Theor Chem Acc (2010) 127:303–309
DOI 10.1007/s00214-009-0716-8

REGULAR ARTICLE

Ab initio study of the cooperativity between NH···N and NH···C hydrogen bonds in H_3N–HNC–HNC complex

Baoan Gong · Bo Jing · Qingzhong Li · Zhenbo Liu · Wenzuo Li · Jianbo Cheng · Qingchuan Zheng · Jiazhong Sun

Received: 21 September 2009 / Accepted: 2 December 2009

Abstract Ab initio calculations at the MP2/aug-cc-pVTZ level have been performed to study the cooperativity of hydrogen bonds in homoclusters (HNC–HNC–HNC and HNC–HNC–HNC–HNC) and heteroclusters (H_3N–HNC–HNC and H_3N–HNC–HNC–HNC). The cooperative energies in the HNC–HNC–HNC and H_3N–HNC–HNC trimers are –2.05 and –2.56 kcal/mol, respectively. The result shows that the cooperativity in the heterotrimer is larger than that in the homotrimer. A similar result also happens in the tetramers. The energy decomposition scheme indicates that orbital interaction is a major contribution to the cooperative energy of N···HN hydrogen bond, whereas the electrostatic and orbital interactions to that of C···HN hydrogen bond. The effect of HNC chain length on the strength of N···HN hydrogen bond has also been considered at the MP2/aug-cc-pVDZ level. It is indicated that the interaction energy of N···HN hydrogen bond trends to be a fixed value when the HNC number tends to be infinite, and the strength of N···HN hydrogen bond is regulated mainly through the electrostatic and polarization interactions although the charge transfer interaction also has an effect on it.

Keywords Hydrogen bond · Ab initio · Cooperativity · Energy decomposition · Hydrogen isocyanide

1 Introduction

Hydrogen bonds are one of the most important intermolecular interactions in many fields of chemistry, physics, and biology [1]. It has been shown that a string of several H-bonds exhibits a substantial amount of cooperativity. Each H-bond can affect the properties of others. Cooperativity effect plays a very important role in understanding the behavior in some chemical and biochemical systems [2]. Unfortunately, experimental studies of small H-bonded clusters have a difficulty in producing and analyzing such systems [3]. Ab initio calculations, however, can provide some useful information about the cooperativity. For example, 1:2 complexes (H_2O:$(HX)_2$, where X denotes F, Cl, Br, or I) were observed in inert matrices [4–7], but their structures were determined with the help of quantum chemical calculations [8, 9].

Hydrogen isocyanide (HNC) has been evidenced in low temperature rare gas matrixes [10] and interstellar space [11]. It is related with prebiotic organic synthesis [12], thus more attention has been paid to the structures and properties of its complexes. The equilibrium structure and hyperpolarizability of HNC dimer have been investigated with theoretical methods [13, 14]. Although experimental studies of HNC complexes are scarce [15], theoretical calculations have been performed for them.

The study of intermolecular interaction between H_3N and HNC molecules is significative because both molecules are connected with the formation of ancient organic compounds. Quantum chemical studies have succeeded in the description of 1:1 H_3N and HNC complexes [16, 17]. It

---

B. Gong (✉) · B. Jing · Q. Li (✉) · Z. Liu ·
W. Li · J. Cheng · Q. Zheng · J. Sun
The Laboratory of Theoretical and Computational Chemistry,
Science and Engineering College of Chemistry and Biology,
Yantai University, Yantai 264005, People's Republic of China
e-mail: gba@ytu.edu.cn

Q. Li
e-mail: liqingzhong1990@sina.com

Q. Zheng · J. Sun
State Key Laboratory of Theoretical and Computational
Chemistry, Institute of Theoretical Chemistry, Jilin University,
Changchun 130023, People's Republic of China

is shown that HNC can act as a proton acceptor rather than a proton donor. The interaction energy between them is –17.17 and –6.41 kJ/mol when HNC is the proton donor and acceptor, respectively. This shows that the ability of HNC proton donor is stronger than that of its proton acceptor. However, the trimer of $H_3N{:}(HNC)_2$ has not been focused with experimental and theoretical methods. The study of such trimer is helpful to understand the cooperativity of hydrogen bonds and its effect on the properties of the molecules.

