Steric Effect is an Additional Possible Cause of Blue-shifting Hydrogen Bonds

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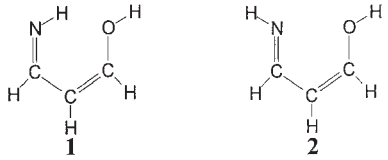
A novel simple example was found that at least sometimes the steric effect could cause a blue-shifting hydrogen bond, which indicates that Hobza's recent theory about the origin of the blue-shifting hydrogen bond is not complete.

The major driving forces leading to a hydrogen bond X–H···Y are generally believed to involve electrostatic interaction and charge transfer, which usually are able to weaken the X–H bond and therefore, elongate the X–H bond length and decrease the X–H stretching vibration frequency. This effect is called a red shift and represents the most important, easily detectable manifestation of the formation of a hydrogen bond.[1]

Thus, the recent observation[2] that in some hydrogen bonds like $F_3CH\cdots OH_2$, a blue shift instead of a red one occurs caused considerable interest immediately.[3] On the basis of various analyses of all the known blue-shifting hydrogen bonds, Hobza claimed that unlike the red-shifting hydrogen bonds, the blue-shifting ones should see no or little electron density transfer from the proton acceptor (Y) to the X–H σ^* antibonding orbital. Instead, increase of electron density was found in a remote part of the proton-donor molecule, e.g. C–F σ^* antibonding orbital in F_3CH, and a secondary unclear structural reorganization was proposed to cause the contraction of the X–H bond.



1 **2**

Here we would like to point out that the Hobza's explanation of blue-shifting hydrogen bonds is not complete because at least sometimes the steric effect can cause a blue-shifting hydrogen bond. This conclusion was drawn on the basis of the structures of the *cis* **1** and *trans* **2** conformers of the following compound.

All the calculations were done with Gaussian 98.[5] Various levels of methods, including molecular mechanics, semi-empirical, HF, and MP2 with different levels of basis sets were used. Frequency calculations were also performed on every optimized structure except that obtained with MP2/aug-CC-pVDZ, which confirmed that the optimized structures are real minima.

In Figure 1 were shown the optimized structures of **1** and **2** with MP2/6-311++g** method. The N–H bond lengths, N–H vibration frequencies, and total energies were summarized in Table 1. According to the results, it is obvious that the N–H bond length is shortened and its vibration frequency blue shifted if the compound is hydrogen bonded. Remarkably, this blue-shifting hydrogen bond does not involve any C–H···Y weak interaction, nor does it have any electron-withdrawing group like F on the proton donor side. Instead, it is a very simple N–H···O hydrogen bond.

1 **2**

Figure 1. MP2/6-311++g** structure of **1** and **2**.

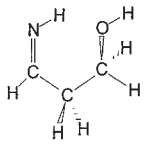
Table 1. The optimized N-H bond lengths, total energies, energy difference, and N-H stretching vibration frequencies of **1** and **2**

Method	N-H bond length /Å		Energy			Frequency/cm^{-1}	
	1	**2**	**1**/a.u.	**2**/a.u.	ΔE /kJ·mol^{-1}	**1**	**2**
UFF	1.0295	1.0231	0.0137	0.0086	−13.4	3727.4	3728.9
DREIDING	1.0223	0.9610	0.0092	0.0072	−5.2	2996.2	2999.9
AM1	0.9993	0.9996	−0.0251	−0.0150	28.6	3413.5	3410.9
PM3	0.9873	0.9877	−0.0152	−0.0091	16.0	3466.7	3474.3
HF/STO-3G	1.0463	1.0471	−242.6123	−242.6063	16.9	3903.6	3878.3
HF/3-21G	1.0124	1.0136	−244.3967	−244.3856	31.2	3638.6	3586.9
HF/6-31G	1.0052	1.0062	−245.6649	−245.6556	26.2	3732.5	3695.4
HF/6-31+G*	1.0034	1.0045	−245.7809	−245.7762	13.0	3772.8	3734.7
HF/6-311++G**	1.0028	1.0036	−245.8487	−245.8446	11.6	3759.7	3728.2
MP2/6-31+G*	1.0254	1.0269	−246.5070	−246.5021	13.8	3493.2	3456.3
MP2/6-311++G**	1.0223	1.0231	−246.6433	−246.6396	10.8	3515.8	3490.6
MP2/Aug-CC-pVDZ	1.0279	1.0283	−246.5990	−246.5955	9.8	—	—

Also interestingly, the above blue shift behavior does not require one to use very sophisticated methods to predict it. Not only very small basis sets like sto-3 g and 3–21 g, but also semi-empirical method like AM1 and PM3 can give qualifiedly correct results. Compared to the fact that low level HF and especially AM1 and PM3 methods cannot correctly predict the blue shift in the systems such as $F_3CH\cdots OH_2$,[6] the current result may indicate that the cause of blue shift here is simpler and therefore, easier to model. Nevertheless, it should be noted that the molecular mechanic methods that we used were not able to predict the blue shift, which may be considered as a novel problem to overcome in the future design of the force fields.

As no electron-withdrawing group like F is present on the proton donor side, the cause of the blue shift here cannot be attributed to any peculiar electron density transfer. Instead, since in **1** the six-membered hydrogen-bonded ring has to adopt a nearly planar geometry because of the double bonds, the H···O distance apparently is shorter than the value a repulsion-free non-bonding atom-atom distance could be. Therefore, it is expected that there is significant repulsion between the N–H and O groups in **1**, and this repulsion presumably forces the N–H to be shortened.

The above argument is supported by the structures of the following compounds **3** and **4**, in which a single C–C bond should enable the six-membered hydrogen-bonded ring free of repulsion. Indeed, MP2/6-311++g** calculations indicated that the N-H bond length in **3** (1.0240 Å) was longer than that in **4** (1.0218 Å), and the N-H vibration frequency was red shifted by the hydrogen bonding, (3488.4 cm^{-1} for **3** *vs* 3510.0 cm^{-1} for **4**) as normally expected. Since the only difference between **1/2** and **3/4** is whether two carbons are connected by a single or double bond, it has to be concluded that the steric repulsion caused by the double bond is the major cause of the blue shift.



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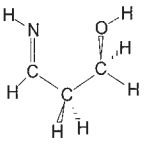

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In addition, it should be mentioned that the energy difference between **1** and **2** is 10.8 kJ mol^{-1}, whereas the energy difference between **3** and **4** is 19.4 kJ mol^{-1} at MP2/6-311++g** level. The much less energetic advantage of hydrogen bonding in **1** compared to **3** can be caused by the steric repulsion between N-H and O in **1** as well as by the fact that oxygen adjacent to a sp^3 carbon is more basic than that adjacent to a sp^2 carbon.

In short, a novel simple example was found that at least sometimes the steric effect could cause a blue-shifting hydrogen bond. Therefore, Hobza's recent theory about the origin of the blue-shifting hydrogen bond is not complete. Finally, it should be pointed out that the current compounds might not represent the best systems to study experimentally. Their small size, however, enables high-level theoretical investigations to demonstrate the principles. We are currently trying to synthesize compounds containing the above skeleton in order to find out if the blue shift caused by the steric effect can be confirmed by the experiment, too.

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