TẠP CHÍ KHOA HỌC
TRƯỜNG ĐẠI HỌC QUY NHƠN

Một cách nhìn mới về phản liên kết hydro C-H···N trong các phức của chloroform với hydrogen cyanite và dẫn xuất fluoride

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TÓM TẮT

Các tương tác không cộng hóa trị của liên kết hydro trong các phức của chlorofrom với hydrogen cyanite và dẫn xuất fluoride đã được nghiên cứu kỹ bằng cách quét bề mặt năng lượng thế năng. Các phức của cả hai hệ thống được nghiên cứu cho kết quả đều thuộc liên kết hydro chuyển dời xanh khi đạt cấu trúc hình học bền. Tất cả các hệ thống đều trải qua sự rút ngắn liên kết C-H khi ở khoảng cách xa. Ở khoảng cách N···H cụ thể, liên kết C-H của phân tử $CHCl_3$ trong các phức chất với FCN có xu hướng chuyển dời xanh nhiều hơn so với liên kết hydro trong phức $CHCl_3$···HCN. Các phân tích SAPT2+ cho thấy tương tác tĩnh điện là thành phần chính giúp ổn định liên kết hydro C-H···N, nhưng không xác định được sự chuyển dời xanh của tần số kéo dài C-H sau khi tạo phức. Đáng chú ý, kết quả thu được cho thấy lực phân tán đóng vai trò quan trọng trong việc kiểm soát sự chuyển của liên kết hydro.

Từ khóa: *Liên kết hydro, chuyển dời xanh, phân tán, tĩnh điện, SAPT2+.*

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An insight into improper hydrogen bond of C-H···N type in complexes of chloroform with hydrogen cyanide and its flouro derivative

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ABSTRACT

Non-covalent interactions in term of hydrogen bond in complexes of chloroform with hydrogen cyanide and its fluoride derivative were investigated thoroughly by scanning the potential energy surface. The complexes of both examined systems show blue-shift at their most stable geometries. All of systems experience the contraction in C-H bond length at long distances. At specific R_{N-H} distance, the C-H bond of $CHCl_3$ molecule in complexes with FCN tends to be more blue-shifted than one in connection with HCN counterpart. The SAPT2+ analyses reveal that electrostatic interaction is the major component which stabilizes the C–H···N hydrogen bond, but does not determine the blue shift of C-H stretching frequency following complexation. Remarkably, the obtained results show that the dispersion force plays a crucial role in controlling the shifting of the hydrogen bond.

Keywords: *Hydrogen bond, blue-shift, dispersion, electrostatic, SAPT2+.*

1. INTRODUCTION

Hydrogen bond (H-bond) is inevitably a crucial non-covalent interaction acquiring massive attention during the past decades. In standard textbooks,[1-3] the bond is usually represented in the form of A-H···B. A is an atom or a group whose ability is to draw electron density from the hydrogen atom, and A-H plays as a proton donor, while B is a fragment with excessive electron cloud served as a proton acceptor. Initially, H-bond was characterized by an A-H lengthening, concomitant red-shift in its frequency and an enhancement in IR intensity. There are two well-recognized fashions which can thoroughly explain the underlying mechanism of such bond. The first explanation is based on the effect of the electrostatic component in the presence of B,[4,5] while the alternative is developed on the contribution of charge transfer effect from B to A-H bond.[6-11]

However, the controversial debates have been triggered since the discovery of another type of interaction which bears totally opposite features than the above-mentioned bond. This interaction, which was later named improper or blue-shifting hydrogen bond, is associated with a contraction in A-H bond length, an increase in its stretching vibrational frequency and a decrease in spectroscopy intensity.[12-17] Up to now, although there have been a number of proposed arguments

