Indian Journal of Chemistry
Vol. 57A, February 2018, pp. 150-162

Theoretical investigation into the cooperativity effect and thermodynamic property of β-nitroguanidine·C_2F_4·H_2O ternary complex

Bin Li*, Guang-ming Zhao & Xiao-juan Guo
School of Environment and Safety Engineering, North University of China, Taiyuan 030051, China
Email: sxzbhjgc@163.com

The H-bonding cooperativity effects in β-NQ (nitroguanidine)···C_2F_4···H_2O ternary complex are investigated by the B3LYP and MP2(full) methods with the 6-311++G(2df,2p) basis set. The thermodynamic cooperativity effects are evaluated at 298.15 K. The result shows that C_2F_4 can be used as a wastewater treatment agent for β-NQ. The influence of the N–H···O or O–H···F H-bonding interaction on the N–H···F interaction is more pronounced than that of the latter on the former. The weak cooperativity effect appears in the linear complex while the notable anti-cooperativity effect is seen in the cyclic system. The enthalpy change is the major factor driving the cooperativity. There is no obvious correlation between the cooperativity effects evaluated by interaction energies and those from thermodynamic data. The complexation energies ($E_{\text{int.}}$) correlate well with the local minima of surface electrostatic potentials ($V_{\text{S,min}}$) or internal charge separations (Π). AIM (atom in molecule) analysis is used to reveal the nature of cooperativity effect. It can be inferred that the wastewater treatment for explosives can be viewed as a cooperativity process of coexisting intermolecular interactions, and also a thermodynamic cooperativity process.

Keywords: Theoretical chemistry, Cooperativity effect, Thermodynamic cooperativity, Atom-in-molecule analysis, MP2 method, Surface electrostatic potential

Recently, the excessive synthesis, production and application of explosives, as well as the wanton discharge of explosive contaminated wastewaters have caused serious water pollution in many parts of the world[1]. Effective treatment of the explosive wastewater has become an important and urgent issue for a long time. In order to eliminate explosive component from wastewater, one of the green, feasible and effective schemes is to discover a wastewater treatment agent, which conforms to two basic features: on the one hand, form strong intermolecular interaction with the explosive molecule and on the other, the intermolecular interaction between treatment agent and H_2O should be weak. Thus, due to the difference of the strengths of intermolecular interactions, the explosive molecule can be eliminated from the wastewater. The effectiveness of this method has been confirmed for about 20 years[2]. For example, by using the extractant acetonitrile, multiple extractions were carried out to quantify the residual TNT (2,4,6-trinitrotoluene) and efficiency of each extraction stage for the TNT-contaminated soil-aggregate mixture in aqueous solution by the ultrasonic extraction methods[3]. Ye *et al.*[4] found, after adsorption by resin, the acute toxicity was greatly reduced for the explosive wastewaters composed of dinitrotoluene sulfonates with small amount of TNT, dinitrotoluene, mononitrotoluene and other derivatives of nitrobenzene.

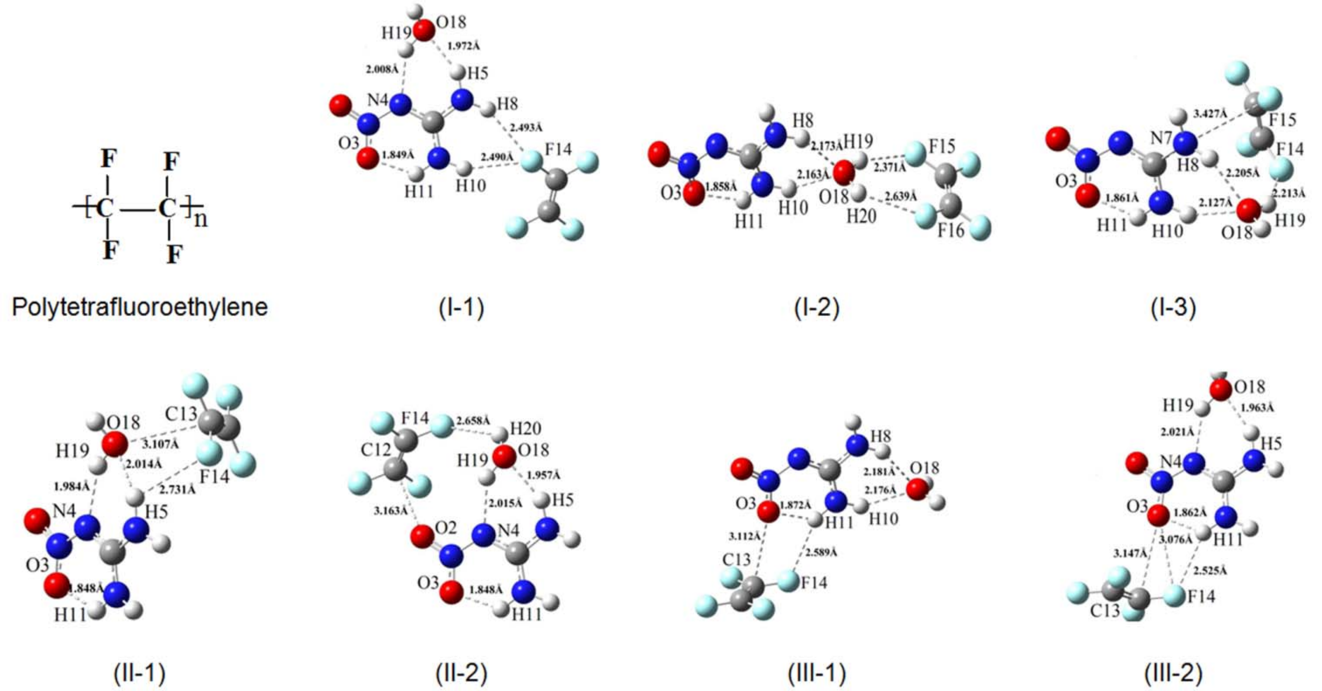
From the perspective of the intermolecular force, in the process of wastewater treatment, there are at least three kinds of intermolecular interactions among explosive, wastewater treatment agent and H_2O. Although the explosive component could be eliminated from wastewater by the intermolecular interaction between explosive and wastewater treatment agent, other intermolecular interactions also exist, i.e., the interaction between the explosive molecule and H_2O, and that between wastewater treatment agent and H_2O. It has been extensively shown from many experimental and theoretical results that the coexistence of the multiple intermolecular interactions can lead to the cooperativity effect[5–8], which may influence the intermolecular interaction between the explosive and wastewater treatment agent, and influence the wastewater treatment of explosive. Therefore, in order to explore the physical nature of wastewater treatment and eliminate effectively explosive from wastewater, it is very necessary to investigate the cooperativity effect in the "explosive-wastewater treatment agent-H_2O" system.

According to Vijay et al.,[9] the cooperativity or anti-cooperativity effect can occur when the coexisting multiple noncovalent interactions in one system mutually enhance or weaken each others' strength. It plays a crucial role in the separation and purification of compounds, chemical reactions, molecular aggregation and recognition, etc.[10] The cooperativity effect involving hydrogen bond (H-bond) is currently a topic of wide ranging interest. A supramolecular structure based on the cooperativity effect of intermolecular C–H···π, C–H···Br H-bonds and Br···Br interactions was observed in the compound $[AsPh_2Br_2]_2[(Br_3)^-\cdots(Br_2)\cdots(Br_3)^-]$ by X-ray crystallography[11]. Bakó *et al.*[12] analyzed the cooperativity effects involving the H-bonds in liquid water by molecular dynamics simulations with the help of network science, and pointed out that the energetic criterion was much more rigorous and reliable than the geometric criterion for the H-bonded network of liquid water[12]. Ahmed *et al.*[13] evaluated the effect of the bioisosteric replacement of a –C=O group with a sulphonyl functionality on the cooperativity between the H-bonds and hydrophobic binding. The cooperativity effects involving hydrogen/lithium/halogen bonds were calculated in the XH_3P^+ complexes with NCY (X = H, F, CN, NH_2, OH; Y = H, Li, F, Cl) by the MP2/aug-cc-pVTZ method of theory[14]. The role of substituents on cooperativity between the N···HF and CH···F H-bonds in the ternary systems involving aromatic azine were explored at the MP2/6-311++G(d,p) level. Hammett constants were used to predict the cooperativity effects[15]. A combination of the differential Raman spectrometrics and contact-angle measurements confirmed the molecular-site-resolved information regarding the O:H–O bond cooperativity in aqueous solutions[16]. McDowell undertook a theoretical study of the cooperative effects between the hydrogen-, halogen-, lithium- and beryllium-bonded interactions in the $H_3P\cdots YZ$ (YZ=HF, ClF, LiF, BeH_2) complexes at the MP2/6-311++G(3df, 3pd) level of theory, and found that the strong cooperative effects led to the bond breakage of the H–P and/or Cl–F bonds[17]. The interplay between hydrogen bond and single-electron tetrel bond in the $H_3C\cdots COX_2\cdots HY$ and $H_3C\cdots CSX_2\cdots HY$ (X = F, Cl; Y = CN, NC) complexes was invastigated at the UMP2/aug-cc-pVTZ level of theory, and many-body interaction energies were calculated[18]. From the atomic energy perspective, the cooperativity, anti-cooperativity, and non-cooperativity were analysed in the clusters of water, methanol, and formaldehyde at the MP2/6-311++G(d,p) and CCSD(T)/6 311++G(d,p) levels[19]. The progress in understanding the phase diagram of water and ice from the perspective of hydrogen bond (O:H–O) cooperative relaxation by the interplaying theoretical prediction, numerical computation, and phonon spectrometric methods has been reviewed[20]. Tang *et al.*[21] found that the positive cooperativity involving the H-bonding interactions was mainly attributed to the polarization and dispersion energies in $F_2SiO\cdots NCH\cdots NCH$ but to the polarization energy in $F_2CO\cdots NCH\cdots NCH$[21]. A spectroscopic and computational study of self-association of 1, 2-cyclohexanediols indicated that the H-bonding cooperativity played an important role in the structure of oligomers[22]. The cooperative or anticooperative character of the interrelation between three types of interactions (H-bonding, halogen-bonding and N···C interactions) was analysed[23]. The experimental evidence of the cooperativity effects of the H-bonding interactions in water molecules was obtained from the broadband rotational spectroscopy[24]. The H-bonding cooperativity effects in cyclic and ladder oligomers of cyanamide were studied in terms of the H-bonding strength, energy per hydrogen bond, excess energy and inter- and intra-molecular distances as well as vibrational frequencies at B3LYP/aug-cc-pvdz level[25]. A combined vibrational, energetic and NBO (natural bond orbitals)/NEDA (natural energy decomposition analysis) study on the amine–water interaction revealed the origin of the effect of H-bonding cooperativity[26]. Vijay *et al.*[27] reported the obvious cooperativity effects between cation···π interaction and H-bonding interactions. Deyà *et al.*[5,6] have also reported some experimental and theoretical evidences of the cooperativity effects involving the H-bonding interactions. Although there have been a large number of experimental and theoretical works devoted to the cooperativity effects involving the H-bonds, however, to our knowledge, no theoretical investigation into the H-bonding cooperativity effect involving the process of wastewater treatment of explosive has been presented.

