A theoretical investigation on the cooperativity effect, reduced density gradient, stability and aromaticity in the benzonitrile···H$_2$O complex with Na$^+$ or Cl$^-$

Jiang-Bo Xie$^a$, * & Wen-Jing Shi$^b$
$^a$College of Materials Science and Engineering, North University of China, Taiyuan 030051, China
Email: xjb209@126.com
$^b$The Third Hospital of Shanxi Medical University, Taiyuan 030053, China

Received 26 May 2014; revised and accepted 15 October 2014

The cooperativity effect between the H-bonding and Na$^+$···σ or Cl$^-$···H···O/C interactions, the reduced density gradient (RDG) and the aromaticity evaluated by nucleus-independent chemical shift in Na$^+$Cl$^-$···benzonitrile···H$_2$O complex are investigated by using the B3LYP and MP2(full) methods with the 6-311++G(2d,p) basis set. The results show that the influence of the Na$^+$···σ or Cl$^-$···H···O/C interaction on H-bond is more pronounced than that of the latter on the former. Most of the ternary complexes with Na$^+$ exhibit the cooperativity effects while most of the Cl$^-$ systems show anti-cooperativities. The cooperativity effect is observed in the complex in which Na$^+$ or Cl$^-$ point towards either benzonitrile or H$_2$O, while the anti-cooperativity effect is seen in the system where the ion points simultaneously to benzonitrile and H$_2$O. The anti-cooperative structures are more stable than the cooperative structures. The cooperativity effect has a notable influence on the aromaticity and π→π* conjugative effect. The analyses of RDG and AIM (atoms in molecules) confirm the existence of cooperativity.

Keywords: Theoretical chemistry, Cooperativity effect, Noncovalent interactions, Reduced density gradient, Stability, Aromaticity

When the noncovalent interactions operate simultaneously and mutually enhance each others’ strength, they are termed as acting cooperatively$^1$. Cooperativity effect involving hydrogen bond is currently a topic of wide ranging interest due to their extremely important role in chemical reaction, molecular recognition and regulation of biochemical process$^2-4$. Furthermore, due to the favorable binding energy of the charged complex, the cooperativity effect of the ion···molecule (ion···σ or ion···π) interaction is notable$^5, 6$. Therefore, recently there have been many works devoted to the cooperativity effects between the H-bonding and ion···molecule interactions$^7, 8$. Deyà’s and Vijay’s groups studied theoretically the cooperativities of cation···π and H-bonding interactions$^9-11$, and those between anion···π and H-bonding interactions$^{12, 13}$ in some representative systems. The influence of cation/anion···π interactions on the strength of N-H hydrogen bonds has been studied using the B3LYP and MP2 methods$^{14, 15}$. The cooperativities of H-bonding and ion···molecule interactions in biological systems have also received much attention in theoretical studies$^{16, 17}$.

It is well-known that the formation of ion···π interaction can lead to the electron redistribution in the atoms of aromatic ring, which thus may result in the change of aromaticity. Then, is there a correlation between the cooperativity effect involving ion···π interaction and change of the aromaticity upon the ternary-complex formation? As a simple and efficient criterion of aromaticity, the nucleus-independent chemical shift (NICS) has been used to characterize the aromaticity$^{18}$. Furthermore, many theoretical works have been carried out to probe the influence of cooperativity on the NMR chemical shifts$^{19-21}$. However, to the best of our knowledge, no theoretical investigation has been reported on the influence of the cooperativity effect between the ion···π and H-bonding interactions on aromaticity evaluated by NICS.

In this paper, we present a theoretical investigation into the cooperativity effect between the H-bonding and ion···molecule interactions in Na$^+$···benzonitrile···H$_2$O and Cl$^-$···benzonitrile···H$_2$O. The influence of cooperativity on the NICS of benzonitrile ring is also probed. Benzonitrile (BN) is the simplest aromatic nitrile species. The H-bonding interactions between the nitrile groups and protic solvents are of considerable interest$^{22, 23}$. The O···H···N and C···H···O H-bonds have been found$^{24, 25}$. Thus, in Na$^+$Cl$^-$···benzonitrile···H$_2$O, the Na$^+$/Cl$^-$···σ, Na$^+$/Cl$^-$···π and hydrogen bonds may
coexist, and the cooperativity effect between them may arise. This investigation will be important to understand the cooperativity effect between the H-bonding and ion···molecule interactions in the system with aromatic monomer.

**Methodology**

All calculations were performed with Gaussian 03 programs. All 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) basis set.

For the binary system, the interaction energy \( E_{\text{int}(\text{BN} \cdots \text{H}_2\text{O})} \), \( E_{\text{int}(\text{Na}+/\text{Cl}^- \cdots \text{BN} \cdots \text{H}_2\text{O})} \) or \( E_{\text{int}(\text{Na}+/\text{Cl}^- \cdots \text{H}_2\text{O})} \) was calculated by evaluating the difference between the total energies of complex and individual monomers and corrected with the basis set superposition error (BSSE).

In the ternary system, \( E_{\text{int}(\text{BN} \cdots \text{H}_2\text{O})} \), \( E_{\text{int}(\text{Na}+/\text{Cl}^- \cdots \text{BN} \cdots \text{H}_2\text{O})} \) or \( E_{\text{int}(\text{Na}+/\text{Cl}^- \cdots \text{H}_2\text{O})} \) represents the interaction energy between both the moieties which are directly interacting with. They correspond to the benzonitrile···\( \text{H}_2\text{O} \), benzonitrile···\( \text{Na}^+ \)/\( \text{Cl}^- \) and \( \text{Na}^+ \)/\( \text{Cl}^- \)···\( \text{H}_2\text{O} \) interaction energies in the presence of \( \text{Na}^+ \) or \( \text{Cl}^- \), \( \text{H}_2\text{O} \) and benzonitrile, respectively. These interaction energies were calculated using Eqs (1), (2) and (3), respectively.

\[
\begin{align*}
E'_{\text{int}(\text{BN} \cdots \text{H}_2\text{O})} & = E_{\text{BN} \cdots \text{H}_2\text{O}} - E_{\text{BN}} - E_{\text{H}_2\text{O}} \\
E'_{\text{int}(\text{Na}+/\text{Cl}^- \cdots \text{BN} \cdots \text{H}_2\text{O})} & = E_{\text{Na}+/\text{Cl}^- \cdots \text{BN} \cdots \text{H}_2\text{O}} - E_{\text{Na}+/\text{Cl}^-} - E_{\text{BN}} - E_{\text{H}_2\text{O}} \\
E'_{\text{int}(\text{Na}+/\text{Cl}^- \cdots \text{H}_2\text{O})} & = E_{\text{Na}+/\text{Cl}^- \cdots \text{H}_2\text{O}} - E_{\text{Na}+/\text{Cl}^-} - E_{\text{H}_2\text{O}} \\
\end{align*}
\]

