JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2004; **17:** 1099–1106
Published online 24 June 2004 in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/poc.785

Blue-shifted dihydrogen bonds

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Received 28 October 2003; revised 25 February 2004; accepted 2 March 2004

ABSTRACT: Blue-shifted dihydrogen bonds were predicted to be present in a number of non-covalent complexes including $F_3C—H\cdots H—Be—X$, $F_3C—H\cdots H—Mg—X$, $F_3C—H\cdots H_4Si$, $F_3Si—H\cdots H—Li$, $F_3Si—H\cdots H—Be—X$, $F_3Si—H\cdots H—Mg—X$, and $F_3Si—H\cdots H_4Si$ ($X = H$, F, Cl and CH_3). Pauli and nuclei–nuclei repulsions between the protonic hydrogen and hydridic hydrogen are proposed as the cause of the blue shift. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: hydrogen bond; dihydrogen bond; blue shift; *ab initio*

INTRODUCTION

Hydrogen bonding is an important type of non-covalent interaction that is present in many chemical and biological processes.[1] The major driving forces for hydrogen bonding ($X—H\cdots Y$) are usually believed to be electrostatic and charge-transfer interactions. Both of these interactions weaken the X—H bond and, consequently, increase the X—H bond length and decrease the X—H stretching vibration frequency. The latter is called a red shift. It represents the most important, easily detectable manifestation of the formation of a hydrogen bond.

However, some recent experimental and theoretical studies have indicated the existence of blue-shifted hydrogen bonds in which hydrogen bond formation leads to X—H bond contraction and to a blue shift of the X—H stretching frequency.[2,3] Initial examples included some $C—H\cdots X$ systems (e.g. $F_3C—H\cdots OH_2$) in which the central carbon atom is connected to a few highly electronegative substituents such as F and Cl. This led to a suggestion 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] Recent studies, however, have shown that N—H, O—H, Si—H and P—H bonds may also form blue-shifted hydrogen bonds, in which the central atom does not necessarily carry any electronegative substituents.[4–7] Therefore, the long-range charge transfer theory is not adequate for blue-shifted hydrogen bonds.

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A better theoretical model for blue-shifted hydrogen bonding has been proposed recently.[8] According to this theoretical model, there is a balance between the X—H elongation effect due to the orbital interactions and the X—H contraction effect due to Pauli and nuclei–nuclei repulsions. If the former effect is dominant, a red shift will occur, otherwise, a blue shift occurs. So far, this theoretical model has been successfully applied to many types of blue-shifted hydrogen bonds that have been reported.[8,9] A recent study demonstrated that this theoretical model can also account for the blue-shifted hydrogen bonds in $F—He—H\cdots X$ systems.[10] It worth noting that another recent theoretical model, which attributes the blue shift to an increase in the s-character of the X—H bond,[7] has difficulty in explaining the $F—He—H\cdots X$ systems where the rehybridization of He is elusive.[10]

In this paper, we report a special group of blue-shifted hydrogen bonds, blue-shifted dihydrogen bonds. We believe that this study is valuable for the following three reasons. (1) The dihydrogen bond is an unusual and intriguing type of hydrogen bond, which has attracted considerable attention recently.[11–13] It has been demonstrated to be able to influence structure, reactivity and selectivity in solution and the solid state, thus finding potential utility in catalysis, crystal engineering and materials chemistry. (2) So far N-, O-, F-, P-, S- and Cl-centered proton acceptors have been found in blue-shifted hydrogen bonds. However, it remains unknown whether an H-centered proton acceptor can also be used to construct blue-shifted hydrogen bonds. (3) It has been demonstrated that the polarization, charge transfer, correlation and higher order energy components are larger in dihydrogen-bonded complexes than classical hydrogen-bonded complexes.[14] Hence the study of blue-shifted dihydrogen bonds may provide novel and important insights into the mechanism of the blue shift.

METHOD

All calculations were performed with the Gaussian 98 suite of programs.[15] A number of theoretical methods, including MP2/6–31+G(d), MP2/6–311++G(d,p), MP2/6–311++G(2d,2p), MP2/cc-pVDZ and QCISD/6–31+G(d), were used for geometry optimization. The optimized structure was confirmed by a frequency calculation at the MP2/6–311++G(d,p) level to be a real minimum without any imaginary vibration. The dihydrogen bonding energy was calculated as the difference between the total energy of the complex and the sum of the total energies of the monomers. This energy was corrected with the zero point energies (ZPEs) (unscaled) and basis set superposition errors (BSSEs) estimated using Boys and Bernardi's counterpoise technique.[16]

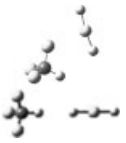
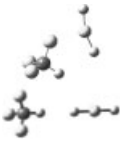
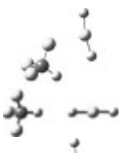
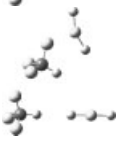
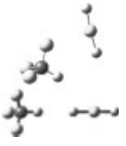
RESULTS AND DISCUSSION

Effects of the computational methods on the calculation results

In order to examine the effects of the theoretical methods on the calculation results, we utilized a number of theoretical methods, including MP2/6–31+G(d), MP2/6–311++G(d,p), MP2/6–311++G(2d,dp), MP2/cc-pVDZ, and QCISD/6–31+G(d), to study a particular complex, F_3C—H···H—Be—H. The results are shown in Table 1.

