Cent. Eur. J. Chem. • 8(5) • 2010 • 1117–1126
DOI: 10.2478/s11532-010-0088-x

VERSITA

Central European Journal of **Chemistry**

Ab initio study of hydrogen bond complexes of ring compounds containing the H_2N-C=Y moiety with water

Research Article

Tao Liu[1,2], Guo-Dong Liu[1], Zhang-Yu Yu[*3,4]

[1]*Department of Chemistry and Chemical Engineering, Jining University, Qufu 273155, Shandong, China*

[2]*College of Chemistry and Chemical Engineering, Graduate School, Chinese Academy of Sciences, Beijing 100049, China*

[3]*School of Chemistry and Chemical Engineering, Shandong University, Jinan 250010, Shandong, China*

[4]*School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, Shandong, China*

Received 13 January 2010; Accepted 8 June 2010

Abstract: *Ab initio* calculations, including natural charge population and natural resonance theory analyses, have been carried out to study the two-way effects between hydrogen bonds (H-bonds) and the intramolecular resonance effect by using the H-bonded complexes of ring compounds containing the H_2N-C=Y moiety (C=Y bond is contained in the six-membered or five-membered rings) with water as models. The amino groups in the four monomers of ring compounds (**FAYs, Y** represents the heavy atoms in the substituent groups, =CH, =N, =SiH, and =P, respectively) can all serve as H-bond donors (**HD**) and H-bond acceptors (**HA**) to form stable H-bonded complexes with water. The **HD** H-bond and resonance effect enhance each other (positive two-way effects) whereas the **HA** H-bond and resonance effect weaken each other (negative two-way effects). The resonance effect in **FAY(1)** (C=Y bond is contained in the six-membered rings) is weaker than that in formamide, and those in **FAY(2)** and **FAY(3)** (C=Y bonds are contained in the five-membered rings). The two-way effects between H-bond and resonance effect exist in the H-bonded complexes of ring compounds containing the H2N-C=Y moiety with water.

Keywords: *Hydrogen bond • Resonance effect • Ab initio*

1. Introduction

The dual ability of amide linkage to function as both a hydrogen bond (H-bond) donor and acceptor makes the linkage versatile in molecular assembly and recognition. It is the capability of the linkage to serve as both H-bond donor and acceptor that makes it important in chemistry, biochemistry and materials science [1,2]. Amide structure and reactivity is conventionally interpreted within the framework of resonance theory [3,4]. We have performed ab initio calculations [5] to study the two-way effects between H-bond and the intramolecular resonance effect by using the H-bonded complexes of formamide and its derivatives with water as models. It has been shown that there are no contradictions to the Pauling's resonance model [3] and the resonance effect influences not only the H-bond strength but also the type.

An understanding of the two-way effects may be helpful in drug design and refinement by modulating the H-bond strength and in building empirical H-bond models to study large biological molecules. In the present work, we will further explore if the two-way effects between H-bond and the intramolecular resonance effect exist in the ring compounds containing the H_2N-C=Y moiety. The models we use in the article are the ring compounds (**FAYs, Y** represents the heavy atoms in the substituent

* *E-mail: zhy_yu@126.com*

groups, =CH, =N, =SiH, and =P, respectively) and their H-bonded complexes with water. Three catalogues of the ring compounds are studied in the present work (see Figs. 1-3). In the ring compounds (**FAY(1)**) of catalogue (1), the C=Y bonds are contained in the Y-C=C-C=C-C six-membered rings. In the ring compounds (**FAY(2)**) of catalogue (2), the C=Y bonds are contained in the Y-C=C-C-C five-membered rings. In the ring compounds (**FAY(3)**) of catalogue (3), the C=Y bonds are contained in the Y-C-C=C-C five-membered rings. It should be clarified that the intramolecular resonance effect we mentioned is the resonance effect among the C, N, and Y atoms as described in Scheme 1, rather than the inherent resonance effect in the six-membered rings of **FAY(1)** and the five-membered rings of **FAY(2)** and **FAY(3)**. We focus on how substitutions influence the resonance effect and consequently the capability to form H-bond and, in reverse, how the formed H-bond affects the geometrical and electronic structures (*i.e.*, the resonance effect).

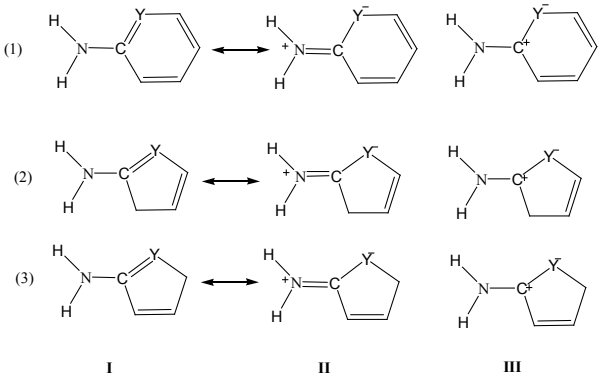
To study the two-way effects, we first study the substituent effects on the resonance effect in the three catalogues of ring compounds by replacing the =CH with =N, =SiH, and =P, respectively. By using water as an H-bond probe, we then investigate how the resonance effect affects their capability to form an H-bond and how the formed H-bond, in reverse, influences the resonance effect. For clarity, the monomers are designated as **FAY(i)** (Y = C, N, Si, P, and i = 1, 2, 3, respectively) with Y representing the heavy atoms in the substituent groups. In the present article, we will discuss **FAY(1)** and their H-bonded complexes in detail, and discuss the **FAY(2)** and **FAY(3)** briefly.