For cyclic structure of \( \text{Cl}^- \cdots \text{benzonitrile} \cdots \text{H}_2\text{O} \),

\[
\begin{align*}
E'_{\text{int}(\text{BN} \cdots \text{H}_2\text{O})} & = E_{\text{BN} \cdots \text{H}_2\text{O}} - E_{\text{BN}} - E_{\text{H}_2\text{O}} \quad \text{(1)'} \\
E'_{\text{int}(\text{Cl}^- \cdots \text{BN} \cdots \text{H}_2\text{O})} & = E_{\text{Cl}^- \cdots \text{BN} \cdots \text{H}_2\text{O}} - E_{\text{Cl}^- \cdots \text{BN}} - E_{\text{H}_2\text{O}} \quad \text{(2)'}
\end{align*}
\]

\( E''_{\text{int}(\text{BN} \cdots \text{H}_2\text{O})} \), \( E''_{\text{int}(\text{Na}+/\text{Cl}^- \cdots \text{BN} \cdots \text{H}_2\text{O})} \) and \( E''_{\text{int}(\text{Na}+/\text{Cl}^- \cdots \text{H}_2\text{O})} \) are defined as the through-space interaction energy between both the moieties with which they are not directly interacting. They were calculated at the binary frameworks (not be optimized) of the optimized ternary geometries.

The cooperativity \( \left( E_{\text{coop.}} \right) \) 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 sum of all pair interaction energies as given in Eq. (4) or (5).

\[
\begin{align*}
E_{\text{coop.}} &= E_{\text{int}(\text{Na}+/\text{Cl}^- \cdots \text{BN} \cdots \text{H}_2\text{O})} - E_{\text{int}(\text{Na}+/\text{Cl}^- \cdots \text{BN})} - E_{\text{int}(\text{BN} \cdots \text{H}_2\text{O})} - E_{\text{int}(\text{Na}+/\text{Cl}^- \cdots \text{H}_2\text{O})} \\
E_{\text{coop.}} &= E_{\text{int}(\text{BN} \cdots \text{Na}+/\text{Cl}^- \cdots \text{BN})} - E_{\text{int}(\text{BN} \cdots \text{Na}+/\text{Cl}^- \cdots \text{H}_2\text{O})} - E_{\text{int}(\text{Na}+/\text{Cl}^- \cdots \text{BN})} - E_{\text{int}(\text{BN} \cdots \text{H}_2\text{O})} \\
\end{align*}
\]

For cyclic structure of \( \text{Cl}^- \cdots \text{benzonitrile} \cdots \text{H}_2\text{O} \),

\[
\begin{align*}
E_{\text{coop.}} &= E_{\text{int}(\text{BN} \cdots \text{H}_2\text{O} \cdots \text{Cl}^-)} - E_{\text{int}(\text{BN} \cdots \text{H}_2\text{O})} - E_{\text{int}(\text{H}_2\text{O} \cdots \text{Cl}^-)} \\
\end{align*}
\]

Except for \( E''_{\text{int}(\text{BN} \cdots \text{H}_2\text{O})} \), \( E''_{\text{int}(\text{BN} \cdots \text{Na}+/\text{Cl}^- \cdots \text{H}_2\text{O})} \) and \( E''_{\text{int}(\text{H}_2\text{O} \cdots \text{Na}+/\text{Cl}^- \cdots \text{H}_2\text{O})} \), all the energies at the right side of equations correspond to the systems optimized separately.

**Results and Discussion**

**Structure and RDG analysis**

Benzonitrile···\( \text{H}_2\text{O} \) (I, II, III, IV and V), benzonitrile···\( \text{Na}^+/\text{Cl}^- \) and \( \text{Na}^+/\text{Cl}^- \cdots \text{H}_2\text{O} \) binary complexes were selected at the B3LYP/6-311++G(2d,p) level (see Supplementary Data, Fig. S1). Similar to that reported in earlier literature, the O···H···N and C···H···O H-bonds are found in the benzonitrile···\( \text{H}_2\text{O} \) systems. The O···H···N H-bonding interactions are larger than those of the C···H···O links at two levels of theory (see Supplementary Data, Table S1). The \( \text{Na}^+/\text{···N} \), \( \text{Na}^+/\text{···π} \) and \( \text{Na}^+/\text{···O} \) interactions are found in benzonitrile···\( \text{Na}^+ \) and \( \text{Na}^+/\text{···H}_2\text{O} \), respectively. The C···H···\( \text{Cl}^- \) and O···H···\( \text{Cl}^- \) anionic H-bonds are confirmed in benzonitrile···\( \text{Cl}^- \) and \( \text{Cl}^- \cdots \text{H}_2\text{O} \), respectively.

At the B3LYP/6-311++G(2d,p) level, the optimizations of systems from \( \text{Na}^+ \) I and II, III, IV, V result in three (I-1(Na)~3(Na)), one (II-1(Na)), one (III-1(Na)), two (IV-1(Na)~2(Na)) and two (V-1(Na)~2(Na)) ternary complexes, respectively. The optimizations of systems from \( \text{Cl}^- \) I, II, III, IV, V lead to two (I-1(Cl)~2(Cl)), one (II-1(Cl)), two (III-1(Cl)~2(Cl)), one (IV-1(Cl)) and one (V-1(Cl)) ternary complexes, respectively (Fig. 1).

According to Johnson et al., the reduced density gradient (RDG) can be used to reveal the intermolecular interactions in real space based on the electron density. It is defined as follows:
Fig. 1 – (A) Plots of the RDG versus the electron density multiplied by the sign of the second Hessian eigenvalue ($\lambda_2$) and (B) RDG isosurface ($s = 0.5$) of ternary complexes at the B3LYP/6-311++G(2d,p) level. [The surfaces are colored on a blue-green-red scale according to values of sign ($\lambda_2$) (a.u.) ranging from −0.05 to 0.05 au. Blue indicates stronger attractive interactions, red indicates stronger nonbonding overlap].

(A) 

(B)
\[ \text{RDG} = \frac{1}{2(3\pi^2)^{1/3}} \left| \frac{\nabla \rho(r)}{\rho(r)^{4/3}} \right| \]

The sign of \( \lambda_2 \) (the second eigenvalue of the electron density Hessian matrix) can be used to distinguish the bonded (\( \lambda_2 < 0 \)) from non-bonded (\( \lambda_2 > 0 \)) interactions. The spikes can be classified into three types, viz., (i) large, negative values of sign (\( \lambda_2 \rho \)) indicative of attractive interactions such as dipole dipole or H-bonding, (ii) large and positive sign (\( \lambda_2 \rho \)) indicating nonbonding interaction such as strong repulsion or steric effect in the ring/cage, and, (iii) values near zero indicate of very weak interactions, such as van der Waals interaction\(^{29}\). The plots of the RDG versus the electron density \( \rho \) multiplied by the sign of \( \lambda_2 \) can allow for analysis and visualization of a wide range of interaction types. Figure 1 depicts the results calculated and plotted by the Multiwfn 2.6 suite\(^{30}\) and VMD programs\(^{31}\).