In the present paper, we thus perform a study of the $H_3N{:}(HNC)_2$ complex with quantum chemical calculations. In order to get an insight into synergistic effects, calculations on the dimers and the individual monomers of which it is composed are also carried out with the same level of accuracy. The origin of the cooperativity is analyzed using energy decomposition scheme. We also consider the effect of HNC chain length on the strength of N···HN hydrogen bond.

2 Theoretical methods

The equilibrium structures of the complexes (H_3N–HNC, HNC–HNC, H_3N–HNC–HNC, HNC–HNC–HNC, H_3N–HNC–HNC–HNC, HNC–HNC–HNC–HNC, and H_3N–HNC–HNC–HNC–HNC) and corresponding monomers were optimized at the MP2/aug-cc-pVTZ level. This level of theory has been confirmed to adequately describe the hydrogen bonding interaction in H_3N–HNC [16] and HNC–HNC dimers [18]. The H_3N–$(HNC)_N$, where $N = 1$–8, clusters have also been calculated at the MP2/aug-cc-pVDZ level on consideration of calculation cost. The harmonic vibrational frequencies were then calculated at the same levels to assure the minimum nature of the monomers and complexes. The interaction energies of the dimers, $\Delta E_{AB} = E_{AB} - (E_A + E_B)$, have been calculated as the difference between the energy of the dimer and the total energy of the monomers. The interaction energies of molecular pairs in the higher polymers were calculated with a two-body approximation. The interaction energies were corrected for the basis set superposition error (BSSE) using the counterpoise correction method of Boys and Bernardi [19]. All calculations have been performed with Gaussian 03 program [20].

To elucidate the origin of the cooperativity of hydrogen bonds, the interaction energies were decomposed with the energy decomposition scheme in ADF program [21]. The big basis set of QZ4P with small core type was adopted here for the reliability of the results. The BLYP method with this basis set in ADF software was used because the interaction energies obtained with it are close to those with supermolecular method at the MP2 level.

3 Results and discussion

3.1 Synergistic effects

Figure 1 shows the optimized structures of the investigated complexes (H_3N–HNC, H_3N–HNC–HNC, H_3N–HNC–HNC–HNC, and H_3N–HNC–HNC–HNC–HNC). These complexes take on a linear structure of C_{3v} symmetry. Based on the fact that both H_3N and HNC can act as a proton donor and acceptor in formation of hydrogen bonds, thus H_3N–HNC dimer has two isomers. Considering the stronger proton donor of HNC molecule and the stronger electron donor of H_3N molecule, we only display a more stable isomer as shown in Fig. 1. When a second HNC molecule is added into this dimer, two trimers also exist. However, only one of which is presented due to the same reason. The interaction energy and cooperative energy in