2. Details of Calculation

All structures in this work were fully optimized at the MP2 level with basis sets, 6-31G**, 6-311+G**, and cc-pVTZ and characterized to be minima (no imaginary frequency) by frequency analyses at the MP2/6-31G** level. The H-bond energies used in the discussions were calculated with Eq.1.

$$\Delta E_{H\text{-}bond} = E_{complex} - E_{water} - E_{FAY(i)} + \Delta E_{BSSE} + \Delta E_{ZPE} \quad (1)$$

where $E_{complex}$, E_{water}, and $E_{FAY(i)}$ are the MP2/aug-cc-pVTZ//MP2/cc-pVTZ single-point energies of the H-bonded complex, water, and **FAY(i)** (Y = C, N, Si, P, and i = 1, 2, 3, respectively), respectively. ΔE_{BSSE} is the basis set superposition error (BSSE) correction estimated at the same level by using the standard counterpoise method [6] implemented in Gaussian 03 [7], and ΔE_{ZPE} is the



Scheme 1. The resonance effect among the C, N, and Y atoms

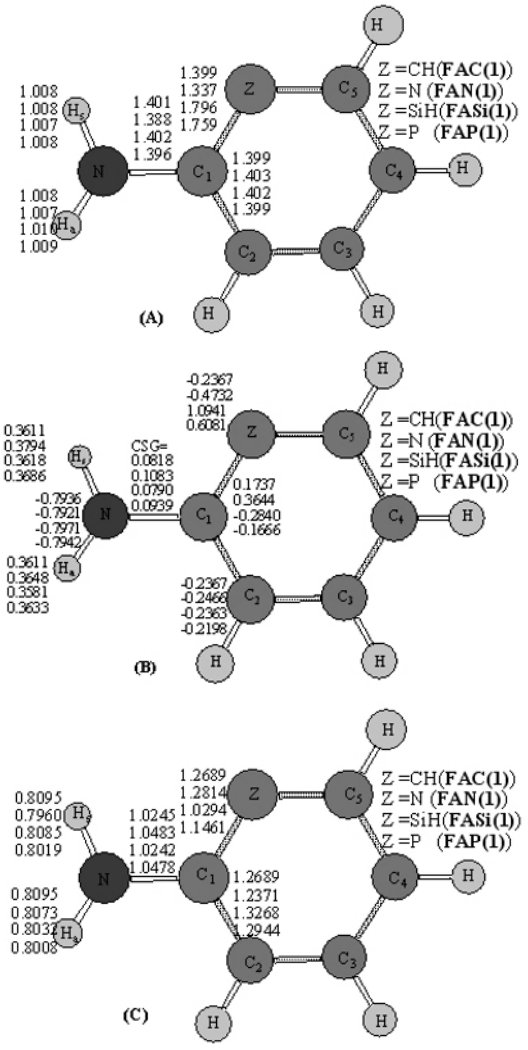


Figure 1. (A) MP2/cc-pVTZ geometries of **FAY(1)** (Y=C, N, Si, and P) with the bond lengths in angstroms. (B) MP2/6-311++G**//MP2/cc-pVTZ natural charges (in e) of individual atoms, and the charge shifts relative to the reference (methylamine) on amino groups (CSG). (C) MP2/6-311++G**//MP2/cc-pVTZ WBIs.

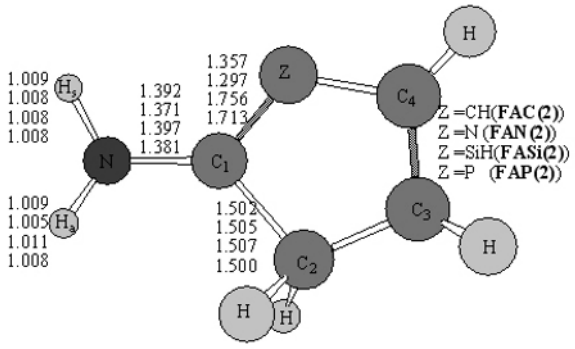


Figure 2. MP2/cc-pVTZ geometries of **FAY(2)** (Y=C, N, Si, and P) with the bond lengths in angstroms.

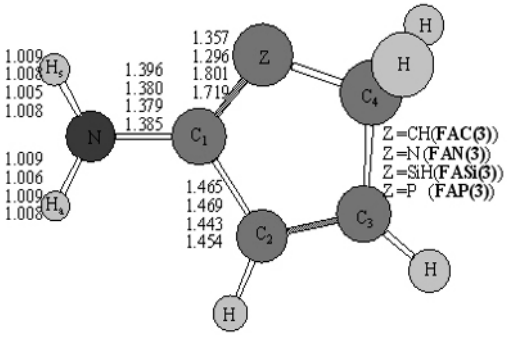


Figure 3. MP2/cc-pVTZ geometries of **FAY(3)** (Y=C, N, Si, and P) with the bond lengths in angstroms.

zero point energy (ZPE) correction at the MP2/6-31G** level.

The previous study [5] indicates the reliability of the MP2/cc-pVTZ level in describing this class of compounds. The H-bond energies calculated at the level can produce a reliable trend. The MP2/cc-pVTZ geometries and the energies based on Eq. 1 are used in the following discussions.

The NPA (Natural Population Analysis) [8-10], NRT (Natural Resonance Theory) [11-13] and WBI (Wiberg Bond Index) [14] performed at MP2/6-311++G**//MP2/cc-pVTZ level with the MP2 wavefunctions were used to characterize the electronic structures of the monomers and the H-bonded complexes. All calculations were carried out by using the Gaussian 03 program [7], and the NPA, NRT, and WBI were performed with the NBO 5.0 package [15].

