

Coexistence of S–H...O and N–H...O Blue-shifted Hydrogen Bonds in a Small System: HSO...HNO

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Theoretical study indicates that the HSO...HNO complex possesses simultaneously two substantial blue-shifted H bonds: S–H...O and N–H...O. The blue shift of the S(N)–H stretching frequencies is due to an intricate combination of two shortening effects of the electron density decrease in the $\sigma^*[\text{S(N)}\text{--H}]$ and the rehybridization of sp^n S(N)–H hybrid orbitals.

Hydrogen bond is essential to many chemical and biochemical processes. A characteristic feature of X–H...Y H bond formation is X–H bond lengthening with a concomitant red shift of the X–H stretching frequency. However, a number of experimental and theoretical studies have reported the existence of an unusual class of blue-shifted H bonds in which H-bond formation leads to X–H bond shortening and to a blue shift of the X–H stretching frequency.¹ From its very discovery, blue-shifted H bonds received much attention from theoreticians who suggested several explanations for this phenomenon. Hobza and Havlas proposed that there was difference in nature between the red-shifted and blue-shifted H bonds and that the structural reorganization is the fundamental reason for the blue-shifted H bond.² Some other researchers considered that there was no difference between the blue-shifted and red-shifted H bonds in nature.³ Alabugin et al. suggested that the X–H bond length in X–H...Y H bond is determined by a subtle balance of the opposing effects: X–H bond elongating effect due to hyperconjugative $n(\text{Y}) \rightarrow \sigma^*(\text{X}\text{--H})$ interaction and X–H bond shortening effect due to rehybridization.⁴ To the best of our knowledge, the origin of blue-shifted H bond is still not completely known because it is much more complicated than the red-shifted H bond. Consequently, it is significant to provide novel insights into the origin of blue-shifted H bond. In addition, it is worthy of mentioning that the H bonds in stable molecule and radical systems have been paid much attention because of the importance of prereactive complexes in molecule–radical reactions in recent years.⁵ The deepening investigation on the nature of H bonds in the prereactive complex HSO...HNO is very interesting.

It should be noted that both theoretical and experimental researches on blue-shifted H bond were mainly concentrated on the C–H bond and very scarcely on the N–H and S–H bonds. Alabugin et al. predicted that the X–H...Y blue-shifted H bond is likely to be observed only when the X–H bond elongating hyperconjugative $n(\text{Y}) \rightarrow \sigma^*(\text{X}\text{--H})$ interaction is relatively weak.⁴ Consequently, S–H...Y and N–H...Y blue-shifted H bonds are interesting because $\sigma^*(\text{S}\text{--H})$ and $\sigma^*(\text{N}\text{--H})$ orbitals are better acceptors than $\sigma^*(\text{C}\text{--H})$ orbital. Surprisingly, S–H...O and N–H...O blue-shifted H bonds were found in our study to coexist in a very small system of HSO...HNO complex. Furthermore, a reasonable explanation for the origin of the S–H...O and N–H...O blue-shifted H bonds was proposed.

The characteristics of the HSO...HNO complex determined by both standard and counterpoise-corrected optimizations⁶ at MP2/6-311++G(2d,2p) and B3LYP/6-311++G(2d,2p) levels are presented in Table 1 and Figure 1. The results of these optimizations correspond to energy minima since no imaginary frequencies were found. From X–H stretching frequency change between the monomers HSO and HNO and the complex HSO...HNO shown in Table 1, we can see that there is a slight difference between MP2 and B3LYP calculations. Taking the $(\text{HF})_2$ complex as an example, Hobza and Havlas have pointed out the necessity of using the CP-corrected optimization.⁷ However, the blue shift of the X–H stretching frequency in the complex HSO...HNO by CP-corrected optimization is still in reasonable agreement with that of the X–H stretching frequency by standard optimization. It should be pointed out that the N5–H4 stretching frequency displays very large blue shift (more than 100 cm^{-1}) in the complex HSO...HNO. For the S–H...O H bond, all the methods also suggest that the S2–H1 bond is shortened by about 0.0045 \AA owing to the complex formation. Furthermore, all the methods predict that the blue shift of the S–H stretching frequency in the complex HSO...HNO is about 45 cm^{-1} . On the basis of these analyses, we can confirm that the complex HSO...HNO exhibits simultaneously two substantial blue-shifted H bonds: N5–H4...O3 and S2–H1...O6.