As can be seen from Fig. 1, there are several spikes in the low density and low gradient region, suggesting weak interactions in the ternary complexes. Figure 1A shows the data for the (anionic) hydrogen bonding and \( \text{Na}^+ \)–molecule (\( \text{Na}^+ \)–\( \text{O} \), \( \text{Na}^+ \)–\( \text{N} \), \( \text{Na}^+ \)–\( \pi \)) interactions with the low density, low-gradient spikes placed at negative values. The low density, low-gradient spikes at positive values and the values near zero indicate the lack of bonding and steric effect in the central area of ring, respectively.

The interaction regions can also be located by generating RDG isosurface enclosing the corresponding regions in the real molecular space, which also can provide direct information about the strength of interaction by different colors\(^{29}\) (see Fig. 1B). Also, except for I-2(Na), all the systems are hydrogen-bonded complexes in which the ion–molecule or nonbonding interactions are also exhibited at the overlapping density ranges. For example, for I-1(Na), the low-density and low-gradient region corresponds to the isosurface between hydrogen donor (\( \text{H}_2\text{O} \)) and nitrogen atom, as well as the isosurface between oxygen atom (\( \text{H}_2\text{O} \)) and \( \text{Na}^+ \). The blue or green region clearly shows the strong attractive interaction between hydrogen and nitrogen atoms, or oxygen atom and \( \text{Na}^+ \). The blue region falls on the interaction of \( \text{H} \cdots \text{N}(\text{O}) \) and the green region falls on the \( \text{Na}^+ \cdots \text{O} \) or \( \text{Cl} \cdots \text{H} \) interaction, which is in agreement with the result that the \( \text{Na}^+ \cdots \text{O} \) or \( \text{Cl} \cdots \text{H} \) interaction is larger than that of the \( \text{H} \cdots \text{N}(\text{O}) \) hydrogen-bonding interaction. In each of the complexes, in the center of the six-member ring where steric repulsion is expected, the red region shows the effect clearly. Furthermore, there are several regions with blue and green colors, which indicate that several interactions coexist simultaneously. These results indicate that the \( \text{Na}^+ \cdots \text{O} \), \( \text{Na}^+ \cdots \text{N} \), \( \text{Na}^+ \cdot \pi \), and the \( \text{O} \cdots \text{H} \cdots \text{N} \) and \( \text{C} \cdots \text{H} \cdots \text{O} \) H-bonding interactions exist in the ternary complexes with \( \text{Na}^+ \), and the \( \text{O} \cdots \text{H} \cdots \text{N} \), \( \text{C} \cdots \text{H} \cdots \text{O} \), \( \text{O} \cdots \text{Cl} \) and \( \text{C} \cdots \text{H} \cdots \text{Cl} \) anionic hydrogen bonds are confirmed in those with \( \text{Cl}^- \). In other word, for each of the ternary complexes, two or three kinds of the interactions coexist. The \( \text{Na}^+ \cdots \text{O} \) interaction and the \( \text{O} \cdots \text{H} \cdots \text{N} \), \( \text{Na}^+ \cdots \text{N} \) or \( \text{Na}^+ \cdot \pi \) interaction coexist in the ternary complex I-1(Na)(C), I-2(Na)(C\(_2\)) or I-3(Na)(C\(_3\)). Both the C–H⋯O and \( \text{Na}^+ \cdot \pi \) interactions are found in II-1(Na)(C), IV-2(Na)(C\(_2\)) and V-2(Na)(C\(_3\)). The coexistence of the C–H⋯O and \( \text{Na}^+ \cdot \pi \) interactions is confirmed in III-1(Na)(C), IV-1(Na)(C\(_1\)) and V-1(Na)(C\(_3\)). For the ternary complexes with \( \text{Cl}^- \), the O⋯H⋯N and C⋯H⋯Cl H-bonds coexist in I-1(Cl)(C\(_1\)) and I-2(Cl)(C\(_2\)). Each of the complexes II-1(Cl)(C\(_1\)), III-1(Cl)(C\(_1\)), III-2(Cl)(C\(_2\)) and V-1(Cl)(C\(_3\)) can be described as a cyclic structure with one C⋯H⋯O H-bond and two anionic H-bonds (O⋯H⋯Cl and C⋯H⋯Cl\(^\dagger\)). The O⋯H⋯Cl\(^\dagger\) and C⋯H⋯Cl H-bonds are also found in IV-1(Cl)(C\(_1\)).

For the ternary complexes with \( \text{Na}^+ \) (Table 1 and Fig. S1), when compared to the binary benzonitrile⋯\( \text{H}_2\text{O} \) systems, except for I-2(Na) and I-3(Na), the H⋯N and H⋯O distances decrease, indicating that the O⋯H⋯N and C⋯H⋯O H-bonding interactions are strengthened due to the addition of \( \text{Na}^+ \). Similar results are also found for the \( \text{Na}^+ \)⋯\( \text{N} \), \( \text{Na}^+ \cdot \pi \) and \( \text{Na}^+ \)⋯\( \text{O} \) distances, which increase in I-2(Na) and I-3(Na) while decreasing in the other ternary complexes in comparison with those in \( \text{Na}^+ \)⋯\( \text{BN}(\text{A}) \), \( \text{Na}^+ \)⋯\( \text{BN}(\text{B}) \) and \( \text{Na}^+ \)⋯\( \text{H}_2\text{O} \), respectively. Thus, the benzonitrile⋯\( \text{Na}^+ \) and \( \text{Na}^+ \)⋯\( \text{O} \) interactions are weakened in I-2(Na) and I-3(Na), and strengthened in II-1(Na), III-1(Na), IV-1(Na), IV-2(Na), V-1(Na) and V-2(Na).

For the ternary systems of \( \text{Cl}^- \) (Table 2 and Fig. S1), when compared to the binary benzonitrile⋯\( \text{H}_2\text{O} \), the H⋯N distance decreases in I-1(Cl) and I-2(Cl); the H⋯O distance increases in III-1(Cl) and the H⋯O H-bond is broken in IV-1(Cl). Thus, the O⋯H⋯N H-bonding interaction is strengthened in I-1(Cl) and I-2(Cl),
Interestingly, the C–CN bond lengths decrease perceptibly in I-2(Na), III-1(Na), IV-1(Na), V-1(Na) and all the ternary systems with Cl⁻ in comparison with those in the corresponding binary complexes. Thus, the C–CN bond becomes strong and the π→π conjugative effect between the ring and C≡N bond may be strengthened upon the ternary-complex formations.

