DFT Study on the Complexation of Bambus[6]uril with the Perchlorate and Tetrafluoroborate Anions

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Abstract

By using quantum mechanical DFT calculations, the most probable structures of the bambus[6]uril·ClO_4^- and bambus[6]uril·BF_4^- anionic complex species were derived. In these two complexes having C_3 symmetry, each of the considered anions, included in the macrocyclic cavity, is bound by 12 weak hydrogen bonds between methine hydrogen atoms on the convex face of glycoluril units and the respective anion.

Keywords: Bambus[6]uril; perchlorate and tetrafluoroborate anions; complexation; 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.[1–3]

Cucurbit[6]uril (abbrev. CB[6]) is the oldest and the most accessible representative of the CB family of macrocycles and its supramolecular interactions with various guests have been extensively investigated.[1,2] The ability of CB[6] to behave as a synthetic receptor was described in detail by Mock and co-workers together with the discovery of the macrocyclic structure of the molecule.[4] Guest positioning and complex stability strongly depended on the length of alkyl chain of the guest.[5–8] Since then the complexation between CB[6] and many organic guests has been studied, including polyamines,[9,10] viologen derivatives,[11] organic dyes,[12] polypeptides,[13] amino acids, and dipeptides.[14]

New macrocycles prepared by the acid-catalyzed condensation of ethyleneurea and formaldehyde were named hemicucurbit[*n*]urils (*n* = 6,12),[15,16] as their structures resemble the motif obtained when the corresponding cucurbit[*n*]uril is cut in half along the equator. In contrast to cucurbit[*n*]urils, hemicucurbit[*n*]urils are soluble in nonpolar solvents, such as chloroform. Furthermore, hemicucurbit[*n*]urils form complexes with anions, but no interaction with common metal cations was observed in an aqueous solution.[17,18]

Recently, the synthesis of a cyclic hexamer, bambus[6]uril (abbrev. BU[6]; see Scheme 1), which combi-
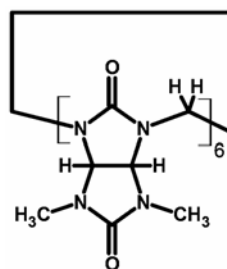
Scheme 1. Structural formula of bambus[6]uril (abbrev. **BU[6]**).

nes the structural features of both cucurbit[*n*]urils and he-micucurbit[*n*]urils, was described.[19] An acid-catalyzed condensation between 2,4-dimethylglycoluril and formal-dehyde in HCl resulted in the mentioned macrocycle BU[6], in which the glycoluril units are connected through methylene bridges (Scheme 1). This macrocycle was isolated as a white powder in a maximum yield of 30%, when the reaction was carried out in 5.4 M HCl at room temperature.[19] Further, it is necessary to emphasize that BU[6] showed a good affinity for halide anions; the crystal structure of the anionic complex BU[6] · Cl⁻ was presented as well.[19] On the other hand, in the current work, applying quantum mechanical DFT calculations, the most probable structures of the BU[6] · ClO_4^- and BU[6] · BF_4^- anionic complex species are solved.

