Journal of Chemistry, Vol. 47 (6), P. 779 - 785, 2009

THE INTERACTION OF BH_2NH_2 WITH HNZ (Z: O, S) IN THE GAS PHASE: THEORETICAL STUDY OF THE BLUE SHIFT OF N-H...H-B DIHYDROGEN BONDS AND THE RED SHIFT OF N-H...O AND N-H...S HYDROGEN BONDS

Received 13 September 2007

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ABSTRACT

Theoretical calculations at the MP2/6-311++G(2d,2p) level were performed to study the origin of the B-H...H-N blue-shifting dihydrogen bonds in the complexes of BH_2NH_2...HNZ (Z = O, S). The stably optimized cyclic structures of the complexes are displayed in figure 1, with interaction energies as table 1. The blue shift of the N5-H7 bond stretching frequencies is observed in the B9-H4...H7-N5 dihydrogen bonds for BH_2NH_2...HNO and BH_2NH_2...HNS, corresponding to contraction of the N5-H7 bonds (except for slight elongation of the N5-H7 bond found in the complex BH_2NH_2...HNS), increase of stretching frequencies and decrease of infrared intensities respectively.

I - INTRODUCTION

Very recently, the 1990s, a new type of interaction named *dihydrogen bond* was detected for metal organic crystal structure [1, 2] which was coined to describe an interaction of the type X-H...H-E; where X is a typical hydrogen donor such as N or O; and E are transition metals such as Ir, Re or B. These bonds are of type "proton-hydride", i.e. between $X-H^{\delta+}$ and $H^{\delta-}-E$. The Cambridge Structural Databases (CSD) have shown that the main characteristics of X-H...H-E systems are: the d(H...H) distances are typically 1.7-2.2 Å, significantly less than the sum of van der Waals for two hydrogen atoms, 2.4 Å; interaction energies in the range of classical hydrogen bonds (12-28 $kJ.mol^{-1}$) [3]. The importance of dihydrogen bond in chemical, physical, and bio-chemical processes was studied [4, 5]. The authors have pointed out that similar processes were observed for biological systems such as the enzyme hydrogenate in bacteria and algae. To increase the understanding of dihydrogen bonds, Thomas et al. [6] carried out an ab-initio theoretical study on the dimmer $(BH_3NH_3)_2$. Popelier [7] characterized a dihydrogen bond by means of AIM quantities on the basis of electron density. To the best of our knowledge, the X-H...H-E blue-shifting dihydrogen bond have just reported for some the recent papers [8 - 10]. We believe that this study is valuable and interesting. One goal of this paper is to find cases of the X-H...H-E blue-shifting dihydrogen bonds in the complexes between BH_2NH_2 and HNZ (Z: O, S), and to expect for providing a remarkable explanation about the origins of the blue-shifting dihydrogen bonds.

2. Computational methods

Interaction energies are corrected by zero point energy (ZPE) and basis set superposition error (BSSE) which is estimated using the function counterpoise procedure proposed by Boys and Bernardi. Atomic charge, electron density, population of molecular orbitals, hyperconjugation energies and rehybridization are determined using natural bond orbital model (NBO). Hyperconjugation energy takes from the second-order Moller-Plesset perturbation. To avoid vibrational coupling between the $\nu(NH_2)$ and $\nu(XH_2)$ modes, the frequencies were calculated in the X9D3H4N81H1D2 isotopomers in both the monomers and complexes. All the calculations in this study were performed by making use of the Gaussian 03 program.[11] The positions of the critical points were detected using the eigen-vector method. Electron density ($\rho(r)$) and Laplacian ($\nabla^2(\rho(r))$) of bond critical points (BCPs) were evaluated by AIM 2000 program[12] All calculations were performed at the MP2/6-311++G(2d,2p) high level of theory.

III - RESULTS AND DISCUSSION

1. Geometries and interaction energies

The optimized structures of the monomers and their complexes at the MP2/6-311++G(2d,2p) level are displayed in figure 1.