### Table 1 — The intermolecular distances (R) and the results of AIM (ρ and \( \nabla^2 \rho \)) in Na⁺–benzonitrile–H₂O at the B3LYP/6-311++G(2d,p) level

<table>
<thead>
<tr>
<th></th>
<th>I-1(Na)</th>
<th>I-2(Na)</th>
<th>I-3(Na)</th>
<th>II-1(Na)</th>
<th>III-1(Na)</th>
<th>IV-1(Na)</th>
<th>IV-2(Na)</th>
<th>V-1(Na)</th>
<th>V-2(Na)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{\text{Na}^+–O} ) (Å)</td>
<td>2.151</td>
<td>2.255</td>
<td>2.242</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \rho_{\text{Na}^+–O} ) (a.u.)</td>
<td>0.0312</td>
<td>0.0236</td>
<td>0.0243</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \nabla^2 \rho_{\text{Na}^+–O} ) (a.u.)</td>
<td>0.2161</td>
<td>0.1527</td>
<td>0.1594</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( a \): H(BN): hydrogen atom in BN.
\( b \): rc: center of ring.
\( c \): In I-1(Na), the values of \( R_{\text{Na}^+–(H₂O)} \), \( \rho_{\text{Na}^+–(H₂O)} \) and \( \nabla^2 \rho_{\text{Na}^+–(H₂O)} \) are 1.734 Å, 0.0446 a.u. and 0.1124 a.u., respectively.

### Table 2 — The intermolecular distances (R) and the results of AIM (ρ and \( \nabla^2 \rho \)) in Cl⁻–benzonitrile–H₂O at the B3LYP/6-311++G(2d,p) level

<table>
<thead>
<tr>
<th></th>
<th>I-1(Cl)</th>
<th>I-2(Cl)</th>
<th>II-1(Cl)</th>
<th>III-1(Cl)</th>
<th>III-2(Cl)</th>
<th>IV-1(Cl)</th>
<th>V-1(Cl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{\text{Cl}^––O} ) (Å)</td>
<td>2.005</td>
<td>2.006</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \rho_{\text{Cl}^––O} ) (a.u.)</td>
<td>0.0227</td>
<td>0.0227</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \nabla^2 \rho_{\text{Cl}^––O} ) (a.u.)</td>
<td>0.0803</td>
<td>0.0803</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( a \): H(BN): hydrogen atom in BN.
\( b \): H(H₂O): hydrogen atom in H₂O.

### Interaction energy and cooperativity effect

The interaction energies in ternary complexes computed by the B3LYP and MP2(full) methods with the 6-311++G(2d,p) basis set, respectively are summarized in Tables 3 and 4 (See also Supplementary Data, Tables S2 and S3). In most cases, the MP2(full) interaction energies are more negative than the corresponding B3LYP results.

For the ternary complexes with Na⁺ (Table 3 and Supplementary Data, Tables S1, S2), except for I-2(Na) and I-3(Na), the values of \( E_{\text{int}}(\text{BN}–\text{H₂O}) \) are larger than those for the corresponding benzonitrile–H₂O complexes at two levels of theory, showing that the O–H…N and C–H…O H-bonding interactions are strengthened on the ternary-complex
Table 3 — Interaction energy ($E'_{int}$, $E''_{int}$ or $E_{int}$) and cooperativity energy ($E_{coop}$) in Na$^+$--benzonitrile--H$_2$O at the MP2(full)/6-311+G(2d,p) level

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E'_{int}$ (BN--H$_2$O) (kJ/mol)</th>
<th>$E'_{int}$ (BN--H$_2$O--Na$^+$) (kJ/mol)</th>
<th>$E''_{int}$ (kJ/mol)</th>
<th>$E_{int}$ (Na$^+$--BN--H$_2$O) (kJ/mol)</th>
<th>$E_{coop}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-1(Na)</td>
<td>−83.8 (−80.0)b</td>
<td>−167.9 (−164.4)b</td>
<td>−52.6</td>
<td>−188.2 (−175.5)</td>
<td>−8.6</td>
</tr>
<tr>
<td>I-2(Na)</td>
<td>−127.5 (−121.5)c</td>
<td>−191.5 (−185.0)</td>
<td>7.3</td>
<td>−231.9 (−216.6)</td>
<td>8.4</td>
</tr>
<tr>
<td>I-3(Na)</td>
<td>−57.4 (−47.6)c</td>
<td>−98.1 (−91.7)</td>
<td>0.6</td>
<td>−161.7 (−142.5)</td>
<td>8.7</td>
</tr>
<tr>
<td>II-1(Na)</td>
<td>−39.0 (−34.1)</td>
<td>−79.2 (−69.4)</td>
<td>−23.6</td>
<td>−102.6 (−86.8)</td>
<td>9.2</td>
</tr>
<tr>
<td>III-1(Na)</td>
<td>−24.6 (−20.2)</td>
<td>−153.3 (−147.3)</td>
<td>−6.6</td>
<td>−165.0 (−153.8)</td>
<td>−5.6</td>
</tr>
<tr>
<td>IV-1(Na)</td>
<td>−26.2 (−21.6)</td>
<td>−153.8 (−147.8)</td>
<td>−6.6</td>
<td>−166.6 (−155.3)</td>
<td>−6.2</td>
</tr>
<tr>
<td>IV-2(Na)</td>
<td>−38.0 (−33.4)</td>
<td>−88.8 (−79.1)</td>
<td>−23.6</td>
<td>−101.7 (−86.1)</td>
<td>−0.5</td>
</tr>
<tr>
<td>V-1(Na)</td>
<td>−24.2 (−19.9)</td>
<td>−153.3 (−147.3)</td>
<td>−6.6</td>
<td>−164.6 (−153.3)</td>
<td>−5.4</td>
</tr>
<tr>
<td>V-2(Na)</td>
<td>−35.4 (−31.1)</td>
<td>−87.8 (−78.0)</td>
<td>−23.6</td>
<td>−99.0 (−83.4)</td>
<td>0.9</td>
</tr>
</tbody>
</table>

*The values in parenthesis are corrected for BSSE; those in bold are for $E'_{int}$ (H$_2$O--Na$^+$).  
b$E'_{int}$ (BN--H$_2$O) = $E_{BN}$--H$_2$O--Na$^+$ -- $E_{BN}$ -- $E_{H2O}$--Na$^+$;  
c$E''_{int}$ (BN--H$_2$O) = $E_{BN}$--H$_2$O--Na$^+$ -- $E_{BN}$--H$_2$O -- $E_{Na}$.

forms. Furthermore, for III-1(Na), IV-1(Na) and V-1(Na) with the Na$^+$--N interaction, the values of $E'_{int}$ (BN --Na$^+$) are larger than that in Na$^+$--BN(A). In I-1(Na), the value of $E'_{int}$ (H$_2$O--Na$^+$) is also larger than that in H$_2$O--Na$^+$. These results show that the Na$^+$--σ interactions in I-1(Na), III-1(Na), IV-1(Na) and V-1(Na) are strengthened on formation of the ternary complex. The Na$^+$--π interactions in II-1(Na), III-1(Na), IV-2(Na) and V-2(Na) are also strengthened as shown by their larger $E'_{int}$ (H$_2$O--π) values than that in Na$^+$--BN(B) at two levels of theory. When the value of $E''_{int}$ is larger than that of $E_{int}$ in the corresponding binary complex, it indicates that the stabilization of the dimers gets enhanced in the presence of the third component and thus giving rise to the cooperativity effects. Therefore, the cooperativity effects may occur in these seven complexes with the H-bonding and Na$^+$--σ or Na$^+$--π interactions. However, in I-2(Na) and I-3(Na), the values of $E'_{int}$ (BN --Na$^+$) and $E'_{int}$ (H$_2$O--Na$^+$) are lower than those in Na$^+$--BN(A), Na$^+$--BN(B) and H$_2$O--Na$^+$ at two levels of theory, respectively, indicating the possible anti-cooperativity effects. These results are in accordance with the analyses of structures.

