

On the Correlation between the Blue Shift of Hydrogen Bonding and the Proton Donor-Proton Acceptor Distance

WANG, Jin-Ti(王金娉) FENG, Yong(封勇) 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

It is demonstrated that in all types of hydrogen bonds ($X-H\cdots Y$) there is a balance between the long-range attractive orbital interactions and short-range Pauli/nucleus repulsions. When the proton acceptor approaches the proton donor from distance, the hydrogen bonding energy becomes more negative at relatively large distance, goes through a minimum, and then starts to become less negative when the short-range repulsive forces come into effect. Meanwhile, the $X-H$ bond length increases at relatively large distances, goes through a maximum and starts to shorten when the short-range repulsive forces come into effect. Whether the hydrogen bond is red or blue shifted is dictated by the energy minimum position. If at the energy minimum position the $X-H$ bond length is shorter than that for the free monomer, the hydrogen bond is blue shifted and vice versa. Further studies demonstrate that the recent report about the correlation of $C-H$ bond lengths with proton donor-acceptor distance in $F_3C-H\cdots OH_2$ and $F_3C-H\cdots Cl^-$ is not fully correct because the authors conducted an inappropriate comparison. Furthermore, it is shown for the first time that the Pauli/nucleus repulsion theory is applicable to the blue-shifted hydrogen bonds in the $X-H\cdots\pi$ complexes and the blue-shifted lithium bonds in the $X-Li\cdots Y$ complexes.

Keywords hydrogen bond, blue shift, lithium bond, *ab initio*

Introduction

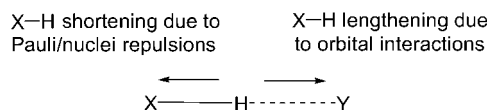
Hydrogen bonding ($X-H\cdots Y$) is a fundamental concept in chemistry.¹ The driving forces for its formation include electrostatic and charge-transfer interactions. Both of the interactions should weaken the $X-H$ bond, increase the $X-H$ bond length, and decrease the $X-H$ stretching frequency. This effect is called a red shift. It represents the most important, easily detectable manifestation of the formation of a hydrogen bond.

However, it was found recently that blue-shifted hydrogen bonds also exist where hydrogen bond formation leads to $X-H$ bond contraction and to a blue shift of the $X-H$ stretching frequency.^{2,3} Initial examples were mainly the $C-H\cdots Y$ systems (*e.g.*, $F_3C-H\cdots OH_2$) in which the central C atom has a few highly electronegative substituents such as F. This led to a theory that charge transfer from the proton acceptor to the remote electronegative moieties (*e.g.*, F in F_3C-H) is the cause of the blue shift.² Very recent studies, however, showed that $N-H$ and $O-H$ may also form blue-shifted hydrogen bonds where the central atom does not need to carry any electronegative substituent.⁴ Therefore, the charge transfer theory is not adequate for blue-shifted hydrogen bonds.

Recently we proposed a different theory for blue-shifted hydrogen bonds.⁵ According to it there is a balance between the $X-H$ elongation effect due to the

orbital interactions and the $X-H$ contraction effect due to the Pauli and nucleus-nucleus repulsions (see Scheme 1). If the former effect wins, a red shift will occur. Otherwise, a blue shift will take place. So far this theory has been successfully applied to many types of blue-shifted hydrogen bonds^{5,6} such as $F-He-H\cdots N_2$.⁷ It is worthy mentioning that another recent theory, which attributes the blue shift to increase in the *s*-character of the $X-H$ bond,⁸ fails to explain the blue shift in $F-He-H\cdots N_2$ because He is incapable of rehybridization.

Scheme 1



A more detailed description of our Pauli/nucleus repulsion theory for the blue-shifted hydrogen bonds is shown in Figure 1. As seen from Figure 1, at long $X\cdots Y$ distance the hydrogen bonding energy ΔE becomes more negative when the $X\cdots Y$ distance d decreases. This is clearly due to the orbital interactions between $X-H$ and Y which include electrostatic attraction, dispersion interaction, and charge transfer interaction. On the other hand, at short $X\cdots Y$ distance the hydrogen bonding energy becomes less negative when the $X\cdots Y$

* E-mail: qxguo@ustc.edu.cn; Fax: 86-551-3606689

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distance decreases. This is undoubtedly caused by the Pauli/nucleus repulsions between H and Y.

