

Substituent Effects on the Blue-Shifting Hydrogen Bonds between $X - C \equiv C - CF_2 - H$ and Water

FAN, Jian-Miao(范剑淼) ZHANG, Ke-Chun(张科春) LIU, Lei(刘磊)
LI, Xiao-Song(李晓松) GUO, Qing-Xiang*(郭庆祥)

Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China

MP2/6-31 + g(d) calculations were performed verifying the existences of blue-shifting $X - C \equiv C - CF_2 - H \cdots OH_2$ hydrogen bonds. Detailed analyses revealed that the interaction energy and donor-acceptor distance had good correlations with the substituent Hammett constants. However, the extent of C—H bond contraction and the blue shift of the C—H stretching vibration did not show any good correlation with the traditional substituent constants, indicating that certain more complicated mechanisms might be involved in the present systems. Nevertheless, it was found that highly electron-withdrawing substituents were not favorable to the C—H bond contraction, and it was suggested that the attractive interaction between water and the carbon of $-CF_2H$ probably played an important role in the blue shift.

Keywords hydrogen bond, blue shift, vibration, bond contraction, substituent effect.

Introduction

Hydrogen bond is crucially important in chemistry and biochemistry fields. Therefore, people have been showing tremendous interest in the details of this interaction for many years. Usually, it was believed that the formation of $X-H \cdots Y$ hydrogen bond should result in the elongation of the X—H bond and concomitantly red shift of the X—H stretching vibration frequency. However, it was recently found both experimentally¹ and theoretically² that blue-shifting hydrogen bonds also exist, where the X—H bond surprisingly contracts upon hydrogen bond formation.

So far a number of blue-shifting hydrogen bonds

have been studied, but many important aspects of the blue-shifting hydrogen bonds still remain unknown.³ For example, the substituent effects have not been investigated on the blue-shifting hydrogen bonds, which, however, should be able to provide much important information about the interaction. Thus, we performed a high-level *ab initio* computational study on the substituent effects in $X - C \equiv C - CF_2 - H \cdots OH_2$ hydrogen bonding.

Methods

All the calculations were performed with GAUSSIAN 98.⁴ The monomers and complexes were optimized with MP2/6-31 + g(d) method, which is quite CPU-consuming for the present systems, but is necessary for the reliability of the calculations on noncovalent interactions.³ Frequency calculations were also performed at MP2/6-31 + g(d) level, which confirmed that the optimized complexes corresponded to true minima as no negative vibration frequency was found. Interaction energy was computed as difference in energy between the complex and the sum of isolated monomers, and basis set superposition error (BSSE) was corrected by the counterpoise procedure of Boys and Bernardi.⁵

Results and discussion

In Fig. 1 is shown a typical $X - C \equiv C - CF_2 - H \cdots OH_2$ hydrogen bond at its energy minimum, whose major structural parameters are summarized in Table 1.

* E-mail: qxguo@ustc.edu.cn; Fax: 86-551-3601592

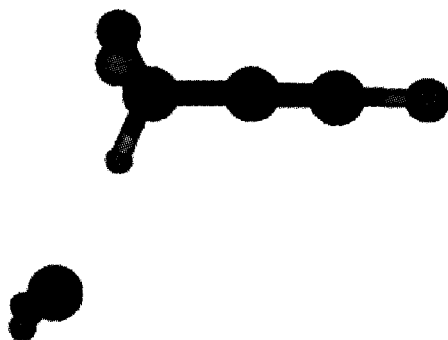
Received June 29, 2001; revised October 8, 2001; accepted October 16, 2001.

Project supported by the National Natural Science Foundation of China (No. 29972038).