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in order to explain the origin of this H-bond, no interpretation achieves consensus among scientists universally. Some authors proposed that the blue-shifting effect was derived from the reorganization of the host molecule. Such restructuring can be consequences of the charge transfer contribution,[13] or the rehybridization.[18] Meanwhile, others managed to justify the nature of H-bond as a balance of opposing interactions.[19, 20] For a long time, our group has pursued another way of explanation for this bond of interest. Among hydrogen bonded systems, we have paid more attention to the interactions of C-H donors with various proton acceptors. This is due to the fact that C-H type hydrogen bond is of great importance in biological systems;[21-23] gaining understanding about them, thus, can pave the way for having more insight into our bodies. Moreover, this type of H-bond is categorized into the pro-improper donor, according to Joseph and Jemmis,[20] whose shifts in C-H bond strongly depend on the nature of proton acceptors. In our article published in 2017,[24] we found that the stabilities of the complexes are influenced by the gas phase basicity of the donor,[24] and the polarization of the C-H bond. Specifically, the majority of the interactions between halofrom and acceptor proton Y are CHF_3 for blue-shifted hydrogen bond while $CHBr_3$ gives mainly red-shifted hydrogen bond. As for $CHCl_3$ gives both of H-bond types, therefore the polarity of the C-H bond in the CHX_3 monomers increases in substituted order of X in going to from F to Cl and then to Br. Thus, we carried out fixing the distance N···H and optimized the geometric parameters of the complexes. Besides, for a specific donor, the basicity is directly associated with the change in C-H bond length. Therefore, we held a belief that as the dependence of C-H bond length on the Lewis base's origin was clarified, they must be interactions from the acceptor, not internal changes in donor's structure, controlling the shift of the C-H covalent bond. It prompted a need to investigate the role of single interactions that contribute to the stability of a dimer upon complexation.

In the above study and another previous work,[25] we conducted SAPT calculations in order to decompose the total interaction energy into four physically meaningful forces, namely electrostatic, dispersion, induction, and exchange. This way of analysis has been proved to provide reliable energy decomposition results.[26] Furthermore, we reported some significant comments on the role of energy components to H-bond, especially the importance of dispersion in blue-shifting systems.[25] Hence, in this work, we utilized SAPT as a productive tool to examine the change in contributions of these interactions during the complex formation comprehensively and expected to shed light on the nature of blue-shifting hydrogen bond.

2. COMPUTATIONAL DETAILS

All the *ab initio* calculations were performed by the Gaussian 09 package.[27] For the purpose of the present work, we constrained the distance between a proton donor and an acceptor R_{N-H} (R_{N-H} = 1.7 – 3.5 A) and the C_{3v} symmetry. The remaining parts of complexes were optimized at MP2/6-311++G(3df,2pd) level of theory. Stretching frequencies are calculated at the same level in order to investigate the shift of C-H bond's stretching frequency. Single point energy (SPE) and basis set superposition error (BSSE) via the counterpoised correction of Boys and Bernadi[28] for all the monomers and complexes are obtained at the CCSD(T)/6-311++G(3df,2pd)//MP2/6-311++G(3df,2pd) level. Interaction energies are estimated as the difference in energy between complexes and their fragments, corrected for both of ZPE and BSSE (ΔE*). Topological parameters of complexes at the bond critical points (BCPs) were computed using the AIM2000 software.[29]

The SAPT2+ calculations for the complexes were applied with the aug-cc-pVDZ basis set using Psi4 software.[30] The total intermolecular interaction energy was separated into five fundamental components which are so-called electrostatic (E_{elst}), dispersion (E_{disp}), induction (E_{ind}), exchange (E_{exch}) and δE^{HF}, where δE^{HF} contributing to the interaction energy includes all third and higher-order induction and exchange-induction terms. The total intermolecular interaction energy is calculated as shown in equation:

$$E_{SAPT2+} = E_{elst} + E_{ind} + E_{exch} + E_{disp} + \delta E^{HF} (1)$$

III. RESULTS AND DISCUSSION

3.1. Changes of the C-H bond length and its stretching frequency

The changes in C-H bond length and the corresponding stretching frequency in the two complex systems are presented in Table 1. The Δr value is negative at large separation and decreases until the minimum is reached, then increases to positive ones, indicating that the C-H shortening occurs over the long distances and the elongation occurs at short range. The change of its stretching frequency further supports this observation as Δν value is positive at large distances and gradually increases until reaching its maximum value and then decreases to negative values. The shift from blue- to red-shifting when the proton acceptor comes closer is similar to some previous studies.[20, 31, 32]

Table 1. Changes in bond length (Δr(C-H), in Å), stretching vibrational frequency (ΔνC-H in cm^{-1}) of the C–H bond and the interaction energy corrected by both ZPE and BSSE (ΔE* ($kJ.mol^{-1}$))