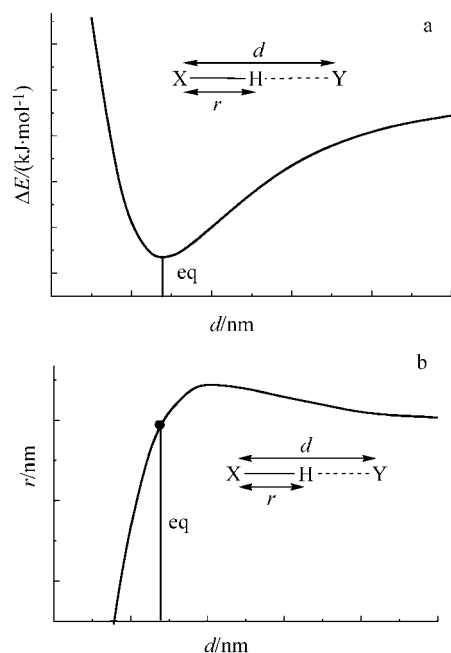


Figure 1 Correlation between the X...Y distance and the hydrogen bonding energy (a) and correlation between the X...Y distance and the X—H bond length (b).

Also in Figure 1, at long X...Y distance the X—H bond length r increases when d decreases. This should stem from the charge transfer from Y to the antibonding X—H orbital. On the other hand, at short X...Y distance r decreases when d decreases. This should originate from the Pauli/nucleus repulsions between H and Y. At this point, it is clear that whether the hydrogen bond is red or blue shifted relies on the equilibrium position. If at the equilibrium position the r value is larger than the X—H bond length of the free monomer, the hydrogen bond is red shifted. Otherwise, the hydrogen bond is blue shifted.

In the previous study⁵ we showed that the correlations in Figure 1 could be applied to three hydrogen bonding systems, *i.e.*, $\text{F}_3\text{C—H}\cdots\text{FH}$, $\text{F}_2\text{N—H}\cdots\text{FH}$, and $\text{FO—H}\cdots\text{FH}$. Among the three, the first one has a strong blue-shift, the second has only a small blue-shift, and the third has a strong red-shift. On the basis of these three systems we believed that the correlations in Figure 1 can be applied to all types of hydrogen bonds. However, in a recent paper by Alabugin *et al.*⁸ it was claimed that the correlations in Figure 1 could not be applied to two particular systems, *i.e.*, $\text{F}_3\text{C—H}\cdots\text{OH}_2$ and $\text{F}_3\text{C—H}\cdots\text{Cl}^-$. It was claimed that the correlation of C—H bond lengths with H...Y distance in $\text{F}_3\text{C—H}\cdots\text{OH}_2$ and $\text{F}_3\text{C—H}\cdots\text{Cl}^-$ follows a different trend compared to $\text{F}_3\text{C—H}\cdots\text{FH}$ because H_2O and Cl^- are better Lewis donors than FH.⁸

In the present study, we investigate why Alabugin *et al.* obtained different correlations between the X—H bond length and proton donor-acceptor distance com-

pared to our previous study. We believe that such a study would be important because of the following two reasons. (1) Except for Alabugin *et al.* and us, no one has ever studied the correlation between X—H bond length and X...Y distance in hydrogen bonding. Therefore, more detailed study on this subject should be performed. (2) Whether the correlations in Figure 1 are valid or not determines whether the Pauli/nucleus repulsion theory for the blue-shifted hydrogen bonds is correct or not. Therefore, a clarification is necessary.

Method

All the calculations were performed using Gaussian 98 softwares.⁹ MP2/6-31+G(d) and MP2/6-311++G(d,p) methods were used in geometry optimization under various constraints. The hydrogen bonding energy was calculated as the difference between the total energy of the complex and the sum of the total energies of the monomers. For just seeking the trend of the hydrogen bonding energy change, this energy was not corrected with the zero point energies (ZPE) and basis set superposition errors (BSSE) estimated using the counterpoise technique.¹⁰

Results and discussion

Correlation between C—H bond length and C...O or C...Cl distance

The structures of the hydrogen bonded complexes, $\text{F}_3\text{C—H}\cdots\text{OH}_2$ and $\text{F}_3\text{C—H}\cdots\text{Cl}^-$, were optimized using MP2/6-311++G(d,p) method (Figure 2). In the optimal structures, the C...O distance is 0.32814 nm and the C...Cl distance is 0.33400 nm. The hydrogen bonding energy is -19.10 kJ/mol for $\text{F}_3\text{C—H}\cdots\text{OH}_2$ and -69.14 kJ/mol for $\text{F}_3\text{C—H}\cdots\text{Cl}^-$. In $\text{F}_3\text{C—H}\cdots\text{OH}_2$ the C—H bond length is shortened from 0.10877 to 0.10854 nm and the C—H stretching frequency is blue shifted from 3223.3 to 3260.1 cm^{-1} . In $\text{F}_3\text{C—H}\cdots\text{Cl}^-$ the C—H bond length is lengthened from 0.10877 to