Table 1 Structural parameters of the X—C≡C—CF₂—H···OH₂ hydrogen bonds

X	C—H bond length ($\times 10^{-1}$ nm)			C···O distance ($\times 10^{-1}$ nm)	C—H···O angle (deg.)
	In the monomer	In the complex	Variation (ΔL)		
H	1.0911	1.0890	-0.0021	3.2520	175.491
F	1.0909	1.0887	-0.0022	3.2502	179.117
Cl	1.0913	1.0890	-0.0023	3.2481	177.571
OH	1.0911	1.0888	-0.0023	3.2629	174.976
OCH ₃	1.0912	1.0891	-0.0021	3.2678	174.246
SH	1.0915	1.0893	-0.0022	3.2486	174.550
NH ₂	1.0914	1.0891	-0.0023	3.2770	172.150
NO ₂	1.0914	1.0896	-0.0018	3.2048	171.891
NHCH ₃	1.0916	1.0892	-0.0024	3.2808	172.953
OC ₂ H ₅	1.0910	1.0889	-0.0021	3.2702	174.841

According to Table 1, the C···O distances (0.320—0.328 nm) are of reasonable values for hydrogen bonds, and the C—H···O angles are all about 180 degree. Therefore, it is apparent that the systems are stabilized with C—H···O hydrogen bonding, a weak non-covalent interaction that recently has caused much attention.⁶ It should also be noted that the substituent groups are far away from the hydrogen bond so that their influence to the interaction should only be electronic in nature.

**Fig. 1** Structure of optimized F—C≡C—CF₂—H···O₂ hydrogen bond.

Interestingly, according to Table 1 it is obvious that all of the C—H bonds are shortened upon hydrogen bond formation, which means that the C—H bonds are strengthened as it interacts with H₂O. This behavior is also confirmed by the frequency calculations, with the results summarized in Table 2 with the interaction energies. According to Table 2, the C—H stretching vibration frequencies increase upon the hydrogen bond forma-

tion (blue shifting), which presumably could be easily observed with infrared spectroscopic studies.² The reliability of this blue shift can also be shown by the excellent correlation between the C—H bond lengths and stretch vibration frequencies of the monomers as well as complexes (Fig. 2). Thus, the blue-shifting hydrogen bonding phenomenon is also verified in the present study.

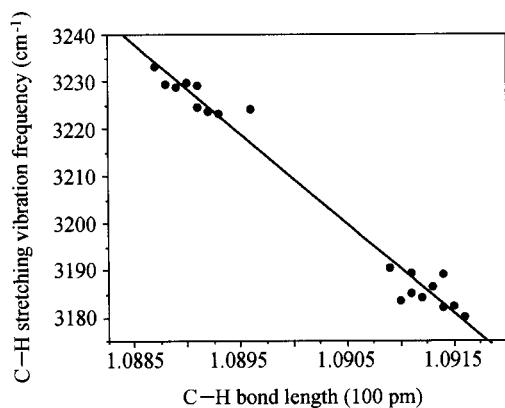
According to Table 2, it can be seen that the interaction energies of the C—H···O hydrogen bonds are decently large. However, it should be noted that the BSSE in calculation of the interaction energy is also nontrivial. Therefore, failure to correct the BSSE in studying the analogous systems might lead to erroneous results. Interestingly, plotting the interaction energies and the C···O distances vs. substituent σ_p constants give two straight lines as shown in Fig. 3. Both the slopes are negative, indicating that the more electron-withdrawing group should enhance the strength of the hydrogen bonding. Such a result is not hard to understand, as similar substituent effects were also found recently in the C—H···N (or O, F) hydrogen bonds between X—C≡C—H and NH₃, H₂O, and HF.⁷

