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A theoretical investigation into the cooperativity effect involving anionic hydrogen bond, thermodynamic property and aromaticity in $Cl^-\cdots$benzonitrile$\cdots H_2O$ ternary complex

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ABSTRACT

The cooperativity effects involving the $O/C{-}H\cdots Cl^-$ anionic H-bonding interactions in $Cl^-\cdots$benzonitrile$\cdots H_2O$ ternary complexes are investigated by using the B3LYP and MP2(full) methods with the 6-311++G(2d,p) and aug-cc-pVTZ basis sets. The thermodynamic cooperativity and the influence of the H-bond cooperativity effect on the aromaticity of benzonitrile ring are also evaluated. The result shows that the influence of the $O/C{-}H\cdots Cl^-$ anionic H-bonding interaction on the $O{-}H\cdots N$ or $C{-}H\cdots O$ interaction is more pronounced than that of the latter on the former. The cooperativity effect appears in the linear complex while the anti-cooperativity effect is found in the cyclic system. The enthalpy change is the major factor driving the cooperativity in forming the linear ternary complex while entropy change turns into the favorable factor in forming the cyclic system. The aromaticity characterized by nucleus-independent chemical shifts (NICS) is weakened and the bond dissociation energy (*BDE*) of the C—CN bond increase upon the ternary-complex formation. The cooperativity effect ($E_{coop.}$) correlates well with R_c (NICS$(1)_{ternary}$/NICS$(1)_{binary}$), $R_{BDE(C{-}CN)}$ ($BDE_{(C{-}CN)ternary}/BDE_{(C{-}CN)binary}$) and the change of chemical shift $\Delta\Delta\delta$ ($\Delta\delta_{ternary} - \Delta\delta_{binary}$), respectively.

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1. Introduction

When the noncovalent interactions operate simultaneously and mutually enhance each others' strength, they are termed as acting cooperatively [1]. Cooperativity effect involving hydrogen-bonding interaction is currently a topic of wide ranging interest due to their extremely important role in chemical reaction, molecular recognition and regulation of biochemical process [2–4]. Mignon et al. found that the $\pi\cdots\pi$ interaction had a significant influence on the hydrogen-bonding capacity of stacked DNA/RNA bases [5]. Vijay's, Frontera's and Deyà's groups reported many theoretical evidences of the cooperativity effects in some representative hydrogen-bonded systems [6,7]. Recently two reviews on the cooperativity effect in weak bonds (including hydrogen bonds) were published [8,9].

In general, the stronger the noncovalent interaction, the more notable the cooperativity effect is. Due to the favorable binding energies of charged complexes, the cooperativity effects in the anionic systems are often notable [7,10,11]. Recently there have been many works devoted to the cooperativity effects involving the hydrogen bonds in the anionic complexes, such as those between anion$\cdots\pi$ and hydrogen-bonding interactions [12–14].

The $H\cdots X^-$ (X = F, Cl, Br, etc.) anionic hydrogen bond is one kind of the typical and strong interactions [15]. There are a great number of the $H\cdots X^-$ anionic H-bonding interactions in biological systems [16–19]. Properly characterizing the cooperativity effect involving the $H\cdots X^-$ anionic H-bonding interaction is crucial to understanding some biological processes [20]. Very recently, we studied theoretically the cooperativity effect of the $H\cdots F^-$ anionic hydrogen bond in the complex with non-aromatic N-(Hydroxymethyl)acetamide [21]. To our knowledge, no theoretical investigation into the cooperativity effect involving the $H\cdots X^-$ anionic H-bonding interaction in the complex with aromatic monomer has been presented.

Benzonitrile (BN) is the simplest aromatic nitrile species. The hydrogen-bonding interactions between the nitrile groups of benzonitrile and its derivatives and protic solvents are of considerable interest [22–26]. For example, the hydrogen-bonding interaction between benzonitrile and H_2O [27], HCN [28] or *N*,*N*-dimethylformamide [29] was studied by theoretical calculations. A forecast of H-bond changes in the electronic excited state for benzonitrile

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and its derivatives was carried out by using the time-dependent density function theory [30].