For the ternary complexes I-1(Cl) and I-2(Cl) with Cl$^-$, the values of $E'_{int}$ (BN--H$_2$O) and $E'_{int}$ (Cl--BN) are larger than those in the corresponding benzonitrile--H$_2$O and benzonitrile--Cl$^-$ complexes at two levels of theory, showing that the O--H···N and C--H···Cl$^-$ H-bonding interactions are strengthened upon the ternary-complex formations (Table 4 and Supplementary Data, Tables S1 and S3). Thus, the possible cooperativity effects occur in I-1(Cl) and I-2(Cl), in agreement with the analysis of the structure. For IV-1(Cl), the value of $E'_{int}$ (Cl--H$_2$O) is lower than that of Cl$^-$--H$_2$O, indicating that the O--H···Cl$^-$ interaction is weakened. According to Eqs (1)' and (2)' for cyclic trimer, the difference

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E'_{int}$ (BN--H$_2$O) (kJ/mol)</th>
<th>$E'_{int}$ (Cl--BN) (kJ/mol)</th>
<th>$E'_{int}$ (Cl--H$_2$O) (kJ/mol)</th>
<th>$E_{int}$ (BN--H$_2$O--Cl) (kJ/mol)</th>
<th>$E_{coop}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-1(Cl)</td>
<td>−28.5 (−24.7)</td>
<td>−74.6 (−66.1)</td>
<td>−94.8 (−81.9)</td>
<td>−98.0 (−85.2)</td>
<td>−7.1</td>
</tr>
<tr>
<td>I-2(Cl)</td>
<td>−31.7 (−27.9)</td>
<td>−77.8 (−69.3)</td>
<td>−103.6 (−95.2)d</td>
<td>−127.1 (−110.6)</td>
<td>24.0</td>
</tr>
<tr>
<td>II-1(Cl)</td>
<td>−63.6 (−58.7)c</td>
<td>−110.8 (−102.4)d</td>
<td>−59.5 (−54.1)</td>
<td>−122.5 (−106.4)</td>
<td>16.8</td>
</tr>
<tr>
<td>III-1(Cl)</td>
<td>−59.0 (−54.2)d</td>
<td>−118.9 (−111.0)d</td>
<td>−59.7 (−54.3)</td>
<td>−130.5 (−114.4)</td>
<td>6.6</td>
</tr>
<tr>
<td>IV-1(Cl)</td>
<td>−67.1 (−62.8)c</td>
<td>−128.6 (−120.1)</td>
<td>−56.7 (−51.4)</td>
<td>−123.0 (−109.7)</td>
<td>0.8</td>
</tr>
<tr>
<td>V-1(Cl)</td>
<td>−66.1 (−61.9)c</td>
<td>−118.4 (−109.9)d</td>
<td>−59.7 (−54.2)</td>
<td>−129.6 (−113.5)</td>
<td>9.5</td>
</tr>
</tbody>
</table>

*The values in parenthesis are corrected for BSSE.  
bThe value of $E'_{int}$ (H$_2$O--Cl) in I-1 and I-2 is −7.3 and −3.8 kJ/mol, and that of $E'_{int}$ (BN--H$_2$O--Cl) in IV-1 is 5.6 kJ/mol, respectively.  
c$E'_{int}$ (BN--H$_2$O--Cl) = $E_{BN}$--H$_2$O--Cl$^-$ -- $E_{BN}$--H$_2$O -- $E_{Cl}$.
between the $E'_{\text{int.}}$ and the sum of two corresponding interaction energies in binary complexes amounts to the value of cooperativity. Therefore, the cooperative effect for cyclic system can be judged from the comparison of the $E'_{\text{int.}}$ with the sum of the two corresponding interaction energies. In the cyclic ternary-complexes, II-1(Cl), III-1(Cl), III-2(Cl) and V-1(Cl), the values of $E'_{\text{int.}}(\text{BN} \cdots \text{H}_2\text{O} \cdots \text{Cl})$ are lower than the sum of the $E_{\text{int.}}(\text{BN} \cdots \text{H}_2\text{O})$ and $E_{\text{int.}}(\text{BN} \cdots \text{Cl})$ in the corresponding benzonitrile···$\text{H}_2\text{O}$ and benzonitrile···$\text{Cl}^-$ systems at two levels of theory. Furthermore, the values of $E'_{\text{int.}}(\text{Cl} \cdots (\text{BN} \cdots \text{H}_2\text{O}))$ are also lower than the sum of the $E_{\text{int.}}(\text{BN} \cdots \text{Cl})$ and $E_{\text{int.}}(\text{H}_2\text{O} \cdots \text{Cl})$. These results suggest the possible anti-cooperativity effects in II-1(Cl), III-1(Cl), III-2(Cl) and V-1(Cl).