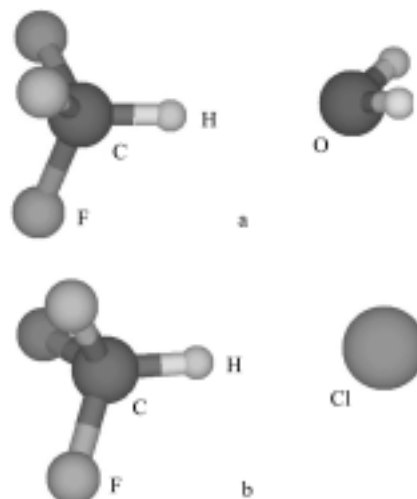


Figure 2 Optimized structures for $\text{F}_3\text{C—H}\cdots\text{OH}_2$ (a) and $\text{F}_3\text{C—H}\cdots\text{Cl}^-$ (b).

0.10951 nm and the C—H stretching frequency is red shifted from 3223.3 to 3094.0 cm^{-1} . All the results are in agreement with Alabugin's study.⁸

By fixing the C \cdots O distance in $\text{F}_3\text{C—H}\cdots\text{OH}_2$ and by optimizing the remaining coordinates of the complex, we obtained curves of the hydrogen bonding energies and the optimized C—H bond lengths as functions of the C \cdots O distance using the MP2/6-311++G(d,p) method (Figure 3). As seen from Figure 3, both the energy-distance and the bond length-distance curves are very similar to those in Figure 1 in shape. The equilibrium position is located at the place where the C—H bond is shortened. Therefore, the hydrogen bond in $\text{F}_3\text{C—H}\cdots\text{OH}_2$ is blue shifted.

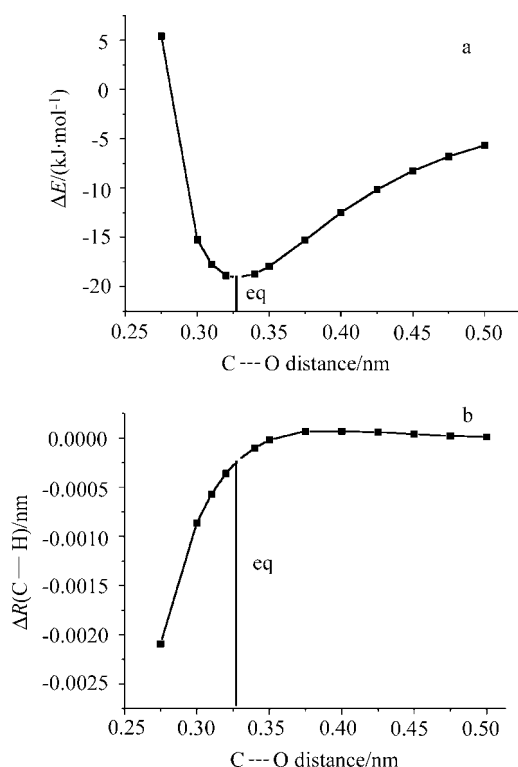


Figure 3 Correlation between the C \cdots O distance and the hydrogen bonding energy (a) and correlation between the C \cdots O distance and the C—H bond length (b) in $\text{F}_3\text{C—H}\cdots\text{OH}_2$.

Similarly by fixing the C \cdots Cl⁻ distance in $\text{F}_3\text{C—H}\cdots\text{Cl}^-$ we obtained curves of the hydrogen bonding energies and the optimized C—H bond lengths as functions of the C \cdots Cl distance (Figure 4). Both the energy-distance and the bond length-distance curves in Figure 4 are also very similar to those in Figure 1 in shape. The equilibrium position is located at the place where the C—H bond is lengthened. Therefore, the hydrogen bond in $\text{F}_3\text{C—H}\cdots\text{Cl}^-$ is red shifted.