From the intermolecular interaction point of view, when the complexation energy (the difference in the energy of complex and sum of the energies of monomers) is larger than the sum of the individual intermolecular interaction energies, the noncovalent interactions act cooperatively, while the anti-cooperativity effect occurs when the former is weaker than the latter. Besides the intermolecular interaction, the cooperativity effect can also be evaluated by the change of the thermodynamic data[28]. The positive cooperativity can be observed when the Gibbs' free energy of the overall binding is stronger than the summation of the Gibbs' free energies of binding of individual interactions; the negative cooperativity indicates that the change in Gibbs free energy of binding is smaller than what could be achieved[29–33]. There have also been many studies that address the enthalpic and entropic origin of the H-bonding cooperativity[34–36]. For example, by experimental data, Ksenia *et al*.[37] found that the enthalpies of the H-bonding interaction of amines in aliphatic alcohols were lower than those in 1:1 amine–alcohol complexes in base media, and the enthalpies of H-bonding in multi-particle complexes were sensitive to the influence of cooperative effect[37]. Sedov *et al*.[38] investigated the Gibbs free energy of H-bonding of aliphatic alcohols with liquid water at 298K by experiment, and found that the strong cooperative effects led to huge negative values of the Gibbs energies. However, the formation of the second and third H-bonds of an alcohol molecule with water was much less favorable, accompanied by the anti-cooperative effect[38]. We have evaluated the thermodynamic H-bonding cooperativity in $Cl^-\cdots$benzonitrile$\cdots H_2O$ ternary complexes using the B3LYP and MP2(full) methods with the 6-311++G(2d,p) and aug-cc-pVTZ basis sets[39].

Nitroguanidine (NQ), one of the important high energetic and insensitive explosives as propellant and explosive charge component, has been extensively used in civil and military activities. Unfortunately, NQ can leach into the surface waters, and present an environmental threat. The wastewater treatment for NQ explosive is imperative. Although a suitable wastewater treatment agent for NQ is not available at present, polytetrafluoroethylene (see Fig. 1) is reported to desensitize NQ explosive with the moderate intermolecular interaction[40-42] as a nonpolar polymer and bind to the polar H_2O very weakly[43]. This implies that if polytetrafluoroethylene is added into the wastewater of NQ explosive, NQ will be extracted from wastewater by the difference of intermolecular interactions, and polytetrafluoroethylene could be used as a wastewater treatment agent of NQ.

Nitroguanidine exists in two forms: α and β, labeled α-NQ and β-NQ, respectively. β-NQ is more stable than α-NQ and energetically lower by 28.16 kJ /mol (corrected with zero point vibrational energy) at the MP2/6-31G(d,p) level[44]. Therefore, only β-NQ has been considered in this study. β-NQ contains two



Polytetrafluoroethylene (I-1) (I-2) (I-3)

(II-1) (II-2) (III-1) (III-2)

Fig. 1 — Polytetrafluoroethylene and the optimized geometries of seven ternary-system conformations at the B3LYP/6-311++G(2df,2p) level.

–NH_2 groups and the –F_2C–CF_2– moiety is the structural unit of polytetrafluoroethylene. Thus, in the NQ complex with polytetrafluoroethylene (or F_2C=CF_2), the N–H F intermolecular interaction may be found. In the β-NQ C_2F_4 H_2O ternary system, the N–H F, N–H O, O–H F and O–H O hydrogen bonds may coexist, giving rise to the cooperativity effect between them. Therefore, the β-NQ C_2 F_4 H_2O complex can serve as a model system to investigate the cooperativity effect involving the H-bonding interaction in the "explosive-wastewater treatment agent-H_2O" system. Herein, the H-bonding cooperativity effects in the β-NQ C_2F_4 H_2O ternary complexes were investigated by quantum chemistry theoretical method. The thermodynamic origin of cooperativity effect were revealed. This investigation will be useful to explore the physical nature of the process of wastewater treatment, and further in selecting the wastewater treatment agent for explosive and eliminate effectively explosive from wastewater.

Methodology

All calculations were performed with Gaussian 03 programs[45]. The monomers and complexes were fully optimized using the DFT-B3LYP method with the 6-311++G(2df,2p) 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(2df,2p) basis set.

For the binary system, the intermolecular interaction energy ($E_{\text{int.}(\beta\text{–NQ}\ldots.C_2F_4)}$, $E_{\text{int.}(\beta\text{–NQ}\ldots.H_2O)}$ or $E_{\text{int.}(C_2F_4\ \ H_2O)}$) was calculated by evaluating the difference between the energy of complex and sum of energies of individual monomers.

In the ternary system of linear structure, $E_{\text{int.}(\beta\text{–NQ}\ldots.C_2F_4)}$, $E_{\text{int.}(\beta\text{–NQ}\ldots.H_2O)}$ or $E_{\text{int.}(C_2F_4H_2O}$ represent the interaction energy between both the moieties which directly interact with, i.e., it corresponds to the β-NQ···C_2F_4, β-NQ···H_2O or C_2F_4···H_2O interaction energy in the presence of H_2O, C_2F_4 or β-NQ (Eq. 1),

$$E'_{\text{int.}(A\cdots B)} = E_{A\cdots B\cdots C} - E_{B\cdots C} - E_A$$

$$\text{or}\ \ E'_{\text{int.}(B\cdots C)} = E_{A\cdots B\cdots C} - E_{A\cdots B} - E_C \qquad \text{...(1)}$$

where A, B, or C refers to β-NQ, C_2F_4, or H_2O. When the value of $E'_{\text{int.}}$ is larger than that of $E_{\text{int.}}$, the stabilization of binary complex is enhanced in the presence of the third component, and thus the cooperativity effects occur in ternary system.

$E''_{\text{int.}(A\cdots C)}$ is defined as the through-space interaction energy between both the moieties with which they do not directly interact. It was calculated at the ternary geometry by employing Eq. (2),

$$E''_{\text{int.}(A\cdots C)} = E'_{A\cdots C} - E_A - E_C i \qquad \text{...(2)}$$

where $E'_{A\cdots C}$ represents the total energy 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 ($E_{\text{int.}(A\cdots B\cdots C)}$) and the sum of all pair interaction energies as given in Eqs (3) or (4).

$$E_{\text{coop.}} = E_{\text{int.}(A\cdots B\cdots C)} - E_{\text{int.}(A\cdots B)} - E_{\text{int.}(B\cdots C)} - E_{\text{int.}(A\cdots C)}$$
$$\text{for cyclic structure} \qquad \text{…(3)}$$

$$E_{\text{coop.}} = E_{\text{int.}(A\cdots B\cdots C)} - E_{\text{int.}(A\cdots B)} - E_{\text{int.}(B\cdots C)} - E''_{\text{int.}(A\cdots C)}$$
$$\text{for linear system} \qquad \text{…(4)}$$

where $E_{\text{int.}(A\cdots B\cdots C)} = E_{A\cdots B\cdots C} - E_A - E_B - E_C$.

Except for $E'_{A\cdots C}$ in Eq. (2), all the energies at the right side of equations correspond to the systems optimized separately.