When two or more noncovalent interactions operate in a system, it is interesting to see how the noncovalent interactions influence each other. So the proportion of the increment of interaction energy to the corresponding value in binary system was investigated. At the MP2(full)/6-311++G(2d,p) level, the proportion of the increment of the $E'_{\text{int.}}(\text{BN} \cdots \text{H}_2\text{O})$ and $E_{\text{int.}}(\text{BN} \cdots \text{Cl})$ in ternary complex to the corresponding $E_{\text{int.}}$ in binary system, defined as $[E'_{\text{int.}}-E_{\text{int.}}]/E_{\text{int.}}$, is in the ranges of 47.25–269.22%, −4.28–63.37% and −6.24–30.67% for H-bonding, Na$^+$$\cdots$$\sigma$ and Na$^+$$\cdots$$\pi$ interactions, respectively. The proportion of the increment of the H-bonding interaction is far larger than that of the Na$^+$$\cdots$$\sigma$ or Na$^+$$\cdots$$\pi$ interaction, showing that the change of the H-bonding interaction energy is more notable than that of the Na$^+$$\cdots$$\sigma$ or Na$^+$$\cdots$$\pi$ interaction energy on the ternary-complex formation. In other words, the cooperativity effect of the charged Na$^+$$\cdots$ molecule interaction on the neutral H-bond is more pronounced than that of the neutral H-bond on the Na$^+$$\cdots$ molecule interaction. This result is very similar to that in the ternary system with Cl$^-$. For example, at the MP2(full)/6-311++G(2d,p) level, the proportion of the increment of the O–H···$\text{N}$ interaction energy to $E_{\text{int.}}(\text{BN} \cdots \text{Cl})$ is in the range of 34.52–46.77%, while that of the C–H···Cl$^-$ anionic H-bonding energy to $E_{\text{int.}}(\text{BN} \cdots \text{Cl})$ is the range of 11.35–17.62%. The influence of the C–H···Cl$^-$ anionic H-bonding interaction on the O–H···$\text{N}$ interaction is more pronounced than that of the O–H···$\text{N}$ interaction on the C–H···Cl$^-$ interaction. It should be noted that the values of $E'_{\text{int.}}(\text{BN} \cdots \text{H}_2\text{O})$ obtained by Eq. (1) are not the “real” neutral H-bonding interaction energy but partly the ion···molecule interaction energy since both Na$^+$/Cl$^-$···$\text{BN} \cdots \text{H}_2\text{O}$ and Na$^+$/Cl$^-$···$\text{BN}$ in Eq. (1) are charged complexes. The binding energy of charged complex is considerably favorable since there is notable electrostatic effect. Therefore, the values of $E'_{\text{int.}}(\text{BN} \cdots \text{H}_2\text{O})$ are larger than those of the “real” neutral H-bonding interaction energies.

The results of cooperativity effects have been obtained using the B3LYP and MP2(full) methods with the 6-311++G(2d,p) basis set. At two levels of theory, the values of cooperativity effect are negative in I-1(Na), III-1(Na), IV-1(Na) and V-1(Na), while the ternary complexes I-2(Na), I-3(Na) and II-1(Na) have the positive $E_{\text{coop.}}$ values (Table 3 and Supplementary Data, Table S2). These results indicate that the cooperativity effect is present in I-1(Na), III-1(Na), IV-1(Na) and V-1(Na), while the anti-cooperativity effect is confirmed in I-2(Na), I-3(Na) and II-1(Na). At two levels of theory, the values of the cooperativity effects follow the order: I-1(Na) < IV-1(Na) < III-1(Na) < V-1(Na) < IV-2(Na) < V-2(Na) < I-3(Na) ≈ I-2(Na) ≈ I-1(Na). The values of the cooperativity effects in the Na$^+$$\cdots$$\sigma$ interaction complexes are more negative than those in the conformations with the Na$^+$$\cdots$$\pi$ interactions.

For I-1(Cl), the value of cooperativity effect is negative at the MP2(full)/6-311++G(2d,p) level. At two levels of theory, the value of cooperativity effect is negative in I-2(Cl), while the ternary conformations II-1(Cl), III-1(Cl), III-2(Cl), IV-1(Cl) and V-1(Cl) have the positive $E_{\text{coop.}}$ values (Table 4 and Supplementary Data, Table S3). These results indicate that the cooperativity effects are present in I-1(Cl) and I-2(Cl), while the anti-cooperativity effects are confirmed in II-1(Cl), III-1(Cl), III-2(Cl), IV-1(Cl) and V-1(Cl), in accordance with the results of structure and energy. At two levels of theory, the values of the cooperativity effects follow the order: I-2(Cl) < I-1(Cl) < IV-1(Cl) < III-2(Cl) < V-1(Cl) < III-1(Cl) < II-1(Cl). The values of the cooperativity effects in the linear complexes are more negative than those in the cyclic conformations.

As can be seen from Tables 3 and 4 (see also Supplementary Data, Tables S2 and S3) most of the ternary complexes with Na$^+$ show the cooperativity effects, whereas most of the ternary complexes with Cl$^-$ have the anti-cooperativity effects. In other words, the cooperativity effect prefers to be in the Na$^+$ ternary-complexes while the anti-cooperativity effect tends to be in the Cl$^-$ ternary-systems. Note that in the complexes, I-1(Na), III-1(Na), IV-1(Na), IV-2(Na),
V-1(Na), V-2(Na), I-1(Cl) and I-2(Cl) with the cooperativity effects, the Na$^+$ and Cl$^-$ point toward either benzonitrile or H$_2$O, whereas in the ternary systems with the anti-cooperativity effects (except for II-1(Na)), the Na$^+$ or Cl$^-$ points simultaneously to benzonitrile and H$_2$O. Therefore, the cooperativity effect prefers to be in the complexes in which the Na$^+$ and Cl$^-$ point to either benzonitrile or H$_2$O, while the anti-cooperativity effect tends to be in the ternary systems where the ion points simultaneously toward benzonitrile and H$_2$O.

At two levels of theory, the complexation energies of the ternary complexes where the Na$^+$ or Cl$^-$ points simultaneously to benzonitrile and H$_2$O are always stronger than those of the complexes in which the ion points only one monomer, i.e., the former are more stable than the latter. Thus, the anti-cooperative structures are more stable than the cooperative structures. This is not always the case; there is no significant correlation between the cooperativity effects and stabilities. In most cases, the complex where the ion points simultaneously toward the other two monomers is more stable. The reason is that it has more ion···molecule interactions and more favorable charge delocalizations for ion, which make the system more stable. The cooperativity/anti-cooperativity reveals how the non-covalent interactions influence each other. The cooperativity effect indicates that the two interactions work together and enhance each other's strength, whereas the anti-cooperativity effect indicates that they weaken each other’s strength. The cooperativity or anti-cooperativity effects are mainly attributed to the polarization induced in each subunit and charge transfer. For example, for the APT, NBO and Mulliken charges in ternary system I-1(Cl), the proton donor H atom has a more positive charge (0.480, 0.496, 0.410) than that in the binary complex (0.439, 0.488, 0.383) (See Supplementary Data, Tables S4 and S5). The charge increase leads to the increase of the polarization of the O–H bond, making it easier for the hydrogen atom to form the H-bond. Simultaneously, the proton acceptor N atom in ternary system has a more negative charge. Thus, the H-bonding interactions are strengthened upon the formations of ternary complexes, and the cooperativity effect occurs. Similar to the ternary systems with Cl$^-$, the cooperativity effects in the ternary systems with Na$^+$ are also confirmed according to the APT, NBO and Mulliken charges (Supplementary Data, Table S6). In general, the cooperative structures are more stable than the anti-cooperative structures. However, in some cases, it is reversed.