However, it turns out that the extent of C—H contraction (ΔL) does not have any good correlation with either substituent σ_p or σ_p^+ constants. Only a marginally acceptable correlation could be obtained even if the electronic effect is considered explicitly as its field/inductive and resonance components.⁸

$$\Delta L = 0.0021 - 2.38F - 3.66R \quad (n = 10, r = 0.78)$$

Table 2 C—H stretching vibration frequencies and interaction energies

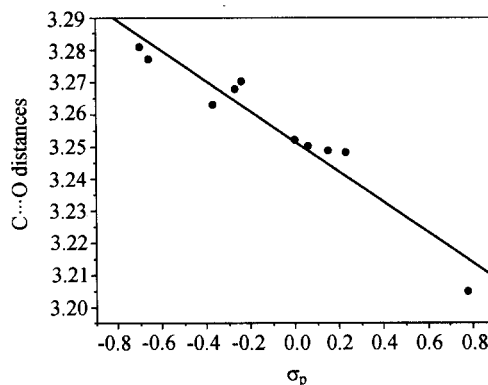
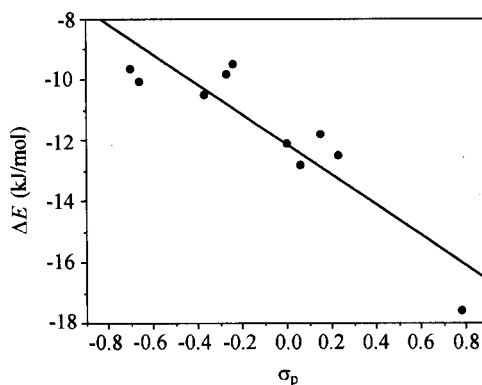
X	C—H vibration frequency (cm^{-1})			BSSE (kJ/mol)	Interaction Energy (kJ/mol)
	In the monomer	In the complex	Variation ($\Delta\nu$)		
H	3189.402	3229.771	+ 40.369	2.70	- 12.10
F	3190.506	3233.166	+ 42.660	2.73	- 12.81
Cl	3186.528	3229.740	+ 43.212	2.81	- 12.49
OH	3185.173	3229.394	+ 44.221	2.76	- 10.50
OCH ₃	3184.264	3229.162	+ 44.898	2.70	- 9.82
SH	3182.444	3223.236	+ 40.792	2.91	- 11.78
NH ₂	3182.127	3224.605	+ 42.478	2.70	- 10.05
NO ₂	3189.182	3224.160	+ 34.978	2.89	- 17.56
NHCH ₃	3180.151	3223.697	+ 43.546	2.68	- 9.63
OC ₂ H ₅	3183.578	3228.800	+ 45.222	2.76	- 9.48

**Fig. 2** Correlation between the C—H bond lengths and stretching vibration frequencies of the monomers as well as complexes.

This indicates that certain electronic effects other than normally known ones may be involved in blue-shifting hydrogen bonding. It is clear that electron-withdrawing substituents do not favor the blue shift, as the correlation coefficients before F and R constants are both negative. The conclusion is also supported by the fact that the NO_2 substituted system has the smallest value of C—H contraction.

In agreement with the above result, the extent of vibration blue shift does not have any good correlation with the normally used substituent constants (*e. g.* σ_p , σ_p^+ , F , and R), either. It should be mentioned that the correlation between the variation of the vibration frequencies ($\Delta\nu$) and the hydrogen bonding interaction energies is good as shown in Fig. 4. This again indicates

that the electron-withdrawing substituents do not favor the blue shift, as stronger electron-withdrawal increases the hydrogen bonding interaction energy.

**Fig. 3** Substituent effects on the interaction energies and C...O distances.

In order to understand the substituent effects on the blue-shifting hydrogen bonds further, we then calculate the Mulliken charges and energies of the frontier orbitals