Results and Discussion

Binary system

The most stable binary complexes β-NQ C_2F_4 (I, II and III), β-NQ···H_2O (A and B) and C_2F_4· H_2O were selected at the B3LYP/6-311++G(2df,2p) level (see Supplementary Data, Fig. S1). All the binary complexes have C_1 symmetry. The H F distances in the N–H···F–C contact are 2.444, 2.346, and 2.536 Å in I, II, and III at B3LYP/6-311++G(2df,2p) level, respectively, which are close to the accepted H···F H-bond distance, suggesting the formation of the intermolecular N–H F H-bonding interaction. The N–H···O H-bonding interaction is found in the β-NQ···H_2O system due to the short H···O distances (1.963 and 2.189 Å in A and B, respectively). The O–H F H-bonding interaction is confirmed in C_2F_4 H_2O with the H F distance of 2.236 Å.

The intermolecular interaction energies in the β-NQ···C_2F_4 complexes are in the range between –6.8 and –13.5 kJ/mol at the MP2(full)/6-311++G(2df,2p) level (Supplementary Data, Fig. S1). The interaction energies obtained at two levels of theory are in the same order of II > III > I. As mentioned above, the H···F distance in II is the shortest. The interaction energy in C_2F_4···H_2O is very weak (only –6.9 kJ/mol) at the MP2(full)/6-311++G(2df,2p) level. The intermolecular interactions between C_2F_4 and β-NQ are stronger than those between C_2F_4 and H_2O, and the strongest interaction between C_2F_4 and β-NQ is about twice as large as that between C_2F_4 and H_2O is, suggesting that C_2F_4 can be used as a wastewater treatment agent to remove β-NQ from wastewater. For β-NQ···H_2O, the conformation A is more stable than B (–49.6 versus –37.2 kJ/mol at the MP2(full)/6-311++G(2df,2p) level), is in agreement with the increase of the N–H···O distances.

Ternary systems

Structure of ternary system

The optimizations of the complexes from H_2O and the β-NQ C_2F_4 binary systems I, II, and III result in three ((I-1)~(I-3)), two (II-1~2), two (III-1~2) ternary complexes at the B3LYP/6-311++G(2df,2p) level, respectively (Fig. 1). The complexes I-1, I-2, III-1 and III-2 can be regarded as linear structures, while the complexes I-3, II-1 and II-2 can be described as cyclic, in which three monomers are arranged in a ring with the intermolecular H-bond between every two molecules. Both the N–H···O and N–H···F H-bonds coexist in the ternary complexes I-1, II-1, III-1 and III-2. In I-2, I-3 and II-1, the coexistence of N–H···O and N–H···F H-bonds are suggested. The O–H···N H-bond between the H atom of H_2O and lone pair electrons of N atom in I-1, II-1, II-2 and III-2 is confirmed by the short H···N distances (no more than 2.1 Å) and large second-order perturbation delocalization interactions with the $E^{(2)}_{LP(N)\rightarrow\sigma^*(H\text{–}O)}$ in the range of 27.8~39.5 kJ/mol based on the natural bond orbital analysis[46] at the B3LYP/6-311++G(2df,2p) level. In the complex of nitro explosive, the intermolecular H-bond involving the oxygen atom of the $–NO_2$ group is often present[47]. However, despite considerable efforts, it was not found in the title complex, or else the complexes with it were more unstable than the title systems.

For the linear ternary complexes I-1, I-2, III-1 and III-2, when compared to the corresponding binary systems, some of the H-bonded distances are shortened and some are elongated (Fig. 1 and Fig. S1), although the changes are very slight. For example, the largest difference of the N–H· F H-bonded distances between the binary complex I and ternary system I-1 is not more than 0.05 Å. The intermolecular H-bonded distance is almost unaffected when the third molecule is added, suggesting that the cooperativity effect might be weak in the linear ternary complexes.

However, when compared to the binary systems, in the cyclic ternary complexes the changes in the intermolecular H-bonded distances are notable. For instance, the difference between the N–H···F H-bonded distances of the binary complex II and ternary system II-1 is up to 0.385 Å. Furthermore, most of the H-bonded distances are increased in comparison with those in binary complexes. In particular, some of the H-bonds are broken upon the formation of ternary complexes. These results suggest that the anti-cooperativity effect may be found in the cyclic ternary complexes.

Interaction energy and cooperativity effect

Table 1 summarizes the intermolecular interaction energies of ternary complexes using the B3LYP and MP2(full) methods with the 6-311++G(2df,2p) basis set. There is an obvious trend that the MP2(full) interaction energies are more negative than the corresponding B3LYP results, which is in agreement with those of previous investigations[39]. It is well known that B3LYP does not include dispersion energy, while MP2(full) can predict reliable binding energies of the complexes. Therefore, in most cases, the

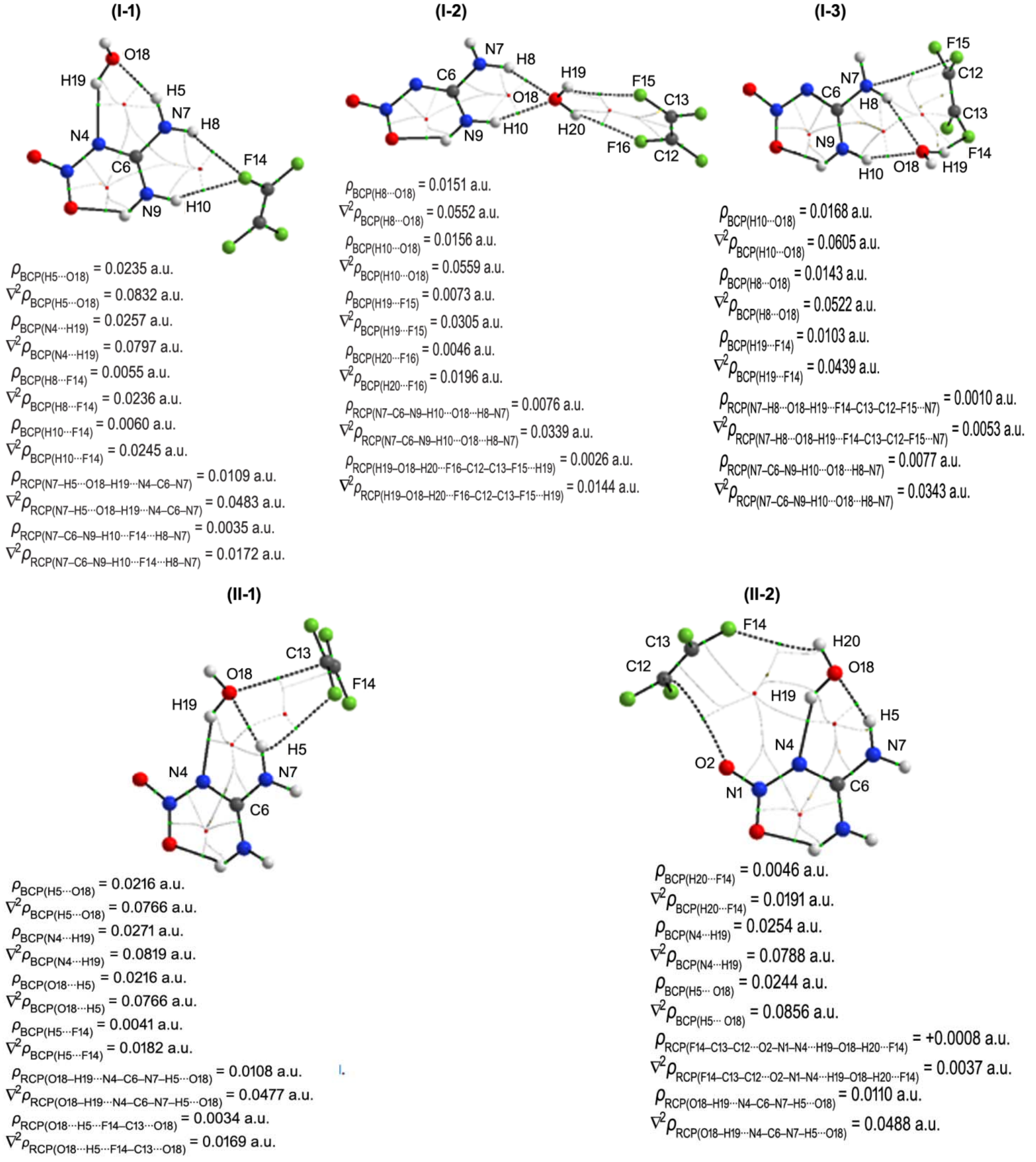
Table 1 — Interaction energy ($E'_{\text{int.}}$[a], $E''_{int.}$ or $E_{\text{int.}}$, kJ/mol) and cooperativity energy ($E_{coop.}$, kJ/mol) at the B3LYP/6-311++G(2df,2p) and MP2(full)/6-311++G(2df,2p) (in parantheses) levels