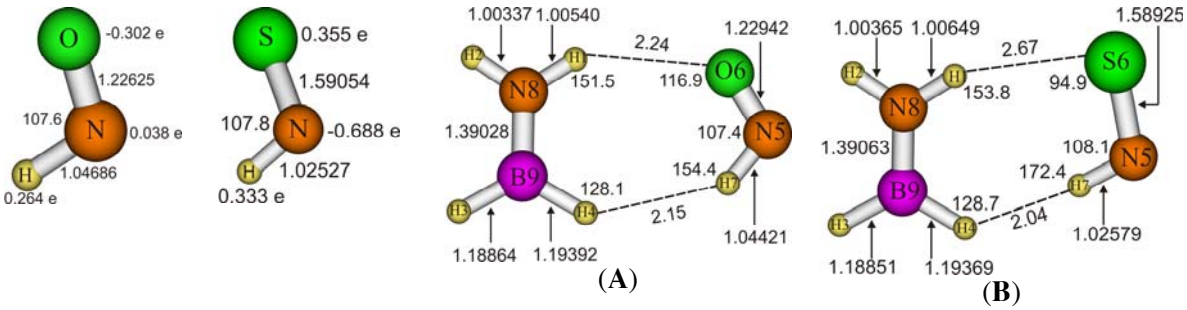

Figure 1: The optimized structures of the HNZ, BH_2-NH_2....HNZ, in which the Z are the O, S atoms at the MP2/6-311++G(2d,2p) level of theory

Two complexes of BH_2NH_2...HNZ have symmetry point group C_s and all atoms are in a plane. All structures are minimized on potential energy surfaces (PESs), and characteristic parameters of bond lengths and angles are obviously described here. It is clear that there are changes of geometry in the examined complexes compared to monomers respectively. Change of bond lengths and interaction energies with both ZPE and BSSE corrections is tabulated in the table 1.

Table 1: Change of bond lengths Δr (Å), interaction energies (kcal.mol^{-1}) corrected by ZPE (^{a}ΔE) and BSSE (^{b}ΔE) at the MP/6-311++G(2d,2p) level of theory

	Δr(B9H4)	Δr(N8H1)	Δr(N5H7)	Δr(N5Z6)	Δr(B9H3)	Δr(N8H2)	Δr(B9N8)	^{a}ΔE	^{b}ΔE
A	0.0044	0.0020	-0.0027	0.0032	-0.0009	0.0000	-0.0034	-2.37	-1.66
B	0.0042	0.0031	0.0005	-0.0013	-0.0010	0.0003	-0.0030	-2.38	-1.58

Z: O, S; a: only corrected by ZPE; b: corrected by both ZPE and BSSE.

As displayed in figure 1, there are N8-H1...Z6 (Z: O, S) contacts and B9-H4...H7-N5 contacts in the examined complexes, forming cyclic structures quite stably. The intermolecular interaction energies are equal -2.37, -2.38 kcal.mol^{-1} corrected by ZPE and -1.66, -1.58 kcal.mol^{-1} with both ZPE and BSSE corrections for **A** and **B** respectively. This means that the examined plane-cycle complexes are relatively stable and their strength is similar.