For comparison, the structures of the ternary complexes with Ne in place of Na$^+$ and Cl$^-$ were optimized at the B3LYP/6-311++G(2d,p) level (Supplementary Data, Fig. S2), and the APT, NBO and Mulliken charges are collected in Tables S7 and S8 respectively (Supplementary Data). As can be seen except for I-2(Ne(Na)), I-3(Ne(Na)), II-1(Ne(Na)) and V-1(Ne(Cl)), the absolute values of the APT, NBO, Mulliken charges for the O, N and proton donor H atoms as well as NBO charge transfers of H$_2$O ($Q_{CT(H\cdot\cdotO)}$) in the ternary complexes with Ne are all smaller than those in the corresponding ternary systems with Na$^+$ and Cl$^-$ (Supplementary Data, Tables S5–S8). Here, Ne(Na) and Ne(Cl) are the ternary complexes with Ne instead of Na$^+$ and Cl$^-$.

Note that the structures of I-2(Ne(Na)), I-3(Ne(Na)) and II-1(Ne(Na)) change greatly in comparison with those of the corresponding ternary systems with Na$^+$. In particular, the absolute values of the APT, NBO, Mulliken charges of the O, N and proton donor H atoms in the ternary complexes with Ne are almost equal to those in the corresponding binary benzonitrile···H$_2$O systems (Supplementary Data, Table S4). Furthermore, three kinds of charges of Ne in ternary complexes are all near to zero. These results suggest that there is no more polarization induced in each subunit or charge transfer in the ternary system with Ne relative to those of the corresponding binary benzonitrile···H$_2$O system, i.e., the cooperativity effect do not occur in the ternary complex with Ne.

**AIM analysis**

In order to further obtain an insight into the origin of cooperativity effect, AIM (atom in molecule) analysis was carried out, and are presented in Tables 1, 2 and Fig. S1 (Supplementary Data). The values of $\rho_{BCP(Na^+-N)}$ and $\rho_{BCP(Na^+-O)}$ in the ternary conformation I-1(Na) increase in comparison with those in the binary system I, indicating that the O–H···N and Na$^+$···O interactions are strengthened upon the ternary-complex formation. The increase of charge densities $\rho_{BCP(H\cdot\cdotO)}$ and $\rho_{BCP(Na^+-N)}$ is also found in III-1(Na), IV-1(Na) and V-1(Na), showing that the C–H···O and Na$^+$···N interactions mutually enhance each other. These results confirm the cooperativity effect in these four complexes. Although the values of
\( \rho_{BCP(H-O)} \) in IV-2(Na) and V-2(Na) are larger than those in the corresponding binary systems, \( \rho_{BCP(Na^+-\pi)} \) are very close to that in Na\(^+\)-\( \cdots \)BN(B). Therefore, the cooperativity effects are not notable. However, for I-2(Na), the values of \( \rho_{BCP(Na^+-\cdot)} \) and \( \rho_{BCP(Na^+\cdots O)} \) decrease in comparison with those in Na\(^+\)-\( \cdots \)BN(A) and H\(_2\)O\( \cdots \)Na\(^+\). In I-3(Na), the decreases of the charge density \( \rho_{BCP(Na^+\cdots O)} \) and \( \rho_{CCP(Na^+-\pi)} \) are also observed. In the binary system II, there is a large charge density in the bond critical point \((3, -1)\) of the O–H\( \cdots \)N contact, whereas it has disappeared in II-1(Na). Thus, the anti-cooperativity effect occurs in I-2(Na), I-3(Na) and II-1(Na).

For the ternary systems of Cl\(^+\), the values of \( \rho_{BCP(N-H)} \) in I-1(Cl) and I-2(Cl) increase in comparison with those in the binary system I, suggesting that the O–H\( \cdots \)N interactions are strengthened upon the formation of the ternary complex (Table 2 and Supplementary Data, Fig. S1). Furthermore, the values of \( \rho_{BCP(Cl^+H-H)} \) and \( \rho_{BCP(H-C)} \) in I-1(Cl) and I-2(Cl) are also larger than those in Cl\(^+\)-\( \cdots \)BN(A), indicating the strengthening of the C–H\( \cdots \)Cl\(^−\) anionic H-bonding interactions and thus the cooperativity effect between the O–H\( \cdots \)N and C–H\( \cdots \)Cl\(^−\) interactions. For IV-1(Cl), the values of \( \rho_{BCP(H\cdots Cl^+)} \) decrease in comparison with those in IV and Cl\(^+\)-H\(_2\)O, suggesting the anti-cooperativity effect between the O–H\( \cdots \)Cl\(^−\) and C–H\( \cdots \)Cl\(^−\) interactions. In II-1(Cl), III-1(Cl), III-2(Cl) and V-1(Cl), although the values of \( \rho_{BCP(O\cdots H)} \) and \( \rho_{BCP(Cl\cdots O\cdots H)} \) increase in comparison with those in the corresponding binary systems, one of the bond paths linking Cl\(^+\) with the hydrogen atom of the C–H moiety is not found, showing that one of the C–H\( \cdots \)Cl\(^−\) H-bonds is broken upon formation of the ternary complex. Thus, the anti-cooperativity effects arise in these four complexes.

**NICS and BDE of the C-CN bond**

The NICS (0, \( \pi \)) (in the ring center and midpoint of C\( =\)N bond) and total NICS (1) (1 Å above the ring and C\( =\)N bond) were computed at the B3LYP/6-311++G(2d,p) level using the gauge-independent atomic orbital (GIAO) method\(^{10} \) and the isotropic and anisotropic NICS (0, \( \pi \)) and NICS (1) were collected (Supplementary Data, Table S9). For the ternary systems of Na\(^+\), except for the NICS (1) in I-2(Na), all the values of the isotropic NICS (0, \( \pi \)) and NICS (1) involving ring are lower than those in the corresponding benzonitrile\( \cdots \)H\(_2\)O and benzonitrile\( \cdots \)Na\(^+\) binary complexes. Furthermore, except for I-3(Na), all the anisotropic NICS (0, \( \pi \)) and NICS (1) in the ternary systems are lower than those in the corresponding benzonitrile\( \cdots \)Na\(^+\) complexes. Similar to the systems of Na\(^+\), for the ternary systems of Cl\(^+\), the values of the isotropic and anisotropic NICS (0, \( \pi \)) in the ring centers are also lower than those in the corresponding benzonitrile\( \cdots \)H\(_2\)O complexes. Except for the isotropic NICS (1) involving the ring in II-1(Cl), III-1(Cl) and III-2(Cl), all the NICS (1) in the ternary systems are lower than those in benzonitrile\( \cdots \)H\(_2\)O. These results show that the aromaticities of benzonitrile ring are weakened upon the ternary-complex formations.