System	$E'_{\text{int.(β-NQ···C2F4)}}$ (kJ/mol)	$E'_{\text{int.(β-NQ···H2O)}}$ (kJ/mol)	$E'_{\text{int.(C2F4···H2O)}}$ (kJ/mol)	$E''_{\text{int.}}$ (kJ/mol)	$E_{\text{int.(β-NQ···C2F4···H2O)}}$ (kJ/mol)	$E_{\text{coop.}}$ (kJ/mol)
I-1	–5.1 (–6.9)	–41.3 (–50.1)		0.2 (–1.1)	–46.0 (–58.6)	–0.7 (–1.1)
I-2		–32.5 (–38.6)	–6.1 (–7.1)	–0.2 (–0.9)	–37.3 (–46.3)	–0.1 (–1.3)
I-3	–6.4 (–6.5)	–33.0 (–35.1)	–5.5 (–6.3)		–38.7 (–51.7)	5.1 (11.6)
II-1	–7.0 (–8.9)	–36.8 (–37.0)	–5.0 (–6.6)		–47.8 (–57.5)	9.9 (12.5)
II-2	–7.1 (–8.6)	–36.9 (–39.2)	–5.1 (–5.9)		–47.9 (–60.8)	9.7 (9.2)
III-1	–8.0 (–9.2)	–32.9 (–38.6)		–0.5 (–1.3)	–40.2 (–50.0)	–0.3 (–2.4)
III-2	–7.2 (–9.3)	–41.7 (–51.0)		–0.3 (–1.1)	–48.0 (–61.1)	–0.4 (–1.3)

[a]The computational method of $E'_{\text{int.}}$ for the cyclic structure is similar to that for the linear structure.

MP2(full) method will be used to predict the cooperativity effect.

For the linear ternary-complexes I-1 and III-2, the values of $E'_{\mathrm{int.(\beta\text{-}NQ\cdots C_2F_4)}}$ are slightly lower than those of the corresponding β-NQ C_2F_4 complexes at the B3LYP/6-311++G(2df,2p) level (Fig. 2 and Fig. S2). Except for the above cases, the values of $E'_{\mathrm{int.(\beta\text{-}NQ\cdots C_2F_4)}}$, $E'_{\mathrm{int.(\beta\text{-}NQ\cdots H_2O)}}$ and $E'_{\mathrm{int.(C_2F_4\cdots H_2O)}}$ in four linear ternary-complexes I-1, I-2, III-1 and III-2 are all larger than those in the corresponding β-NQ···C_2F_4, β-NQ···H_2O and C_2F_4···H_2O binary complexes at two levels of theory. These results show that the N–H···F,



(I-1)

$\rho_{\mathrm{BCP(H5\cdots O18)}}$ = 0.0235 a.u.
$\nabla^2\rho_{\mathrm{BCP(H5\cdots O18)}}$ = 0.0832 a.u.
$\rho_{\mathrm{BCP(N4\cdots H19)}}$ = 0.0257 a.u.
$\nabla^2\rho_{\mathrm{BCP(N4\cdots H19)}}$ = 0.0797 a.u.
$\rho_{\mathrm{BCP(H8\cdots F14)}}$ = 0.0055 a.u.
$\nabla^2\rho_{\mathrm{BCP(H8\cdots F14)}}$ = 0.0236 a.u.
$\rho_{\mathrm{BCP(H10\cdots F14)}}$ = 0.0060 a.u.
$\nabla^2\rho_{\mathrm{BCP(H10\cdots F14)}}$ = 0.0245 a.u.
$\rho_{\mathrm{RCP(N7\text{–}H5\cdots O18\text{–}H19\cdots N4\text{–}C6\text{–}N7)}}$ = 0.0109 a.u.
$\nabla^2\rho_{\mathrm{RCP(N7\text{–}H5\cdots O18\text{–}H19\cdots N4\text{–}C6\text{–}N7)}}$ = 0.0483 a.u.
$\rho_{\mathrm{RCP(N7\text{–}C6\text{–}N9\text{–}H10\cdots F14\cdots H8\text{–}N7)}}$ = 0.0035 a.u.
$\nabla^2\rho_{\mathrm{RCP(N7\text{–}C6\text{–}N9\text{–}H10\cdots F14\cdots H8\text{–}N7)}}$ = 0.0172 a.u.

(I-2)

$\rho_{\mathrm{BCP(H8\cdots O18)}}$ = 0.0151 a.u.
$\nabla^2\rho_{\mathrm{BCP(H8\cdots O18)}}$ = 0.0552 a.u.
$\rho_{\mathrm{BCP(H10\cdots O18)}}$ = 0.0156 a.u.
$\nabla^2\rho_{\mathrm{BCP(H10\cdots O18)}}$ = 0.0559 a.u.
$\rho_{\mathrm{BCP(H19\cdots F15)}}$ = 0.0073 a.u.
$\nabla^2\rho_{\mathrm{BCP(H19\cdots F15)}}$ = 0.0305 a.u.
$\rho_{\mathrm{BCP(H20\cdots F16)}}$ = 0.0046 a.u.
$\nabla^2\rho_{\mathrm{BCP(H20\cdots F16)}}$ = 0.0196 a.u.
$\rho_{\mathrm{RCP(N7\text{–}C6\text{–}N9\text{–}H10\cdots O18\cdots H8\text{–}N7)}}$ = 0.0076 a.u.
$\nabla^2\rho_{\mathrm{RCP(N7\text{–}C6\text{–}N9\text{–}H10\cdots O18\cdots H8\text{–}N7)}}$ = 0.0339 a.u.
$\rho_{\mathrm{RCP(H19\text{–}O18\text{–}H20\cdots F16\text{–}C12\text{–}C13\text{–}F15\cdots H19)}}$ = 0.0026 a.u.
$\nabla^2\rho_{\mathrm{RCP(H19\text{–}O18\text{–}H20\cdots F16\text{–}C12\text{–}C13\text{–}F15\cdots H19)}}$ = 0.0144 a.u.

(I-3)

$\rho_{\mathrm{BCP(H10\cdots O18)}}$ = 0.0168 a.u.
$\nabla^2\rho_{\mathrm{BCP(H10\cdots O18)}}$ = 0.0605 a.u.
$\rho_{\mathrm{BCP(H8\cdots O18)}}$ = 0.0143 a.u.
$\nabla^2\rho_{\mathrm{BCP(H8\cdots O18)}}$ = 0.0522 a.u.
$\rho_{\mathrm{BCP(H19\cdots F14)}}$ = 0.0103 a.u.
$\nabla^2\rho_{\mathrm{BCP(H19\cdots F14)}}$ = 0.0439 a.u.
$\rho_{\mathrm{RCP(N7\text{–}H8\cdots O18\text{–}H19\cdots F14\text{–}C13\text{–}C12\text{–}F15\cdots N7)}}$ = 0.0010 a.u.
$\nabla^2\rho_{\mathrm{RCP(N7\text{–}H8\cdots O18\text{–}H19\cdots F14\text{–}C13\text{–}C12\text{–}F15\cdots N7)}}$ = 0.0053 a.u.
$\rho_{\mathrm{RCP(N7\text{–}C6\text{–}N9\text{–}H10\cdots O18\cdots H8\text{–}N7)}}$ = 0.0077 a.u.
$\nabla^2\rho_{\mathrm{RCP(N7\text{–}C6\text{–}N9\text{–}H10\cdots O18\cdots H8\text{–}N7)}}$ = 0.0343 a.u.

(II-1)

$\rho_{\mathrm{BCP(H5\cdots O18)}}$ = 0.0216 a.u.
$\nabla^2\rho_{\mathrm{BCP(H5\cdots O18)}}$ = 0.0766 a.u.
$\rho_{\mathrm{BCP(N4\cdots H19)}}$ = 0.0271 a.u.
$\nabla^2\rho_{\mathrm{BCP(N4\cdots H19)}}$ = 0.0819 a.u.
$\rho_{\mathrm{BCP(O18\cdots H5)}}$ = 0.0216 a.u.
$\nabla^2\rho_{\mathrm{BCP(O18\cdots H5)}}$ = 0.0766 a.u.
$\rho_{\mathrm{BCP(H5\cdots F14)}}$ = 0.0041 a.u.
$\nabla^2\rho_{\mathrm{BCP(H5\cdots F14)}}$ = 0.0182 a.u.
$\rho_{\mathrm{RCP(O18\text{–}H19\cdots N4\text{–}C6\text{–}N7\text{–}H5\cdots O18)}}$ = 0.0108 a.u.
$\nabla^2\rho_{\mathrm{RCP(O18\text{–}H19\cdots N4\text{–}C6\text{–}N7\text{–}H5\cdots O18)}}$ = 0.0477 a.u.
$\rho_{\mathrm{RCP(O18\cdots H5\cdots F14\text{–}C13\cdots O18)}}$ = 0.0034 a.u.
$\nabla^2\rho_{\mathrm{RCP(O18\cdots H5\cdots F14\text{–}C13\cdots O18)}}$ = 0.0169 a.u.