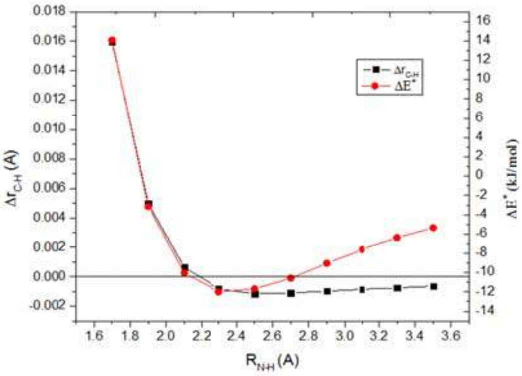
R_{N-H} (Å)	$CHCl_3\cdots NCH$			$CHCl_3\cdots NCF$		
	Δr(C-H)	Δν(C-H)	ΔE*	Δr(C-H)	Δν(C-H)	ΔE*
1.7	0.01599	-138.53	14.07	0.01412	-112.05	15.02
1.9	0.00497	-28.08	-3.15	0.00402	-14.30	-2.28
2.1	0.00063	12.24	-10.04	0.00014	19.40	-9.11
2.3	-0.00083	21.43	-12.00	-0.00107	25.07	-11.09
2.5	-0.00115	19.3	-11.68	-0.00126	21.06	-10.82
2.7	-0.00110	15.18	-10.57	-0.00116	15.97	-9.74
2.9	-0.00097	12.04	-9.04	-0.00100	12.97	-8.30
3.1	-0.00085	10.09	-7.61	-0.00087	10.26	-6.96
3.3	-0.00075	8.77	-6.38	-0.00076	8.92	-5.80
3.5	-0.00064	7.62	-5.36	-0.00067	7.80	-4.85

Table 1 shows that, at long distances, the C-H bond in $CHCl_3\cdots NCF$ decreases much more than that of the NCH, and also fewer increases at short range. Specifically, the contraction of the C-H bond in $CHCl_3$ increases from 0.00067 Å to 0.00126 Å when interacting with FCN. These values are about 0.00004-0.00023 Å more than those of the remaining system, where the C-H bond is shortened *ca.* 0.00064-0.00115 Å. In both systems, the C-H bond lengths reach minima at R_{N-H} = 2.5 Å. The complexes, then, exhibit increases in C-H bond lengths when the acceptor comes closer. The $CHCl_3\cdots NCH$ system shows an increase at *ca.* 0.00024-0.00187 Å more than the $CHCl_3\cdots NCF$ system. Overall, the blue shift is more preferred in the FCN system as compared to the HCN one. The level of contraction and elongation of C-H length bond is different, when the complexes are formed by the electrostatic energy and the ability to electron density transfer from n(N) lone pair to the σ*(C-H) orbital. Both of factors depend on the increase of the gas phase basicity at the N site of these proton acceptors. Indeed, we calculated the proton affinities at N sites in two acceptors at CCSD(T)/6-311++G(3df,2pd)//MP2/6-311++G(3df,2pd) and the obtained results show that the PA values at N sites in FCN (679 $kJ.mol^{-1}$) is smaller than that in HCN (700 $kJ.mol^{-1}$).

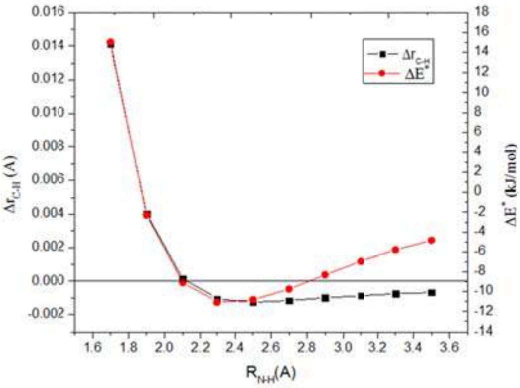
3.2. Interaction energy, and its relation with N···H intermolecular distance

The interaction energies taken into account both ZPE and BSSE (ΔE*) calculated at the CCSD(T)/6-311++G(3df, 2pd)//MP2/6-311++G (3df, 2pd) level are also gathered in Table 1. In general, the interaction energies lie in the range from -5.36 to -12 kJ.mol^{-1} and from -4.85 to -11.09 kJ.mol^{-1} corresponding to the interactions of HCN and FCN with $CHCl_3$. At the N···H distance is 2.3 Å which the interaction energies are the most negative for the two complexes.