3. Results and Discussions

3.1. Substituent effects on the geometries and resonance effect of the monomers

The MP2/cc-pVTZ structures of the four monomers of **FAY(1)** are displayed in Fig. 1A (The input structures of **FAY(1)** (**FAC(1)**, **FAN(1)**, **FASi(1)**, and **FAP(1)**) for geometrical optimizations are given in the supporting information). As the Y atom moves from left to right along either the second or third row in the periodic table, the N-C_1 bond is contracted progressively; the N-C_1 bond lengths in **FAC(1)** and **FAN(1)** are 1.401 and 1.388 Å, respectively, and those in **FASi(1)** and **FAP(1)** are 1.402 and 1.396 Å, respectively. All values are substantially smaller than the standard single N-C bond length (1.4626 Å) in NH_2CH_3 and larger than the N-C bond length (1.3576 Å) in formamide [5]. The apparent shortening of the N-C_1 bond indicates the double bond character of N-C_1 bonds in the monomers. The increase in the electronegativity of X atom decreases the N-C_1 bond length and enhances the resonance effect. Consistently, the elongation of C_1=Y bonds (Y = C and N) in the monomers relative to that in CH_2=Y, being 0.066 and 0.062 Å, is less pronounced than the C_1=Y (Y = Si and P) elongation (0.085 and 0.086 Å, relative to the corresponding CH_2=Y) in the monomers, in agreement with the fact that the formal C=Y (Y = C and N) double bonds are stronger than the formal C=Y (Y= Si and P) double bonds.

The MP2/cc-pVTZ structures of the four monomers of **FAY(2)** and **FAY(3)** are displayed in Figs. 2 and 3. The values of the N-C_1 bond lengths in **FAY(2)** and **FAY(3)** are smaller than the corresponding values in **FAY(1)**, showing that the resonance effect is stronger in **FAY(2)** and **FAY(3)** than that in **FAY(1)**. In the structure of **FASi(3)** the Si-H bond is out of the five-membered-ring plane (the corresponding C-H bond in **FAC(3)** (Y = C) is in the ring plane), which leads to the N-C_1 bond lengths being shortest in **FASi(3)** of the four **FAY(3)** monomers.

The substituent effects on the geometries are supported by the quantitative NRT analyses. Table 1 lists the weights of the three most predominant resonance structures (among C, N, and X atoms) calculated at MP2/6-311++G**//MP2/cc-pVTZ level. The resonance I in the four monomers of **FAY(1)** consistently is the most weighted (21.11 - 27.84%), resonance II ranks second (1.51 - 2.17%, we do not find the resonance II in **FASi(1)** and its corresponding H-bonded complexes (see below)), and resonance III only exist in **FAN(i)** (i =1, 2, 3, respectively) and some of the corresponding H-bonded complexes. As shown in Table 1 and Fig. 1A, the weights of resonance II in **FAY(1)** at the second row in the periodic table are in qualitative agreements with the N-C_1 bond lengths.

It can be seen that the weights of resonances I and II in **FAY(i)** are smaller than the corresponding values of formamide and its derivatives (resonance I: 77.6 - 57.2%, resonance II: 8.2 - 29.4%) [5] since the inherent resonance effect of the six-membered or five-membered

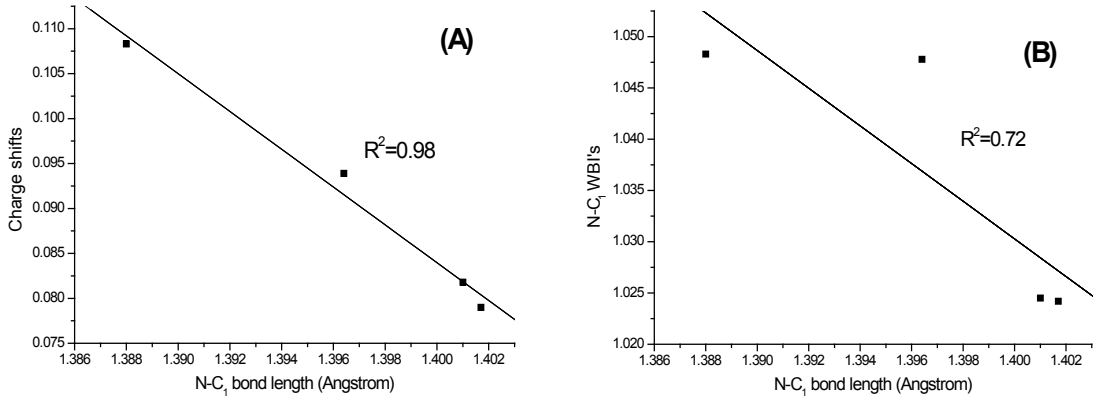


Figure 4. Various correlations among the N-C_1 bond lengths, charge shifts, and WBIs for the isolated monomers.

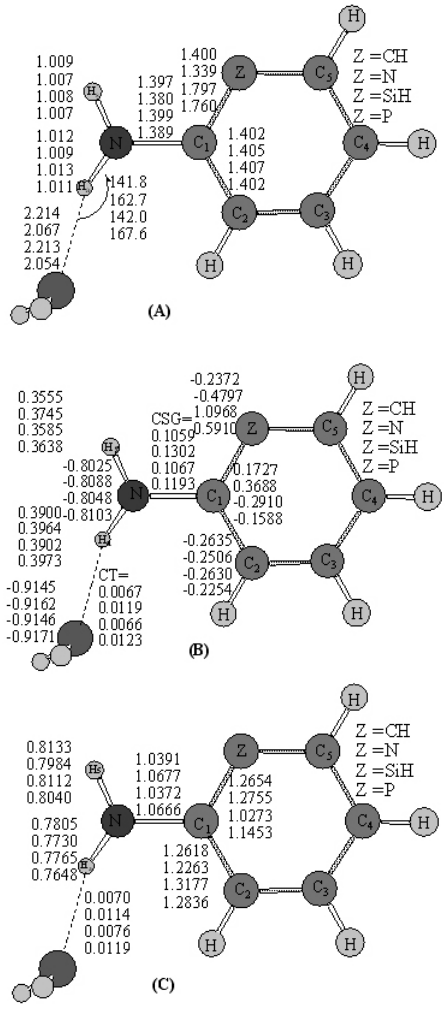


Figure 5. (A) MP2/cc-pVTZ optimized geometries of **FAY(1)-HD** (Y = C, N, Si, and P) complexes, with the bond lengths in angstroms. (B) MP2/6-311++G**//MP2/cc-pVTZ natural charges (ine) of partial charges, and the charge transfer (CT) from $NH_2 + H_2O$ groups (CSG). (C) MP2/6-311++G**//MP2/cc-pVTZ WBIs.

ring of **FAY(i)**. Similarly, as the inherent resonance effect in the five-membered ring is not as strong as that in the six-membered ring, the weights of resonances I and II in **FAY(2)** and **FAY(3)** are larger than the corresponding values in **FAY(1)** as shown in Table 1.