At this point, it is clear that both $\text{F}_3\text{C—H}\cdots\text{OH}_2$ and $\text{F}_3\text{C—H}\cdots\text{Cl}^-$ follow the correlations in Figure 1. The blue shift in $\text{F}_3\text{C—H}\cdots\text{OH}_2$ and the red shift in $\text{F}_3\text{C—H}\cdots\text{Cl}^-$ can also be successfully explained using our Pauli/nucleus repulsion theory. Alabugin's claim that the change of C—H bond length in $\text{F}_3\text{C—H}\cdots\text{OH}_2$ and

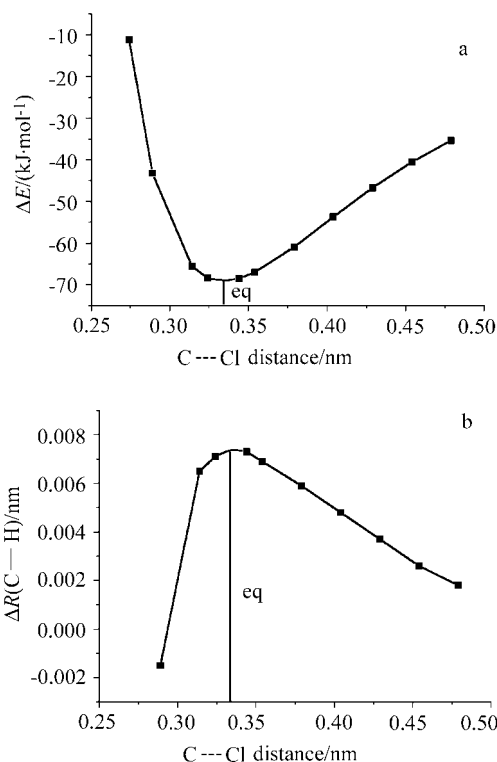


Figure 4 Correlation between the C \cdots Cl distance and the hydrogen bonding energy (a) and correlation between the C \cdots Cl distance and the C—H bond length (b) in $\text{F}_3\text{C—H}\cdots\text{Cl}^-$.

$\text{F}_3\text{C—H}\cdots\text{Cl}^-$ should follow a different trend⁸ is invalid. Further examination of Alabugin's paper⁸ reveals that Alabugin *et al.* fixed the H \cdots O and H \cdots Cl distances and optimized the remaining coordinates of the complexes. Therefore, they wrongly compared their results with ours which were obtained from completely different methods.

Correlation between C—H bond length and H \cdots O or H \cdots Cl distance

Although Alabugin *et al.* drew an incorrect conclusion on the basis of inappropriate comparisons, it is interesting to re-investigate and to explain the correlation between C—H bond length and H \cdots O or H \cdots Cl distance in $\text{F}_3\text{C—H}\cdots\text{OH}_2$ or $\text{F}_3\text{C—H}\cdots\text{Cl}^-$. Therefore, we fixed the H \cdots O and H \cdots Cl distances in $\text{F}_3\text{C—H}\cdots\text{OH}_2$ and $\text{F}_3\text{C—H}\cdots\text{Cl}^-$ and optimized the remaining coordinates of the complexes using the MP2/6-311++G(d,p) method. The results are shown in Figures 5 and 6.

As seen in Figures 5 and 6, at long H \cdots Y distance the X—H \cdots Y hydrogen bonding energy becomes more negative when the H \cdots Y distance decreases. This can be explained by the distance dependence of the orbital interactions. On the other hand, at short H \cdots Y distance the X—H \cdots Y hydrogen bonding energy becomes less negative when the H \cdots Y distance decreases. This is clearly due to the Pauli/nucleus repulsions.

In Figures 5 and 6, the C—H bond length at long H \cdots Y distance decreases when the H \cdots Y distance de-

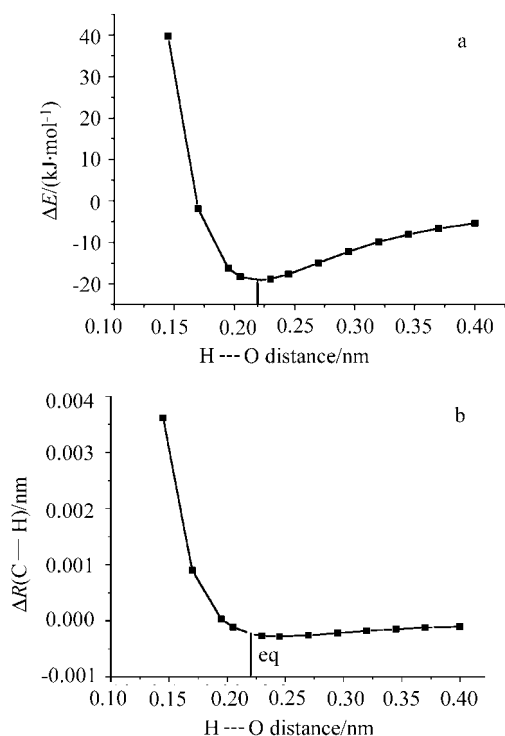


Figure 5 Correlation between the H...O distance and the hydrogen bonding energy (a) and correlation between the H...O distance and the C—H bond length (b) in $F_3C-H\cdots OH_2$.