Interestingly, for the ternary systems of Cl\(^+\), a good linear correlation (\( R^2 = 0.9675 \)) is found between \( \Delta \delta \) and \( E_{coop} \) (\( \Delta \delta = \Delta \delta_{\text{ternary}} - \Delta \delta_{\text{binary}} \) for the anisotropic NICS (1)) (Fig. 2). \( \Delta \delta_{\text{ternary}} \) and \( \Delta \delta_{\text{binary}} \) are the

---

Fig. 2 – \( \Delta \delta \) (anisotropic NICS (0, \( \pi \)), ppm) involving the ring versus \( E_{coop} \) at the B3LYP/6-311++G(2d,p) level. [(a) Ternary complex with Na\(^+\); (b) Ternary complex with Cl\(^+\)].
chemical shifts in the ternary system and the corresponding benzonitrile···H₂O binary complex, respectively. For the ternary systems of Na⁺, two linear correlations are also found between ∆Δδ and $E_{\text{coop}}$. for the Na⁺···σ and Na⁺···π complexes, respectively (Fig. 2). Note that when compared to the binary benzonitrile···H₂O, the anisotropic NICS (0, π) and NICS (1) decrease in the ternary-systems with the Na⁺···σ interactions, and increase in the complexes with the Na⁺···π contacts.

For the ternary systems with Cl⁻, a good linear correlation ($R^2 = 0.9683$) is again obtained between $R_c'$ and $E_{\text{coop}}$. ($R_c = \text{NICS (1)_{ternary}}/\text{NICS (1)_{binary}}$) at the B3LYP/6-311++G(2d,p) level (Fig. 3). NICS (1) indicates the anisotropic value in the ternary system or benzonitrile···H₂O binary complex. Similar results are also observed in the Na⁺ ternary-systems with two linear correlations between $R_c$ and $E_{\text{coop}}$. ($R_c = \text{NICS (0, π)_{ternary}}/\text{NICS (0, π)_{binary}}$) for the anisotropic NICS (Fig. 3).

The above results show that the cooperativity effect has a great influence on the magnitude of the NICS (0, π) and NICS (1) involving the ring, i.e., the cooperativity effect has a notable influence on the aromaticity of benzonitrile ring.

For the isotropic and anisotropic NICS (0, π) in the midpoint of the C≡N bond, the values in the ternary systems with the Na⁺···σ contact are larger than those in benzonitrile···H₂O, while the opposite trend is found in those with the Na⁺···π interaction (Supplementary Data, Table S9). In other words, the values of the NICS (0, π) in the ternary systems with the Na⁺···π contact are lower than those in the corresponding Na⁺···N or Na⁺···O interaction complexes. In the ternary systems with Cl⁻, both the isotropic and anisotropic NICS (0, π) with the C≡N bond are larger than those of benzonitrile···H₂O.

For the anisotropic NICS (1) involving the C≡N bond in the Na⁺ ternary-systems, a good linear correlation ($R^2 = 0.9700$) between $R_c$ and $E_{\text{coop}}$. ($R_c' = \text{NICS (1)_{ternary}}/\text{NICS (1)_{binary}}$) at the B3LYP/6-311++G(2d,p) level is obtained (Supplementary Data, Fig. S3).

The changes in the NICS (0, π) and NICS (1) in the ring and C≡N bond may lead to the changes in the π→π* conjugative effect between the ring and C≡N bond. In order to obtain further insight into the changes in the π→π* conjugative effect, the changes in bond dissociation energy (BDE) in the C–CN bond were investigated.

The MP2 method cannot be used to adequately describe BDEs due to the serious spin contamination. Therefore, the B3LYP method with the 6-311++G(2d,p) basis set was selected. The BDEs in the C–CN bond in ternary complexes with the Na⁺···σ contact are larger than those in the corresponding binary systems, while the BDEs in the Na⁺···π interaction ternary complexes are lower than those in the binary complexes (Supplementary Data, Tables S10 and S11). These results show that the strength of the C–CN bond is enhanced and the π→π* conjugative effect between the ring and C≡N bond is strengthened upon formation of the Na⁺···σ contact ternary-complex, while the opposite trend is found in the Na⁺···π interaction complexes.
observed in the systems with the Na\textsuperscript{+}···\pi interaction. For the ternary complexes with Cl\textsuperscript{−}, the BDEs in the C–CN bond are larger than those in binary systems, showing that the strength of the C–CN bond is enhanced and the \pi→\pi\textsuperscript{*} conjugative effect between the ring and C≡N bond is strengthened. These results are all in agreement with the analyses of structures.

Two linear correlations are obtained between $R_{\text{BDE(C-CN)}}$ and $E_{\text{coop.}}$. ($R_{\text{BDE(C-CN)}}=\frac{\text{BDE(C-CN)}}{\text{binary}}/\text{BDE(C-CN)}}{\text{ternary}}$) for the Na\textsuperscript{+}···σ and Na\textsuperscript{+}···π interaction systems, respectively. For the ternary systems with Cl\textsuperscript{−}, a good linear correlation ($R^2 = 0.9820$) is also obtained between $R_{\text{BDE(C-CN)}}$ and $E_{\text{coop.}}$. (Fig. 4). $\text{BDE(C-CN)}}{\text{binary}}$ is the BDE of the C–CN bond in benzonitrile···H\textsubscript{2}O. These results show that the cooperativity effect has a great influence on the \pi→\pi\textsuperscript{*} conjugative effect also.

**Conclusions**

The cooperativity effect between the H-bonding and Na\textsuperscript{+}···σ or Cl\textsuperscript{−}···H–O/C interactions, RDG and aromaticity in Na\textsuperscript{+}/Cl\textsuperscript{−}···benzonitrile···H\textsubscript{2}O were investigated using the B3LYP and MP2(full) methods. The result indicate that most of the ternary complexes with Na\textsuperscript{+} show the cooperativity effects while most of the Cl\textsuperscript{−} systems exhibit the anti-cooperativity effects. The anti-cooperative structures are more stable than the cooperative structures. The aromaticity of ring is weakened while the BDE of the C–CN bond increases on ternary-complex formation. The cooperativity effect ($E_{\text{coop.}}$) correlates with $R_e$ (NICS(1)\textsubscript{ternary}/NICS(1)\textsubscript{binary}), $\Delta\delta$ ($\delta_{\text{ternary}}-\delta_{\text{binary}}$) involving the ring and C≡N bond, and $R_{\text{BDE(C-CN)}}$ (BDE(C-CN)\textsubscript{ternary}/BDE(C-CN)\textsubscript{binary}). The cooperativity effect has a large influence on the \pi→\pi\textsuperscript{*} conjugative effect. This investigation is useful to understand the cooperativity effect involving the H-bonding and ion–molecule interactions in the system with aromatic monomer.

**Supplementary Data**

Supplementary data associated with this article, i.e., some geometrical parameters of the binary and ternary complexes, the interaction energies of the binary systems, the structures of the Ne(Na) and Ne(Cl) ternary complexes and charges of atoms, Figs S1–S3, and, Tables S1–S11, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/ijca_53A(11)1359-1370_SupplData.pdf.

**References**

26 Gaussian 03, Revision B.03, (Gaussian, Inc., Pittsburgh PA) 2003.