponding carbonyl oxygen atoms (1.72, 1.72 and 1.50 Å) of the parent receptor **1**.

The lowest-energy-level structure obtained by the full DFT optimization of the **1**·$(H_3O^+)_2$ cationic complex species is shown in Figure 3, together with the lengths of the corresponding hydrogen bonds (in Å). Compared to the free macrocycle **1** (Figure 1), the cucurbit[7]uril part of the complex **1**·$(H_3O^+)_2$ is somewhat distorted so that its
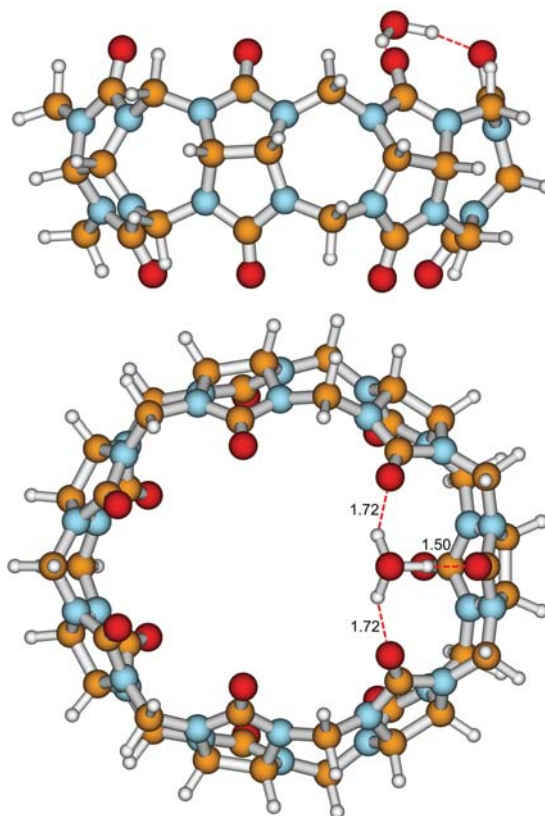

Figure 2. Two projections of the DFT optimized structure of the **1**·H_3O^+ complex **[**B3LYP/6-31G(d)]. Hydrogen bond lengths of H_3O^+ to the three corresponding carbonyl oxygens of **1** are 1.72, 1.72 and 1.50 Å.

structure has a plane symmetry (Figure 3). In this complex species, the "first" of the two considered H_3O^+ cations is bound by three H-bonds to the three corresponding carbonyl oxygens (1.72, 1.72 and 1.48 Å), while the "second" H_3O^+ cation is bound only by two H-bonds to the two respective carbonyl oxygen atoms (1.45 and 1.45 Å) of the parent macrocyclic receptor **1**.

Finally, the calculeted binding energies of the complexes **1** · H_3O^+ and **1** · $(H_3O^+)_2$ are –405.3 and –629.1 kJ/mol, respectively, confirming the relatively high stabilities of these cationic complex species.

In conclusion, it should be noted that the binding energies of the **2** · H_3O^+ and **2** · $(H_3O^+)_2$ complexes, where **2** denotes cucurbit[6]uril, were found to be –404.8 and -608.5 kJ/mol,[28] respectively. This means that the stabilities od the corresponding cationic complexes [i.e., **1** · H_3O^+ and **2** · H_3O^+, as well as **1** · $(H_3O^+)_2$ and **2** · $(H_3O^+)_2$**]** are comparable.
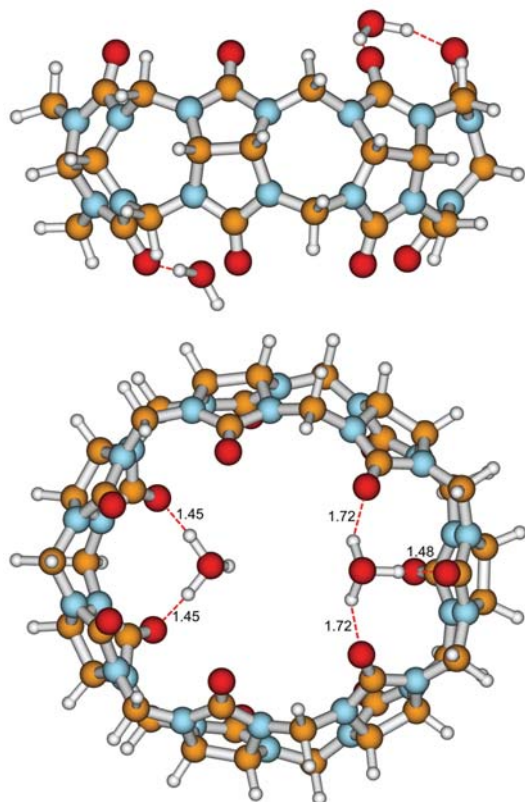
3. Acknowledgements

Figure 3. Two projections of the DFT optimized structure of the $1 \cdot (H_3O^+)_2$ complex [B3LYP/6-31G(d)]. Hydrogen bond lengths of the "first" H_3O^+ to the three corresponding carbonyl oxygens of **1** are 1.72, 1.72 and 1.48 Å; hydrogen bond lengths of the "second" H_3O^+ to the two corresponding carbonyl oxygens of **1** are 1.45 and 1.45 Å.

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Povzetek

Z uporabo kvantno mehanskih DFT izračunov smo določili najbolj verjetno strukturo kationskih kompleksov kukurbit[7]uril·H_3O^+ in kukurbit[7]uril·$(H_3O^+)_2$. Ugotovili smo, da imajo kompleksi planarno simetrijo, kjer je H_3O^+ z relativno močnimi vodikovimi vezmi vezan na kisikove atome v karbonilni skupini kukurbit[7]urila.