Resonance II implies that if the resonance effect is turned off, the amino nitrogen will become more negatively charged and the oxygen will become less negatively charged, while resonance III implies no charge shifts on nitrogen atom. The charges of the individual atoms, given by NPA analyses, are collected in Fig. 1B. In the four monomers of **FAY(1)**, the charges (-0.7921 to -0.7971 e) on nitrogen atoms are all smaller than the -0.8281 e on the nitrogen in NH_2CH_3, which indicates the resonance effect results in the charge shifts on nitrogen atoms. In the following, we use the charge population of NH_2CH_3 as a reference to discuss the charge shift values. Note that the choice of a reference does not influence the changing trend among the monomers. As the resonance effect occurs, all electrons are reorganized to adapt to the new chemical environment, the hydrogen atoms in amino groups therefore also play a role, and the charge shifts on the amino groups are more informative, so we will consider the total charge shifts on the amino groups (CSG). By using the total charge (-0.1562 e) on the NH_2 group in NH_2CH_3 as a reference, the CSG's in **FAY(1)**, **FAY(2)**, and **FAY(3)** (Y=C, N, Si, and P) are 0.0818, 0.1083, 0.0790, and 0.0939 e, 0.0897, 0.1267, 0.0725, and 0.1098 e, 0.0851, 0.1106, 0.1202, and 0.1087 e, respectively. The value of the CSG in **FASi(3)** is largest of the four monomers of **FAY(3)** for the strange structure of **FASi(3)** (Y = Si), as stated above. As shown in Fig. 4A, the group charge shifts are well correlated with the N-C_1 bond lengths. The correlation coefficient in **FAY(1)** is 0.98 and the corresponding value in **FAY(2)** is 0.99.

The double bond character of N-C_1 bonds is also

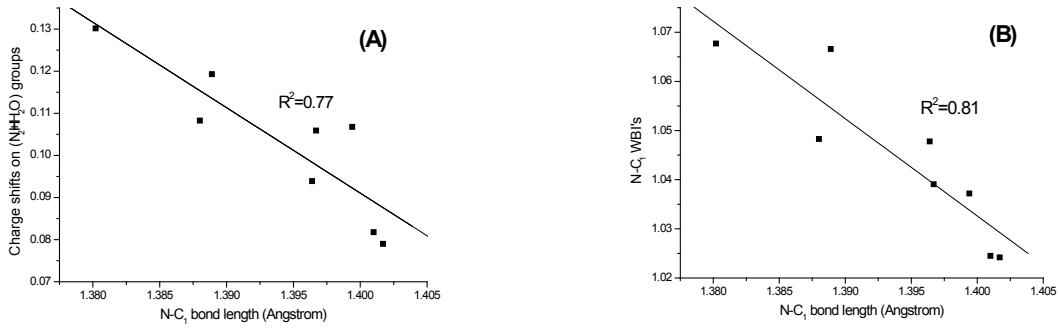


Figure 6. Various correlations among the N-C_1 bond lengths, charge shifts, and WBIs for the isolated monomers and **FAY(1)-HD** complexes.

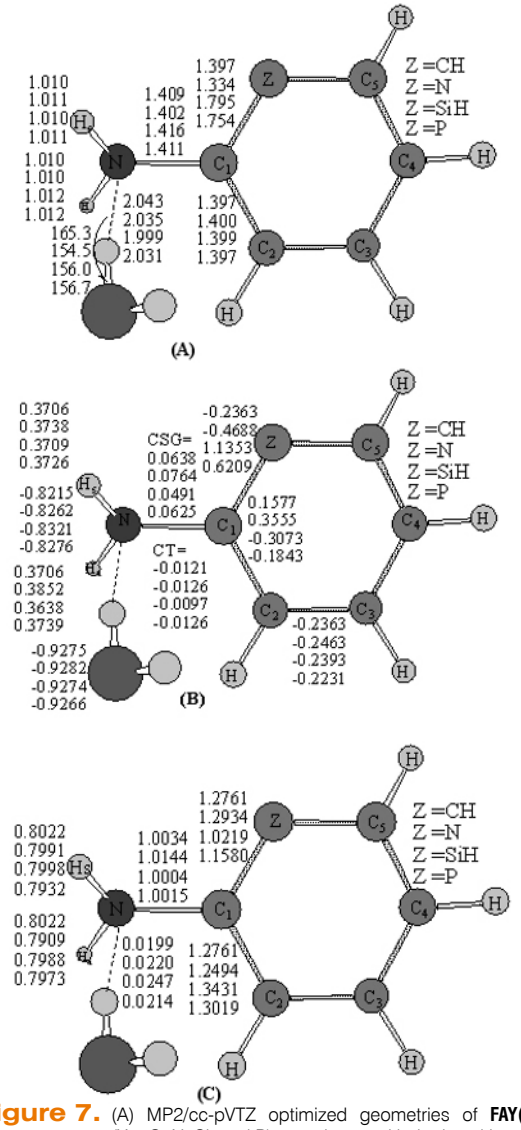


Figure 7. (A) MP2/cc-pVTZ optimized geometries of **FAY(1)-HA** (X= C, N, Si, and P) complexes, with the bond lengths in angstroms. (B) MP2/6-311++G**//MP2/cc-pVTZ natural charges (in e) of partial charges, and the charge transfer (CT) from NH_2+H_2O groups (CSG). (C) MP2/6-311++G**//MP2/cc-pVTZ WBIs.