In order to clearly see the relationship between the changes in the C-H bond length and the interaction energy, we plot correlations as shown in Figure 1. The most stable complexes experience blue-shifting with the intermolecular distance between the proton donor and proton acceptor to be in the range of 2.1 – 2.3 Å. Flexible optimization results at MP2/6-311++G(3df,2pd) level confirm this observation. Specifically, at the equilibrium geometries, the distance of N···H contacts is 2.21 Å in $CHCl_3$···NCH and $CHCl_3$···NCF dimers. This result is in accordance with a recent study investigating the interaction of two molecules in the Ar matrix.[33]



$CHCl_3$···NCH



$CHCl_3$···NCF

Figure 1. Relationship between the interaction energies and Δr(C-H) in the complexes: $CHCl_3$···HCN and $CHCl_3$···FCN

Additional examination on the effect of the interaction energy on the shift from blue- to red- shifting. We make a comparison based on the value of interaction energies among the checked systems as presented in Figure 2. Figure 2 indicates that the interaction energies are negative when the N···H distances are in the range of 1.9 ÷ 3.5 Å and they get the positive values with R_{N-H} smaller than 1.9 Å. Namely, the interaction energies decrease until reaching its minimum value at long distance and then gradually increase at short range when the N···H distance continues decreasing. On the other hand, at the same distance, the durability of the $CHCl_3$···FCN complexes is smaller than the $CHCl_3$···HCN complexes, which is consistent with previous reports.[24, 34-36] The difference in the stability of the two systems can be due to the higher gas-phase basicity of HCN, whose effect was proposed in our previous study.[24]

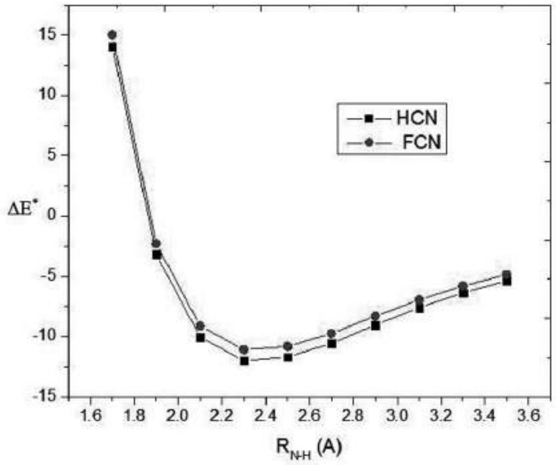


Figure 2. Comparison of the interaction energy between two systems

3.3. AIM analysis

In an attempt to further understand the properties of C-H···N hydrogen bond in the complexes, we carried out QTAIM analysis for the complexes at MP2/6-311++G(3df,2pd). Results of topological geometries as given in Table 2 show that the bond critical point (BCP) appears at a very long distance. In general, when XCN comes closer to $CHCl_3$, the electron density at the BCP of N···H contact in each system rises linearly in the range of 0.0010-0.0519 au. There is virtually no significant difference in the electron density at the BCP of the intermolecular contact in the two systems with the same N···H distance. Nevertheless, for the alike N···H distance the electron density at BCP of N···H contact is slightly larger for $CHCl_3$···NCH than $CHCl_3$···NCF.

Table 2. The topological parameters at BCPs of the N···H contacts at MP2/6-311++G(3df.2pd) and the individual hydrogen bond energy (E_{HB})

