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ORIGINAL PAPER

Theoretical study on the complexation of the sodium cation with a hexaarylbenzene-based receptor

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Abstract By means of theoretical calculations at density functional level, the complex structure of a hexaarylbenzene-based receptor with Na^+ was derived. In the resulting complex having C_3 symmetry, the sodium cation synergistically interacts with the hydrophilic polar ethereal oxygen fence and with the central hydrophobic benzene bottom of the parent receptor via cation–π interaction.

Keywords Receptors · Macrocycles · Complexation · DFT · Structure

Introduction

Hexaarylbenzene (HAB) derivatives attract great attention because of their unique propeller-shaped structure and potential application in molecular electronics and nanotechnology. NMR spectroscopy and X-ray crystallography have shown that the HAB-based receptor **1** (Scheme 1) binds a single potassium cation because it interacts both with the polar ethereal fence and with the central benzene ring via cation–π interaction [1]. Cation–π interaction is a well-established phenomenon in the gas phase and solid state [2], and is known to play an important role in the stabilization of tertiary structures of various proteins [3].

Recently, protonation of valinomycin, some calix[4]arenes, dibenzo-18-crown-6, and receptor **1** has been investigated [4–15]. Moreover, by using affinity capillary electrophoresis, the K^+/Na^+ selectivity for the HAB-based receptor **1** has been studied in methanolic medium [16]. However, up to now, the complex structure of receptor **1** with the sodium cation has not been solved. Therefore, in the current work, density functional theory (DFT) calculations were applied to derive the most probable structure of the cationic complex species $\mathbf{1}\cdot Na^+$.

Results and discussion

The quantum mechanical calculations were carried out at the density functional level of theory (DFT, B3LYP functional) using the Gaussian 03 suite of programs [17]. 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

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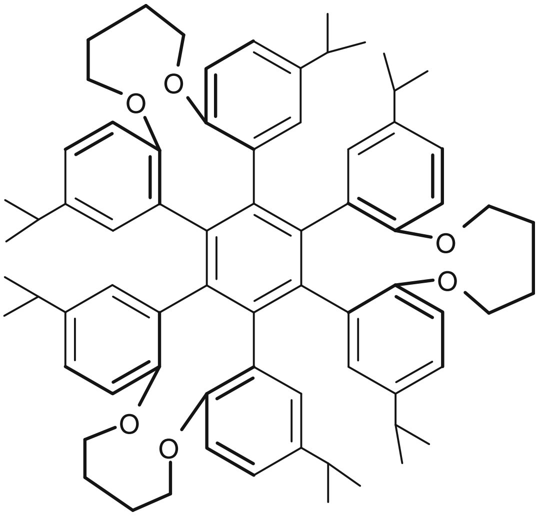

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Scheme 1

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 **1** and the **1**·Na$^+$ complex species could be imagined, our quantum mechanical calculations in similar cases, performed in an analogous way, showed very good agreement of experiment with theory [18–23].

In the model calculations, we optimized the molecular geometries of the parent HAB-based receptor **1** and its complex with Na$^+$. The optimized structure of a free receptor **1** having C_3 symmetry, involving a bowl-shaped cavity comprising an aromatic bottom (i.e., central benzene ring) and an ethereal fence formed by six oxygen atoms from the peripheral aryl groups, is illustrated in Fig. 1. The depth of the cavity, i.e., the distance between the mean plane of the aromatic bottom and that of the ethereal fence, is 2.15 Å (1 Å = 0.1 nm); the diameter of this cavity in **1** is 6.19 Å (Fig. 1).