(II-2)

$\rho_{\mathrm{BCP(H20\cdots F14)}}$ = 0.0046 a.u.
$\nabla^2\rho_{\mathrm{BCP(H20\cdots F14)}}$ = 0.0191 a.u.
$\rho_{\mathrm{BCP(N4\cdots H19)}}$ = 0.0254 a.u.
$\nabla^2\rho_{\mathrm{BCP(N4\cdots H19)}}$ = 0.0788 a.u.
$\rho_{\mathrm{BCP(H5\cdots O18)}}$ = 0.0244 a.u.
$\nabla^2\rho_{\mathrm{BCP(H5\cdots O18)}}$ = 0.0856 a.u.
$\rho_{\mathrm{RCP(F14\text{–}C13\text{–}C12\cdots O2\text{–}N1\text{–}N4\cdots H19\text{–}O18\text{–}H20\cdots F14)}}$ = +0.0008 a.u.
$\nabla^2\rho_{\mathrm{RCP(F14\text{–}C13\text{–}C12\cdots O2\text{–}N1\text{–}N4\cdots H19\text{–}O18\text{–}H20\cdots F14)}}$ = 0.0037 a.u.
$\rho_{\mathrm{RCP(O18\text{–}H19\cdots N4\text{–}C6\text{–}N7\text{–}H5\cdots O18)}}$ = 0.0110 a.u.
$\nabla^2\rho_{\mathrm{RCP(O18\text{–}H19\cdots N4\text{–}C6\text{–}N7\text{–}H5\cdots O18)}}$ = 0.0488 a.u.

Fig. 2 — AIM results of seven ternary systems at B3LYP/6-311++G(2df,2p) level. (*Contd.*)

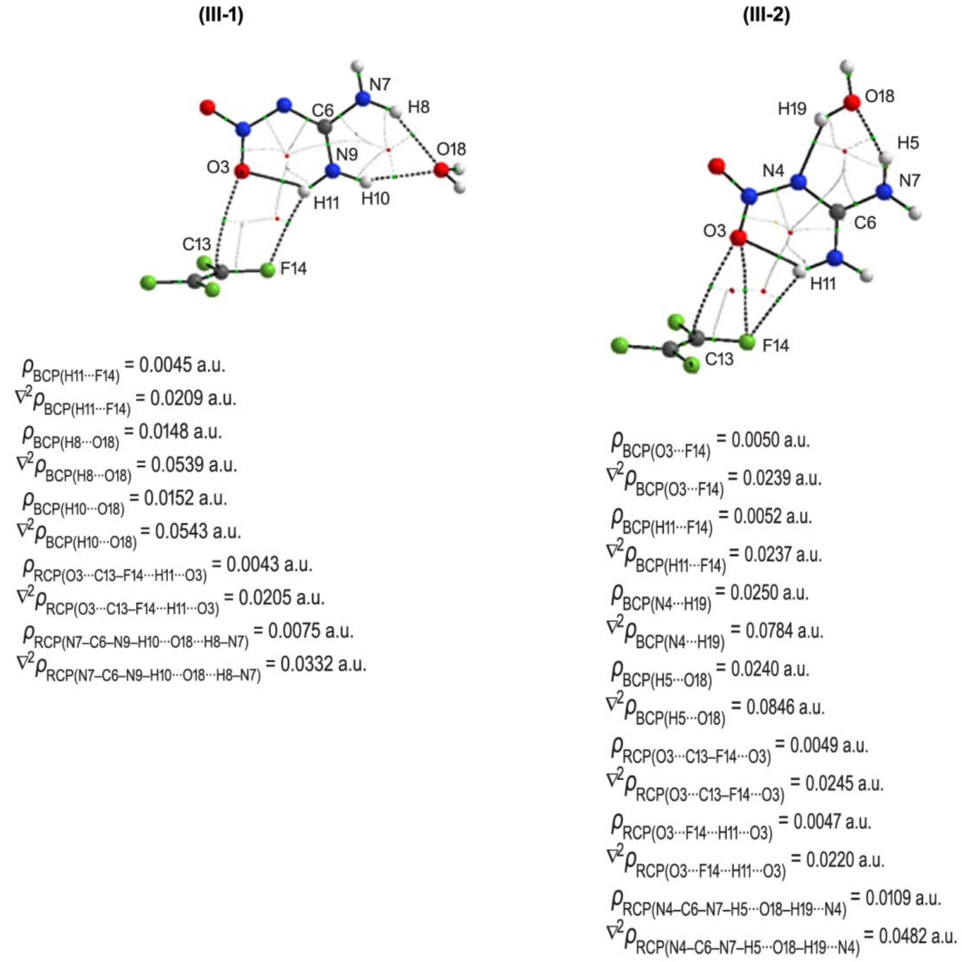


Fig. 2 (*Contd.*) — AIM results of seven ternary systems at B3LYP/6-311++G(2df,2p) level.

N–H···O, O–H···F H-bonding interactions are strengthened upon the ternary-complex formations. Thus, the possible cooperativity effects occur in the linear ternary-complexes. However, similar to the H-bonded distances, the changes of all the interactions upon the formation of ternary systems are very slight. For example, the difference of the N–H F interactions between β-NQ H_2O (III) and III-1 is only 0.1 kJ/mol at the MP2(full)/6-311++G(2df,2p) level. This indicates that the cooperativity effect may be weak. For three cyclic complexes I-3, II-1 and II-2, the values of $E'_{\text{int.(β-NQ}\cdots C_2F_4)}$, $E'_{\text{int.(β-NQ}\cdots H_2O)}$ and $E'_{\text{int.}(C_2F_4\cdots H_2O)}$ are all lower than those in the corresponding β-NQ···C_2F_4, β-NQ···H_2O and C_2F_4···H_2O binary complexes at two levels of theory. These results show that the N–H···F, N–H···O, O–H···F H-bonding interactions are weakened upon the cyclic ternary-complex formations. Thus, the possible anti-cooperativity effects occurs in the cyclic ternary-complexes.

When several noncovalent interactions coexist, it is interesting to see how they influence each other. Hence, the proportion of change of the interaction energy to the corresponding value in binary system was investigated. At the MP2(full)/6-311++G(2df,2p) level, for the linear ternary complexes, the proportion of the increment of N–H F interaction energy to $E_{\text{int.(β-NQ}\cdots C_2F_4)}$ (=$[E'_{\text{int.(β-NQ}\cdots C_2F_4)}–E_{\text{int.(β-NQ}\cdots C_2F_4)}]/E_{\text{int.(β-NQ}\cdots C_2F_4)}$) is no more than 2.2%, and that of the N–H···O or O–H F H-bonding energy to $E_{\text{int.(β-NQ}\cdots H_2O)}$ or $E_{\text{int.}(C_2F_4\cdots H_2O)}$ is also very small, with the largest value of 1.61% or 2.90% respectively. These results show that the strengths of the noncovalent interactions are almost not affected by each other upon the formation of the linear ternary complex, suggesting the weak cooperativity effect. However, the influence between the H-bonding interactions is remarkable upon the cyclic ternary-complex formations, as can be shown from the larger proportion of the decrement of the N–H···F, N–H···O or O–H···F interaction energy in the ternary complex to that of the corresponding binary system. For example, the proportion is up to 36.3%, 29.2% or 14.5% for the N–H···F, N–H···O or O–H···F H-bonding interaction, suggesting the large cooperativity effect. These results show that the N–H···F H-bonding interaction is changed more remarkable than the N–H O or O–H F H-bonding interaction upon the ternary-complex formation. In other words, the influence of the N–H···O or O–H F H-bonding interaction on the N–H···F interaction is more pronounced than that of the N–H···F interaction on the N–H···O or O–H F interaction upon the cyclic ternary-complex formations.

Table 1 shows that at two levels of theory, the linear ternary systems have the negative $E_{coop.}$ values, while the values of cooperativity effect are positive in the cyclic complexes. Thus, the cooperativity effects occur in the linear structures, while the cyclic complex suffers the anti-cooperativity effect, as is consistent with the analysis of structure and energy. The cooperativity effects are weak while the anti-cooperativity effects are large. At the MP2(full)/6-311++G(2df,2p) level, the values of cooperativity effect are in the range of –1.1 and –2.4 kJ/mol. In the cyclic complexes, they are within a range of 9.2 to 12.5 kJ/mol. In the previous investigations, the values of the cooperativity effect in acetonitrile trimer were found to be in the range of –0.33 to –3.76 kJ/mol at the MP2/6-311G* level[48], and those in $F_3CCl(Br)\cdots NCH(CNH)\cdots HMgH$ complex were within a range of –1.02 to –2.31 kJ/mol at MP2/cc-pVTZ level[49].

At two levels of theory, in most cases, the complexation energies of three cyclic ternary complexes are stronger than four linear complexes, indicating that the stability of the cyclic structure with the anti-cooperativity effect is higher than that of the linear structure with the cooperativity effect, as was also found in our previous investigations[39]. Note that there is no notable correlation between the cooperativity effects and stabilities[50, 51]. The number of H-bonds in cyclic ternary complex is more than that of linear structure. This is perhas one of reasons that the cyclic system is more stable than the linear complex. The cooperativity/anti-cooperativity reveals how the noncovalent interactions influence each other. It is mainly attributed to the induced polarization[52] and charge transfer[53] in each subunit. The favourable polarization and charge transfer can lead to the strengthened intermolecular interaction formed between/among subunits, accompanied by the cooperativity effect. On the contrary, the unfavourable polarization and charge transfer can lead to the weakened intermolecular interaction with the anti-cooperativity effect[54].