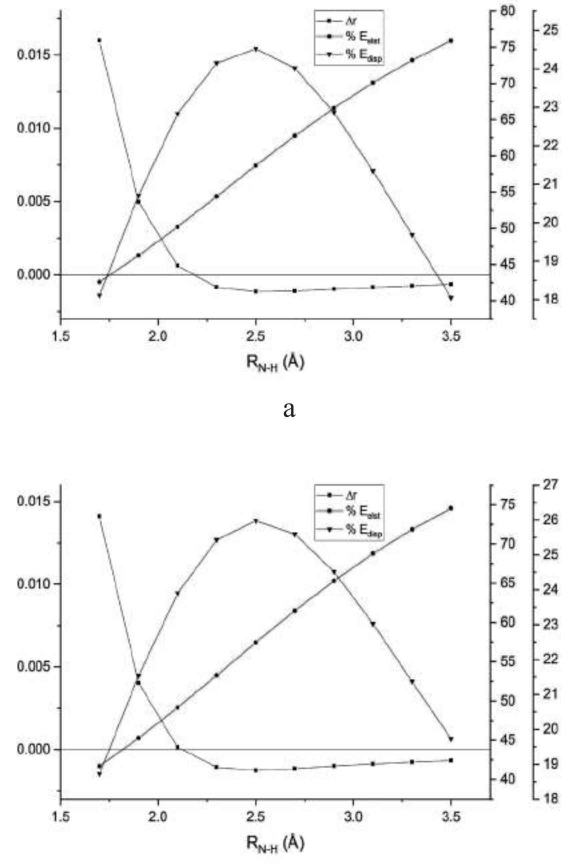
d_{HB} (Å)		1.7	1.9	2.1	2.3	2.5	2.7	2.9	3.1	3.3	3.5
$CHCl_3$···HCN	ρ(r)(au)	0.0519	0.0326	0.0207	0.0134	0.0087	0.0057	0.0038	0.0025	0.0016	0.0010
	∇^2(r)(au)	0.122	0.099	0.071	0.047	0.030	0.019	0.013	0.009	0.006	0.004
	H(r)	-0.0115	-0.0016	0.0014	0.0016	0.0012	0.0009	0.0007	0.0005	0.0004	0.0003
	E_{HB} (kJ.mol^{-1})	-70.8	-36.9	-19.6	-11.0	-6.5	-3.9	-2.5	-1.5	-0.9	-0.6
$CHCl_3$···FCN	ρ(r)(au)	0.0510	0.0319	0.0202	0.0131	0.0085	0.0056	0.0036	0.0024	0.0016	0.0010
	∇^2(r)(au)	0.123	0.099	0.070	0.047	0.029	0.019	0.012	0.008	0.006	0.004
	H(r)	-0.0109	-0.0013	0.0015	0.0018	0.0013	0.0009	0.0007	0.0005	0.0004	0.0003
	E_{HB} (kJ.mol^{-1})	-69.1	-35.9	-19.1	-10.7	-6.3	-3.8	-2.4	-1.5	-0.9	-0.5

The Laplacians (∇^2(r)) and H(r) at BCPs fall within the criteria of the hydrogen bond formation. As a result, the C-H···N intermolecular interactions in the complexes are considered as hydrogen bonds. To be more specific, ∇^2(r) of all systems is greater than 0. When the intermolecular distance of the two molecules decreases, the ∇^2(r) increases from 0.004 to 0.122 au in $CHCl_3$···NCH and from 0.004 to 0.123 au in $CHCl_3$···FCN. H(r) at BCP of N···H contact in two systems gives a value larger than 0 at a distance larger than 2.0 Å, while for R_{N-H} = 1.7 and R_{N-H} = 1.9 Å, H(r) values are negative. Hence, it can be concluded that the interaction formed between proton donor and acceptor at distances of larger than 1.9 Å are weak hydrogen bonds and the others are moderate ones that take a part of covalent nature.

3.4. Role of energy component

To elucidate the role of each energy component in the red- or blue-shifting of hydrogen bond in the complexes, SAPT2+ analyzes at the aug-cc-pVDZ basis set were performed for the optimized structures at the MP2/6-311++G(3df,2pd) level. The value of the energy components as well as the contribution percentage to the stability of the complexes at each specified distance are shown in Table S1-S2 in Supporting Information. In all of the energy components, there are three main energy components, including electrostatic, dispersion and induction, contribute to stability of complexes, whereas exchange interaction causes a decrease in complex durability.

Two examined systems share similar patterns in the contributions of interaction forces. The electrostatic energy component plays a dominant role in the stabilization of these complexes, especially at large distances. Thus, for the $CHCl_3$···NCH system, as R_{N-H} decreases, the electrostatic energy decreases from -4.90 to -62.6 kJ.mol^{-1}, which accounts for 47-76% of the total stabilizing energy. Meanwhile, this type of forces is responsible for about 46-75% in the intermolecular interactions of $CHCl_3$ with NCF. For further analysis, we plot the correlations of the contribution percentage of energy components and the changes in C-H bond length with respect to the intermolecular distance. Particularly, those of electrostatic and dispersion component are presented in Figure 3, and that of induction term is illustrated in Figure S1 of Supporting Information.



a

b

Figure 3. Relationship between %E$_{elst}$, %E$_{disp}$ and Δr in: a) $CHCl_3 \cdots HCN$ and b) $CHCl_3 \cdots FCN$

As shown in Figure 3, while the Δr significantly fluctuates during the formation of complexes, the contribution percentage of the electrostatic component in stabilizing energy decreases monotonously. This indicates that such correlation gives no clue to determine when the interaction turns from blue- to red-shifting hydrogen bond. In other words, even though playing a pivotal role in stabilizing the complexes, electrostatic is not the key factor that identify the shift of hydrogen bond.

