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Competition and cooperativity between hydrogen bond and halogen bond in HNC···$(HOBr)_n$ and $(HNC)_n$···HOBr ($n = 1$ and 2) systems

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ABSTRACT

A computational study of the complexes formed between HNC and HOBr has been undertaken at the MP2/aug-cc-pVTZ theoretical level. Eight dyads and fourteen triads formed through hydrogen bonding and halogen bonding were studied. It was found that the halogen bond is weaker than the hydrogen bond in HNC–HOBr dyad. The C atom in HNC is found to be a better electron donor than the O atom in HOBr. The cooperative effect is present between the hydrogen bond and halogen bond in the triads. The most stable triad corresponds to the complex combined with OH···C and NH···C hydrogen bonds. However, the largest cooperative effect occurs in the complex combined with NH···O and OBr···C interactions, in which the cooperative energy is about 23% of the total interaction energy. The cooperative effect is negative when HOBr acts as the proton and halogen donors simultaneously.

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1. Introduction

Noncovalent interactions have attracted much attention due to their extensive applications in fields of chemistry, biology, and physics [1]. Hydrogen bond certainly holds the most important position among the intermolecular interactions. It has been demonstrated that the electrostatic interaction, together with induction and dispersion interactions, contributes jointly to the formation of hydrogen bond [2]. Like hydrogen bond, halogen bond is also an important noncovalent interaction between a covalently-bonded halogen atom and a negative site in another molecule, and it has been characterized mainly as the electrostatic interaction [3,4]. Extensive studies have shown that halogen bonding shares some similar properties with hydrogen bonding [5,6].

When two molecules can be combined with different intermolecular forces, there is competition between them. This competition behavior not only occurs between hydrogen bonds [7] but also is present between different types of interactions [8]. In many cases, halogen bonding is comparable in strength to hydrogen bonding and they can compete with each other in formation of the cluster [9]. Metrangolo and his coworkers thought that halocarbons are effective in breaking hydrogen bonds through the formation of halogen bonds [10]. In the previous study, we reported the competitive behavior between hydrogen bond and halogen bond in the complexes of hypohalous acids with formaldehyde [11].

A cooperative phenomenon is observed when two or more intermolecular forces are present in complexes. Like the competition behavior, the cooperativity is another important feature of intermolecular interactions. It results in great changes in geometrical, spectroscopic, and energetic properties. The cooperativity in hydrogen-bonded complexes has been investigated extensively [12–21]. Recently, the cooperativity between different types of interactions has drawn much attention [22,23]. It has been shown that the cooperativity between different types of interactions is usually more prominent than that between the same contacts [24].

The bromine-containing species are more effective in depletion of stratospheric ozone [25,26], thus they have drawn much attention. Among the bromine-containing species, hypobromous acid (HOBr) has been confirmed to play an important role in depleting the ozone [27–29]. Hydrogen isocyanide (HNC) was observed for the first time as a photoisomerization product of HCN in low-temperature rare gas matrixes and later in interstellar space [30,31]. Considering the HNC and HOBr may coexist in the interstellar space, it is thus significant to study the interaction between the two molecules. The study may help us understanding the existence form and functions of both molecules in the interstellar space.

In this paper, we thus investigate the interaction between HNC and HOBr with quantum chemical calculations. The HNC can act as a Lewis base (the C end) and provide a proton. The HOBr can provide the halogen (Br) besides the base center (O) and the acid center. Thus both molecules can be combined through a hydrogen bond or a halogen bond. In HNC···HOBr binary system, there is competition between the hydrogen bond and halogen bond. We also study HNC···$(HOBr)_2$ and HOBr···$(HNC)_2$ ternary systems to

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investigate the cooperativity between hydrogen bond and halogen bond.

2. Theoretical methods

The equilibrium structures of HNC···$(HOBr)_n$ and $(HNC)_n$···HOBr ($n = 1, 2$) complexes as well as the corresponding monomers were optimized at the MP2/aug-cc-pVTZ level. Harmonic frequency calculation has then been performed at the same level to confirm that these structures are local minima on the energy surfaces. The interaction energy of the dyad, $\Delta E_{AB} = E_{AB} - (E_A + E_B)$, is calculated as the difference between the energy of the dyad and the energy sum of the monomers. The interaction energy of molecular pairs in the triad is calculated with a two-body approximation. For example, the interaction energy between A and B in ABC triad is calculated as $\Delta E_{AB} = E_{ABC} - (E_A + E_{BC})$. In this calculation, BC is taken as a whole. All interaction energies were corrected with the basis set superposition error (BSSE). The BSSE was evaluated by using the counterpoise method of Boys and Bernardi [32]. All calculations have been performed with Gaussian 09 program [33].

3. Results and discussion

3.1. Competitive behavior in the dyads

We designed three dyads composed of HNC and HOBr, one HNC dyad, and four HOBr dyads. For convenience of description, HNC and HOBr are denoted with A and B, respectively. Thus, the eight dyads are denoted as A-B-1, A-B-2, A-B-3, A-A, B-B-1, B-B-2, B-B-3, and B-B-4, respectively. Fig. 1 shows their geometrical structures optimized at the MP2/aug-cc-pVTZ level. In the eight structures, A-B-2 and B-B-2 dyads are combined with a halogen bond, A-B-1, A-B-3, A-A, and B-B-1 dyads with a hydrogen bond, and B-B-3 and B-B-4 dyads with two hydrogen bonds. The latter two dyads are cyclic structure.