In this paper, we present a theoretical investigation into the cooperativity effects involving the H···Cl^- anionic hydrogen bonds in the Cl^-···benzonitrile···H_2O ternary complexes. In benzonitrile···H_2O, the conventional O—H···N and C—H···O H-bonds were found [27], and the O—H···π H-bond might exist. For the Cl^{--}···benzonitrile···H_2O ternary system, the anionic hydrogen bonds (O—H···Cl^- and C—H···Cl^-) and conventional hydrogen bonds mentioned above can coexist, and the cooperativity effect between them might arise. Therefore, the Cl^-···benzonitrile···H_2O complex can serve as a model system to investigate the cooperativity effect involving the anionic hydrogen-bonding interaction in the complex with aromatic monomer. This investigation will be useful to understand the biological process involving the anionic hydrogen-bonding interaction in the system with aromatic monomer.

The changes of the geometry, interaction energy, vibration frequency, dipole moment, charge transfer and chemical shift in the process from binary to ternary complexes have been as the measurements of the cooperative effects for several decades [31–34]. In fact, the cooperativity effect can also be evaluated by using the change of the thermodynamic data, such as the change of Gibbs' free energy ΔG_{coop} [35]. The positive cooperativity can be observed by experimental methods when the overall binding is greater than the summation of the Gibbs' free energies of binding for the individual interactions; the negative cooperativity means that the change in Gibbs free energy of binding is smaller than what could be achieved [36]. According to experimental results, Williams and Birdsall et al. postulated that on binding ligands under conditions of positive cooperativity there would be a shrinking of the protein structure while for negative cooperativity there would be an expansion of the structure of the protein–ligand complex [37,38]. Gupta et al. found that the equilibrium constant for the $X + X_n \rightarrow X_{n+1}$ ($n \geqslant 2$) hydrogen bond formation was approximately 10 times larger than that for the $2X \rightarrow X_2$ hydrogen bond due to the cooperativity effect [39]. Recently, the thermodynamic cooperativity between tertiary interactions in different regions of the RNA was discussed [40]. Furthermore, there have been a few studies that address the enthalpic and entropic origin of cooperativity ($\Delta\Delta H$ and $-T\Delta\Delta S$) in experimental investigations [41–43]. Experimental evidences suggest that, in most cases, due to the large and long hydrophobic side chain in biomacromolecule system, the cooperativity mainly results from the favorable entropic contribution "$-T\Delta\Delta S$" [44]. In sum, the thermodynamic cooperativity effect has been of great chemical interests in experimental studies. However, to our knowledge, few theoretical investigations into the thermodynamic cooperativity effect have been presented [45]. In this work, in order to reveal the thermodynamic origin of cooperativity effect, the changes of the thermodynamic properties ($\Delta G_{coop.}$, $\Delta\Delta H$ and $-T\Delta\Delta S$) are also discussed.

2. Methodology

All calculations were performed with Gaussian 03 programs [46]. The monomers and complexes were fully optimized using the DFT-B3LYP method with the 6-311++G(2d,p) basis set. The structures corresponding to the minimum energy points at the molecular energy hypersurface (NImag = 0) were obtained. Single point energy calculations were carried out using the B3LYP and MP2(full) methods with the 6-311++G(2d,p) and aug-cc-pVTZ basis sets.

For the binary system, the interaction energy ($E_{int.(BN\cdots H2O)}$, $E_{int.(Cl-\cdots H2O)}$ or $E_{int.(Cl-\cdots BN)}$) was calculated by evaluating the difference between the total energies of complex and individual monomers. They were corrected with the basis set superposition error (BSSE) [47,48].