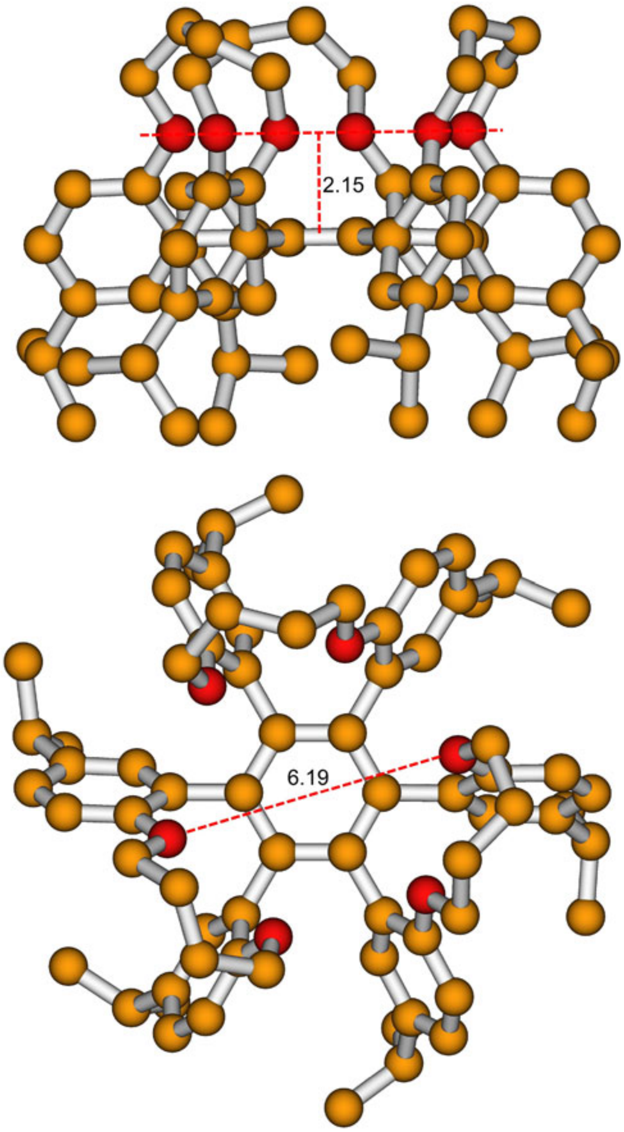

Fig. 1 Two projections of the DFT-optimized structure of a free HAB-based receptor **1** (B3LYP/6-31G(d)) (hydrogen atoms omitted for clarity)

The structure obtained by the full DFT-optimization of the cationic complex species **1**·Na$^+$ is depicted in Fig. 2. In this complex, which also has C_3 symmetry, the “central” cation Na$^+$ synergistically interacts with the hydrophilic polar ethereal oxygen fence (the corresponding Na$^+ \cdots$O distances are 3.02, 2.85, 3.02, 2.85, 3.02, and 2.85 Å) and with the central hydrophobic benzene bottom of the parent receptor **1** via cation–π interaction. The distance between the mean plane of the bottom benzene ring and the Na$^+$ cation is 2.35 Å, as pictured in Fig. 2. At this point it should be noted that the depth of the cavity in the **1**·Na$^+$ complex is about 2.30 Å, whereas its diameter is roughly 5.87 Å. This means that the formation of the cationic complex species **1**·Na$^+$ results in a small tapering and deepening of the cavity.

Finally, the interaction energy, E(int), of the **1**·Na$^+$ complex [calculated as the difference between the electronic energies of **1**·Na$^+$ and isolated Na$^+$ and **1** species, $E(\text{int}) = E(\mathbf{1}\cdot\text{Na}^+) - E(\text{Na}^+) - E(\mathbf{1})$] was found to be

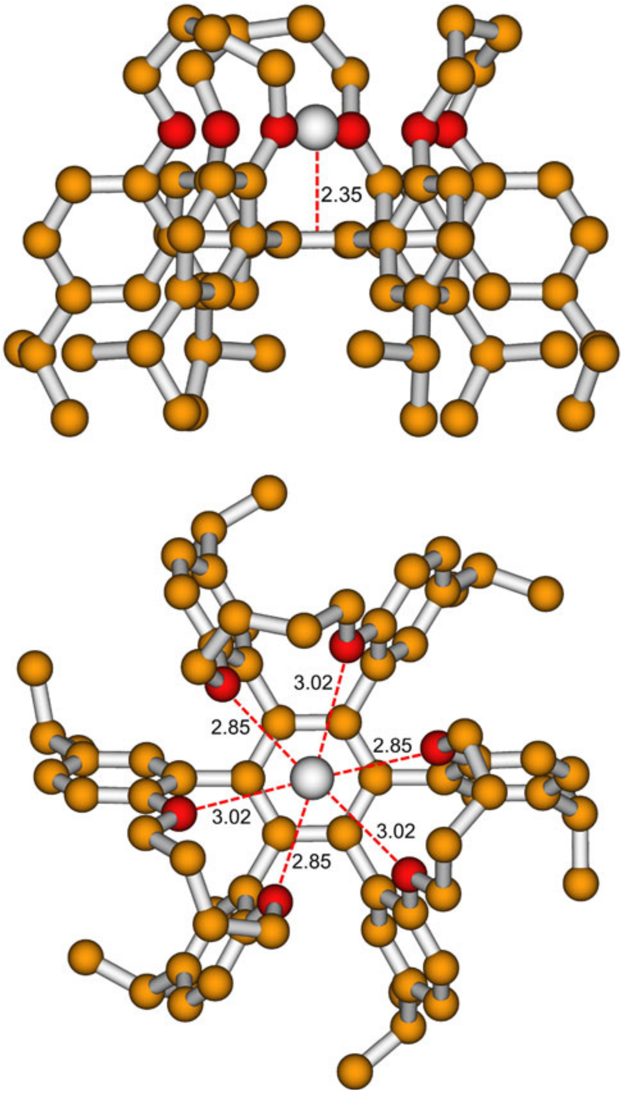

Fig. 2 Two projections of the DFT-optimized structure of the **1**·Na^+ complex (B3LYP/6-31G(d)) (hydrogen atoms omitted for clarity)

-350.9 kJ mol^{-1}, which confirms the formation of the considered cationic complex **1**·Na^+.

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