In order to investigate the origin of the blue-shifted H bond, the NBO analysis⁸ is performed at MP2/6-311++G(2d,2p) level and the corresponding results are listed in Table 2. In the

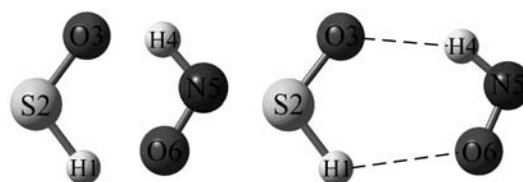


Figure 1. Optimized structure of the monomers and complex.

Table 1. Characteristics of the complex HSO...HNO with different (standard and CP-corrected) optimizations at MP2/6-311++G(2d,2p) and B3LYP/6-311++G(2d,2p) levels

	Standard	CP
$r(\text{O3}\cdots\text{H4})/\text{\AA}$	2.0963 (2.2236) ^a	2.1599 (2.2521)
$r(\text{O6}\cdots\text{H1})/\text{\AA}$	2.4923 (2.5568)	2.5523 (2.5800)
$\Delta r^b(\text{S2}\text{--}\text{H1})/\text{\AA}$	–0.0045 (–0.0047)	–0.0039 (–0.0042)
$\Delta \nu^c(\text{S2}\text{--}\text{H1})/\text{cm}^{-1}$	+50 (+48)	+44 (+43)
$\Delta r(\text{N5}\text{--}\text{H4})/\text{\AA}$	–0.0056 (–0.0073)	–0.0059 (–0.0071)
$\Delta \nu(\text{N5}\text{--}\text{H4})/\text{cm}^{-1}$	+115 (+126)	+121 (+121)

^aB3LYP/6-311++G(2d,2p) level in the brackets. ^bChange of bond length. ^cChange of stretching frequency.

Table 2. NBO analysis of the monomers HSO and HNO and the complex HSO...HNO at the MP2/6-311++G(2d,2p) level

	HSO	HNO	HSO...HNO
n(O6) → $\sigma^*(S2-H1)^a$	—	—	3.47
n(O3) → $\sigma^*(N5-H4)$	—	—	17.03
n(O3) → $\sigma^*(S2-H1)$	99.04	—	83.89
n(O6) → $\sigma^*(N5-H4)$	—	73.76	57.15
$\sigma^*(S2-H1)^b$	0.05317	—	0.04655
$\sigma^*(N5-H4)$	—	0.02858	0.02686
%s char(S2-H1) ^c	11.41% ^{α}	—	11.92% ^{α} ,
	13.56% ^{β}	—	14.29% ^{β}
%s char(N5-H4)	—	19.97%	21.92%

^aEnergy of hyperconjugative n(O6) → $\sigma^*(S2-H1)$ interaction (kJ/mol). ^bElectron density value in the S2-H1 antibonding orbital (e). ^cS character in the spⁿ S2-H1 hybrid orbital for α and β spin systems.