As seen from table 1 and figure 1, it becomes evident that there are considerable elongations of B9-H4 and N8-H1 bonds involved in the B9-H4...H7-N5 and N8-H1...Z6 contacts. The B9-H4 bonds are lengthened more than the N8-H1 bonds upon complexation as shown in table 1. All these elongations will be obviously explained in the following section. It is interesting that there is a large contraction of the N5-H7 bond observed in **A** and a slight elongation of the N5-H7 bond found in **B** with value of 0.0027 Å and 0.0005 Å respectively. It may be roughly explained by higher polarization of the N-H bond in the HNS isolated monomer compared to that in the HNO isolated monomer. The polarization is higher for the former than for the latter because as displayed in figure 1 the NBO charge on N atom in HNS gets the negative value of -0.688 e while it is positively charged with the value of 0.038 e in HNO. Furthermore, the NBO charge on H atom is also charged more positive in HNS than in HNO. Compared to monomers, all B9-N8 bonds are decreased by 0.0034 Å and 0.0030 Å for **A** and **B** respectively. This implies that the interaction between BH_2NH_2 and HNZ can strengthen the B9-N8 bonds. Upon formation, the slight contractions of B9-H3 bond lengths are observed with the value 0.0009 Å, 0.0010 Å in **A** and **B** respectively. However, there are very small elongations of N8-H2 bonds as listed in Table 1. Distance of N5=Z6 bond is lengthened by 0.0032 Å in **A** and that is shortened in **B** with the value of 0.0013 Å.

With respect to two examined complexes, the $d_{H...H}$ distances (figure 1) fall within the range of dihydrogen bond[3] as displayed in figure 1, and are shorter than 2.4 Å (the sum of van der Waals radii for two hydrogen atoms). Simultaneously, distances of H1...Z6 contacts are 2.24 Å, 2.67 Å in A and B respectively, those are also shorter than the sum of van der Waals radius of H and O atom (2.6 Å), and of H and S atom (3.05 Å). It indicates that there simultaneously exist hydrogen bond and dihydrogen bond in the examined complexes. This conclusion will be obviously demonstrated by means of AIM analysis in the subsection. All computed B9-H4...H7 and N5-H7...H4 dihydrogen bond angles are from 128.1 to 172.4^0. The average of these bond angles is in good agreement with the experimental range of 90^0 and 171^0.[3] All hydrogen bond angles N8-H1...Z6 are bent from linearity upon complex formation as shown in Figure 1. Besides, bond angle N5=S6...H1 is also bent amount of 94.9^0 which is more than in N5=O6...H1 bond angle (116.9^0). Although the energy values do not fall within the range of 12-28 $kcal.mol^{-1}$ for forming dihydrogen bond,[3] one should not prematurely conclude that there is not dihydrogen bond in the examined complexes, that dihydrogen bond formation has roughly proved due to the bond length and angle above. Topological analysis of electron density and its Laplacian will obviously confirm whether having or not having dihydrogen bonds in these complexes.

2. Topological analysis

To confirm the existence of the hydrogen and dihydrogen bond in complexes A and B, we performed AIM topological analysis. Poperlier et al. [13, 14] suggested a set of criteria for existence of hydrogen bonds, among which three are most often applied. The first criterion states that the bond path with the bond critical point between the proton and proton acceptor should exist. Such paths for H...Z and H...H contacts are observed for all complexes here as displayed in figure 2.

Two other criteria are electron density ($\rho(r)$) and Laplacian ($\nabla^2(\rho(r))$) at critical point. Both parameters for closed-shell interactions as hydrogen bond are positive and should be within the following ranges: 0.002 - 0.034 au for the electron density and 0.024 - 0.139 au for its Laplacian. The topological parameters of bond critical points (BCPs) and ring critical points (RCPs) at MP2/6-311++G(2d,2p) level are gathered in table 2.

In all complexes, there are BCPs in N8-H1...Z6-N5, B9-H4...H7-N5 contacts because two of three λ_i are negative and the remaining one is positive. In addition, it is worth mentioning that there is existence of a ring structure in one complex because one of three λ_i is negative and the other two are positive.

