The Effects of Hybridization and Hyperconjugation in the Intramolecular Blue-shifted H-Bonds N–H···O

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Theoretical study of an example of intramolecular blue-shifted H-bond N–H···O shows that the blue shift of the N–H bond is caused by an increase in s-character of the N-hybrid AO of the N–H bond upon formation of the H-bond. The effect of hyperconjugation was also analyzed.

In recent years the blue-shifted H-bond has attracted the attention[1,2] of many chemists; it is much more complicated than the red-shifted H-bond and its essences are still not completely known. The blue-shifted H-bond X–H···Y is characteristic of contraction of the XH bond and increase of the XH stretch frequency. For explaining the blue shift, the theory of hyper-conjugation and rehybridization proposed by Alabugin, Weinhold, et al.[3] is acceptable, which suggested that the XH bond length in X–H···Y hydrogen-bonded complexes is controlled by a balance of two main factors acting in opposite directions: XH bond lengthening due to n(Y) → σ^*(HX) hyperconjugation and XH bond shortening due to increase in the s-character and repolarization of the XH bond. The intermolecular hyperconjugation causes formation of red-shifted H-bonds, and as the author pointed out, the rehybridization as the reason of blue shift is not a new thing but just an example of Bent's rule.

The theory of Alabugin is further developed[4] by introducing the intramolecular hyperconjugation n(Z) → σ^*(HX) in the proton donor H–XZ, which is important in H-bonding because it can adjust electron density on σ^*(HX) upon formation of the H-bond. In most cases, there is a lone pair orbital in Z as the donor orbital participating in this interaction; in some cases a σ orbital, especially a σ(ZH) orbital can also act as the donor orbital. Here we will give an example.

The theory of hyperconjugation and rehybridization has successfully been applied to intermolecular H-bonds.[5] Here we give an interesting example of intramolecular H-bonds. In ref. 6, it has been shown that the structure **2** in Figure 1 has a blue-shifted H-bond N–H···O, the NH bond is short and its stretch frequency is large relative to structure **1**. The authors have explained this using the steric effect, and strengthened their viewpoint by the blue shift of the NH bond in structure **6** relative to **5** in Figure 3. The authors' analysis sounds reasonable, but we can give a more reasonable explanation by use of Bent's rule and the concept of intramolecular hyperconjugation.

We performed the calculation at the MP2 level of theory with the two basis sets 6-311++G(d,p) and 6-311++G(2df,2p) using Gaussian 03.[7] For the 2π conjugate systems, except for the open-pentagon frame molecules **1** and **2**, we also calculated the linear frame molecules **3** and **4**, as shown in Figure 2, in order to study the intramolecular hyperconjugation.

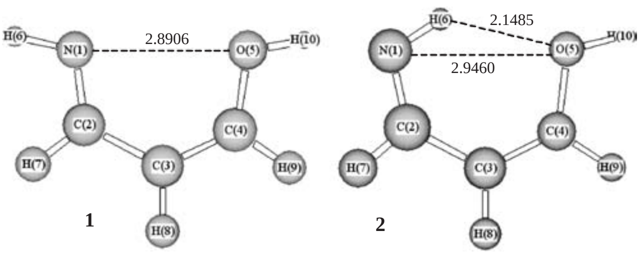

Figure 1. Geometry structures of **1** and **2** (MP2/6-311++G(d,p)).

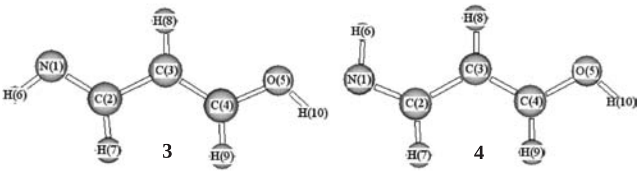

Figure 2. Geometry structures of **3** and **4** (MP2/6-311++G(d,p)).