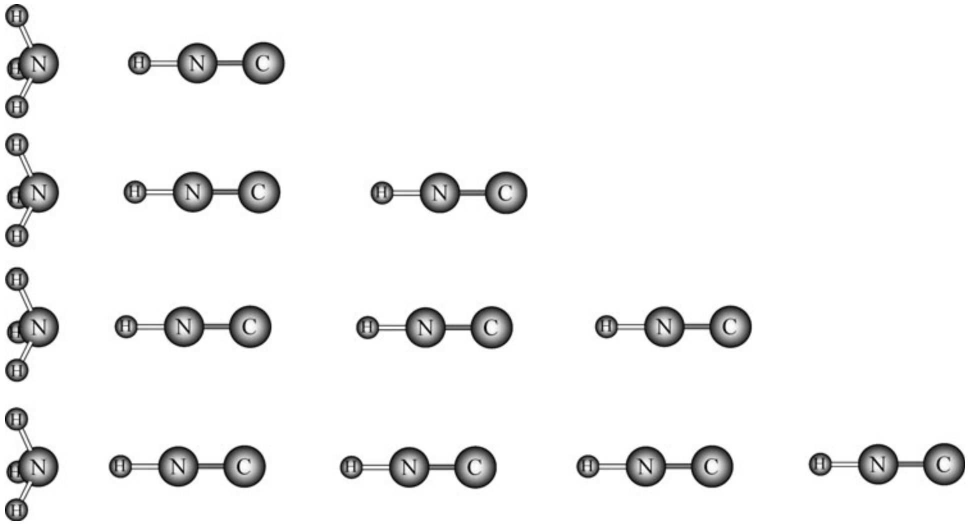

Fig. 1 Optimized structures of A–B2, A–B2–B3, A–B2–B3–B4, and A–B2–B3–B4–B5 complexes. A and B denote H_3N and HNC, respectively

these complexes are given in Table 1. For comparison, the corresponding parts in the HNC dimer, trimer, and tetramer are also presented in Table 1. For convenience, H_3N and HNC are denoted by A and B, respectively. A conventional hydrogen bond occurs between molecules A and B, whereas an unconventional hydrogen bond [22] is present among B molecules.

At the MP2/aug-cc-pVTZ level, all interaction energies were calculated according to the supermolecular method and corrected for BSSE. For example, for A–B2–B3 complex, $\Delta E_{\mathrm{A-B2}} = E_{\mathrm{A-B2-B3}} - (E_{\mathrm{A}} + E_{\mathrm{B2-B3}})$. The interaction energy is calculated to be –11.07 and –7.65 kcal/mol for the A–B2 and B2–B3 dimers, respectively. This result shows that A is a better electron donor than B. However, B exhibits far better proton donor ability than A when another B acts as an electron donor [17]. The interaction energy in the complex with B as a proton donor is more negative than that with B as a proton acceptor. This also supports the conclusion that the proton donor contributes more to the strength of a hydrogen bond [23].

In the A–B2–B3 heterotrimer, the interaction energy of the N···HN hydrogen bond is –14.41 kcal/mol, whereas that of the C···HN is –11.04 kcal/mol. With comparison to those in the respective dimers, the interaction energies in the A–B2–B3 trimer increase by about 30 and 44% for the N···HN and C···HN hydrogen bonds, respectively. It is consistent with the conclusion that the stronger hydrogen bond has a bigger effect on the weaker one [24]. This result gives us an idea that if we plan to increase the strength of a weak hydrogen bond, it should combined with a strong hydrogen bond. The interaction energies of the C···HN hydrogen bond is –9.70 and –10.47 kcal/mol for the B1–B2 and B2–B3 pairs, respectively, in the B1–B2–B3 homotrimer, which increase by about 27 and 37% related to that in the B dimer. This result further shows that molecule B often acts as a proton donor. The strength enhancement of the C···HN hydrogen bond is larger in the A–B2–B3 heterotrimer than that in the B1–B2–B3 homotrimer. This also illustrates the above idea of enhancing a hydrogen bond. Similar results happen in the homotetramer and heterotetramer. These results indicate that synergistic effect is also present between different types of hydrogen bonds in the heteroclusters.

For both homocluster $(\mathrm{B})_N$ and heterocluster A–$(\mathrm{B})_N$, where the subscript N represents the number of the B unit, the total binding energy of the polymers displays significant changes with expansion of the B unit. For the step $(\mathrm{B})_2 \rightarrow (\mathrm{B})_3 \rightarrow (\mathrm{B})_4$, the total interaction energy increases from –7.65 to –27.83 kcal/mol. In the case of the heterocluster, an increase of –10.20, –20.84, and –31.72 kcal/mol has been obtained for $(\mathrm{B})_2$, $(\mathrm{B})_3$, and $(\mathrm{B})_4$, respectively, as the cluster varies from A–B to A–$(\mathrm{B})_4$, showing that the clusters bond stronger and become more stable with the extendibility of the B unit.