Similar circumstances were seen in Figure S1. The induction energy increases linearly in both of its values and its percentage contribution to the stabilizing energy. In studied complexes, the induction energy contributes from 5-7% at R_{N-H} = 3.5 Å to 32-33% at R_{N-H} = 1.7 Å. Although this force is also proposed to be partly responsible for the red-shifting behaviors to some extent,[24] it, here, shows no significant relationship with changes in the shift of C-H stretching vibrational frequencies. Therefore, we can assume that the role of this interaction in controlling the change of the C-H bond is minor and can be ignorable.

Remarkably, we can see a direct connection when considering the relationship between dispersion energy and the change in the C-H bond length. It is obvious from Figure 3 that when the contribution percentage of dispersion interaction increases, the shortening of the C-H bond length increases as well and vice versa. The former trend occurs when the donor-acceptor range decreases from 3.5 to 2.5 Å in the complexes of HCN and FCN, while the latter happens in the remaining regions, where the two fragments come closer. Also, there are coincident extreme points obtained in dispersion contribution line and the C-H bond length variation line in all systems, indicating that the blue-shifting effect reaches its maximum when the participation of dispersion in the stabilizing energy is highest. Thus, it is reasonable to conclude the vital importance of the dispersion in the blue-shifting hydrogen bond.

Further examination on the effect of the dispersion term on the shift of hydrogen bonds is considered. We make a comparison based on the contribution of such interaction among the examined systems, which is demonstrated in Figure 4.

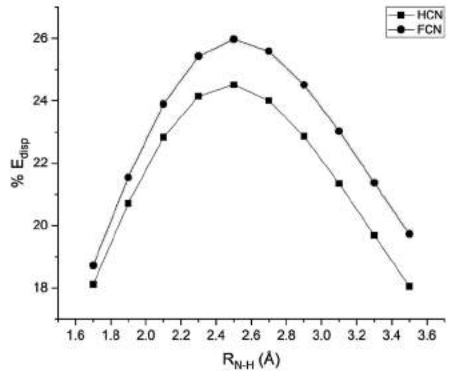


Figure 4. Comparison of the % E_{disp} between two systems

In the $CHCl_3\cdots HCN$ complexes, the highest percentage of dispersion component is about 24%. Meanwhile, the largest participation of dispersion term reaches at around 27% in the complexes of FCN. The contribution of dispersion energy, thus, increases in the order of HCN < FCN proton acceptor. Remarkably, this order is of great consistency with the pattern of the increase of blue-shifting effect, which has been well described in Section 3.1. Again, it is evident that the greater the dispersion interaction is, the higher the blue-shifting of the hydrogen bond is.

4. CONCLUDING REMARKS

The stable complexes of chloroform with cyanide derivatives XCN (X= H, F) were thoroughly examined at the CCSD(T)/6-311++G(3df,2pd)//MP2/6-311++G(3df,2pd) level of theory. The stability of the complex of chloroform with hydrogen cyanite is larger than its flouro derivative at the same donor-acceptor distance. The obtained results show that the change from blue- to red-shift of C-H stretching frequency in the C-H···N hydrogen bond increases in order of FCN < HCN derivative, which results from the increase in the gas phase basicity at N site. The SAPT2+ analysis indicates that the electrostatic term of *ca.* 47-76% predominates over both the induction and dispersion terms in stabilization energy of complexes. The electrostatic and induction terms do not drive the change of C-H bond length or the shift from blue- to red-shifting hydrogen bond. However, it is noteworthy that dispersion term plays an important role in change from blue- to red- shifting hydrogen bond for the complexes of $CHCl_3$ with HCN and FCN. Our work will prompt further exploration of the role of dispersion energy in the red- and blue-shifting hydrogen bond for a better understand of the types of bond.

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