Table 1. Bond length (Å) and stretch frequency (cm^{-1}) of NH, and the energy ΔE (kJ/mol) of the structure **1** to **4** (the energy of **1** is taken as zero point) and **5** to **6** (the energy of **5** is taken as zero point), and results of NBO analysis: the net charges q of atoms, s-character of N hybrid of NH bond, and hyperconjugation energies $E\{n, \sigma \rightarrow \sigma^*\}$ (kcal/mol), at the MP2 level of theory with the basis sets 6-311++G(d,p) and 6-311++G(2df,2p) (in the brackets)

Systems	**1**	**2**	**3**	**4**	**5**	**6**
r(NH)	1.0231 (1.0190)	1.0223 (1.0187)	1.0223 (1.0183)	1.0255 (1.0216)	1.0261 (1.0221)	1.0240 (1.0207)
υ(NH)	3490.5 (3493)	3515.7 (3513)	3502.8 (3504.7)	3461.1 (3460.1)	3453.6 (3452.9)	3488.3 (3480.4)
ΔE	0.00	−9.51 (−9.51)	−21.90 (−21.10)	−18.61 (−18.30)	0.00	−0.82 (−1.17)
q(H(N))	0.3175 (0.3203)	0.3367 (0.3375)	0.3215 (0.3238)	0.3084 (0.3110)	0.3096 (0.3128)	0.3347 (0.3312)
q(N)	−0.6429 (−0.6574)	−0.6416 (−0.6528)	−0.6734 (−0.6871)	−0.6621 (−0.6755)	−0.6410 (−0.6521)	−0.6516 (−0.6600)
s(N)% in σ(NH)	20.48% (20.83%)	22.16% (22.50%)	20.93% (21.24%)	20.78% (21.11%)	20.69% (21.05%)	21.83% (21.90%)
σ^*(NH)	0.0067 (0.0068)	0.0102 (0.0103)	0.0058 (0.0059)	0.0100 (0.0101)	0.0112 (0.0113)	0.0116 (0.0113)
$E\{\sigma(C_{(2)}C_{(3)}) - \sigma^*(NH)\}$	2.98 (3.08)	—	3.04 (3.17)	—	—	—
$E\{\sigma(C_{(2)}H_{(7)}) - \sigma^*(NH)\}$	0.95 (0.97)	5.35 (5.63)	0.92 (0.91)	5.78 (6.02)	6.16 (6.42)	5.76 (6.09)
$E\{n(O) - \sigma^*(NH)\}$	—	1.48 (1.56)	—	—	—	1.14 (0.83)

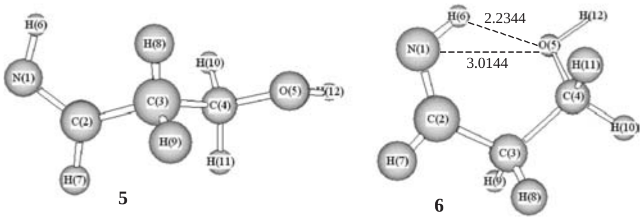

Figure 3. Geometry structures of **5** and **6** (MP2/6-311++G(d,p)).

For the 1π conjugate systems, the structure **4** in ref. 6, similar to the structure **1** here of the 2π conjugate systems, was not obtained, we think it is not stable because the single C–C bond and C–O bond can freely rotate. The NH bond length and its stretch frequency and the relative energies with corrections of BSSE[8] and zero-point energy, and the results of NBO analysis[9] are listed in Table 1, the results of the two basis sets are consistent with each other.