The cooperative energy (E_{coop}) is applied here to evaluate the cooperativity of the hydrogen bonds in these systems. The cooperative energy is calculated as a difference between the total interaction energy in the polymer and the sum of interaction energy in the corresponding dimers. From Table 1, it is seen that the value of E_{coop} in the B1–B2–B3 trimer is –2.05 kcal/mol at the MP2/aug-cc-pVTZ level, which is very close to –2.06 kcal/mol at the MP2/6-311++g(d,p) level [25]. This result supports the conclusion that the sensitivity of H-bond cooperativity to basis set is surprisingly low [26]. The value of E_{coop} in the B1–B2–B3–B4 tetramer is –4.89 kcal/mol, which is about two times as that in the B1–B2–B3 trimer. The value of E_{coop} in the B trimer and tetramer amounts to about 12 and 17% of the total interaction energy, respectively. This shows that the cooperative energy contributes more to the stability of higher polymer.

When the marginal proton acceptor B1 in the B1–B2–B3 trimer is replaced with an A molecule, the cooperative energy is calculated to be –2.56 kcal/mol in the A–B2–B3 trimer. This value is larger than that in the corresponding homotrimer (–2.05 kcal/mol). A similar result happens in

Table 1 Interaction energies (ΔE, kcal/mol) and cooperative energy (E_{coop}, kcal/mol) in the investigated complexes calculated at the MP2/aug-cc-pVTZ level

	A–B2–B3	A–B2–B3–B4	A–B2–B3–B4–B5	B1–B2–B3	B1–B2–B3–B4
ΔE_{AB2}	−14.41 (−11.07)	−16.23	−17.55		
ΔE_{B1B2}				−9.70	−12.14
ΔE_{B2B3}	−11.04 (−7.65)	−14.83	−16.92	−10.47	−14.10
ΔE_{B3B4}		−12.37	−16.42		−12.15
ΔE_{B4B5}			−13.55		
$\Delta E_{\mathrm{total}}$	−21.27	−31.91	−42.79	−17.35	−27.83
E_{coop}	−2.56	−5.55	−8.78	−2.05	−4.89

All energies were corrected for BSSE. Values in parentheses are from the dimers. The interaction energies between the two pairs are calculated with the supermolecular method. The cooperative energy is calculated by subtracting the sum of the interaction energy of the corresponding dimers from the total interaction energy of the polymer. A and B denote H_3N and HNC, respectively the A–B2–B3–B4 and B1–B2–B3–B4 tetramers, in which the cooperative energies are –5.55 and –4.89 kcal/mol, respectively. These results are consistent with the conclusion that the cooperativity is more prominent between different types of hydrogen bonds than that between the same types of hydrogen bonds [18, 24, 28]. The proportion of E_{coop} to the total interaction energy is about 12 and 17% in the heterotrimer and heterotetramer, respectively. This proportion in the heteroclusters is close to that in the homoclusters. Although the cooperativity is more prominent in heterocluster, the contribution of cooperative energy to the total interaction energy is similar in heterocluster and homocluster, at least in the clusters presented here. If the number of B molecule in the heterocluster increases continuously, such as A–B2–B3–B4–B5 polymer, the value of E_{coop} also grows (–8.78 kcal/mol). This value amounts to more than three times as much as that in the A–B2–B3 trimer. It corresponds to about 20% of the total interaction energy. Analyzing the change of E_{coop} proportion to the total interaction energy with the increase of B molecule, it can be found that the average contribution of each B molecule decreases.

The frequency shift in infrared spectroscopy is also a useful tool for the characterization of hydrogen-bonded cluster. Here, we just investigate the NH stretching vibration in the proton donor HNC molecule. The results are given in Table 2. As expected, the NH stretching vibration in all complexes has a red shift upon complexation. The red shift of NH stretch frequency is 670 cm^{-1} in the A–B2 dimer, which is two times more than that in the B2–B3 dimer (314 cm^{-1}). The result is consistent with the interaction energies in both dimers. Upon trimeration, the red shift increases, indicating there is a cooperativity of hydrogen bonds in these trimers. The increase of the red shift in the A–B2–B3 trimer is larger than that in the B1–B2–B3 trimer. The red shift for B2 NH stretch frequency is increased by 223 cm^{-1} when it is from the A–B2 dimer to the A–B2–B3 trimer. This red shift from the addition of B3 as the proton donor is far smaller than that from the contribution of A as the electron donor. The result supports the conclusion that the electron donor plays a more important role in the cooperativity of hydrogen bond [25].