Table 3 Mulliken charges and energies of the frontier orbitals of the systems

X	Mulliken charges in the monomer		Mulliken charges in the complex			HOMO of	LUMO of
	C (-CF ₂ -)	H (-CF ₂ H)	C (-CF ₂ -)	H (-CF ₂ H)	X-C≡C-CF ₂ -H	X-C≡C-CF ₂ -H	X-C≡C-CF ₂ -H
H	0.8498	0.2235	0.5091	0.3017	-0.00462	-0.4294	0.0665
F	0.8820	0.2258	0.5242	0.3041	-0.00407	-0.4401	0.0623
Cl	1.0760	0.2249	0.6093	0.3034	-0.00466	-0.4129	0.0522
OH	0.8094	0.2213	0.4359	0.2991	-0.00433	-0.4038	0.0456
OCH ₃	1.0905	0.2188	0.7534	0.2964	-0.00425	-0.3914	0.0691
SH	1.0012	0.2242	0.5293	0.3029	-0.00464	-0.3712	0.0474
NH ₂	0.9603	0.2154	0.6956	0.2918	-0.00526	-0.3715	0.0451
NO ₂	1.2218	0.2432	0.8038	0.3219	-0.00387	-0.4794	-0.0056
NHCH ₃	0.9399	0.2146	0.6856	0.2910	-0.00490	-0.3578	0.0565
OC ₂ H ₅	1.1857	0.2176	0.8864	0.2953	-0.00404	-0.3881	0.0721

of the monomers and complexes as summarized in Table 3. According to Table 3, the HOMO and LUMO energies are not hard to expect with the conventional theories of substituent effect, as electron-withdrawing substituents lower the orbital energy whereas the electron-donating substituents make it higher. By contrast, it is quite interesting to notice that both the C and H of -CF₂H carry positive charges in the monomer as well as in the complexes, and the proton of -CF₂H carries more positive charge in the complexes than in the monomers whereas carbon of -CF₂ carries less positive charge in the complexes than in the monomers. The total effect is that in the complex X - C≡C - CF₂ - H always carries net negative charge.

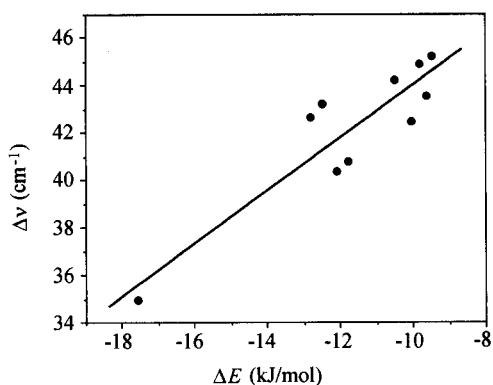


Fig. 4 Correlation between the blue shifts of the C—H stretching vibration and the hydrogen bonding interaction energies.

The above results may have some implications for

the mechanism of the blue shift. First, it should be noticed that the traditional theory of hydrogen bonding is not fully consistent with the blue-shifting hydrogen bonds. According to the conventional point of view, the formation of hydrogen bond (X—H···Y) should involve the charge transfer from the hydrogen bond acceptor (Y) to the X—H anti-bonding molecular orbital. The net effect should be the increase of electron density near proton, which is not observed here as proton carries more positive charge in the complexes. However, the fact that the electron density near proton is decreased here as a result of hydrogen bond formation is not fully unexpected, if one notices that fluorination makes the carbon of -CF₂H highly electron deficient. This is substantially different from the usual hydrogen bonds, where proton is normally bonded to negatively-charged electronegative atom. In other words, in addition to the interaction between proton and the hydrogen bond acceptor (H₂O), the interaction between carbon and H₂O should also be considered here. Presumably, this carbon-H₂O attractive interaction pushes the proton as well as its electrons from H₂O to carbon, so that C—H bond contracts and H carries more positive charge in the complex.

It should be mentioned that the charge transfer from the hydrogen bond acceptor (Y) to the X—H anti-bonding molecular orbital should still occur in the X - C≡C - CF₂ - H···OH₂ complexes, which results in weakening of the C—H bond. Intuitively, a strongly electron-withdrawing substituent should cause more such charge transfer. Although this increases the hydrogen bonding energy, it disfavors the C—H contraction at the

same time. Therefore, stronger electron-withdrawing substituent is not favorable to the blue shift hydrogen bonds, as observed above. It could be expected that stronger electron-donating substituent is not necessary to favor the blue shift, because at that time the complexation should be energetically too weak.