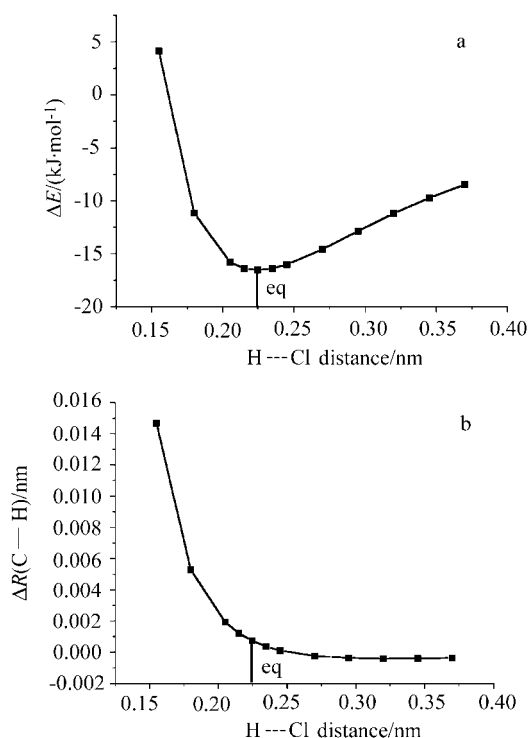
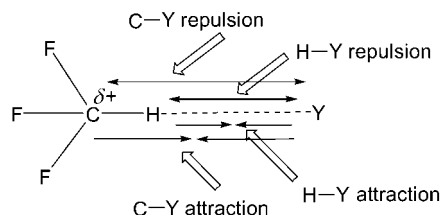


Figure 6 Correlation between the H...Cl distance and the hydrogen bonding energy (a) and correlation between the H...Cl distance and the C—H bond length (b) in $F_3C-H\cdots Cl^-$.

increases. This effect is also reported in Alabugin's paper.⁸ We believe that this effect can be explained using the following theory. In F_3C-H because of the high electronegativity of F the central carbon is positively

charged (Scheme 2). Therefore, in the complex of $F_3C-H\cdots Y$ there is an attraction interaction between C and Y in addition to the attraction interaction between H and Y. Certainly there are also Pauli/nucleus repulsions between C and Y and between H and Y. At long H...Y distance, the C—Y repulsion is negligible. Therefore, when the relative positions of H and Y are fixed, C should sense attraction from Y and force the C—H bond to contract.

Scheme 2



However, at short H...Y distance the C—Y repulsion increases much faster than the C—Y attraction. Therefore, when the H...Y distance decreases the C—H bond length has to increase. This prediction is in excellent agreement with the real calculation results shown in both Figures 5 and 6. Similar results have also been reported by Alabugin *et al.*⁸

Whether the hydrogen bond is red or blue shifted is determined again by the equilibrium position. In $F_3C-H\cdots OH_2$ the C—H bond length at the equilibrium position is smaller than that in the free monomer. Therefore, $F_3C-H\cdots OH_2$ is blue shifted. On the other hand, in $F_3C-H\cdots Cl^-$ the C—H bond length at the equilibrium position is shorter than that in the free monomer. Therefore, $F_3C-H\cdots Cl^-$ is red shifted.

Correlation between C—H bond length and C... π distance in C—H... π interaction

The above results demonstrated that the correlations in Figure 1 are completely valid for $F_3C-H\cdots OH_2$ or $F_3C-H\cdots Cl^-$ despite a recent contradictory report. Herein, we wish to demonstrate that the correlations in Figure 1 can also be applied to a special type of blue-shifted hydrogen bonds, *i.e.*, C—H... π complexes. In this type of complexes, the proton acceptor is not a single atom but a π plane. Therefore, it is important to examine whether a π plane functions in the same way as the atomic acceptors in the bond length-distance correlations.

Because of its large size, the structure of the C—H... π complex between F_3C-H and C_6H_6 was optimized using the MP2/6-31+G(d) method (Figure 7). In the optimal structure, the C... π distance is defined as the vertical distance between C and the π plane and this distance is found to be 0.33537 nm. The hydrogen bonding energy is -23.66 kJ/mol. Compared to the free F_3C-H molecule, in the complex the C—H bond length is shortened from 0.10881 to 0.10840 nm and the C—H stretching frequency is blue shifted from 3250.0

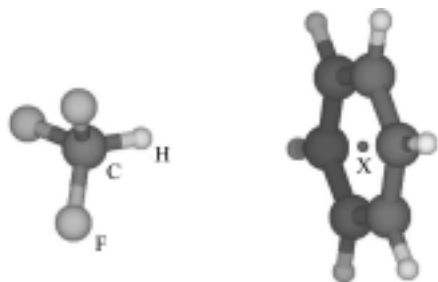


Figure 7 Optimized structure of $F_3C-H\cdots C_6H_6$.

to 3320.7 cm^{-1} .