3.2 Energy decomposition

Kar and Scheiner [26] thought that cooperativity is typically attributed in large degree to the polarization induced in each subunit by the presence of its H-bonding partner. However, King and Weinhold [27] studied the cooperative effects of the B trimer and tetramer using second-order Møller–Plesset method and suggested that most of the cooperativity arises from the donor–acceptor ($n_N \rightarrow {}_{CH}*$) electron density transfer in the C–H···N bonding. In order to unveil the origin of the hydrogen bonding cooperativity, the interaction energies in these complexes were decomposed into electrostatic interaction energy (E_{elstat}), Pauli repulsion energy (E_{Pauli}), and orbital interaction energy (E_{oi}). The term E_{elstat} corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the molecules. The Pauli repulsion energy, E_{Pauli}, comprises the destabilizing interactions between occupied orbitals. The orbital interaction energy, E_{oi}, accounts for charge transfer (i.e., donor–acceptor interactions between occupied orbitals on one moiety with unoccupied orbitals of the other) and polarization (empty/occupied orbital mixing on one fragment due to the presence of another fragment). The energy decomposition was performed on the equilibrium geometries obtained at the MP2/aug-cc-pVTZ level with BLYP/QZ4P (small core) in the ADF program. The results are shown in Table 2. The steric interaction energy (E_{steric}) is the sum of E_{elstat} and E_{Pauli}, and the interaction energy (ΔE_{int}) is the sum of E_{elstat}, E_{Pauli}, and E_{oi}. It can be seen from the table that the values of E_{elstat} and E_{oi} are negative, while that of E_{Pauli} is

Table 2 Frequency shifts ($\Delta \nu$, cm^{-1}) of NH stretching vibration in the proton donor calculated at the MP2/aug-cc-pVTZ level and energy components (kcal/mol) of the interaction energies in the complexes

	B2–B3	B1–B2–B3		A–B2	A–B2–B3	
		B1–B2	B2–B3		A–B2	B2–B3
E_{elstat}	−10.22	−12.56 (23%)	−13.20 (29%)	−18.54	−22.33 (20%)	−14.18 (39%)
E_{Pauli}	9.94	12.01 (21%)	12.37 (24%)	20.54	25.18 (23%)	13.24 (33%)
E_{oi}	−5.99	−7.90 (32%)	−7.63 (27%)	−12.18	−16.18 (33%)	−8.19 (37%)
E_{steric}	−0.28	−0.55 (96%)	−0.83 (196%)	2.01	2.84 (41%)	−0.94 (236%)
ΔE_{int}	−6.27	−8.45 (35%)	−8.46 (35%)	−10.17	−13.34 (31%)	−9.13 (46%)
$\Delta \nu_{HN}$	−314	−443, −395		−670	−893	−444

$E_{steric} = E_{elstat} + E_{Pauli}$ and $\Delta E_{int} = E_{elstat} + E_{Pauli} + E_{oi}$. Values in parentheses indicate the increase percentage of interaction components in the trimers relative to the corresponding dimers. The energy decomposition was performed at the BLYP/QZ4P level on the MP2/aug-cc-pVTZ geometries. For B1–B2–B3 trimer, the NH symmetric and antisymmetric stretching frequencies of two proton donor B molecules are listed. The NH stretch frequency is 3,818 cm^{-1} in the isolated B molecule. A and B denote H_3N and HNC, respectively positive in these complexes. The negative values of E_{elstat} and E_{oi} indicate that they play a positive contribution to the stability of the complexes, whereas the positive E_{Pauli} means that its contribution is negative. The sum of E_{elstat} and E_{oi} is larger in absolute than E_{Pauli}, and thus these complexes are stable.