In the ternary system, $E'_{int.(BN\cdots H2O)}, E'_{int.(Cl-\cdots BN)} and E'_{int.(Cl-\cdots H2O)}$ represent the interaction energy between both the moieties which are directly interacting with. They correspond to the benzonitrile···H_2O, benzonitrile···Cl^- and Cl^-···H_2O interaction energies in the presence of Cl^-, H_2O and benzonitrile, respectively. These interaction energies were calculated using the following equations, respectively.

$$\begin{aligned} E'_{int.(BN\cdots H_2O)} &= E_{Cl^-\cdots BN\cdots H_2O} - E_{Cl^-\cdots BN} - E_{H_2O} \text{ for linear structure} \\ E'_{int.(BN\cdots(H_2O\cdots Cl^-))} &= E_{BN\cdots H_2O\cdots Cl^-} - E_{BN} - E_{H_2O\cdots Cl^-} \text{ for cyclic structure} \end{aligned} \tag{1}$$

$$\begin{aligned} E'_{int.(Cl^-\cdots BN/H_2O)} &= E_{Cl^-\cdots BN\cdots H_2O} - E_{BN\cdots H_2O} - E_{Cl^-} \text{ for linear structure} \\ E'_{int.(Cl^-\cdots(BN\cdots H_2O))} &= E_{Cl^-\cdots BN\cdots H_2O} - E_{Cl^-} - E_{BN\cdots H_2O} \text{ for cyclic structure} \end{aligned} \tag{2}$$

when the value of $E'_{int.}$ is larger than that of $E_{int.}$ (or the sum of two corresponding interaction energies for cyclic structure) in the corresponding binary complex, it means that the stabilization of the dimers gets enhanced in the presence of the third component and thus the cooperativity effects occur.

$E''_{int.H_2O\cdots BN}$ and $E''_{int.(H_2O\cdots Cl)}$ are defined as the through-space interaction energy between both the moieties with which they are not directly interacting. They were calculated at the ternary geometry by employing the following equation:

$$E''_{int.(H_2O\cdots BN/Cl)} = E'_{H_2O\cdots BN/Cl^-} - E_{H_2O} - E_{BN/Cl^-} \tag{3}$$

where $E'_{H2O\cdots BN/Cl}$ represent the total energies of the binary framework (not be optimized) at the optimized ternary geometry.

The cooperativity ($E_{coop.}$) was calculated as the difference between the binding energy of ternary complex (i.e., the energy involved in the direct assembly of the ternary complex from its constituent monomers) and the binding energy of the sum of all pair interaction energies as given in Eq. (4) or (5).

$$\begin{aligned} E_{coop.} = {} & E_{int.(BN\cdots H_2O\cdots Cl)} - E_{int.(BN\cdots H_2O)} - E_{int.(H_2O\cdots Cl)} \\ & - E_{int.(BN\cdots Cl)} \text{ for cyclic structure} \end{aligned} \tag{4}$$

$$\begin{aligned} E_{coop.} = {} & E_{int.(BN\cdots H_2O\cdots Cl)} - E_{int.(BN/Cl\cdots H_2O)} - E_{int.(BN\cdots Cl)} \\ & - E''_{int.(H_2O\cdots BN/Cl)} \text{ for linear system} \end{aligned} \tag{5}$$

The synergetic energies were calculated using the following equation:

$$\begin{aligned} E_{syn.} = {} & E_{int.(BN\cdots H_2O\cdots Cl)} - E_{int.(BN/Cl\cdots H_2O)} \\ & - E_{int.(BN\cdots Cl)} \text{ for linear structure} \end{aligned} \tag{6}$$

Except for $E'_{H2O\cdots BN/Cl}$ in Eq. (3), all the energies at the right side of equations correspond to the systems optimized separately.

3. Results and discussion

3.1. Binary system

Six benzonitrile···H_2O binary complexes (I, II, III, IV, V and VI), two benzonitrile···Cl^- systems (A and B) and Cl^-···H_2O were selected at the B3LYP/6-311++G(2d,p) level (see Figs. 1S and 2S). Similar to literature [27], the O—H···N and C—H···O H-bonding interactions are found in the benzonitrile···H_2O systems, and the O—H···N H-bonding interaction is larger than that of the C—H···O link at four levels of theory (see Table 1S). The calculation also shows that the H atom of H_2O can bind electrostatically to negative carbon center at the para-position of the nitrile group in VI. Attah

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