By fixing the $C\cdots\pi$ distance and by optimizing the remaining coordinates of the complex, we obtained curves of the hydrogen bonding energies and the optimized $C-H$ bond lengths as functions of the $C\cdots\pi$ distance using the MP2/6-31+G(d) method (Figure 8). As seen from Figure 8, both the energy-distance and the bond length-distance curves are very similar to those in Figure 1 in shape. The equilibrium position is located at the place where the $C-H$ bond is shortened. Therefore, the hydrogen bond in $F_3C-H\cdots C_6H_6$ is blue shifted. These results demonstrate that the Pauli/nucleus repulsion theory is also applicable to the blue shift in an $X-H\cdots\pi$ complex.

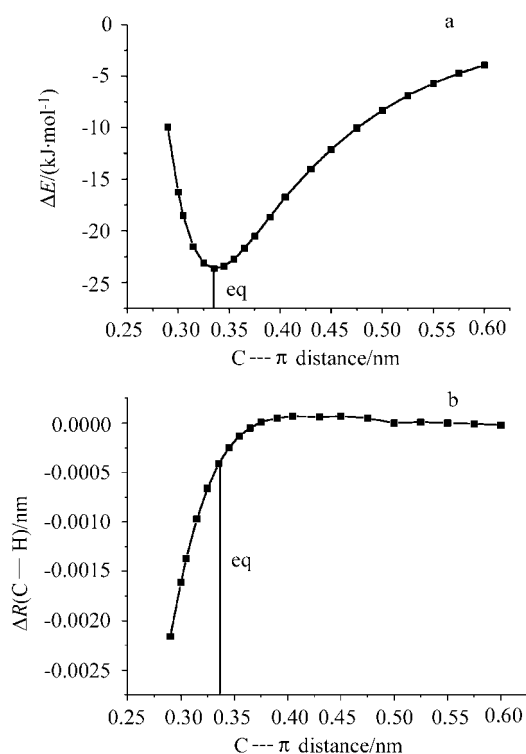


Figure 8 Correlation between the $C\cdots\pi$ distance and the hydrogen bonding energy (a) and correlation between the $C\cdots\pi$ distance and the $C-H$ bond length (b) in $F_3C-H\cdots C_6H_6$.

Correlation between $C-Li$ bond length and $C\cdots Y$ distance in $C-Li\cdots Y$ interaction

So far the blue-shifted hydrogen bonds have drawn considerable attention but no one has ever considered

whether there is any blue-shifted lithium bond.¹¹ In the present study we wish to report that the complex between F_3C-Li and Ne has a blue-shifted lithium bond whereas the complex between F_3C-Li and H_2O has a red-shifted lithium bond.

The structures of the lithium-bonded complexes, $F_3C-Li\cdots Ne$ and $F_3C-Li\cdots OH_2$, were optimized using the MP2/6-311++G(d,p) method (Figure 9). In the optimal structures, the $C\cdots Ne$ distance is 0.41972 nm and the $C\cdots O$ distance is 0.39678 nm. The lithium bonding energy is -7.65 kJ/mol for $F_3C-Li\cdots Ne$ and -91.96 kJ/mol for $F_3C-Li\cdots OH_2$. In $F_3C-Li\cdots Ne$ the $C-Li$ bond length is shortened from 0.20218 nm to 0.20208 nm. In $F_3C-Li\cdots OH_2$ the $C-Li$ bond length is lengthened from 0.20218 to 0.20391 nm. Therefore, $F_3C-Li\cdots Ne$ is a blue-shifted lithium bond and $F_3C-Li\cdots OH_2$ is a red-shifted lithium bond.

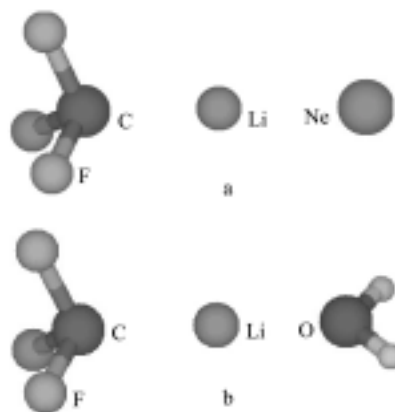


Figure 9 Optimized structures for $F_3C-Li\cdots Ne$ (a) and $F_3C-Li\cdots OH_2$ (b).