In the B2–B3 dimer, the ratio of E_{elstat} to E_{oi} is about 1.71. This value indicates that the electrostatic interaction makes a main contribution to the C···HN hydrogen bond although the contribution from the orbital interaction is also important. As a B1 molecular as a proton acceptor is inserted into the B2–B3 dimer, the interaction energies of the B1–B2 and B2–B3 pairs in the B1–B2–B3 trimer increase by about 35% relative to that of the B2–B3 dimer. The E_{elstat} value in the B2–B3 pair is larger than that in the B1–B2 pair, whereas E_{oi} value in the B2–B3 pair is smaller than that in the B1–B2 pair. For the B1–B2 pair in the trimer, E_{elstat} and E_{oi} increase by 23% and 32%, respectively. For the B2–B3 pair in the trimer, the two terms increase by 29 and 27%, respectively. The increase percentage of the two terms is close to each other, and thus the cooperative energy in the trimer results from the combined effect of the electrostatic and orbital interactions.

In the A–B2 dimer, the ratio of E_{elstat} to E_{oi} is about 1.52, which is smaller than that in the B2–B3 dimer. It means that the orbital interaction plays a major role in the A–B2 dimer than in the B2–B3 dimer. This conclusion supports the fact that molecule A is a stronger electron donor. For the A–B2 and B2–B3 pairs in the A–B2–B3 heterotrimer, the interaction energy increases by 31 and 46%, respectively. The values of E_{elstat} and E_{oi} are larger in the A–B2 pair than those in the B2–B3 pair. For the A–B2 pair in the trimer, the increase percentage of E_{oi} is 1.65 times as much as that of E_{elstat}. For the B2–B3 pair in the trimer, however, the increase percentage of E_{oi} is close to that of E_{elstat}. The results show that the orbital interaction plays a major contribution to the increase in interaction energy of the N···HN hydrogen bond, whereas the electrostatic and orbital interactions are responsible for the C···HN hydrogen bond. The same reason can be used to understand the reason that the strength of the B2–B3 pair in the heterotrimer is stronger than that in the homotrimer.

The steric interaction energy, E_{steric}, can be considered as the sum of E_{elstat} and E_{Pauli}. From Table 2, it can be seen that the value of E_{steric} is positive for the C···HN hydrogen bond but negative for the N···HN hydrogen bond. Negative E_{steric} means that the contribution of electrostatic interaction is larger than that of Pauli repulsive interaction, whereas positive E_{steric} indicates that the contribution of Pauli repulsive interaction is larger than that of the electrostatic interaction. The positive E_{steric} further shows the importance of orbital interaction in the formation of C···HN hydrogen bond.

3.3 Effect of HNC chain length on the strength of N···HN hydrogen bond

From Table 1, it is seen that the interaction energy of N···HN hydrogen bond increases from A–B2 dimer to A–B2–B3–B4–B5 complex. Thus two questions arise: (1) how much is the effect of B chain length on the strength of N···HN hydrogen bond; and (2) how this effect happens. To answer these questions, we optimized the structures of A–(B)$_N$, where $N = 1$–8, complexes at the MP2/aug-cc-pVDZ level. The subscript N denotes the number of B molecule in the complex. The interaction energy of N···HN hydrogen bond in these complexes is decomposed into three parts, E_{elstat}, E_{Pauli}, and E_{oi}, which is performed with BLYP/QZ4P (small core) method on the MP2/aug-cc-pVDZ geometry. The results are summarized in Table 3.

From Table 3, it is seen that the interaction energy (ΔE_{int}) of N···HN hydrogen bond is enhanced with increase in the number of B molecule. The interaction energy difference of N···HN hydrogen bond between the two adjacent complexes decreases with increase in the B number. For example, it is –1.36 kcal/mol between A–(B)$_2$ and A–(B)$_3$ complexes, whereas it is –0.15 kcal/mol between A–(B)$_6$ and A–(B)$_7$ complexes. This result means that the interaction energy of N···HN hydrogen bond trends to be a fixed value when the B number tends to be infinite. To obtain this value, we constructed Fig. 2 by plotting the interaction energy of the N···HN hydrogen bond versus $1/N$ where N refers to the number of B molecule. A linear relationship is found between them. By extrapolating the line to $1/N = 0$, a maximum (–16.93 kcal/mol) of the interaction energy of N···HN hydrogen bond is obtained. The above analyses show that the strength of N···HN hydrogen bond is affected the most by the first B molecule added to A–(B)$_1$ dimer, whereas this influence is minuscule when the added B number is larger than 3. This result indicates that

