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ORIGINAL PAPER

Theoretical study on the complexation of bambus[6]uril with the chloride, bromide, and iodide anions

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Abstract By using quantum mechanical DFT calculations, the most probable structures of the bambus[6]uril·Cl^-, bambus[6]uril·Br^-, and bambus[6]uril·I^- anionic complex species were derived. In these three complexes, each of the considered univalent halide anions, included in the center of the macrocyclic cavity, is bound by 12 weak $C–H\cdots X^-$ ($X^- = Cl^-, Br^-, I^-$) hydrogen bonds between methine hydrogen atoms on the convex face of the glycoluril units and the respective anion. The lengths of the $C–H\cdots X^-$ hydrogen bonds increase in the order $Cl^- < Br^- < I^-$.

Keywords Receptors · Macrocycles · Complexation · Halide anions · Ab initio calculations · Complex structure

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 negatively charged rims of carbonyls on both sides of the macrocycle. This structure makes the macrocycles capable of binding organic guests bearing one or more positive charges in their structures [1–3].

Cucurbit[6]uril (abbreviated **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, who also discovered the macrocyclic structure of the molecule [4]. Guest positioning and complex stability strongly depended on the length of the alkyl chain of the guest [5–8]. The complexation between **CB[6]** and many organic guests, including polyamines [9, 10], viologen derivatives [11], organic dyes [12], polypeptides [13], amino acids, and dipeptides [14], has since been studied.

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

Recently, the synthesis of a cyclic hexamer, bambus[6]uril (abbreviated **BU[6]**; Scheme 1), which combines the structural features of both cucurbit[*n*]urils and hemicucurbit[*n*]urils, was described [19]. An acid-catalyzed condensation between 2,4-dimethylglycoluril and formaldehyde in HCl resulted in the 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

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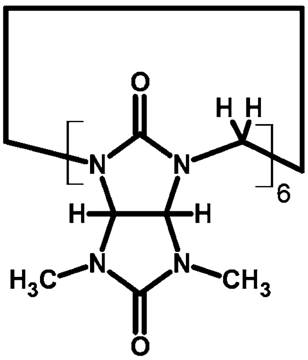

BU[6]

Scheme 1

[19]. Further, it is necessary to emphasize that **BU[6]** had strong affinity for halide anions. The crystal structure of the anionic complex **BU[6]**$\cdot$Cl^{-} was also reported [19].

In this work, the most probable structures of the **BU[6]**$\cdot$Cl^{-}, **BU[6]**$\cdot$Br^{-}, and **BU[6]**$\cdot$I^{-} anionic complex species have been solved by use of quantum mechanical DFT calculations.

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 LanL2DZ basis set was used and the optimizations were unconstrained. To increase the numerical accuracy and to reduce oscillations during the molecular geometry optimization, two-electron integrals and their derivatives were calculated by use of 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 effect of a polar solvent on the detailed structures of **BU[6]**, **BU[6]**$\cdot$Cl^{-}, **BU[6]** $\cdot$Br^{-}, and **BU[6]**$\cdot$I^{-} could be imagined, our quantum mechanical

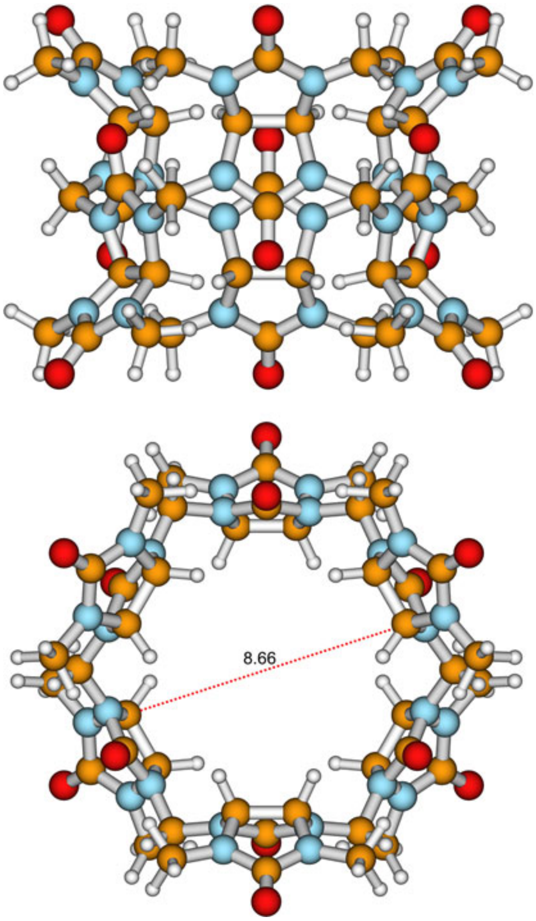

Fig. 1 Two projections of the DFT-optimized structure of free macrocycle **BU[6]** (B3LYP/LanL2DZ). The diameter of the cavity in **BU[6]** is 8.66 Å