In order to explain the blue and red-shifted lithium bonds, we fixed the $C\cdots Ne$ and $C\cdots O$ distances in $F_3C-Li\cdots Ne$ and $F_3C-Li\cdots OH_2$ and optimized the remaining coordinates of the complexes using the MP2/6-311++G(d,p) method. We obtained curves of the lithium bonding energies and the optimized $C-Li$ bond lengths as functions of the $C\cdots Y$ distances (Figures 10 and 11). As shown in Figures 10 and 11, the correlation between the $C\cdots Y$ distance and the lithium bonding energies is in exactly the same shape as that for the $X-H\cdots Y$ interactions. At long $C\cdots Y$ distance, the lithium bonding energy becomes more negative when the $C\cdots Y$ distance decreases. This is due to the orbital interactions. At short $C\cdots Y$ distance, the lithium bonding energy becomes less negative when the $C\cdots Y$ distance decreases. This is caused by the Pauli/nucleus repulsions.

The correlation between the $C\cdots Y$ distance and the $C-Li$ bond length is also in exactly the same shape as that for the $X-H\cdots Y$ interactions. At long $C\cdots Y$ distance, the $C-Li$ bond length increases when the $C\cdots Y$ distance decreases. This is due to the orbital interactions. At short $C\cdots Y$ distance, the $C-Li$ bond length decreases when the $C\cdots Y$ distance decreases. This is caused by the Pauli/nucleus repulsions.

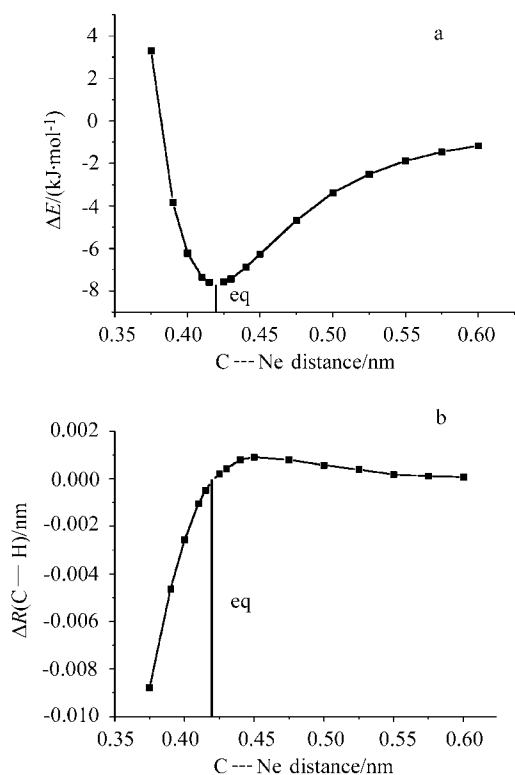


Figure 10 Correlation between the C...Ne distance and the lithium bonding energy (a) and correlation between the C...Ne distance and the C—Li bond length (b) in $F_3C-Li\cdots Ne$.

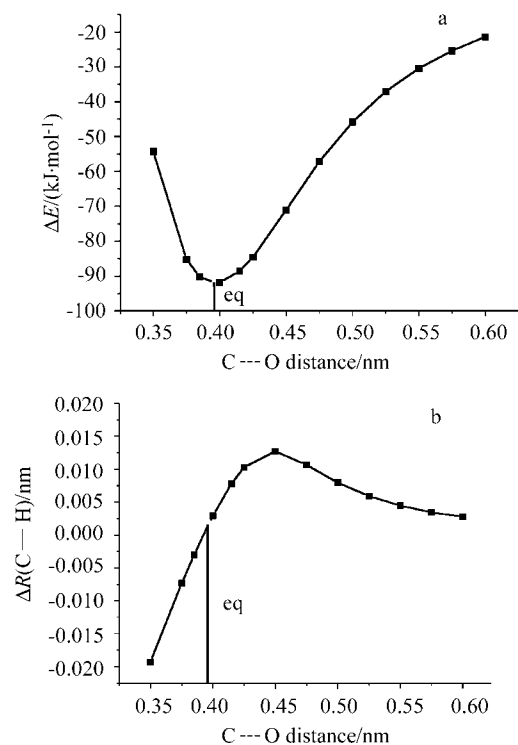


Figure 11 Correlation between the C...O distance and the lithium bonding energy (a) and correlation between the C...O distance and the C—Li bond length (b) in $F_3C-Li\cdots OH_2$.