Table 3 Ineteraction energy components (kcal/mol) of N···HN hydrogen bond in the A–(B)$_N$ clusters, where $N = 1$–8

	E_{elstat}	E_{Pauli}	E_{oi}	ΔE_{int}
A–(B)$_1$	−18.63	20.70	−12.54	−10.47
A–(B)$_2$	−22.58	25.57	−16.83	−13.84
A–(B)$_3$	−24.09	27.55	−18.66	−15.20
A–(B)$_4$	−24.75	28.41	−19.50	−15.83
A–(B)$_5$	−25.09	28.87	−19.94	−16.16
A–(B)$_6$	−25.19	28.94	−20.06	−16.31
A–(B)$_7$	−25.38	29.26	−20.34	−16.46
A–(B)$_8$	−25.43	29.33	−20.41	−16.52

The decomposition of interaction energy was carried out with BLYP/QZ4P (small core) method on the MP2/aug-cc-pVDZ geometry: $\Delta E_{\mathrm{int}} = E_{\mathrm{elstat}} + E_{\mathrm{Pauli}} + E_{\mathrm{oi}}$. A and B denote H_3N and HNC, respectively

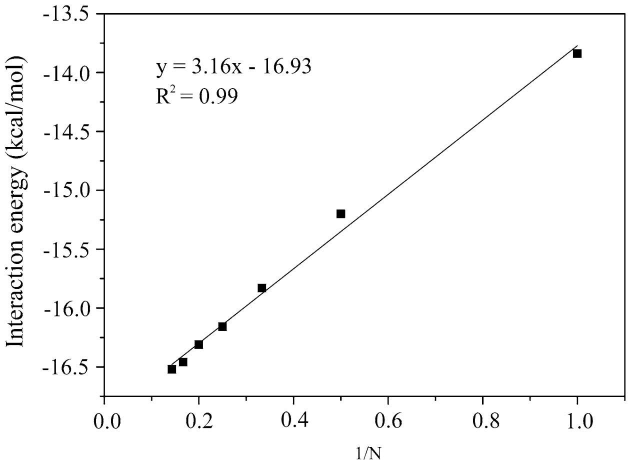

Fig. 2 Relationship of the interaction energy of N···HN hydrogen bond with 1/*N*, where *N* is the number of B molecule in A–$(B)_N$ clusters. A and B denote H_3N and HNC, respectively

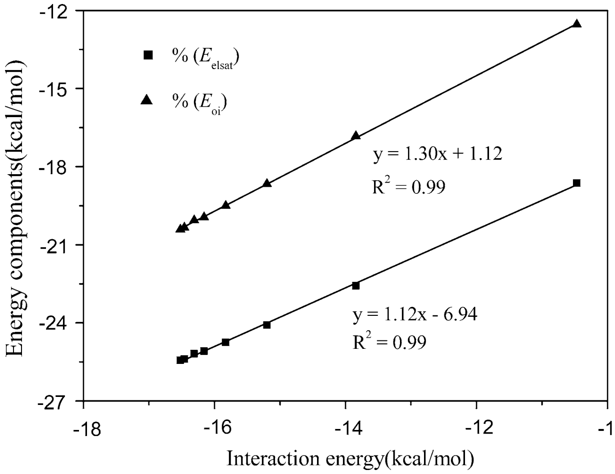

Fig. 3 Relationship of the interaction energy with E_{elstat} and E_{oi}

electrostatic induction interaction plays a dominant role in enhancing the strength of N···HN hydrogen bond. This conclusion can be further validated through analyzing the change of the components of the interaction energy, which was decomposed with ADF program. Figure 3 shows the relationship of the interaction energy with E_{elstat} and E_{oi}. Clearly, their relationship is linear which indicates that the change of E_{elstat} and E_{oi} is similar to that of the interaction energy. The term E_{oi} accounts for charge transfer and polarization [29], and thus the strength of N···HN hydrogen bond is regulated mainly through the electrostatic and polarization interactions although the charge transfer interaction also has an effect on it. This conclusion is consistent with the nature of N···HN hydrogen bond in A–B dimer obtained according to symmetry-adapted perturbation theory (SAPT) [16].