indicated by the WBIs (shown in Fig. 1C). The WBIs of N-C_1 bonds in the monomers of **FAY(1)**, ranging from 1.0242 to 1.0483, are larger than the value of 0.9610 in NH_2CH_3. The WBIs of N-C_1 bonds in the monomers of **FAY(2)** and **FAY(3)** are larger than the corresponding values in **FAY(1)**, which further indicates that the strength of the resonance effect in **FAY(1)** is weaker than that in **FAY(2)** and **FAY(3)**. The correlation of the N-C_1 WBIs with N-C_1 bond lengths of **FAY(1)** is plotted in Fig. 4B, which shows the good correlations (R^2=0.72).

3.2. Two-way effects between H-bond and resonance effect

As in our previous study [5], the amino groups in the six monomers of formamide and its derivatives all serve as H-bond donors to form stable H-bonded complexes with water, and only two are able to function as H-bond acceptors to form stable H-bonded complexes with water. In contrast, the amino groups in the four monomers of **FAY(i)** can all serve as H-bond donors and H-bond acceptors to form stable H-bond complexes with water. We designate the two types of H-bonds as **HD** (H-bond donor) and **HA** (H-bond acceptor), and label the corresponding complexes as **FAY(i)-HD** (Y = C, N, Si, P, and i = 1, 2, and 3, respectively) and **FAY(i)-HA** (Y = C, N, Si, P, and i = 1, 2, and 3, respectively).

3.2.1. Positive two-way effects between HD H-bond and the resonance effect

The geometries of the four **HD** complexes **(FAY(1)-HD)** are displayed in Fig. 5A. Comparison of the geometries of the **FAY(1)** moieties in the complexes with their corresponding monomers (Fig. 1A) shows similar trends of N-C_1 bond contraction and C_1-Y bond elongation to those in the free monomers as Y moves across the periodic table. Nevertheless, the H-bonds have appreciable influences on the geometries of the **FAY(1)** moieties. Relative to the isolated monomers,

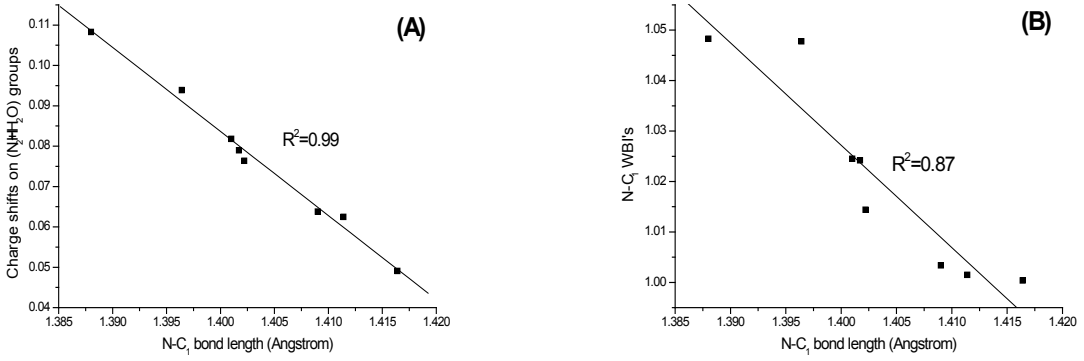


Figure 8. Various correlations among the N-C_1 bond lengths, charge shifts, and WBIs for the isolated monomers and **FAY(1)-HA** complexes.

the N-C_1 bonds are further shortened by 0.002 - 0.008 Å, and the C_1-Y bonds are further elongated by 0.001 - 0.002 Å. The geometrical deviations to the isolated monomers signify that the **HD** H-bond enhances the resonance effect. Intuitively, because the amino groups are **HDs**, there are negative charge transfers (CTs, Fig. 5B) from water to the monomers through amino groups. The charge accumulation on the amino groups pushes more negative charge away from the group. Comparing Fig. 1B with Fig. 5B, one can notice that the charge shifts on NH_2 + H_2O moieties are larger than those in the free monomers. As shown in Table 1, the weights of resonance II in **FAY(1)-HD** are lager than the corresponding values in the monomers of **FAY(1)** (the resonance II can not be found in **FASi(1)-HD**). The changes in the geometries are also consistent with the larger weights of resonance II (ca. 0.02 - 0.38%) and WBIs of N-C_1 bonds in the complexes than those in the corresponding monomers. The N-H_a bond lengthening in the complexes can be interpreted by the electrostatic interaction model [16-18], according to which the oxygen of water pulls the H-bond proton away from nitrogen, or the hyperconjugation model [19], which attributes the lengthening to the donation of the oxygen lone pair to the N-H antibonding orbital. With respect to the monomer, the C_1-C_2 bond lengths become longer, and N-H_s bond lengths only change marginally. Comparing the corresponding values in **FAY(2)-HD** and **FAY(3)-HD** with those in **FAY(1)-HD**, one can notice that there are larger weights of resonance II, shorter N-C_1 bond lengths, larger values of shifted charges, and larger WBIs of N-C_1 bonds in **FAY(2)-HD** and **FAY(3)-HD**.

The correlations described in Fig. 6 can even be extended to include the four **FAY(1)-HD** complexes together. Figs. 6A,B shows the various correlations corresponding to Figs. 4A,B, respectively. The R^2 values, 0.77 and 0.81, are compared with the values of the monomer case, 0.98 and 0.72, respectively.