2. Results and Discussion

The quantum mechanical calculations were carried out at the density functional level of theory (DFT, B3LYP functional)[20,21] using the Gaussian 03 suite of programs.[22] The 6-31G(d) basis set was used and the optimizations were unconstrained. In order to increase the numerical accuracy and to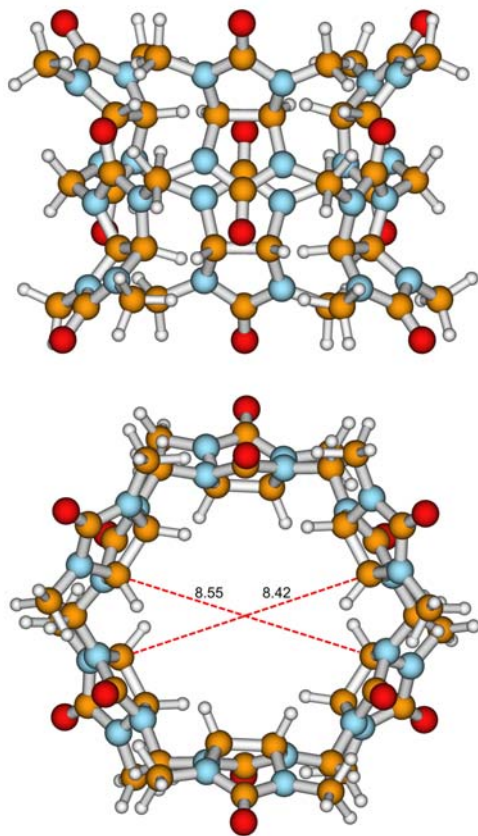 reduce oscillations during the molecular geometry optimization, two-electron integrals and their derivatives were calculated by using the pruned (99,590) integration grid, having 99 radial shells and 590 angular points per shell, which was requested by means of the Gaussian 03 keyword "Int = UltraFine".

Although a possible influence of a polar solvent on the detailed structures of BU[6], BU[6] · ClO_4^- and BU[6] · BF_4^- could be imagined, our quantum mechanical calculations in similar cases, performed in an analogous way, showed very good agreement of experiment with theory.[23-30]

In the model calculations, we optimized the molecular geometries of the parent macrocycle BU[6] and its anionic complex species with ClO_4^- and BF_4^-. The optimized structure of the free macrocyclic receptor BU[6] with C_3 symmetry is illustrated in Figure 1. At this point it should be noted that the six glycoluril units in the considered macrocycle adopt alternate conformations; the methine hydrogen atoms on the convex face of each unit point into the cavity – its diameter is alternately 8.42 and 8.55 Å (see Figure 1). This macrocycle can be divided into two identical parts by a plane defined by the carbon atoms of
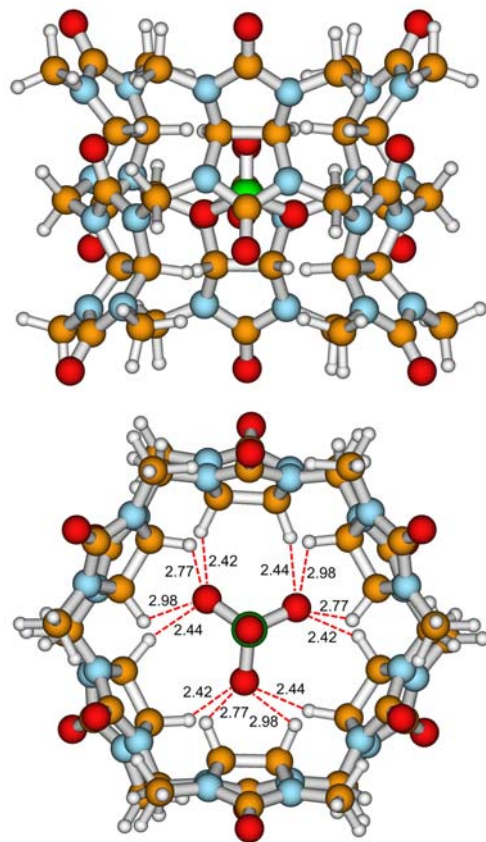

Figure 1. Two projections of the DFT optimized structure of free macrocycle **BU[6]** [B3LYP/6-31G(d)]. The diameter of the cavity in **BU[6]** is alternately 8.42 and 8.55 Å.