The calculated results show that the H-bond N–H···O in **2** and **6** is blue shifting, respectively relative to **1** and **5**. Comparing **2**(**6**) with **1**(**5**), we found that the hydrogen bonded to nitrogen in **2**(**6**) has larger positive charge than that in **1**(**5**), so the NH bond has larger polarization in **2**(**6**) than in **1**(**5**), and correspondingly the s-character of the N-hybrid of the NH bond in **2**(**6**) is also larger than that in **1**(**5**). So according to Bent's rule, the NH bond in **2**(**6**) contracts and its stretch frequency blue shifts relative to **1**(**5**). In **2** and **6**, the hyperconjugation n(O) $\rightarrow$ σ^*(NH), which can lead to a red-shifted H-bond, is small, so the charge transfer from n(O) to σ^*(NH) is negligible. The n(O) $\rightarrow$ σ^*(NH) interaction has negligible contribution to the frequency shift of the formed H-bond because the n(O) lone pair orbital is a $sp^{1.3}$ hybrid orbital, and has large s-character and small diffusion. The occupancies of σ^*(NH) in **5** and **6** are equal, however, the occupancy of σ^*(NH) in **2** is 0.003e larger than that in **1**. The difference between these two cases is caused by the $\sigma \rightarrow \sigma^*$ hyperconjugation. In structures **2**, **5**, and **6**, $N_{(1)}H_{(6)}$ and $C_{(2)}H_{(7)}$ are of trans-configuration, but in **1**, they are of cis-configuration. Both $\sigma(C_{(2)}H_{(7)})$ and $\sigma(C_{(2)}C_{(3)})$ can interact with $\sigma^*(N_{(1)}H_{(6)})$, but σ(CH) is a stronger hyperconjugation donor than σ(CC), and only when the donor σ and acceptor σ^* are of trans-configuration, the overlap, hyperconjugation, and electron density transfer between them are appreciable. So in **2**, **5**, and **6**, the large hyperconjugation $\sigma(C_{(2)}H_{(7)}) \rightarrow \sigma^*(N_{(1)}H_{(6)})$ transfers large electron density from σ(CH) to σ^*(NH) such that the occupancy of σ^*(NH) has large increment and larger than that in **1**. It is this orbital interaction that explains the blue shift (-0.002 Å, 35 cm^{-1}) of **6** relative to **5** is larger than the blue shift (-0.0008 Å, 25 cm^{-1}) of **2** relative to **1**.

To observe further the effect of the hyperconjugation $\sigma \rightarrow \sigma^*$, we compared the two structures **3** and **4**. The NH bond length in **3** is shorter than that in **4** and its stretch frequency is larger than that in **4**. These differences between **3** and **4** are also due to the $\sigma \rightarrow \sigma^*$ hyperconjugation. In **3**, $N_{(1)}H_{(6)}$ and $C_{(2)}H_{(7)}$ are of cis-configuration, but in 4 they are of trans-configuration. So in 4 the σ(CH) $\rightarrow$ σ^*(NH) hyperconjugation transfers more electron density from σ(CH) to σ^*(NH), than that from σ(CC) to σ^*(NH) by σ(CC) $\rightarrow$ σ^*(NH) in **3**. The occupancy in σ^*(NH) of **4** is about 0.010e, larger than that of **3**, 0.0058e. Because of the effect of this $\sigma \rightarrow \sigma^*$ interaction, the blue shift of the H-bond N–H···O in **2** should be calculated not with respect to **1** but with respect to **4**, because the structures **2** and **4** have the same $\sigma \rightarrow \sigma^*$(NH) interaction, their relationship is similar to that of **6** and **5**. So the blue shift of the H-bond N–H···O in **2** are $\Delta r(\mathrm{NH}) = -0.0032$ Å, $\Delta \upsilon(\mathrm{NH}) = 54.6\,\mathrm{cm}^{-1}$, relative to **4**, within the 6-311++G(d,p) basis set. The blue shift of **2** with respect to **4** is larger than the blue shift of **2** relative to **1**, because the former is the pure blue shift caused by an increase in the s-character, but the latter is the net result of the NH bond contraction caused by an increase in the s-character and the NH bond elongation caused by the σ(CH) $\rightarrow$ σ^*(NH) hyperconjugation where the NH contraction is larger than the NH elongation.

Summarily, for these intramolecular H-bonds, the blue shift of the NH bond is caused by an increase of s-character of the N-hybrid and polarization of the NH bond, this NH bond shortening is larger than the NH bond lengthening owing to the hyperconjugations σ(CH) $\rightarrow$ σ^*(NH) and n(O) $\rightarrow$ σ^*(NH). The n(O) $\rightarrow$ σ^*(NH) interaction is negligible.

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