Bambus[6]uril as a Novel Macrocyclic Receptor for the Nitrate Anion

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Abstract

By using quantum mechanical DFT calculations, the most probable structure of the bambus[6]uril·NO_3^- anionic complex species was derived. In this complex having C_3 symmetry, the nitrate anion NO_3^-, included in the macrocyclic cavity, is bound by twelve weak hydrogen bonds between methine hydrogen atoms on the convex face of glycoluril units and the considered NO_3^- ion.

Keywords: Bambus[6]uril, nitrate anion, complexation, DFT calculations, 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]
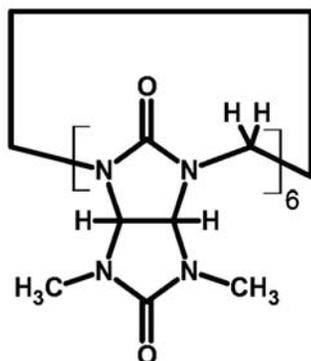
Scheme 1. Structural formula of bambus[6]uril(abbrev. **BU[6]**).

The synthesis of a cyclic hexamer bambus[6]uril (abbrev. **BU[6]**; see Scheme 1) was first described in 2010.[15] 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. This macrocycle was isolated as a white powder in a maximum yield of 30%, when the reaction was carried out in 5.4 mol/L HCl at room temperature.[15] Further, it is necessary to emphasize that the receptor **BU[6]** showed a good affinity for halide anions; the crystal structure of the anionic complex **BU[6]**·Cl⁻ was presented as well.[15]

From a map of the electrostatic surface potential it unambiguously follows that the interior cavity of **BU[6]** is significantly positively charged, whereas negative charge is located on the carbonyl oxygen atoms of the portal.[15] Quantum mechanical density functional theory (DFT) calculations were used to derive the most probable structures of the **BU[6]** · Cl⁻, **BU[6]** · Br⁻ and **BU[6]** · I⁻ anionic complex species. 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···X⁻ (X⁻ =Cl⁻, Br⁻, I⁻) hydrogen bonds between methine hy-

drogen atoms on the convex face of the glycoluril units and the respective anion. The lengths of the C–H···X⁻ hydrogen bonds increase in the order Cl⁻<Br⁻<I⁻ .[16] On the other hand, the fluoride anion F⁻ is bound in the macrocyclic **BU[6]** · F⁻ complex cavity only by 6 weak C–H···F⁻ hydrogen bonds, as proved theoretically.[17]

Recently, the anionic complex **BU[6]** · NO$_3^-$ has been proved experimentally.[18] This means that the **BU[6]** macrocycle can be considered as an effective receptor for the NO$_3^-$ anion. However, up to now, the structure of the **BU[6]** · NO$_3^-$ complex has not been solved. Therefore, in the current work, applying quantum mechanical DFT calculations, the most probable structure of the mentioned anionic complex species is predicted. It is apparent that this structure may be an important contribution to the theoretical study of the **BU[6]** macrocyclic receptor.

2. Results and Discussion

The quantum mechanical calculations were carried out at the density functional level of theory (DFT, B3LYP)[19,20] using the Gaussian 03 suite of programs.[21] The LanL2DZ basis set was used and the optimizations were unconstrained. In order to increase the numerical ac-

curacy 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]** and **BU[6]** · NO$_3^-$ could be imagined, our quantum mechanical calculations in similar cases, performed in an analogous way, showed very good agreement of experiment with theory.[22–29]

