



# Theoretical study on halide anion recognitions by pyrrole- and benzene-strapped calix[4]pyrroles

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## ABSTRACT

Equilibrium geometries of two anion receptors, pyrrole- and benzene-strapped calix[4]pyrrole (PCP and BCP), and their complexes with halide anions ( $X^-$ /receptor, receptor = PCP and BCP,  $X^- = F^-$ ,  $Cl^-$  and  $Br^-$ ) were optimized using density functional theory (DFT) at the B3LYP/6-311G(d,p) level of theory. Natural bond orbital (NBO) method, atoms in molecules (AIMs) theory, and energy decomposition analysis (EDA) have been used to characterize the orbital interaction between anion and receptors, to construct three-dimensional electron density (ED) maps of all complexes, and to investigate into the binding contribution to the anion recognitions. Two types of hydrogen bonds,  $N-H \cdots X^-$  and  $C-H \cdots X^-$ , were confirmed in complex structures, and the halide anions offer lone pair electrons to the binding  $\sigma^*$  (N-H) or  $\sigma^*$  (C-H) antibond orbital of receptors. These H-bonds in  $F^-$ /receptor were obviously stronger than those in the other two ( $Cl^-$ /receptor and  $Br^-$ /receptor). The intermolecular interaction energies were predicted by using B3LYP/6-311G(d,p) methods with basis set superposition error (BSSE) correction. The order of the anion recognition selectivity was predicted as  $F^- > Cl^- > Br^-$ , and PCP possessed a higher anion affinity than BCP under identical conditions. These calculation results were qualitatively in good agreement with the experimental results.

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## 1. Introduction

In the course of the life movement, more than 70% of all enzyme substrates and cofactors are involved in anion in natural [1]. Considerable attention has been paid to anion recognition, and the design of host systems for anion-recognition applications is an ever-increasing field of research [2]. Calixpyrrole is one of the most promising molecules currently being explored for the purpose of anion binding [3–5], especially for the halide anions. Efforts to improve the anion affinity of calixpyrrole and to enhance its selectivity have led to the synthesis of a variety of new calixpyrrole derivatives [6,7]. Among various modifications, introduction of “strap” such as pyrrole, furan, and aromatic rings on one side of the calix[4]pyrrole, are one of the most effective approaches [8–12]. Experimental results show that the halide anion affinities are considerably enhanced in pyrrole- and benzene-strapped calix[4]pyrroles relative to the parent octamethylcalix[4]pyrrole. However, furan-strapped calix[4]pyrrole displays a lower anion affinity relative to the former two [11].

The binding interactions of anions with receptors are directed by a number of factors, for example, receptor-anion strength, influence of solvents, and the conformational arrangements. Their

detailed studies by theoretical approaches are very important in interpretation of experiments concerning the anion recognitions as well as in guiding the design and synthesis of new functionalized calixpyrroles [13–18].

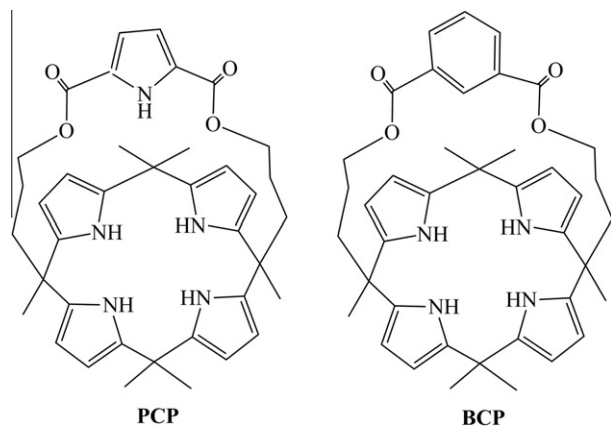
In this paper, we report a quantum mechanics study on the geometric parameters and anion recognition of pyrrole- and benzene-strapped calix[4]pyrroles (PCP and BCP, Fig. 1). Some of the practical theoretical methods, such as atoms in molecules (AIMs), natural bond orbital (NBO) and energy decomposition analyses (EDA), are employed to analyze the nature of the interaction between halide anions and receptors.

