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A MP2(full) theoretical investigation on the π-halogen interaction between OCB≡BCO and X1X2 (X1, X2 = F, Cl, Br)

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ABSTRACT

The π-halogen bond interactions are found between the B≡B triple bond and X1X2 (X1, X2 = F, Cl, Br) employing MP2(full) method at 6-311+G(2d), aug-cc-pVDZ and aug-cc-pVTZ levels according to the "CP (counterpoise) corrected potential energy surface (PES)" methodology, accompanied by the B≡B bond contraction. The (2, 3) extrapolated energies using the two-point approximation are also reported. All the π-halogen complexes are of electronic state $^1A_1$ with the C_{2V} symmetry. The dipole moment of dihalogen, the effects of the polarization of the halogen atom X1 and the electron withdrawing of X2 influence the strength of π-halogen bond interaction. The analyses of the natural charges, natural bond orbital (NBO), atoms in molecules (AIM) theory and electron density shifts reveal the nature of the π-halogen bond interactions, and explain the origin of the B≡B bond contraction. The energy decomposition analysis at B3LYP/TZ2P level shows that the interaction energy in the OCB≡BCO···X1X2 is mainly determined by the orbital energy. The values of ΔE_{int}, ΔE_{elstat}, ΔE_{pauli} and ΔE_{orb} are all arranged in the order of OCB≡BCO···BrF > OCB≡BCO···ClF ≈ OCB≡BCO···FCl > OCB≡BCO···BrCl > OCB≡BCO···Br_2 > OCB≡BCO···Cl_2 > OCB≡BCO···ClBr > OCB≡BCO···FBr. The binding energy of the complex of OCB≡BCO with X1X2 is stronger than that of the corresponding HC≡CH···X1X2 complex. OCB≡BCO···F_2 is indicative of covalent interaction. These results confirm that OCB≡BCO can be as π-electron donor to form the π-halogen bond interaction.

1. Introduction

Recently the π-halogen intermolecular interactions have received much attention due to their extremely important roles in a wide range of biological and chemical fields including crystal engineering, supramolecular structures, new high-value materials and drug design, etc [1–23]. In particular, they are often involved in protein–ligand interactions of the amino acids [24–26]. Furthermore, in most cases, the π-halogen bonded complexes are key intermediates in the electrophilic halogenations of alkenes, alkynes, allenes and aromatic systems [15,16,21]. It has been shown from many experimental and theoretical results that this kind of interactions can be established between the electron-rich multiple-bonds, aromatic rings and their derivatives as the electron donors, and dihalogens X1X2 (X1, X2 = F, Cl, Br, I) as well as organic halides [1–26]. Then, can the electron-deficient multiple-bond be as potential electron donor to form π-halogen bond? Compared to π-hydrogen and cation-π interactions, π-halogen bond interactions are not extensively investigated to date, especially from a theoretical point of view for those involving the triple-bonds as the electron donors. In fact, the π-halogen bond interactions between triple-bonds and halogen atoms play an even important role in the enantioselective host molecule [27]. With these in mind, we focus our attention on the π-halogen bond interactions between dihalogens and the electron-deficient triple-bonds as the electron donors.

OCB≡BCO is one of the typical species with the electron-deficient triple-bond. The investigation of the OCB≡BCO complex involving the B≡B triple-bond as the electron donor has always been of the interesting topic [28–30]. Very recently we have found that, although the B≡B triple-bond is electron-deficient, the electron is easy to be released to form the strong π-hydrogen bond and cation-π interaction [28–30]. Furthermore, for a long time, an acceptable and dominant notion is that, in the intermolecular interaction complex, the multiple-bond as the electron donor is always weakened and elongated. However, we have observed that it is not the case for the electron-deficient B≡B triple-bond in OCB≡BCO. Moreover, the binding energy is obviously stronger than that of the complex with the electron-rich C≡C triple-bond [30]. The analyses of the AIM charge density and electron density shifts explain that the more lost density from the

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electron-donating CO group in the complex than in the monomer is shifted to the bonding orbital of the B≡B bond, leading to the electron density accumulation in the BB bond, therefore the strengthened B≡B bond and the increased interactions [28–30]. These results suggest that, akin to the cation-π and π-hydrogen-bonded complexes, if much of the lost electron density from the C≡O group is transferred to the bonding orbital of the B≡B bond, the B≡B triple-bond of OCB≡BCO will turn into the "electron-rich" moiety as the electron donor to form the π-halogen interaction, perhaps accompanied by the B≡B bond contraction, too.

In 1973, Infrared spectra of the complexes of $C_2H_2\cdots Cl_2$, $C_2D_2\cdots Cl_2$, $C_2H_4\cdots Cl_2$, $C_2D_4\cdots Cl_2$, and $C_3H_6\cdots Cl_2$ were obtained after simultaneous slow deposition of both components on the cooled window of an optical cryostat at 75°K [31]. After 30 years, the π-halogen bonded complexes formed as essential intermediates from alkenes, alkynes, and allenes with bromine were investigated in different solvents by UV-spectroscopy in combination with stopped-flow techniques. Calculations by ab initio method revealed the preferred structures and nature of the π-halogen bonds [16]. In 2005, Li et al. studied the π-halogen bonds of ClF with ethylene and its derivatives at MP2/aug-cc-pVDZ level [9]. In 2006, the full geometry optimizations for the π-type halogen-bond systems, $C_2H_4(C_2H_2)$–XY (XY = F_2, Cl_2, Br_2, ClF, BrF, BrCl) were carried out using MP2 at 6-311++G(d,p) and aug-cc-pVDZ levels [32]. In 2009, ab initio calculations were performed to investigate the noncovalent C–Cl$\cdots\pi$ interactions between the triple-bonds and chlorine atoms in the complexes of acetylene with several chloromethanes [33]. Very recently, an advance on halogen bonding has been reviewed [34]. All the previous investigations paid close attention to the π-halogen bond interactions containing only the electron-rich donors. However, to our knowledge, no investigation on the π-halogen bond interaction involving the electron-deficient B≡B triple-bond as the electron donor has been presented.