The values of electron density and Laplacian for N8-H1...Z6-N5 in **A** and **B** do fall within the proposed typical range of the hydrogen bonds as mentioned above. On the basis of AIM topological analysis, we claim that the N8-H1...Z6-N5 contacts can be classified as hydrogen bonds. Simultaneously, inspection of the results in table 2 the values of the electron density of the B9-H4...H7-N5 contacts and their Laplacian also fall within the range of values of $\rho(r)$ and $\nabla^2(\rho(r))$ for hydrogen bond. So, we conclude that the B9-H4...H7-N5 contacts are type of dihydrogen bonds. Therefore, the dihydrogen bond can be considered as another type of the hydrogen bond due to the value of similarly topological parameters despite the dihydrogen bond is very particular as a bond is formed between very particular atoms- two hydrogens. The AIM analysis does not reveal the origin of blue-, red-shifting dihydrogen and hydrogen bonds. These problem will be solved by performing the natural bond orbital (NBO) analysis in the subsection.

3. NBO analysis

For investigating and a better understanding the mechanism on the origin of the blue-shifting dihydrogen bond and red-shifting hydrogen bond, NBO analysis was performed at MP2/6-311++G(2d,2p) level of theory and the corresponding results were gathered in table 3.

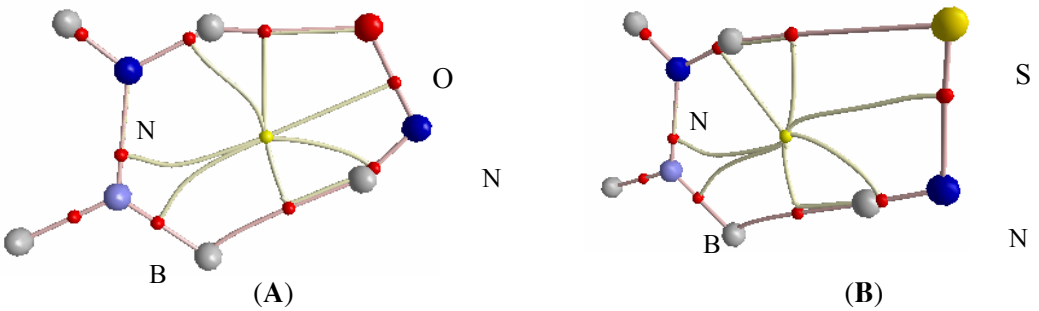

Figure 2: Schematic drawing of the examined complexes, showing the geometry of all their critical points (red small circles are BCPs, yellow small circles are RCPs)

Table 2: Topological analysis of BCPs in BH_2NH_2...HNZ at the MP2/6-311++G(2d,2p) level

		$\rho(r)$	λ_1	λ_2	λ_3	$\nabla^2(\rho(r))$
A	N8-H1...O6-N5	0.0126	-0.0150	-0.0139	0.0794	0.0505
	B9-H4...H7-N5	0.0079	-0.0081	-0.0079	0.0400	0.0240
	RCP	0.0030	-0.0020	0.0077	0.0121	0.0178
B	N8-H1...S6-N5	0.0115	-0.0115	-0.0106	0.0568	0.0346
	B9-H4...H7-N5	0.0093	-0.0099	-0.0098	0.0490	0.0293
	RCP	0.0030	-0.0019	0.0065	0.0116	0.0162

λ_i is an eigenvalue of Hessian matrix of electron density ($\rho(r)$).

The results from table 3 indicate that there is electron density transfer (EDT) from HNZ to BH_2NH_2 upon complex formation with positive values of EDT, which are in turn 0.0046 e and 0.0122 e for **A** and **B** respectively. The stretching frequencies of the B9-H4 bonds and the N8-H1 bonds are decreased corresponding to the negative value of $\Delta\nu$. Simultaneously, there are increases of infrared intensities in these bonds as shown in table 3. Therefore, there exists the red-shifting hydrogen bonds and dihydrogen bonds in two complexes, corresponding to elongation of the N8-H1 and X9-H4 bonds, compared to the monomers,