Based on above discussion, it can be inferred from the perspective of intermolecular force that the wastewater treatment for explosive can be as a process in which the coexisted intermolecular interactions mutually influence each others. In this process, the cooperativity effect plays an important role. When the cooperativity effect leads to an enhanced intermolecular interaction between the wastewater treatment agent and explosive, and simultaneously a weakened interaction between H_2O and explosive or wastewater treatment agent, the purpose of the wastewater treatment will be achieved.

Thermodynamic origin of cooperativity

As mentioned above, one of the aims in this work is to find out a wastewater treatment agent that can take β-NQ out of wastewater. Thus, the ternary complex $C_2F_4\cdots\beta\text{-NQ}\cdots H_2O$ can be regarded as the initial formation of the binary $\beta\text{-NQ}\cdots H_2O$ complex followed by addition of C_2F_4, i.e., wastewater treatment agent C_2F_4 binding to the explosive β-NQ in the presence of H_2O. In order to further examine the origin of cooperativity effect of this process, the thermodynamic cooperativity was investigated by the statistical thermodynamic method at 298.15 K. According to James *et al.*[34], the values of $\Delta G_{coop.}$(Gibbs' free energy change of cooperative effect), $\Delta\Delta H$ (enthalpic contribution of cooperative effect) and $-T\Delta\Delta S$ (entropic contribution of cooperative effect) were calculated at the B3LYP/6-311++G(2df,2p) level as follows:

$$\Delta G_{\text{coop.}} = \Delta G_{(\text{C}_2\text{F}_4\cdots\beta-\text{NQ}\cdots\text{H}_2\text{O})} - \Delta G_{(\beta-\text{NQ}\cdots\text{H}_2\text{O})}$$

$$\Delta\Delta H = \Delta H_{(\text{C}_2\text{F}_4\cdots\beta-\text{NQ}\cdots\text{H}_2\text{O})} - \Delta H_{(\beta-\text{NQ}\cdots\text{H}_2\text{O})}$$

$$-\text{T}\Delta\Delta S = (-\text{T}\Delta S_{(\text{C}_2\text{F}_4\cdots\beta-\text{NQ}\cdots\text{H}_2\text{O})}) - (-\text{T}\Delta S_{(\beta-\text{NQ}\cdots\text{H}_2\text{O})})$$

where the values of ΔG, ΔH, and ΔS of the binary or ternary system were calculated as the difference between the thermodynamical quantities of complex and individual monomers. The results of $\Delta G_{coop.}$, $\Delta\Delta H$ and $-\mathrm{T}\Delta\Delta S$ are presented in Table 2. $\Delta G_{coop.} < 0$ indicates thermodynamical cooperativity effect, i.e., the ligand is bound more strongly[34]. $\Delta\Delta H < 0$ or $-\mathrm{T}\Delta\Delta S < 0$ mean the favorable enthalpic or entropic contribution to cooperativity effect[30].

Except for I-2, the values of $\Delta G_{coop.}$ are negative in the ternary systems, showing the thermodynamic cooperativity effects (Table 2). This indicates that C_2F_4 binding to β-NQ is easier to take place in the presence of H_2O. For example, from the binding constant $K_{\mathrm{a,coop.}}$ ($\Delta G_{coop.} = -\mathrm{RTln}K_{\mathrm{a,coop.}}$[32]), for II-1, C_2F_4 binding to β-NQ is 6.03×10^6 times tightER in the presence of H_2O. However, for I-2, the value of $\Delta G_{coop.}$ is positive, accompanied by the thermodynamic anti-cooperativity effect. This result shows that C_2F_4 binding to β-NQ is more difficult to occur in the presence of H_2O. Indeed, the value of $K_{\mathrm{a,coop.}}$ decreases to 0.123 in the presence of H_2O. It should be mentioned that in I-2, C_2F_4 does not bind to β-NQ but only to H_2O, with the very weak $C_2F_4\cdots H_2O$ intermolecular interaction (–7.1 kJ/mol, see Table 1).

As mentioned above, from the perspective of intermolecular interaction, the cooperativity effects are found in linear complexes I-1, I-2, III-1 and III-2, while the anti-cooperativity effects are suggested in the cyclic ternary complexes I-3, II-1 and II-2. However, the large negative $\Delta G_{\mathrm{coop.}}$ in I-1, I-3, II-1, II-2 or III-2 indicates the notable thermodynamic cooperativity. In other words, the cooperativity effects evaluated by the interaction energy are not always in accordance with those from the thermodynamic data, as is also found in the previous investigations[39]. In fact, there is no certain correlation between the cooperativity effects evaluated by interaction energy and those from $\Delta G_{coop.}$. The former reveals how the noncovalent interactions influence each other, while the latter indicates the characteristics of thermodynamic process: the favorable cooperativity effect leads to the easier and tighter binding to binary complex, while the unfavorable cooperativity effect leads to the more difficult and looser binding.

Table 2 shows that the values of $\Delta\Delta H$ are negative in all the ternary systems, showing that in the process of forming the ternary complexes from the β-NQ···H_2O binary systems followed by addition of C_2F_4, the enthalpy changes support the cooperativity effect. Similar to $\Delta\Delta H$, the values of $-\mathrm{T}\Delta\Delta S$ are also negative in three cyclic ternary complexes, indicating that in the process of forming the cyclic structures, the enthalpy changes also support the cooperativity effects. Thus, the binding of the cyclic ternary complexes can be achieved with favorable enthalpic and entropic contributions, leading to large negative $\Delta G_{\mathrm{coop.}}$ and thus the notable favorable thermodynamic cooperativities. For the linear structural complexes, except for III-2, the others have the positive values of $-\mathrm{T}\Delta\Delta S$, showing that the entropy changes oppose cooperativity in the formation of the linear structural complexes.

Except for I-2 and II-2, the absolute values of $\Delta\Delta H$ are larger than those of $-\mathrm{T}\Delta\Delta S$, suggesting that the enthalpy change is the major factor driving the thermodynamic cooperativity. For I-2, the absolute values of $-\mathrm{T}\Delta\Delta S$ are larger than those of $\Delta\Delta H$, suggesting that the entropy change is the major factor driving the thermodynamic process, and due to the positive values of $-\mathrm{T}\Delta\Delta S$, the thermodynamic anti-cooperativity occurs. For II-2, although the entropy change is the major factor, both the values of entropy change and enthalpy change are negative, leading to the negative $\Delta G_{\mathrm{coop.}}$ and thus the favorable thermodynamic cooperativities. It should be noted that, as mentioned in previous investigation[39], for the

Table 2 — Thermodynamic data ($\Delta\Delta H$, $-\mathrm{T}\Delta\Delta S$ and $\Delta G_{\mathrm{coop.}}$) at 298.15 K and binding constant ($K_{\mathrm{a,coop.}}$) at the B3LYP/6-311++G(2df,2p) level

System	$\Delta\Delta H$ (kJ/mol)	$-\mathrm{T}\Delta\Delta S$ (kJ/mol)	$\Delta G_{\mathrm{coop.}}$ (kJ/mol)	$K_{\mathrm{a,coop.}}$ (kJ/mol)
I-1	−18.2	3.1	−15.1	4.42×10^2
I-2	−11.3	16.6	5.2	1.23×10^{-1}
I-3	−16.5	−12.5	−29.0	1.20×10^5
II-1	−28.9	−9.7	−38.7	6.03×10^6
II-2	−13.7	−15.8	−29.5	1.47×10^5
III-1	−10.8	5.3	−5.5	9.19×10^0
III-2	−15.6	−2.2	−17.8	1.31×10^3

H-bonded complex, harmonic approximation usually leads to a more negative ΔS and thus a more positive ΔG than the experimental result. Therefore, the calculated ΔG and $K_{\mathrm{a,coop.}}$ are more qualitative than quantitative.

It can be inferred that the wastewater treatment for explosive can be as a thermodynamic cooperativity process. When the thermodynamic cooperativity effect leads to a certain process or direction in which wastewater treatment agent can bind tighter to the explosive, the purpose of the wastewater treatment will be achieved. In this process, for the inorganic reaction between small molecules, the enthalpy change is usually the major factor driving the thermodynamic cooperativity[55], while for the organic reaction between macromolecules, in particular biological macromolecules, the entropy change is often the major factor[56].

AIM analysis

To further invesitigate into the origin of cooperativity effect, AIM (atom in molecule)[57] analysis was carried out. The topological charge density was displayed by AIMPAC program[58] at the B3LYP/6-311++G(2df,2p) level. The results of the ternary and binary systems were presented in Fig. 2 and Fig. S2, respectively.