## 2. Computational methods

The geometrical structures of the studied receptors (PCP and BCP) and their complexes with halide anions,  $X^-$ /receptor ( $X = F, Cl, Br$ ), were completely optimized using the Gaussian 09 program package [19]. The exchange potential of Becke [20] and correlation functional of Lee et al. [21] (B3LYP) were used with the 6-311G(d,p) basis set. The calculated interaction energies between receptors and anions were corrected for the basis set superposition error (BSSE) by the Boys–Bernardi full counterpoise method [22]. The natural bond orbital (NBO) analysis was carried out using NBO, version 3.1 [23] (part of the Gaussian 09 package) at the B3LYP/6-311G(d,p) level of theory for all optimized structures.

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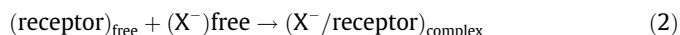
**Fig. 1.** Chemical structures of the used species, pyrrole-strapped calix[4]pyrrole (PCP) and benzene-strapped calix[4]pyrrole (BCP).

The atoms in molecules (AIMs) [24] theory was employed with the AIM2000 program [25] to quantify the noncovalent interactions presented in the supramolecular complexes. AIM is based upon those critical points where the gradient of the electron density vanishes. It is known that the electron density at the bond critical points roughly correlates with the strength of the chemical bonds and interactions. Furthermore, we employed the energy decomposition analysis (EDA) method, which has been developed by Morokuma [26,27] and Ziegler [28] to investigate the binding interaction. The central quantity of the binding analysis is the instantaneous interaction energy  $\Delta E_{\text{int}}$  between the binding fragments. The interaction energy  $\Delta E_{\text{int}}$  can be divided into three main components:

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}} \quad (1)$$

where  $\Delta E_{\text{elstat}}$  is the electrostatic interaction between the fragments, which is calculated with a frozen electron density distribution in the geometry of the final complex.  $\Delta E_{\text{Pauli}}$  is the repulsive interaction between the fragments, which is caused by the fact that two electrons with the same spin cannot occupy the same region in space. The  $\Delta E_{\text{Pauli}}$  term is calculated by enforcing the Kohn–Sham determinant of the molecule to obey the Pauli principle through antisymmetrization and renormalization. The last term  $\Delta E_{\text{orb}}$  is the orbital interaction, which accounts for the stabilizing orbital interactions between occupied and virtual orbitals of the two fragments. Usually, both the  $\Delta E_{\text{elstat}}$  and  $\Delta E_{\text{orb}}$  terms are negative and play a positive role in stabilizing the whole molecules. The EDA were performed using the program package ADF-2010.02 [29] at the BLYP/TZP level of theory [30,31] on the basis of the optimized geometries.

The calculated binding energies ( $\Delta E_{\text{bind}}$ ) of the complexes  $X^-/\text{receptor}$  in the gas phase are gained by the following equations:



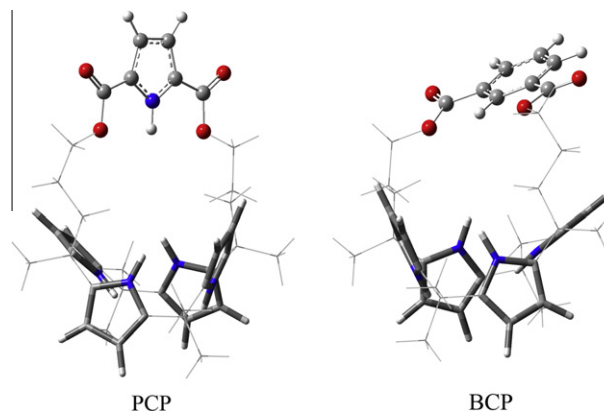
So, the binding energy  $\Delta E_{\text{bind}}$  can use the following equation to calculate:

$$\Delta E_{\text{bind}} = E(X^-/\text{receptor})_{\text{complex}} - E(\text{receptor})_{\text{free}} - E(X^-)_{\text{free}} \quad (3)$$

### 3. Results and discussion

#### 3.1. Molecular structures

The optimized geometrical structures of the receptors (PCP and BCP) and the corresponding complexes  $X^-/\text{receptor}$  ( $X = \text{F}, \text{Cl}, \text{and Br}$ ) are depicted in Figs. 2 and 3, respectively. The calix[4]pyrrole



**Fig. 2.** The optimized geometrical structures of the free receptors, PCP and BCP, calculated with the B3LYP/6-311G(d,p) methods.