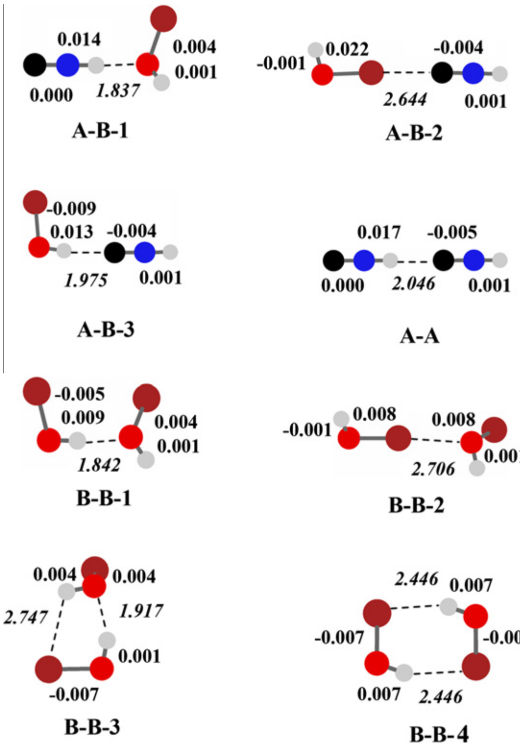

Fig. 1. Optimized structures of the complexes between HNC and HOBr at the MP2/aug-cc-pVTZ level. Red, blue, black, white, and brown balls represent O, N, C, H, and Br atoms, respectively. The binding distance (italic) and change of bond length are also marked with the unit of Å. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

It has been demonstrated that electrostatic potential has been proved to be an effective tool for analyzing and predicting noncovalent interactions [34]. To understand the formation of both interactions, we plotted in Fig. 2 the electrostatic potential maps of the HNC and HOBr monomers at the MP2/aug-cc-pVTZ computational level. One can see that the most positive and negative sites are located at the H and C ends along the H–N–C axis in HNC molecule, respectively. The HOBr molecule has two positive centers with one around the H atom along the O–H direction and another at the Br end of O–Br axis. Thus HOBr can act as proton and halogen donors. The most negative center is around the O atom, so HOBr can also act as proton and halogen acceptors. As expected, eight kinds of interactions are observed. This also proves the important role of electrostatic interaction in the formation of hydrogen bond and halogen bond.

The binding distance and bond length change relative to the monomer are also marked in Fig. 1. The binding distance is 1.837, 1.842, and 1.917 Å for the O···H contact in the A-B-1, B-B-1, and B-B-3 dyads, 1.975 and 2.046 Å for the C···H contact in the A-B-3 and A-A dyads, 2.644 and 2.706 Å for the O···Br contact in the A-B-2 and B-B-2 dyads, and 2.747 and 2.446 Å for the H···Br contact in the B-B-3 and B-B-4 dyads, respectively. It is smaller than the sum of the van der Waals radii of the respective atoms (about 2.5 Å for the O and H atoms, 2.9 Å for the C and H atoms, 3.4 Å for the O and Br atoms, and 3.0 Å for the H and Br atoms). This indicates that there is an attractive force between them.

The interaction energy and some frequency shifts are presented in Table 1. For the three binary systems of HNC and HOBr, the interaction energy increases in order of A-B-2 < A-B-1 < A-B-3. Clearly, the hydrogen-bonded dyad A-B-3 is more stable than the halogen-bonded one A-B-2. The similar conclusion is obtained for the complexes of hypohalous acid with HCN [8], complexes of hypohalous acid with H_2CO [24], and complexes of hypochlorous acid with $(CH_3)_2S$ [35]. At the MP2/aug-cc-pVTZ level, the interaction energy between HCN and HOBr molecules is calculated to be −30.79 and −21.22 kJ/mol for the hydrogen and halogen bonds, respectively, when HCN acts as the electron donor [8]. It is thus concluded that the HCN is a better electron donor than HNC [36].

Solimannejad and coworkers [37] have presented a computational study of HOBr dyads at the MP2/6-311++G(2d,2p) level, and found three minima located on the potential energy surface of the dyads, which are combined with hydrogen bonding. Here we reoptimized the HOBr dyads at the MP2/aug-cc-pVTZ level and found four minima. The cyclic dyad B-B-3 is the most stable one with the interaction energy of −22.73 kJ/mol at the MP2/aug-cc-pVTZ level. It is calculated to be −19.99 kJ/mol at the

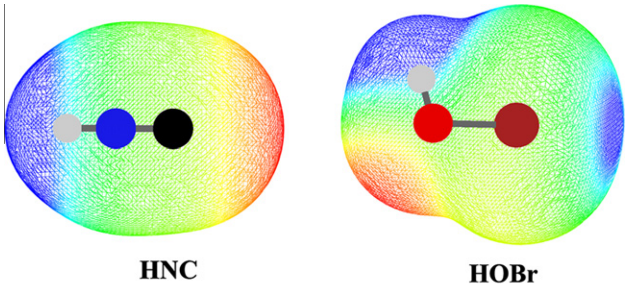

Fig. 2. Electrostatic potentials of HNC and HOBr molecules calculated at the MP2/aug-cc-pVTZ level. The red color represents the negative molecular electrostatic potential and the blue color denotes the positive molecular electrostatic potential. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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