According to the AIM results, for each of the C_2F_4···β-NQ binary system, there is a bond path linking the H atom of the H−N group of β-NQ with the F atom of C_2F_4, accompanied by a bond critical point (BCP) (3, −1). The values of $\rho_{\mathrm{BCP(H\cdots F)}}$ are within the range between 0.0051 and 0.0079 a.u. and the Laplacians $\nabla^2\rho_{\mathrm{BCP}}$ are all positive, suggesting the typical closed-shell kind of interactions. Thus, the N–H···F H-bonding interaction in the N–H F–C contact is confirmed again. Similarly, the N–H···O and O–H N H-bonds in H_2O···β-NQ and O–H···F H-bond in C_2F_4 H_2O binary complexes are also suggested according to their values of ρ_{BCP} and the corresponding $\nabla^2\rho_{\mathrm{BCP}}$. In H_2O···β-NQ, the values of $\rho_{\mathrm{BCP(O–H\cdots O)}}$ are within the range between 0.0230 and 0.0241 a.u., and the value of $\rho_{\mathrm{BCP(O–H\cdots N)}}$ is 0.0237 a.u.. In C_2F_4···H_2O, the value of $\rho_{\mathrm{BCP(O–H\cdots F)}}$ is 0.0057 a.u.. Similar to binary systems, the N–H F, N–H O, O–H···N and O–H···F H-bonds are also confirmed by the AIM results, with several distinct (3, −1) BCPs in the corresponding regions.

The electron density ρ at the bond saddle point indicates the bond strength. The larger the ρ is, the stronger the interaction is[57]. For I-3, the bond path linking the H atom of the H−N group of β-NQ with the F atom of C_2F_4 is not found, showing that the N–H···F H-bonds is broken, as is in agreement with the analysis of structure. For II-1 and II-2, the values of $\rho_{\mathrm{BCP(N–H\cdots F)}}$ decrease in comparison with those in the binary system II, suggesting that the N–H···F interactions are weakened upon the formation of the ternary complex. The value of $\rho_{\mathrm{BCP(O–H\cdots F)}}$ in II-2 is lower than that in C_2F_4···H_2O, and the values of $\rho_{\mathrm{BCP(N–H\cdots O)}}$ and $\rho_{\mathrm{BCP(O–H\cdots N)}}$ in I-3 and II-1 are lower than those in β-NQ···H_2O, indicating the weakened N–H···O and O–H···N H-bonding interactions upon the formation of the ternary complex. Thus, the anti-cooperativity effects in I-3, II-1 and II-1 are confirmed again.

For I-1 and III-2, there is no obvious change of the $\rho_{\mathrm{BCP(N–H\cdots F)}}$, $\rho_{\mathrm{BCP(N–H\cdots O)}}$ or $\rho_{\mathrm{BCP(O–H\cdots N)}}$ value with the formation of ternary complex from the corresponding binary systems. Therefore, the cooperativity effects in them are not obvious. For I-2, the value of $\rho_{\mathrm{BCP(N–H\cdots O)}}$ is lower than that in β-NQ···H_2O, while the that of $\rho_{\mathrm{BCP(O–H\cdots F)}}$ is larger than that in H_2O···β-NQ, indicating the weakened N–H···O while strengthened O–H···F H-bonding interactions upon the formation of ternary complex, leading to a little cooperativity effect, too. For III-1, although the values of $\rho_{\mathrm{BCP(N–H\cdots F)}}$, $\rho_{\mathrm{BCP(N–H\cdots O)}}$ and $\rho_{\mathrm{BCP(O–H\cdots N)}}$ are all lower than those in the corresponding binary systems, as mentioned above, it has the negative $E_{coop.}$ values. It should be noted that, the BCP criterion of AIM theory is too stringent, and the absence of a BCP should not necessarily be considered evidence as to the absence of a intermolecular interaction[59].

Surface electrostatic potential

The electrostatic potentials on the 0.001 a.u. molecular surfaces of the complexes are computed by the Multiwfn programs[60], utilizing the B3LYP/ 6-311++G(2df,2p) optimized geometries. The results are shown in Table 3 (see also Supplementary Data, Fig. S3).

Each of the ternary complexes has several surface minima, which are mainly associated with the lone pairs of the N, O and F, and the strongest is that of F (Fig. S3). The most negative values, i.e., the local minima ($V_{\mathrm{S,min}}$), are in the range between −37.1 and −48.4 kcal/mol. There are also several surface maxima ($V_{\mathrm{S,max}}$) with the H atom of the −OH and −NH groups

Table 3 — Electrostatic potentials on the 0.001 au molecular surfaces of the ternary complexes at the B3LYP/6-311++G(2df,2p) level

System	V_{max} (kcal/mol)	V_{min} (kcal/mol)	σ_+^2 (kcal/mol)^2	σ_-^2 (kcal/mol)^2	v	Π (kcal/mol)
I-1	49.8	−40.5	122.8	137.5	0.2492	16.7
I-2	64.3	−48.4	134.3	235.9	0.2312	20.8
I-3	67.2	−46.3	178.1	235.2	0.2452	18.9
II-1	62.3	−38.3	235.3	131.0	0.2297	14.5
II-2	63.6	−37.4	274.8	83.8	0.1790	15.1
III-1	69.7	−45.3	315.0	174.9	0.2296	18.9
III-2	62.6	−37.1	249.8	99. 7	0.2039	14.6

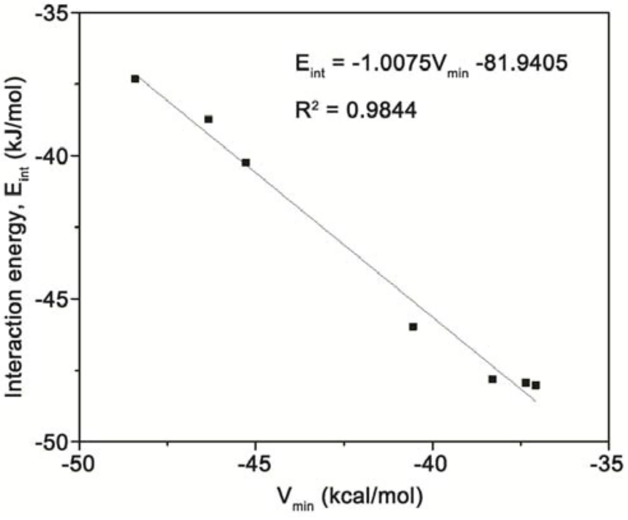


Fig. 3 — Correlation between the complexation energies ($E_{int.}$) and local minima of electrostatic potentials ($V_{S,min}$) of ternary complexes.

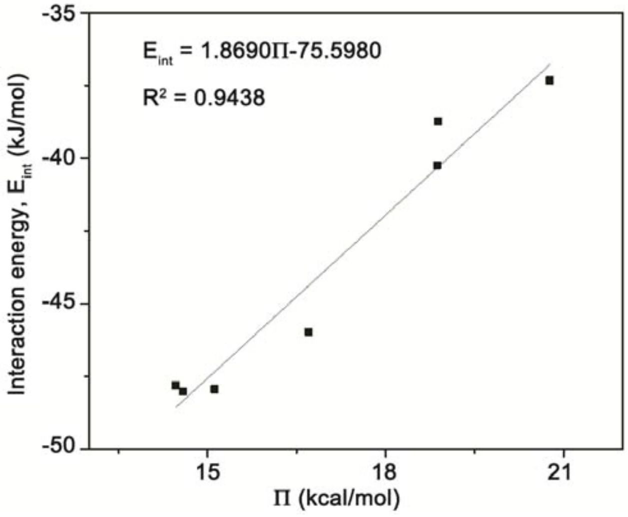


Fig. 4 — Correlation between the complexation energies ($E_{int.}$) and internal charge separation of electrostatic potentials (Π) of ternary complexes.

for each system. The highest is involved with the −NH (I-1, I-3, II-2 and III-2) or −OH group (I-2, II-1 and III-1) in the range of 49.8−69.7 kcal/mol.

The most positive or negative values of $V_{S,max}$ or $V_{S,min}$ correlate well with empirical measures of H-bond-donating and -accepting tendencies[61]. Therefore, in general, the most positive or negative values of $V_{S,max}$ or $V_{S,min}$ are often related to intermolecular interaction energies. Indeed, the correlation between the $V_{S,min}$ and complexation energies ($E_{int.}$) of ternary complexes is found (see Fig. 3) (correlation coefficient (R^2) = 0.9844) and fit the following equation,

$$E_{int.} = -1.0075\ V_{S,min} - 81.9405$$

where $V_{S,min}$ is in kcal·mol^{-1}, and $E_{int.}$ is obtained at the B3LYP/6-311++G(2df,2p) level (in kJ·mol^{-1}).

The relationship between the $E_{int.}$ and internal charge separation (Π) was also investigated (see Fig. 4). The correlation coefficient (R^2) was found to be 0.9438 and fitted the following equation,

$$E_{int.} = 1.8690\ \Pi - 75.5980$$

Further, a poor relationship (R^2=0.8906) is found between the $E_{int.}$ and negative variances of electrostatic potentials (σ_-^2).

While in previous literature[62], the relationship between the synergetic energies and electrostatic potentials has been observed, in this work, a good relationship between the cooperativity effects and surface electrostatic potentials was not found.