The H-bonds in **FAY(1)-HD** complexes become increasingly strong as the X atoms become growingly electronegative in the same row of the periodic table. The H-bond energies in **FAC(1)-HD** and **FAN(1)-HD** (given in Table 2) are -2.59 and -2.90 kcal mol^{-1}, and -2.67 and -2.92 kcal mol^{-1} in **FASi(1)-HD** and **FAP(1)-HD**, respectively. The H-bond energies in **FASi(1)-HD** and **FAP(1)-HD** are respectively larger than their second-row counterparts. As shown by Table 1 and Table 2, the H-bond energies are in qualitative agreement with the weights of resonance II in **FAY(i)-HD** complexes. The agreement indicates that the resonance effect tends to strengthen the **HD** H-bond.

H-bond interactions are dominated by the primary electrostatic attractions between water oxygen and the H-bond hydrogen. For the primary electrostatic attractions, the increasing positive charges on H-bond hydrogen atoms (H_a), and increasing negative charges on the water oxygen atoms are consistent with the increasing H-bond energies, as the X atoms go from left to right in either the second or third rows. The covalent bonding character of an H-bond due to CT is reflected by the WBIs of the H-bond and H-bond angles ($\angle OH_aN$). As the X atoms move from left to right in either the second or third row, the WBI of H-bond increases, the $\angle OH_aN$ H-bond angle becomes closer to 180.0°, and in the meantime the H_a•••O H-bond lengths decrease (Figs. 5A,C).

The intramolecular resonance effect and the H-bond enhance each other in **FAY(i)-HD** complexes, and the positive two-way effects exist in **FAY(i)-HD**.

3.2.2. Negative two-way effect between HA H-bond and resonance effect.

The HA H-bond is the prefered pattern in H_2O•••NH_3 and H_2O•••NH_2CH_3 complexes. As indicated by the N-C_1 bond lengths and the weights of resonance II, the resonance effect in **FAY(i)** monomers is weaker than in

Table 1. Weights of resonance I, II, and III in Scheme 1 at MP2/aug-cc-pVTZ//MP2/cc-pVTZ level by NRT.

	FAC(1)	FAN(1)	FASi(1)	FAP(1)	FAC(1)-HD	FAN(1)-HD	FASi(1)-HD
I	21.11	26.59	17.90	27.84	28.00	25.31	16.04
II	1.51	1.62		2.17	1.53	2.00	
III		1.12					

	FAP(1)-HD	FAC(1)-HA	FAN(1)-HA	FASi(1)-HA	FAP(1)-HA
I	26.51	28.98	27.38	17.47	28.73
II	2.27	0.88	1.34		0.33
III					

	FAC(2)	FAN(2)	FASi(2)	FAP(2)	FAC(2)-HD	FAN(2)-HD	FASi(2)-HD
I	50.68	48.78	48.95	48.18	48.51	42.80	46.90
II	5.06	6.59	5.81	7.84	6.12	13.49	6.90
III		0.72					

	FAP(2)-HD	FAC(2)-HA	FAN(2)-HA	FASi(2)-HA	FAP(2)-HA
I	44.14	49.24	47.90	48.17	47.19
II	12.74	2.72	2.80	3.92	3.57
III			1.10		

	FAC(3)	FAN(3)	FASi(3)	FAP(3)	FAC(3)-HD	FAN(3)-HD	FASi(3)-HD
I	51.24	48.98	36.95	47.35	49.92	47.16	35.26
II	4.08	6.86	10.75	7.50	6.67	7.13	11.17
III		0.76				0.66	

	FAP(3)-HD	FAC(3)-HA	FAN(3)-HA	FASi(3)-HA	FAP(3)-HA
I	45.23	50.25	48.19	37.84	46.72
II	7.91	3.58	3.33	7.13	4.96
III			0.11		

formamide. Therefore, the **FAY(i)** monomers are all able to form stable **FAY(i)-HA** complexes (see Fig. 7A).

The geometries of the four HA complexes are displayed in Fig. 7A. Relative to the free monomers, the N-C_1 bonds in **FAY(1)-HA** are lengthened. Recall that the N-C_1 bonds in the HD complexes are shortened. The N-C_1 bond lengths, 1.409, 1.402, 1.416, and 1.411 Å in **FAC(1)-HA**, **FAN(1)-HA**, **FASi(1)-HA**, and **FAP(1)-HA** complexes, respectively, are longer than those (1.401, 1.388, 1.402, and 1.396 Å) in the **FAC(1)**, **FAN(1)**, **FASi(1)**, and **FAP(1)** and those (1.397, 1.380, 1.399, and 1.389 Å) in **FAC(1)-HD**, **FAN(1)-HD**, **FASi(1)-HD**, and **FAP(1)-HD**. The N-C_1 bond elongations are in agreement with the decreased weights of resonance II (the resonance II in **FASi(1)** and its H-bonded complexes cannot be found). The weights of resonance II, 0.88% in **FAC(1)-HA**, 1.34% in **FAN(1)-HA**, and 0.33% in **FAP(1)-HA**, are smaller than the values in their free counterparts (1.51%, 1.62%, and 2.17%) and the values in the **FAC(1)-HD**, **FAN(1)-HD**, and **FAP(1)-HD** complexes (1.53%, 2.00%, and 2.27%). However, the N-C_1 bonds in **FAC(1)-HA**, **FAN(1)-HA**, and **FAP(1)-HA** are still shorter than the N-C single bond (1.4626 Å) in NH_2CH_3, indicating that the resonance effect is not turned off by the HA H-bond completely.