Conclusion

In summary, MP2/6-31 + g(d) method was used to investigate the substituent effects on the blue-shifting hydrogen bonds between $X - C \equiv C - CF_2 - H$ and water, which showed that the interaction energy and donor-acceptor distance had good correlations with the substituent Hammett constants. However, it was found that the extent of C—H bond contraction and the blue shift of the C—H stretching vibration did not show any good correlation with the traditional substituent constants, presumably because the factors determining their magnitudes were not covered by the usual substituent effects. Nevertheless, it was shown that highly electron-withdrawing substituents were not favorable to the C—H bond contraction, and the attractive interaction between water and the carbon of $-CF_2H$ might play an important role in the blue shift.

References

- Budesinsky, M.; Fiedler, P.; Arnold, Z. *Synthesis* **1989**, 858.
 - Keshavarz, K. M.; Cox, S. D.; Angus, R. O., Jr.; Wudl, F. *Synthesis* **1988**, 641.
 - Boldeskul, I. E.; Tsymbal, I. F.; Ryltsev, E. V.; Latajka, Z.; Barnes, A. J. *J. Mol. Struct.* **1997**, *436*, 167.
 - Hobza, P.; Spirko, V.; Havlas, Z.; Buchhold, K.; Reimann, B.; Barth, H.-D.; Brutschy, B. *Chem. Phys. Lett.* **1999**, *299*, 180.
 - Caminati, W.; Melandri, S.; Moreschini, P.; Favero, P. G. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2924.
 - Mizuno, K.; Imafuji, S.; Ochi, T.; Ohta, T.; Maeda, S. *J. Phys. Chem. B* **2000**, *104*, 11001.
- Hobza, P.; Spirko, V.; Selzle, H. L.; Schlag, E. W. *J. Phys. Chem. A* **1998**, *102*, 2501.
 - Gu, Y.; Scheiner, S. *J. Am. Chem. Soc.* **1999**, *121*, 9411.
 - Hobza, P.; Havlas, Z. *Chem. Phys. Lett.* **1999**, *303*, 447.
 - Cubero, E.; Orozco, M.; Hobza, P.; Luque, F. J. *J. Phys. Chem. A* **1999**, *103*, 6394.
 - Cubero, E.; Orozco, M.; Luque, F. J. *Chem. Phys. Lett.* **1999**, *310*, 445.
 - Hobza, P.; Spöner, J.; Cubero, E.; Orozco, M.; Luque, F. J. *J. Phys. Chem. B* **2000**, *104*, 6286.
 - Muchall, H. M. *J. Phys. Chem. A* **2001**, *105*, 632.
 - Scheiner, S.; Kar, T.; Gu, Y.-L. *J. Biol. Chem.* **2001**, *276*, 9832.
 - Brandl, M.; Meyer, M.; Suhnel, J. *J. Biomol. Struct. Dyn.* **2001**, *18*, 545.
 - Masunov, A.; Dannenberg, J. J.; Contreras, R. H. *J. Phys. Chem. A* **2001**, *105*, 4737.
 - Reimann, B.; Buchhold, K.; Vaupel, S.; Brutschy, B.; Havlas, Z.; Spirko, V.; Hobza, P. *J. Phys. Chem. A* **2001**, *105*, 5560.
- Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253.
- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A. Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A. 7, Gaussian, Inc., Pittsburgh, PA, **1998**.
 - Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
 - Scheiner, S. *Adv. Mol. Struct. Res.* **2000**, *6*, 159.
 - Wahl, M. C.; Sundaralingam, M. *Trends Biochem. Sci.* **1997**, *22*, 97.
 - Desiraju, G. R. *Acc. Chem. Res.* **1996**, *29*, 441.
 - Chen, R.; Zhang, K.-C.; Liu, L.; Li, X.-S.; Guo, Q.-X. *Chem. Phys. Lett.* **2001**, *338*, 61.
 - Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.