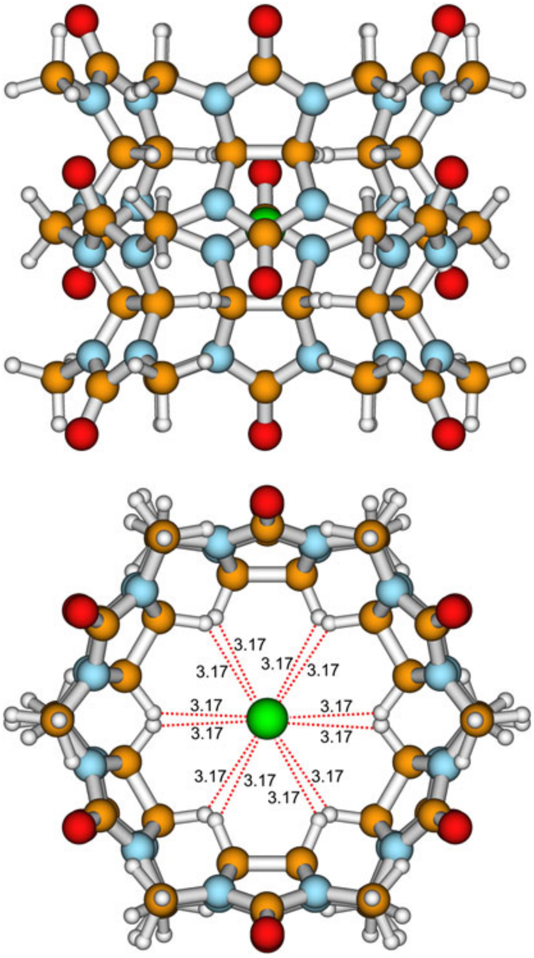

Fig. 2 Two projections of the DFT-optimized structure of the **BU[6]**$\cdot$Cl^{-} complex (B3LYP/LanL2DZ). The lengths of the C–H$\cdots$Cl^{-} hydrogen bonds are 3.17 Å; the diameter of the cavity in **BU[6]**$\cdot$Cl^{-} is 7.81 Å

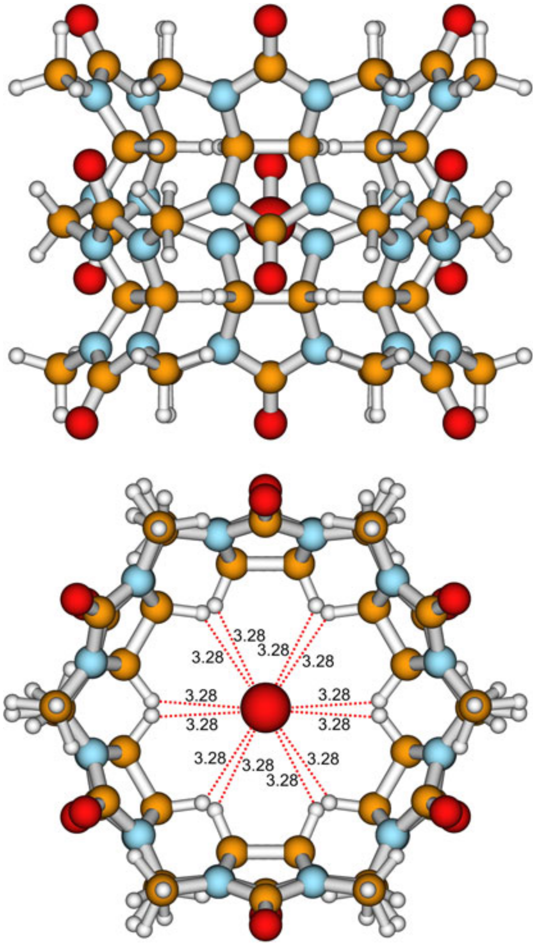

Fig. 3 Two projections of the DFT-optimized structure of the **BU[6]**·Br$^-$ complex (B3LYP/LanL2DZ). The lengths of the C–H···Br$^-$ hydrogen bonds are 3.28 Å; the diameter of the cavity in **BU[6]**·Br$^-$ is 7.97 Å