4 Conclusions

The $(HNC)_N$ and H_3N–$(HNC)_N$ complexes have been studied with quantum chemical calculations. The results show that a larger cooperativity exists in the heterocluster than in the homocluster. According to the analysis of the energy decomposition, the cooperative energy of N···HN hydrogen bond is mostly contributed from the orbital interaction, while for the C···HN hydrogen bond the emergence of cooperative energy is mainly attributed to the electrostatic and orbital interactions. Based on the analysis of the interaction energy of N···HN hydrogen bond, it is found that the interaction energy of N···HN hydrogen bond trends to be a fixed value when the HNC number tends to be infinite, and the strength of N···HN hydrogen bond is dominated mainly through the electrostatic and polarization interactions although the charge transfer interaction also has an effect on it.

Acknowledgments This work was supported by the National Natural Science Foundation of China (grant no. 20973149) and in part by open project of State Key Laboratory of Supramolecular Structure and Materials (SKLSSM200909) from Jilin University, China.

References

1. Jeffrey GA (1997) An introduction to hydrogen bonding. Oxford University Press, New York
2. Cabaleiro-Lago EM, Rios MA (1999) J Phys Chem A 103:6468
3. Gaw JF, Yamaguchl Y, Vincent MA, Schaefer HF (1984) J Am Chem Soc 106:3133
4. Andrews L, Johnson GL (1983) J Chem Phys 79:3670
5. Ayers GP, Pullin ADE (1976) Spectrochim Acta A 32:1641
6. Engdahl A, Nelander B (1986) J Phys Chem 90:6118
7. Hannachi Y, Schriver L, Schriver A, Perchard JP (1989) Chem Phys 135:285
8. Hannachi Y, Silvi B, Bouteiller JY (1992) Chem Phys 97:1911
9. Kreissler M, Lavialle L, Boggio-Pasqua M, Hannachi Y (1998) J Mol Struct 542:55
10. Milligan DE, Jacox ME (1967) J Chem Phys 47:278
11. Brown RD, Godfrey PD, Storey JWV, Clark FO (1976) Nature 262:672
12. Liebman SA, Pesce-Rodriguez RAP, Mattews CN (1994) Adv Space Res 15:71
13. Wang ZX, Zhang JC, Wu JY, Cao WL (2007) J Mol Struct 806:239
14. Wang BQ, Li ZR, Wu D, Hao XY, Li RJ, Sun CC (2004) J Phys Chem A 108:2464
15. Meot-Ner M, Speller CV (1989) J Phys Chem 933:663
16. Wang CX, Zhang JC, Cao WL (2007) Chem J Chin Univ Chin 2:320
17. Alkorta I, Rozas I, Elguero J (1998) Theor Chem Acc 99:116
18. Li QZ, An XL, Luan F, Li WZ, Gong BA, Cheng JB, Sun JZ (2008) J Chem Phys 128:154102
19. Boys SF, Bernardi F (1970) Mol Phys 19:553
20. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA Jr, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R,

Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA (2003) Gaussian 03, Revision E.03. Gaussian, Inc., Pittsburgh, PA

21. ADF2008.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands. http://www.scm.com
22. Cubero E, Orozco M, Hobza P, Luque FJ (1999) J Phys Chem A 103:6394
23. Bian L (2003) J Phys Chem A 107:11517
24. Li QZ, An XL, Gong BA, Cheng JB (2007) J Phys Chem A 111:10166
25. Li QZ, Liu ZB, Cheng JB, Li WZ, Gong BA, Sun JZ (2009) J Mol Struct 896:112
26. Kar T, Scheiner S (2004) J Phys Chem A 108:9161
27. King BF, Weinhold F (1995) J Chem Phys 103:333
28. Li QZ, Hu T, An XL, Gong BA, Cheng JB (2008) Chemphyschem 9:1942
29. Guerra CF, van der Wijst T, Bickelhaupt FM (2005) Struct Chem 16:211