In this paper, our goal is to test theoretically whether the electron-deficient B≡B triple-bond of OCB≡BCO can be as the electron donor to form π-halogen interaction with X1X2 (X1, X2 = F, Cl, Br) or not. Additionally, the B≡B bond length will also be tested whether it is contracted upon the formation of the π-halogen interaction. For this kind of π-halogen interactions, theoretic investigation will reveal the nature of the interaction to further study on structures and activities for the complexes involving the electron-deficient multiple-bond as the electron donors in theory and experiment.

2. Computational methods

It is well established that, employing the MP2 method with the augmented correlation-consistent polarized valence-double/triple-ζ (aug-cc-pVD/TZ) basis set, the distance of the π-halogen bond and the interaction energy compare relatively well to the experimental value. Thus, the MP2/aug-cc-pVD/TZ method has been successfully applied in order to reveal the nature of the π-halogen bond interaction [5,9,35]. Therefore, in this investigation we use the MP2(full) method with aug-cc-pVDZ and aug-cc-pVTZ atomic basis sets. As a comparison, the MP2(full)/6-311+G(2d) method is also considered. On the other hand, it is very necessary to obtain the accurate structure and energy of the π-halogen bond interaction employing the "CP (counterpoise) corrected potential energy surface (PES) [36,37]" method [9]. So the "CP-corrected PES" method is implemented during the process of optimization. As follows in the discussion, the accurate structures from the CP-corrected PES are used.

Except for the decomposition analysis of interaction energy, the other calculations have been performed with Gaussian 03 program [38]. All the possible π-halogen bonded complexes have been fully optimized using MP2(full) method with the 6-311+G(2d) and aug-cc-pVDZ basis sets. The complexes corresponding to the minimum energy points, at which the harmonic frequency analyses have been carried out, at the molecular energy hypersurface have been obtained. Seven stable complexes (NImag = 0) are found, and the π-halogen bonded complexes OCB≡BCO$\cdots F_2$ and OCB≡BCO$\cdots$FCl are not the true minima with two imaginary frequencies, respectively. Single point energy calculations have been performed at MP2(full)/6-311+G(2d), MP2(full)/aug-cc-pVDZ, MP2(full)/aug-cc-pVTZ//MP2(full)/aug-cc-pVDZ levels, respectively. NBO analysis [39] has been carried out at MP2/6-311+G(2d) level. The shifts of the electron densities [40] that accompany the formation of the π-halogen interactions have been displayed at MP2(full)/aug-cc-pVDZ level using GaussView program, and the topological electron charge density has been analyzed by the AIM method [41] using AIMPAC program [42] at the same level. The frequency shifts (Δv), defined as the difference between the frequency of the certain vibrational mode in the complex and isolated X1X2, can be expressed as follows:

$$\Delta v = v_{\text{complex}} - v_{\text{monomer}}$$

In general, the intermolecular interaction energy is computed as the energy difference between the complex and the monomers in the complex geometries neglecting the deformation energy contribution due to the structural deformation of the complex subunits upon complexation. In the preliminary calculation, however, we have found that the X1X2 molecule geometry is drastically changed for the OCB≡BCO$\cdots$X1X2 complex. Such geometric changes could have a notable impact on the computed interaction energy. To estimate the extent of the contribution of the deformation on the computed interaction energies, we give the following diagram:

$$\begin{tikzcd}
\text{OCBBCO}_{(\text{mono.})} + \text{X1X2}_{(\text{mono.})} \arrow[r, "\Delta E_{\text{prep}}"] \arrow[rr, bend right, "\Delta E_{\text{binding}}(D_e)"'] & \text{OCBBCO}_{(\text{fram.})} + \text{X1X2}_{(\text{fram.})} \arrow[r, "\Delta E_{\text{int}}"] & \text{OCBBCO-X1X2}_{(\text{com.})}
\end{tikzcd}$$

Thus, the overall bonding energy ΔE can be divided into two major components as:

$$\Delta E_{\text{binding}} = \Delta E_{\text{prep}} + \Delta_{\text{int}}$$

The preparation energy ΔE_{prep} is the amount of energy required to deform the structures of the free fragments from their equilibrium structure to geometry. Our previous investigations showed that the deformation energy of OCBBCO could be negligible for the complexes of OCBBCO [28–30]. Thus, ΔE can be expressed as follows:

$$\Delta E = \Delta E_{\text{prep(X1X2)}} + \Delta E_{\text{int}}$$

ΔE_{int} is the instantaneous interaction energy between the two fragments in the complex. Here, the energy decomposition analysis of ΔE_{int} for the π-halogen bond in the complex OCB≡BCO$\cdots$X1X2 is carried out at the B3LYP/TZ2P level using ADF program which is based on the methods of Morokuma [43] and Ziegler and Rauk [44]. As a comparison, the energy decomposition analysis of ΔE_{int} for that in HC≡CH$\cdots$X1X2 is also considered. ΔE_{int} can be decomposed into three main components:

$$\Delta E_{\text{int}} = \Delta_{\text{elstat}} + \Delta E_{\text{pauli}} + \Delta_{\text{orb}}$$