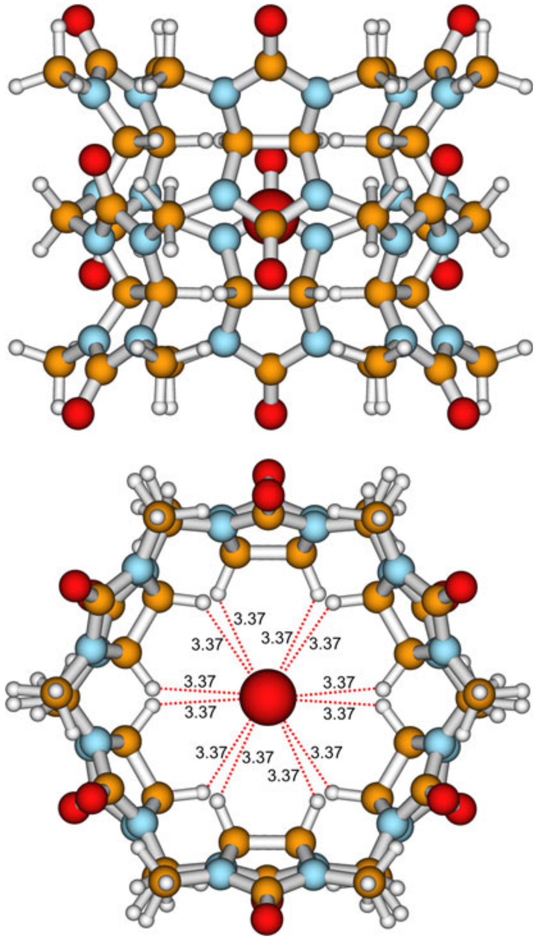

Fig. 4 Two projections of the DFT-optimized structure of the **BU[6]**·I$^-$ complex (B3LYP/LanL2DZ). The lengths of the C–H···I$^-$ hydrogen bonds are 3.37 Å; the diameter of the cavity in **BU[6]**·I$^-$ is 8.12 Å

calculations in similar cases, performed in an analogous way, showed very good agreement of experiment with theory [23–29].

In the model calculations, we optimized the molecular geometries of the parent macrocycle **BU[6]** and its anionic complex species with X$^-$ (X$^-$ = Cl$^-$, Br$^-$, I$^-$). The optimized structure of the free macrocyclic receptor **BU[6]** with C_3 symmetry is illustrated in Fig. 1. At this point it should be noted that the six glycoluril units in this macrocycle adopt alternate conformations; the methine hydrogen atoms on the convex face of each unit point into the cavity—its diameter is 8.66 Å (Fig. 1). This macrocycle can be divided into two identical parts by a plane defined by the carbon atoms of 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.

In Figs. 2, 3, and 4, the lowest-energy-level structures of the anionic complex species **BU[6]**·X$^-$, where X$^-$ = Cl$^-$, Br$^-$, I$^-$, are shown, together with the lengths of the corresponding hydrogen bonds (in Å). In these three complexes, which also have C_3 symmetry, each of the considered halide anions, located in the center of the macrocyclic cavity, is bound by twelve weak C–H···X$^-$ (X$^-$ = Cl$^-$, Br$^-$, I$^-$) hydrogen bonds between methine hydrogen atoms on the convex face of the glycoluril units and the respective anion. The lengths of the C–H···Cl$^-$, C–H···Br$^-$, and C–H···I$^-$ hydrogen bonds are 3.17, 3.28, and 3.37 Å, respectively; the diameters of the cavities in **BU[6]**·Cl$^-$, **BU[6]**·Br$^-$, and **BU[6]**·I$^-$ increase gradually, and are 7.81, 7.97, and 8.12 Å, respectively. This means that both the lengths of the C–H···X$^-$ hydrogen bonds and the diameters of the cavities in **BU[6]**·X$^-$ (X$^-$ = Cl$^-$, Br$^-$, I$^-$) increase in the series of Cl$^-$ < Br$^-$ < I$^-$. For this reason, therefore, the macrocycle **BU[6]** is somewhat flexible, because its cavity size adapts to the size of the X$^-$ anion.

In conclusion, it is possible to assume that the **BU[6]** macrocycle can form—naturally, under suitable conditions—the anionic complexes **BU[6]**·Y$^-$ with other anions Y$^-$ (e.g., CN$^-$, OCN$^-$, or SCN$^-$).

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