(CP) subunit adopts a distorted 1,3-alternate conformation in both of PCP and BCP, whereas a transition to a cone-like conformation occurs upon capture of a single halide anion to form  $X^-/\text{receptor}$ . The most interesting geometrical parameters of  $X^-/\text{receptor}$  are listed in Table 1 as well as the experimental parameters of  $\text{Cl}^-/\text{BCP}$  [9] for comparison. Because of the existence of intermolecular interactions in crystal, such as van der Waals and stronger short-range ones including hydrogen bonding, the calculated bond lengths in the isolated molecule of  $\text{Cl}^-/\text{BCP}$  are consistently shorter than bonds in crystal and the predicted bond angles show slight deviation from the crystal data. Inspection of Table 1 reveals that the difference between the calculated parameters of  $\text{Cl}^-/\text{BCP}$  and the crystal structural parameters is very small. The comparison indicates that the appropriate results can be obtained by using B3LYP method with the 6-311G(d,p) basis set.

As shown in Fig. 3, the interaction models of halide anions and receptors are similar. The CP subunit cavity in the complex appears an oblate spheroid with a halide ion located at its top. Due to the different ionic radii and electronegativity of the three halide anions ( $\text{F}^-$ ,  $\text{Cl}^-$  and  $\text{Br}^-$ ), the calculated geometrical structures of the six complexes are different from each other. Table 1 reveals that the four  $\text{N-H}\cdots\text{F}^-$  H-bond lengths of pyrrole ring in  $\text{F}^-/\text{PCP}$  and  $\text{F}^-/\text{BCP}$  are very short (average distance 1.825 and 1.741 Å, respectively), which indicate the strong hydrogen bonding. However, the calculated strapped pyrrole  $\text{N-H}\cdots\text{F}^-$  distance is 2.329 Å in  $\text{F}^-/\text{PCP}$  indicating weak hydrogen bonding. A similar case is found in  $\text{F}^-/\text{BCP}$  where the strapped benzene  $\text{C-H}\cdots\text{F}^-$  distance is 3.369 Å. In addition, the weak  $\text{C-H}\cdots\text{F}^-$  hydrogen bonds also exist between the methylene or methyl groups and fluoride ion, the latter are weaker than the former roughly predicted from the length of hydrogen bonds. Because of the bigger size of  $\text{Cl}^-$  and  $\text{Br}^-$  ions, their positions in  $X^-/\text{receptor}$  have been shifted up slightly relative to that of  $\text{F}^-$  ion in  $\text{F}^-/\text{receptor}$ . Therefore, the strapped hydrogen bond lengths ( $\text{N-H}\cdots X^-$  in  $X^-/\text{PCP}$  and  $\text{C-H}\cdots X^-$  in  $X^-/\text{BCP}$ ,  $X^- = \text{Cl}^-$  and  $\text{Br}^-$ ) are all shorter than those in  $\text{F}^-/\text{receptor}$ . However, the pyrrole  $\text{N-H}\cdots X^-$ , methylene or methyl  $\text{C-H}\cdots X^-$  hydrogen bonds are all longer than those of  $\text{F}^-/\text{receptor}$ . The bond angle range of all the considered hydrogen bonds is 140–177°. Overall, the interaction between halide ions and CP subunit of strapped calix[4]pyrrole receptor is similar to that between this anion and parent CP [14]. The effect of pyrrole or benzene “strap” on anion binding increases with the increasing size of the halide ions.

#### 3.2. AIM analysis

To better clarify the nature of the interactions between halide ions and the strapped calix[4]pyrrole receptors, the theory of

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