regardless of whether the BH_2NH_2 interactions with HNO or HNS. Inspection of the results in table 3 that upon formation there are slight increases of electron density in the σ*(B9H4) orbitals with the values of 0.0010 e and 0.0006 e for the complex A and B respectively although there are electron density transfers from the σ(B9H4) orbitals to the σ*(N5-H7) orbitals with the relatively small value of the σ(B9-H4)→σ*(N5-H7) intermolecular hyperconjugation energy, 0.82 and 1.05 kcal.mol^{-1} in the complex **A** and **B** respectively. Hence, it should be thought that the electron density redistribution in BH_2NH_2 upon complex formation causes in increase of electron density in the σ*(B9-H4) orbitals. Simultaneously, the NBO charges on the B9, H4 atoms carry the more positive and negative values respectively as listed in Table 3. This means that there is increase of polarization in the B9-H4 bonds when the B9-H4 bonds elongated. It should be thought that the elongation of the B9-H4 bonds is due to attractive interaction of two hydrogens charged inversely. Furthermore, when the complexes are formed, there is decrease of the s-characters and increase of the n-index in the B9-H4 bonds as specifically shown in Table 3, which directs the B9-H4 bonds towards elongation associated with red shift of their stretching frequencies. In summary, the increase of the σ*(B9-H4) electron density, the polarization of the B9-H4 bonds, and decrease of the s-character of the B9-H4 bond play an important role in elongating of the B9-H4 bonds corresponding to the red shifts of their stretching frequencies. From Table 3, there is strong transfer of electron density from n(Z) to σ*(N8-H1) orbitals as demonstrated in large value of the hyperconjugative E(n(Z6)→σ*(N8-H1)) interaction. This strong transfer leads to significant increase in population of the σ*(N8-H1) orbitals. Otherwise, there are increases of both the s-character percentage (decreasing n-index in sp^n) of all N8 atoms and positive charge on H1 atoms, which results in shortening bond and blue shifting of stretching frequency. However, all the N8-H1 bonds are lengthened as discussed above, corresponding to the red shift of their stretching frequencies as shown in table 3. Therefore, it indicates that for the N8-H1 bonds the E(n(Z6)→σ*(N8H1)) intermolecular hyperconjugation effect exceeds the rehybridization effect on the red shift of the N8-H1 bonds.

Table 3: Change of stretching frequencies Δν (cm^{-1}), their infrared intensities ΔI (km.mol^{-1}), hyperconjugation energies (kcal.mol^{-1}) and NBO analysis of the complexes

	A	B
EDT (e)	0.0046	0.0122
Δν(ΔI) (B9-H4)	-38 (48)	-36 (38)
Δν(ΔI) (N8-H1)	-33 (86)	-63 (138)
Δν(ΔI) (N5-H7)	56 (-69)	6 (-36)
$\Delta\sigma^*(B9-H4)$ (e)	0.0010	0.0006
$\Delta\sigma^*(N8-H1)$ (e)	0.0023	0.0074
$\Delta\sigma^*(N5-H7)$ (e)	-0.0020	-0.0001
Δ%s(B9)	-0.71	-0.65
Δ%s(N8)	0.86	1.06
Δ%s(N5)	0.87	1.14
Δq(B9) (e)	0.0003	0.0029
Δq(H1) (e)	0.0209	0.0135
Δq(H4) (e)	-0.0293	-0.0285
Δq(H7) (e)	0.0202	0.0165
$E(n(Z6)\rightarrow\sigma^*(N8-H1)$	2.26	3.56
$E(n(Z6)\rightarrow\sigma^*(N5-H7))$	15.78	7.37
$\Delta E(n(Z6)\rightarrow\sigma^*(N5H7))$	-1.90	-0.77
$E(\sigma(B9-H4)\rightarrow\sigma^*(N5-H7))$	0.82	1.05
Sp^n (B9)	1.94 (1.88)	1.93 (1.88)
Sp^n (N8)	2.71 (2.83)	2.68 (2.83)
Sp^n (N5)	3.77 (3.98)	2.99 (3.18)

The parenthesis in three ending lines is denoted for monomer; the $E(n(Z6)\rightarrow\sigma^*(N5-H7))$ intermolecular hyperconjugation energy of HNO and HNS is 17.68, 8.14 kcal.mol^{-1} respectively.