NBO analysis, the importance of hyperconjugative interaction (electron density transfer) from n(Y) to $\sigma^*(X-H)$ in the X-H...Y H bond is well known, which leads to the electron density increase in the $\sigma^*(X-H)$. From Table 2, the hyperconjugative n(O6) → $\sigma^*(S2-H1)$ interaction is 3.47 kJ/mol, which should contribute to the electron density increase in the $\sigma^*(S2-H1)$. However, the opposite is found. The question is how to explain the electron density decrease in the $\sigma^*(S2-H1)$. We will show below that the electron density redistribution plays a significant role for the unusual phenomenon. In the O3-S2-H1...O6 H bond, the hyperconjugative n(O6) → $\sigma^*(S2-H1)$ interaction leads to electron density increase in the $\sigma^*(S2-H1)$. On the other hand, a decrease in the hyperconjugative n(O3) → $\sigma^*(S2-H1)$ interaction of the complex HSO...HNO, relative to the monomer HSO, has the opposite effect. As a result, the net change of electron density in the $\sigma^*(S2-H1)$ depends on the balance of these two interactions which changed in an antiparallel way. It may be of interest to make a quantitative comparison between these two interactions. Then, we define an index, called *R*. Here, the *R* can be expressed as $R = (E_{1,monomer} - E_{1,complex})/E_2$, where the $E_{1,monomer}$ and $E_{1,complex}$ mean the hyperconjugative n(O3) → $\sigma^*(S2-H1)$ interactions in the monomer HSO and the complex HSO...HNO, respectively. The E_2 denotes the hyperconjugative n(O6) → $\sigma^*(S2-H1)$ interaction in the complex HSO...HNO. According to the definition of the *R*, the *R* can be used to describe the strength of the electron density redistribution. In general, the larger the value of *R*, the stronger the electron density redistribution effect. It can be seen in Table 2 that there a significant decrease of the n(O3) → $\sigma^*(S2-H1)$ in the complex HSO...HNO, relative to the monomer HSO. Furthermore, the value of the *R* is relatively large and attains to 4.37, which indicates that the electron density redistribution effect is very strong in the O3-S2-H1...O6 H bond. Owing to the electron density redistribution, in the O3-S2-H1...O6 H bond, electron density is transferred from n(O6) to $\sigma^*(S2-H1)$ firstly, then more electron density in the $\sigma^*(S2-H1)$ is transferred to n(O3), which leads to electron density decrease in the $\sigma^*(S2-H1)$. Consequently, the electron density decrease in the $\sigma^*(S2-H1)$ can well be interpreted. The mechanism for electron

density decrease of $\sigma^*(N5-H4)$ is quite similar to that of $\sigma^*(S2-H1)$. It is worth pointing out that electron density redistribution is related to the character of the monomer. From Table 2, we can see that for monomer HSO the hyperconjugative n(O3) → $\sigma^*(S2-H1)$ interaction is up to 99.04 kJ/mol and that the electron density in the $\sigma^*(S2-H1)$ is up to 0.05317e. For the monomer HNO, the hyperconjugative n(O6) → $\sigma^*(N5-H4)$ interaction is relatively large and $\sigma^*(N5-H4)$ electron density is 0.02858e. In general, the larger the electron density in $\sigma^*(X-H)$ of the monomer, the stronger the electron density redistribution of the complex. In addition, according to the rehybridization model, the s character of spⁿ hybrid orbital for the S2-H1 bond increases upon the S2-H1...O6 H bond formation. Similarly, the s character of the spⁿ hybrid orbital has a very large increase for the N5-H4 bond, which results in the intense contraction of the N5-H4 bond.

In a summary, there are three factors affecting the red-shifted or blue-shifted H bonds: hyperconjugative n(Y) → $\sigma^*(X-H)$ interaction, electron density redistribution and rehybridization. Hyperconjugative n(Y) → $\sigma^*(X-H)$ interaction contributes to the bond elongating effect. Electron density redistribution and rehybridization contribute to the bond shortening effect. Furthermore, we suggested that red shift and blue shift are mainly determined by two factors: the magnitude of the hyperconjugative n(Y) → $\sigma^*(X-H)$ interaction and the character of the monomer. The magnitude of the threshold (the hyperconjugative n(Y) → $\sigma^*(X-H)$ interaction) which determines the borderline between the red-shifted or blue-shifted H bonds is related to the character of the monomer. In general, the threshold is higher, when the monomer possesses the larger $\sigma^*(X-H)$ electron density.

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