The N-C_1 bond lengths, 1.402, 1.385, 1.411, and 1.396 Å in **FAC(2)-HA**, **FAN(2)-HA**, **FASi(2)-HA**, and **FAP(2)-HA** complexes, and 1.405, 1.392, 1.396, and 1.399 Å in **FAC(3)-HA**, **FAN(3)-HA**, **FASi(3)-HA**, and **FAP(3)-HA** complexes, respectively, are shorter than the values (1.409, 1.402, 1.416, and 1.411 Å) in **FAC(1)-HA**, **FAN(1)-HA**, **FASi(1)-HA**, and **FAP(1)-HA**, respectively. The difference of the N-C_1 bond lengths and weights of resonance II in the three **FAY(i)-HA** complexes (shown in Table 1) shows that the resonance effect in **FAY(1)-HA** is weaker than that in **FAY(2)**-HA and **FAY(3)-HA**.

Table 2. H-bond energies (in kcal mol^{-1}) calculated at MP2 level with various basis sets.

	MP2					
	6-31G**	**6-311+G****	**cc-pVTZ**	**aug-cc-pVTZ[a]**	**aug-cc-pVTZ[a] +ΔZPE[b]**	**aug-cc-pVTZ[a] +BSSE[c] +ΔZPE[b]**
FAC(1)-HD	-6.54	-5.47	-5.79	-4.25	-3.34	-2.59
FAN(1)-HD	-6.34	-5.71	-5.91	-4.35	-3.55	-2.90
FASi(1)-HD	-6.73	-5.67	-6.19	-4.41	-3.46	-2.67
FAP(1)-HD	-6.62	-5.78	-5.94	-4.39	-3.59	-2.92
FAC(1)-HA	-6.84	-6.95	-6.98	-5.47	-4.50	-3.69
FAN(1)-HA	-7.80	-6.47	-7.07	-5.14	-3.77	-3.00
FASi(1)-HA	-9.11	-7.04	-7.90	-5.67	-4.16	-3.28
FAP(1)-HA	-7.65	-6.64	-7.06	-5.12	-3.77	-2.94
FAC(2)-HD	-5.92	-4.99	-5.44	-3.62	-2.84	-2.25
FAN(2)-HD	-6.54	-5.93	-6.17	-4.66	-3.39	-2.61
FASi(2)-HD	-5.44	-4.31	-7.30	-5.66	-4.79	-3.87
FAP(2)-HD	-6.59	-5.77	-6.08	-4.54	-3.87	-3.12
FAC(2)-HA	-8.48	-6.90	-7.81	-5.70	-4.29	-3.47
FAN(2)-HA	-7.81	-6.31	-7.08	-4.96	-3.71	-3.13
FASi(2)-HA	-9.07	-7.44	-8.58	-6.31	-4.96	-4.07
FAP(2)-HA	-8.18	-6.78	-7.49	-5.32	-3.99	-3.26
FAC(3)-HD	-6.33	-5.20	-5.80	-3.97	-3.11	-2.38
FAN(3)-HD	-6.18	-5.68	-5.94	-4.39	-3.48	-2.76
FASi(3)-HD	-7.49	-5.59	-6.09	-4.01	-2.98	-2.33
FAP(3)-HD	-6.62	-5.77	-6.13	-4.52	-3.56	-2.82
FAC(3)-HA	-8.14	-6.98	-7.48	-5.51	-4.10	-3.33
FAN(3)-HA	-7.57	-6.08	-6.79	-4.79	-3.56	-2.98
FASi(3)-HA	-6.90	-6.47	-6.98	-5.12	-3.83	-3.02
FAP(3)-HA	-7.43	-6.40	-6.88	-4.87	-3.62	-2.94
NH_3-HA	-7.92	-7.35	-7.31	-6.23	-4.43	-3.97
NH_2CH_3-HA	-8.66	-8.00	-8.21	-7.16	-5.51	-4.87

*[a] MP2/cc-pVTZ geometries were used. [b] ZPEs calculated at MP2/6-31G** level. [c] BSSEs calculated at MP2/aug-cc-pVTZ//MP2/cc-pVTZ level.*

The correlations described in Fig. 4 can also be extended to include the four **FAY(1)-HA** complexes together. Figs. 8A,B shows the various correlations corresponding to Figs. 4A,B, respectively. The R^2 values, 0.99 and 0.87, are compared with the values of the monomer case, 0.98 and 0.72, and the values of the **FAY(1)-HD** case, 0.77 and 0.81.

The nitrogen atoms in **FAY(1)-HA** are **HAs** and donate negative charges to water molecules, which results in an electron deficiency on nitrogen. The electron deficiency is not favorable for the charge shifts and therefore leads to a weakened resonance effect. Indeed, the charge shifts from NH_2+H_2O groups in **FAC(1)-HA**, **FAN(1)-HA**, **FASi(1)-HA**, and **FAP(1)-HA**, 0.0638, 0.0764, 0.0491, and 0.0625 e, are less than those on NH_2 groups in **FAC(1)**, **FAN(1)**, **FASi(1)**, and **FAP(1)** (0.0818, 0.1083, 0.0790, and 0.0939 e) and those of NH_2 + H_2O moieties in **FAC(1)-HD**, **FAN(1)-HD**, **FASi(1)-HD**, and **FAP(1)-HD** (0.1059, 0.1302, 0.1067, and 0.1193 e), respectively.