We continue discussing the origin of the blue-shifting dihydrogen bonds in the N5-H7 bonds in two complexes. From table 3, it can be

seen that the electron density in the σ*(N5-H7) orbitals decreased, which unambiguously means strengthening and contraction of the N5-H7 bonds and blue shift of stretching frequencies. Indeed, the blue shift is observed for the N5-H7 bond in the complex **A**, corresponding to contraction (0.0027 Å), increase of the stretching frequency (56 cm^{-1}) and decrease of the infrared intensity (69 $km.mol^{-1}$). The slightly blue shift is also detected for the N5-H7 bond with the value 6 cm^{-1} although there is a small elongation of the N5-H7 bond length as shown in table 1. Hence, it is careful not to attribute the red shift to increase of the X-H bond length that decrease of stretching frequency is only attributed to the red shift. The larger decrease of electron density of the σ*(N5-H7) orbital in **A** relative to **B** may be due to both the smaller intermolecular hyperconjugation energy from the σ(B9-H4) to σ*(N5-H7) orbital and the stronger decrease of intramolecular hyperconjugation energy from the n(Z6) to σ*(N5-H7) orbital for the former that for the latter as listed in table 3.

Alabugin et al. [15] have recently proposed that the change of the X-H bond length was determined by a balance of the opposing factors: elongation of the X-H bond due to the strong intermolecular hyperconjugation n(Y)→σ*(X-H)) and rehybridization results in contraction of the X-H bond. In their opinion, the positive charge of the H atom in the X-H...Y hydrogen bond is larger than that in the monomer; according to Bent's rule, rehybridization increases the s-character of the X-H bond, strengthens its polarization, and consequently, shortens the X-H bond. As seen from table 3, for the N5-H7 bonds in both **A** and **B**, our calculated results coincide well with the results of rehybridiation. In two these analyzed complexes; there are increases in positive charges on H7 atoms of the N5-H7 bonds, increase the s-character of the N5 atoms, decrease of n-index of N5 atoms in sp^n hybrid orbitals compared to the monomer respectively. This means that rehybridization effect is advantageous to blue shift of the N5-H7 dihydrogen bonds in the complexes of BH_2NH_2 with HNZ. These blue shifts are also supported by contribution of decrease of electron density in the σ*(N5-H7) antibonding orbitals and small values of intermolecular hyperconjugation energy E(σ(B9-H4)→σ*(N5-H7)) which is only equal 0.82 and 1.05 $kcal.mol^{-1}$ for the complex **A** and **B** respectively.

IV - CONCLUDING REMARKS

The complexes BH_2NH_2....HNZ have been investigated with the MP2/6-311++G(2d,2p) level of theory. It is worth mentioning that both two complexes **A** and **B** belong to the N5-H7 blue-shifting dihydrogen bonds of type B9-H4...H7-N5, corresponding to increase of stretching frequency, and decrease of its infrared intensity. However, a large contraction of the N5-H7 is found in A and a slight elongation of the N5-H7 bond is detected in **B**. Besides, the red-shifting hydrogen bonds of conventional type N8-H1...Z6 (Z = O, N) are observed in two analyzed complexes. From the above analysis, it can be concluded that the blue shifts of the N5-H7 bonds are contributed by increase of the s-character percentage (decreasing n-index in sp^n hybrid orbital), and as well as decrease of electron density in the σ*(N5-H7) orbitals contributed by effect of significant decrease of the intramolecular hyperconjugation E(n(Z6)→σ*(N5-H7)) that overcomes the slightly intermolecular hyperconjugation σ(B9-H4)→σ*(N5-H7).

This work is supported by NAFOSTED under project 104.03.142.09.

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