Conclusions

The H-bonding cooperativity effects in β-NQ···C_2F_4···H_2O ternary complex are investigated by the B3LYP and MP2(full) methods. The thermodynamic cooperativity effects are also evaluated at 298.15 K. The result shows that C_2F_4 can be effective as a wastewater treatment agent to remove β-NQ from wastewater. Weak cooperativity effect appears in the linear complex while notable anti-cooperativity effect is found in the cyclic system. The strengths of the H-bonding interactions are almost unaffected by each other upon the formation of the linear ternary complex. On the other hand, upon the cyclic ternary-complex formation, the influence of the N–H O or O–H F H-bonding interaction on the N–H F interaction is more pronounced than that of the N–H F interaction on the N–H···O or O–H F interaction. The enthalpy change is the major factor driving the cooperativity. There is no obvious correlation between the cooperativity effects evaluated by interaction energies and those from thermodynamic data. The complexation energies ($E_{\text{int.}}$) correlate well with the local minima of the surface electrostatic potential ($V_{\text{S,min}}$) or internal charge separation (Π).

It can be inferred from the perspective of intermolecular force that the wastewater treatment for explosive can be a process in which the coexisting intermolecular interactions mutually influence each other. In this process, the cooperativity effect plays an important role. When the cooperativity effect leads to an enhanced intermolecular interaction between the wastewater treatment agent and explosive, and simultaneously a weakened interaction between H_2O and explosive or wastewater treatment agent, the purpose of the wastewater treatment will be achieved. The wastewater treatment for explosive can also be a thermodynamic cooperativity process. When the thermodynamic cooperativity effect leads to a direction in which wastewater treatment agent can bind tighter to explosive, the purpose of the wastewater treatment will be achieved. This investigation will be useful to further select the wastewater treatment agent for explosive and eliminate effectively explosive from wastewater.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_57A(02) 150-162_SupplData.pdf.

References

1 Schmelling D C, Gray K A & Kamat P V, *Environ Sci Technol*, 30 (1996) 2547.
2 Shiva K & Allen P D, *Wat Envir Res*, 69 (1997) 1238.
3 Williford Jr C W & Bricka R M, *J Hazard Mater*, 66 (1999) 1.
4 Ye Z, Zhao Q, Zhang M & Gao Y, *J Hazard Mater*, 186 (2011) 1351.
5 Garcia-Raso A, Albertí F M, Fiol J J, Tasada A, Barceló-Oliver M, Molins E, Escudero D, Frontera A, Quiñonero D & Deyà P M, *Inorg Chem*, 46 (2007) 10724.
6 Estarellas C, Frontera A, Quiñnero D & Deyà P M, *Chem Phys Lett*, 479 (2009) 316.
7 Escudero D, Frontera A, Quiñnero D & Deyà P M, *Chem Phys Lett*, 456 (2008) 257.
8 Quiñonero D, Frontera A, Escudero D, Ballester P, Costa A & Deyà P M, *Theoret Chem Account*, 120 (2008) 385.
9 Vijay D & Sastry G N, *Chem Phys Lett*, 485 (2010) 235.
10 Meyer E A, Castellano R K & Diederich F, *Angew Chem Int Ed*, 42 (2003) 1210.
11 Silaghi-Dumitrescu L, Attia A A A, Silaghi-Dumitrescu R, Blake A J & Sowerby D B, *Inorg Chim Acta*, (2017), In Press, doi.org/10.1016/j.ica.2017.08.052.
12 Bakó I, Lábas A, Hermansson K, Bencsura Á & Oláh J, *J Mol Liq*, (2017), In press, dx.doi.org/10.1016/j.molliq.2017.08.023.
13 Ahmed M S & David G H, *Bioorg Med Chem Lett*, 26 (2016) 3850.
14 Mehdi D E & Soheila A, *J Mol Graph Model*, 64 (2016) 131.
15 Sotoodeh B, Hamid R M &Asmaa Y, *Comput Theoret Chem*, 1092 (2016) 12.
16 Zhou Y, Huang Y, Ma Z, Gong Y, Zhang X, Sun Y & Sun C Q, *J Mol Liq*, 221 (2016) 788.
17 McDowell S A C, *Chem Phys Lett*, 658 (2016) 12.
18 Zahra R, Mohammad S & Mehdi D E, *Comput Theoret Chem*, 1074 (2015) 101.
19 Laura A & Russell J B, *Comput Theoret Chem*, 1053 (2015) 328.
20 Zhang X, Sun P, Yan T, Huang Y, Ma Z, Zou B, Zheng W, Zhou J, Gong Y & Sun C Q, *Prog Solid State Ch*, 43 (2015) 71
21 Tang Q & Li Q, *Comput Theoret Chem*, 1050 (2014) 51
22 Jesus A J L & Redinha J S, *J Mol Struct*, 1067 (2014) 104.
23 Małgorzata D & Marcin P, *Comput Theoret Chem*, 1027 (2014) 173.
24 Pérez C, Zaleski D P, Seifert N A, Temelso B, Shields G C, Kisiel Z & Pate B H, *Angew Chem Int Ed*, 53 (2014) 14368.
25 Bhagwat K, Vinayak D & Ajay C, *J Mol Liq*, 186 (2013) 131.
26 Jesus A J L & Redinha J S, *Comput Theoret Chem*, 1023 (2013) 74.
27 Vijay D, Zipse H & Sastry G N, *J Phys Chem B*, 112 (2008) 8863.
28 Cera E D, *Chem Rev*, 98 (1998) 1563.
29 Whitesides G M & Krishnamurthy V M, *Q Rev Biophys*, 38 (2005) 385.
30 Willims D H, Stephens E, O'Brien D P & Zhou M, *Angew Chem Int Ed*, 43 (2004) 6596.
31 Jaroslav K & Jiří D, *J Phys Chem B*, 111 (2007) 6118.
32 Gupta R B & Brinkley R L, *AIChE J*, 44 (1998) 207.
33 Behrouzi R, Roh J H, Kilburn D, Briber R M & Woodson S A, *Cell*, 149 (2012) 348.
34 James F, Berry B, Nadezhda V K, Yegor D S, Emna M N P & Vladimir I P, *Biochemistry*, 50 (2011) 3609.
35 Jencks W P, *Proc Natl Acad Sci*, 78 (1981) 4046.
36 Andrea F & Jack G, *J Mol Biol*, 417 (2012) 454.
37 Zaitseva K V, Varfolomeev M A, Novikov V B & Solomonov B N, *J Chem Thermodyn*, 43 (2011) 1083.
38 Sedov I A & Solomonov B N, *Fluid Phase Equilibr*, 315 (2012) 16.
39 Xie J-B & Shi W-J, *Indian J Chem*, 53A (2014) 1359.
40 Hu L, Hu S & Cao X, *Cent Eur J Energy Mater*, 9 (2012) 261.

41 Hu L, Hu S & Cao X, *Cent Eur J Energy Mater*, 11 (2014) 157.

42 Hu L, Hu S, Cao X & Zhang J, *J Energy Mater*, 32 (2014) 27.

43 Xue Z, He J, Zhang J, Zhang X, Chen Y & Ren F, *J Mol Model*, 23 (2017) 346.

44 Wang W, Ren F, Bi Y & Wang W, *Chinese J Chem Phys*, 18 (2005) 765.

45 *Gaussian 03, Rev. D.01* (Gaussian, Inc., Wallingford CT) 2004.

46 Reed A E, Curtis L A & Weinhold F A, *Chem Rev*, 88 (1988) 899.

47 Zhu S, Zhang S, Gou R, Han G, Wu C & Ren F, *J Mol Model*, 23 (2017) 353.

48 Cabaleiro-Lago E M, Hermida-Ramón J M, Peña-Gallego A, Martínez-Núñez E & Fernández-Ramos A, *J Mol Struct (Theochem)*, 498 (2000) 21.

49 Solimannejad M, Malekani M & Alkorta I, *J Phys Chem A*, 114 (2010) 12106.

50 Zabardasti A, Zare N & Arabpour M, *Struct Chem*, 22 (2011) 691.

51 Zabardasti A, Kakanejadi A, Moosavi S, Bigleri Z & Solimannejad M, *J Mol Struct (THEOCHEM)*, 945 (2010) 97.

52 Kar T & Scheiner S, *J Phys Chem A*, 108 (2004) 9161.

53 Glendening E D, *J Phys Chem A*, 109 (2005) 11936.

54 Solimannejad M, Malekani M & Alkorta I, *J Phys Chem A*, 114 (2010) 12106.

55 Calderone C T & Williams D H, *J Am Chem Soc*, 123 (2001) 6262.

56 Nasief N N, Tan H, Kong J & Hangauer D, *J Med Chem*, 55 (2012) 8283.

57 Bader R F W. *Atoms in Molecules, A Quantum Theory*, (Oxford University Press, Oxford, UK) 1990.

58 B-König F W B, Bader R F W & Tang T H, *J Comput Chem*, 3 (1982) 317.

59 Lane J R, Contreras-García J, Piquemal J-P, Miller B J & Kjaergaard H G, *J Chem Theoret Comput*, 9 (2013) 3263.

60 Lu T & Chen F, *J Mol Graphics Model*, 38 (2012) 314.

61 Hagelin H, Brinck T, Berthelot M, Murray J S & Politzer P, *Can J Chem*, 73 (1995) 483.

62 Tian Q, Wang Y, Shi W, Song S & Tang H, *J Mol Model*, 19 (2013) 5171.