Figure 2. Two projections of the DFT optimized structure of the **BU[6]** · ClO_4^- complex [B3LYP/6-31G(d)]. Each of the three oxygens of ClO_4^- is bound by four weak hydrogen bonds (2.44, 2.98, 2.77, and 2.42 Å) with four methine hydrogens on the convex face of glycoluril units; the diameter of the cavity in **BU[6]** · ClO_4^- is alternately 8.14 and 8.26 Å.

the six methylene bridges, and besides, the carbons of six carbonyl groups are arranged alternately above and below the mentioned plane in a "zigzag" manner.
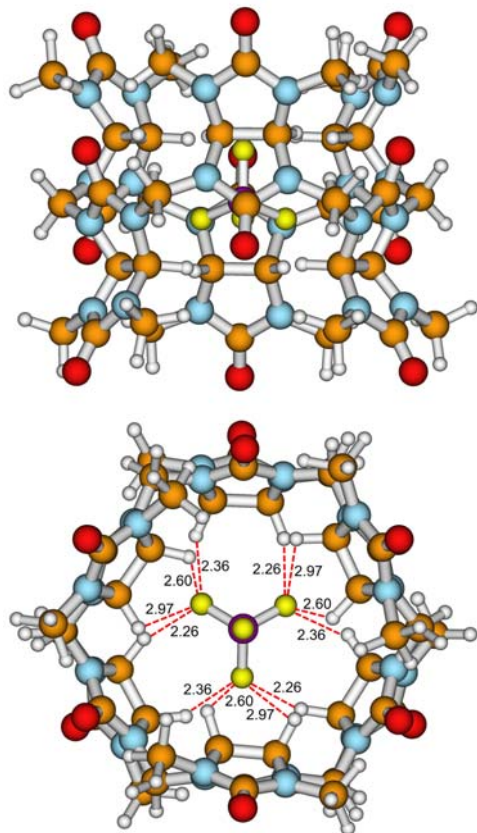

Figure 3. Two projections of the DFT optimized structure of the **BU[6]** · BF_4^- complex [B3LYP/6-31G(d)]. Each of the three fluors of BF_4^- is bound by four weak hydrogen bonds (2.26, 2.97, 2.60, and 2.36 Å) with four methine hydrogens on the convex face of glycoluril units; the diameter of the cavity in **BU[6]** · BF_4^- is alternately 7.85 and 8.07 Å.

In Figures 2 and 3, the lowest-energy-level structures of the anionic complex species BU[6] · ClO_4^- and BU[6] · BF_4^- are shown, respectively, together with the lengths of the corresponding hydrogen bonds (in Å; 1Å = 0.1 nm). In these two complexes having C_3 symmetry, each of the three oxygens of ClO_4^-, as well as each of the three fluors of BF_4^-, is bound by four weak hydrogen bonds with the corresponding four methine hydrogens on the convex face of glycoluril units (see Figures 2 and 3). The diameter of the cavity in BU[6] · ClO_4^- is alternately 8.14 and 8.26 Å, while the diameter of the cavity in BU[6] · BF_4^- is alternately 7.85 and 8.07 Å. Thus, the diameter of the cavity in the parent macrocyclic receptor BU[6] is larger than the mentioned diameters in the anionic complexes BU[6] · ClO_4^- and BU[6] · BF_4^- under study. Therefore, from this point of view, the macrocycle BU[6] is somewhat flexible, as its cavity size adapts to the size of the anions ClO_4^- and BF_4^-.

Finally, the interaction energies of the BU[6] · ClO_4^- and BU[6] · BF_4^- complexes, involving the Boys-Bernardi counterpoise corrections[31–33] of the basis set superposition error, were found to be –158.6 and –182.1 kJ/mol, respectively, confirming the formation of the considered anionic complex species.

3. Acknowledgements

4. References

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Povzetek

Z uporabo kvantno mehanskih računov (DFT) smo določili najbolj verjetne strukture anionskih kompleksov bambus[6]uril·ClO$_4^-$ in bambus[6]uril·BF$_4^-$. Ugotovili smo, da imajo kompleksi C_3 simetrijo, vsak od anionov (vključno z makrociklično praznino) pa je z 12 šibkimi vodikovimi vezmi vezan na enoto glikolurila.