Whether or not the lithium bond is red or blue shifted is determined by the equilibrium position. In

$F_3C-Li\cdots Ne$ the C—Li bond length at the equilibrium position is shorter than that in the free monomer. Therefore, $F_3C-Li\cdots Ne$ is blue shifted. On the other hand, in $F_3C-H\cdots OH_2$ the C—Li bond length at the equilibrium position is shorter than that in the free monomer. Therefore, $F_3C-Li\cdots OH_2$ is red shifted.

Conclusion

In the present paper the correlations between the blue shift of hydrogen bonding and the proton donor-proton acceptor distance were studied systematically and in detail. We found that in all types of hydrogen bonds ($X-H\cdots Y$) there is a balance between the long-range attractive orbital interactions and short-range Pauli/nucleus repulsions. When the proton acceptor approaches the proton donor from distance, the hydrogen bonding energy becomes more negative at relatively large distance, goes through a minimum, and then starts to become less negative when the short-range repulsive forces come into effect. Meanwhile, the X—H bond length increases at relatively large distances, goes through a maximum and starts to shorten when the short-range repulsive forces come into effect. Whether the hydrogen bond is red shifted or blue shifted is dictated by the energy minimum position. If at the energy minimum position the X—H bond length is shorter than that for the free monomer, the hydrogen bond is blue shifted and *vice versa*.

We also demonstrated that the recent report about the correlation of C—H bond lengths with proton donor-acceptor distance in $F_3C-H\cdots OH_2$ and $F_3C-H\cdots Cl^-$ is not fully correct because the authors conducted an inappropriate comparison. Furthermore, we showed for the first time that the Pauli/nucleus repulsion theory is applicable to the blue-shifted hydrogen bonds in the $X-H\cdots \pi$ complexes and the blue-shifted lithium bonds in the $X-Li\cdots Y$ complexes.

References

- Scheiner, S. *Hydrogen Bonding*, Oxford University Press, New York, **1997**.
- (a) Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253.
(b) Hobza, P.; Havlas, Z. *Theor. Chem. Acc.* **2002**, *108*, 325.
- Very recent studies, see:
(a) Meenakshi, P. S.; Biswas, N.; Wategaonkar, S. *J. Chem. Phys.* **2003**, *118*, 9963.
(b) McDowell, S. A. C. *J. Chem. Phys.* **2003**, *118*, 7283.
(c) Li, J.; Xie, D.; Yan, G. *Sci. China, Ser. B* **2003**, *46*, 113.
(d) Mrazkova, E.; Hobza, P. *J. Phys. Chem. A* **2003**, *107*, 1032.
(e) Delanoye, S. N.; Herrebout, W. A.; van der Veken, B. J. *J. Am. Chem. Soc.* **2002**, *124*, 7490.
(f) Scheiner, S.; Kar, T. *J. Am. Chem. Soc.* **2002**, *124*, 13257.
(g) Fan, J.-M.; Zhang, K.-C.; Liu, L.; Li, X.-S.; Guo, Q.-X. *Chin. J. Chem.* **2002**, *20*, 247.
- (a) Fang, Y.; Fan, J.-M.; Liu, L.; Li, X.-S.; Guo, Q.-X. *Chem. Lett.* **2002**, 116.

- (b) Hobza, P. *Int. J. Quantum Chem.* **2002**, *90*, 1071.
(c) Hobza, P.; Spirko, V. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1290.
- 5 Li, X.-S.; Liu, L.; Schlegel, H. B. *J. Am. Chem. Soc.* **2002**, *124*, 9639.
- 6 Fan, J.-M.; Liu, L.; Guo, Q.-X. *Chem. Phys. Lett.* **2002**, *365*, 464.
- 7 Wang, J.-T.; Feng, Y.; Liu, L.; Li, X.-S.; Guo, Q.-X. *Chem. Lett.* **2003**, *32*, 746.
- 8 Alabugin, I. V.; Manoharan, M.; Peabody, S.; Weinhold, F. *J. Am. Chem. Soc.* **2003**, *125*, 5973.
- 9 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**.
- 10 Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
- 11 For lithium bonding please read, see:
(a) Kollman, P. A.; Liebman, J. F.; Allen, L. C. *J. Am. Chem. Soc.* **1970**, *92*, 1142.
(b) Sannigrahi, A. B.; Kar, T.; Niyogi, B. G.; Hobza, P.; von Schleyer, P. V. *Chem. Rev.* **1990**, *90*, 1061.
(c) Duan, X. F.; Scheiner, S. *J. Phys. Chem.* **1992**, *96*, 7971.
(d) Li, L. F.; Fang, W. H.; You, X. Z. *Acta Chim. Sinica* **1995**, *53*, 14 (in Chinese).
(e) Ammal, S. S. C.; Venuvanalingam, P. *J. Phys. Chem. A* **2000**, *104*, 10859.

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