The H-bond lengths in **FAC(1)-HA**, **FAN(1)-HA**, **FASi(1)-HA**, and **FAP(1)-HA**, 2.0434, 2.035, 1.999, and 2.031 Å, are shorter than those in **FAC(1)-HD**, **FAN(1)-HD**, **FASi(1)-HD**, and **FAP(1)-HD**, 2.214, 2.067, 2.213, and 2.054 Å, respectively, and the WBIs of H-bonds, 0.0199, 0.0220, 0.0247, and 0.0214, are larger than those in the corresponding HD complexes, 0.0070, 0.0114, 0.0076, and 0.0119. Consistently, the H-bond energies in **FAC(1)-HA** (-3.69kcalmol^{-1}), **FAN(1)-HA** (-3.00kcalmol^{-1}), **FASi(1)-HA** (-3.28 kcal mol^{-1}), and **FAP(1)-HA** (-2.94 kcal mol^{-1}) are larger than those in **FAC(1)-HD** (-2.59 kcal mol^{-1}), **FAN(1)-HD** (-2.90 kcal mol^{-1}), **FASi(1)-HD** (-2.67 kcal mol^{-1}), and **FAP(1)-HD** (-2.92 kcal mol^{-1}), respectively. Nevertheless, because of the distributions of the resonance effect, the H-bond energies are less than that in H_2O•••NH_3 complex (-3.97 kcal mol^{-1}) and that in H_2O•••NH_2-CH_3 complex (-4.87 kcal mol^{-1}). In agreement with the larger H-bond energies in **FAY(1)-HA** than those in **FAY(1)-HD**, the CT amount between H_2O and monomers in the former, 0.0121, 0.0126, 0.0097, and 0.0126 e are also larger than those in the latter (0.0067, 0.0119, 0.0066, and 0.0123 e, respectively).

The intramolecular resonance effect and the H-bond weaken each other in **FAY(i)-HA** and the negative two-way effects exist in **FAY(i)-HA**.

In conclusion, the two-way effects between H-bond and resonance effect exist in the H-bonded complex of ring compounds containing the H_2N-C=Y moiety (**FAY(i)**) with water.

4. Conclusions

By using the ring compounds which contain the H_2N-C=Y moiety (C=Y bond is contained in the six-membered or five-membered rings), and their H-bonded complexes with water as models, we have performed ab initio

calculations to study the two-way effects between the intramolecular resonance effect and H-bond. The amino groups in the monomers of **FAY(i)** can all serve as **HDs** and **HAs** to form stable H-bonded complexes with water. The NRT analyses and the N-C_1 bond contractions indicate that the resonance effect strengthens **HD** H-bonds and weakens **HA** H-bonds. In reverse, the **HD** H-bonds also enhance the resonance effect, and **HA** H-bonds weaken it. The H-bond energies in the **FAY(i)-HD** and **FAY(i)-HA** complexes are in qualitative agreement with the N-C_1 bond lengths, the weights of resonance II, and the N-C_1 WBIs.

The resonance effect in **FAY(1)** (C=Y bond is contained in the six-membered rings) is weaker than that in formamide, and those in **FAY(2)** and **FAY(3)** (C=Y bonds are contained in the five-membered rings).

The two-way effects between H-bond and resonance effect exist in the H-bonded complex of ring compounds containing the H_2N-C=Y moiety (**FAY(i)**) with water.

The understanding of the two-way effects may be helpful in drug design and refinement by modulating the H-bond strength and in building empirical H-bond models for simulating large biological molecules.

Acknowledgments

This work was supported by the National Natural Science Foundation Committee of China (No. 20773160), Natural Science Foundation Committee of Shandong Province (No. ZR2009BM003), and the Education Department of Shandong Province (No. J09LB54). Dr T. Liu thanks the suggestions of Prof Z.-X. Wang. T. Liu thanks the Youth Fund of Jining University (2009QNKJ08) and Dr Tao Liu.

Supporting Information Available: The input structures of **FAY(1)** (**FAC(1)**, **FAN(1)**, **FASi(1)**, and **FAP(1)**) for geometrical optimizations.

References

[1] A. Greenberg, C.M. Breneman, J.F. Liebman, The Amide Linkage: Structural Significance in Chemistry, Biochemistry, and Materials Science (Wiley, New York, 2000)
[2] A. Greenberg, C.M. Breneman, J.F. Liebman, The Amide Linkage: Structural Significance in Chemistry, Biochemistry, and Materials Science (Wiley, New York, 2002)
[3] L. Pauling, The Nature of the Chemical Bond, 3rd edition (Cornell University, Ithaca, New York, 1960)
[4] E.D. Glendening, J.A. Hrabal, J. Am. Chem. Soc. 119, 12940 (1997)
[5] T. Liu, H. Li, M.–B. Huang, Y. Duan, Z.-X. Wang, J. Phys. Chem. A 112, 5436 (2008)
[6] S.F. Boys, F. Bernardi, Mol. Phys. 19, 553 (1970)
[7] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria,M. A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, GAUSSIAN 03, Revision B.04 (Gaussian, Inc., Pittsburgh, PA, 2003)
[8] A.E. Reed, F. Weinhold, J. Chem. Phys. 78, 4066 (1983)
[9] A.E. Reed, R.B. Weinstock, F. Weinhold, J. Chem. Phys. 83, 735 (1985)
[10] F. Weinhold, J.E. Carpenter, In: R. Naaman, Z. Vager (Eds.), The Structure of Small Molecules and Ions (Plenum, New York, 1988) 227-236
[11] E.D. Glendening, F. Weinhold, J. Comp. Chem. 19, 593 (1998)
[12] E.D. Glendening, F. Weinhold, J. Comp. Chem. 19, 610 (1998)
[13] E.D. Glendening, J.K. Badenhoop, F. Weinhold, J. Comp. Chem. 19, 628 (1998)
[14] K.B.Wiberg, Tetrahedron 24, 1083 (1968)
[15] E.D. Glendening, J.K. Badenhoop, A.E. Reed, J.E. Carpenter, B.J.A. Bohmann, C.M. Morales, F. Weinhold, NBO. 5.0 (Theoretical Chemistry Institute, University of Wisconsin, Madison, Wisconsin, 2001)

[16] S. Scheiner, Hydrogen Bonding (Oxford University Press, New York, 1997)
[17] G.R. Desiraju, T. Steiner, The Weak Hydrogen Bond (Oxford University Press, Oxford, 1999)
[18] C.E. Dykstra, Acc. Chem. Res. 21, 355 (1988)
[19] A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88, 899 (1988)