In the model calculations, we optimized the molecular geometries of the parent macrocycle **BU[6]** and its anionic complex species with NO$_3^-$. 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 8.66 Å (see Figure 1). Besides, this macrocycle can be divided into two identical parts by a plane defined by the carbon atoms of the six methylene bridges so that the carbons of six carbonyl groups are arranged alternately above and below the mentioned plane in a "zigzag" manner.
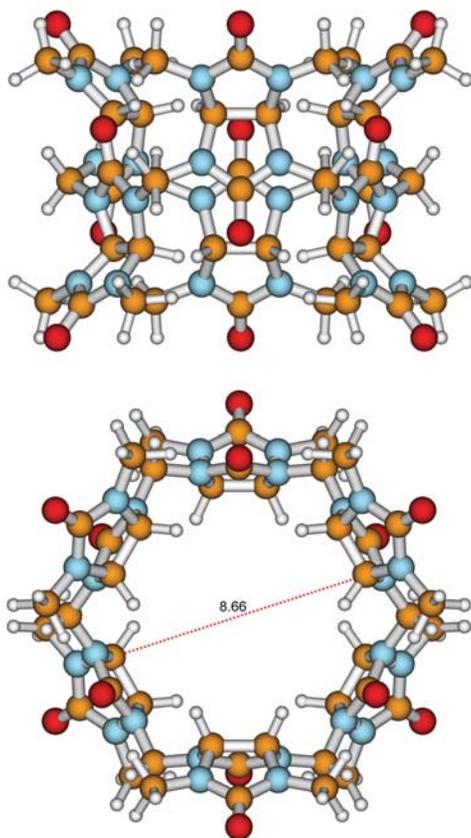

Figure 1. Two projections of the DFT-optimized structure of free macrocycle **BU[6]** (B3LYP/LanL2DZ). The diameter of the cavity in **BU[6]** is 8.66 Å.
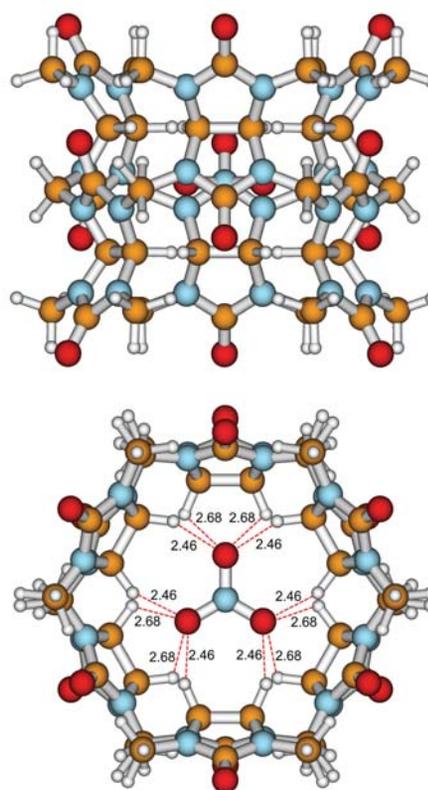

Figure 2. Two projections of the DFT-optimized structure of the **BU[6]** · NO$_3^-$ complex (B3LYP/ LanL2DZ).Each of the three oxygens of NO$_3^-$ is bound by four weak H-bonds (2.46, 2.68, 2.68 and 2.46 Å) with four methine hydrogens on the convex face of glycoluril units; the diameter of the cavity in **BU[6]** · NO$_3^-$ is 8.08 Å.

In Figure 2, the lowest-energy-level structure of the anionic complex species **BU[6]** · NO_3^- is shown, together with the lengths of the corresponding hydrogen bonds (in Å). In this complex having C_3 symmetry, each of the three oxygens of NO_3^- is bound by four weak H-bonds (2.46, 2.68, 2.68 and 2.46 Å) with four methine hydrogens on the convex face of glycoluril units. The diameter of the cavity in **BU[6]** · NO_3^- is 8.08 Å. Thus, the diameter of the cavity in the parent macrocyclic receptor **BU[6]** (8.66 Å) is lager than the mentioned diameter in the anionic complex **BU[6]** · NO_3^-. Therefore, from this point of view, the macrocycle **BU[6]** is somewhat flexible, as its cavity size adapts to the size of the nitrate anion.

Finally, the interaction energy, E(int), of the **BU[6]** · NO_3^- complex, involving the Boys-Bernardi counterpoise corrections[30–32] of the basis set superposition error, was found to be –225.7 kJ/mol, which confirms the formation of the considered anionic complex **BU[6]** · NO_3^-.

3. Acknowledgements

4. References

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Povzetek

Z uporabo kvantno mehanskih DFT izračunov smo napovedali najbolj stabilno strukturo anionskega kompleksa bambus[6]uril·NO_3^-. Izkazalo se je, da ima kompleks C_3 simetrijo, NO_3^- pa je vključen v makrociklični prostor in z dvanajstimi šibkimi vodikovimi vezmi povezan z vodikovimi atomi metina na konveksni površini, sestavljeni iz glikolurilnih enot.