The results show that there are two minima for the complex between F_3C—H and H—Be—H. One of them is a linear complex between C—H and H—Be bonds, whereas the other exhibits both H···H and F···Be interactions. (One of the referees suggested that the double-interaction complex should not be named as a hydrogen bonding complex, because it seems there exists a repulsion between the hydrogen atoms belonging to its consituents which causes it to bent). According to all levels of theory, the linear complex has a lower energy than the double-interaction complex. Nevertheless, the interaction energies of the two complexes are both predicted to be positive by all the theoretical methods. The reason for the positive interaction energy could be the overestimation of BSSE by the counterpoise method,[16] because the interaction energy becomes negative for some methods when the BSSE correction is not applied[17] (stable dihydrogen bonds of BeH_2 have been reported[18]). Overestimation of the ZPE may also be the reason for the calculated interaction energy, because all the interaction energies are negative when ZPE correction is not utilized. Certainly it is also possible that the complex between F_3C—H and H—Be—H is intrinsically unstable. Anyhow, because we shall show in the following section that there are blue-shifted dihydrogen bonds with definitely negative interaction energy, we decided not to

Table 1. Blue-shifted dihydrogen bonds between F_3C—H and H—Be—H predicted by the various theoretical methods

Method	Structure	$\Delta d_{C—H}$ (Å)	$\Delta\nu_{C—H}$ (cm^{-1})	ΔE ($kJ\,mol^{-1}$)[a]	ΔE ($kJ\,mol^{-1}$)[b]	ΔE ($kJ\,mol^{-1}$)[c]
MP2/6–31+G(d)		−0.0009	+16.6	+2.8	−0.4	−5.3
		−0.0010	+17.0	+1.4	+0.0	−4.7
MP2/6–311++G(d,p)		−0.0020	+32.7	+7.1	−1.1	−2.9
		−0.0011	+16.1	+1.7	+0.1	−4.9
MP2/6–311++G(2d,2p)		−0.0015	+24.8	+4.1	−2.2	−4.8
		−0.0007	+12.8	+1.1	−0.2	−5.4
MP2/cc-pVDZ		−0.0037	+57.2	+7.5	−1.2	−3.1
		−0.0019	+25.6	+2.6	+1.5	−3.5
QCISD/6–31+G(d)		−0.0010	+17.2	+2.7	−0.6	−5.1
		−0.0011	+21.2	+1.4	−0.1	−4.5

[a] With both ZPE and BSSE corrections.
[b] With ZPE but not BSSE correction.
[c] With BSSE but not ZPE correction.

spend more time on the positive interaction energy problem of F_3C—H···H—Be—H.

The results in Table 1 also demonstrate that all the methods provide similar results for the complex between F_3C—H and H—Be—H. For the linear structure, all the methods also suggest that the C—H bond of F_3C—H should be shortened by about 0.001–0.002 Å owing to the complex formation. Furthermore, all the methods predict that the blue shift of the C—H stretching frequency in the linear F_3C—H···H—Be—H complex is about $+20\,cm^{-1}$. Therefore, the blue shift in F_3C—H···H—Be—H should be a real effect. This blue shift effect is not very sensitive to how the electron correlation is treated. Also, it is not strongly sensitive to the size of the basis set. Hence it should reliable enough to use a modestly high level theoretical method such as MP2/6–311++G(d,p) to study the blue shift in dihydrogen bonds.

Blue-shifted C—H···H and Si—H···H dihydrogen bonds

Using the MP2/6–311++G(d,p) method, we studied the complexes of F_3C—H and F_3Si—H with H—Li, H—Be—H, H—Be—F, H—Be—Cl, H—Be—CH_3, H—Mg—H, H—Mg—F, H—Mg—Cl, H—Mg—CH_3 and SiH_4. The results are given in Tables 2 and 3.

The results in Tables 2 and 3 suggest that all the dihydrogen bonding complexes should have two minima except for F_3Si—H···H—Li. One of the two minima is a linear complex between X—H and H—Y bonds, except for silane, where there is a bifurcated dihydrogen bond. The other minimum, which in the following will be named the double-interaction complex, exhibits both H···H and the F–metal interactions. For the complexes of F_3C—H with H—Li, SiH_4 and H—MgX (X = H, F, Cl, CH_3) and the complexes of F_3Si—H with SiH_4, H—Be—F, and H—Mg—X (X = H, F, Cl, CH_3), the double-interaction structure is the global minimum. For the remaining complexes, the linear structure is the global minimum.

Despite the complicated structures of the dihydrogen bonds, except for one case (i.e. linear F_3C—H···H—Li), all the complexes exhibit contraction of the C—H or Si—H bond and blue shift of the C—H or Si—H stretching vibration. For the complexes of F_3C—H with H—BeX and H—MgX, the double-interaction complexes ($\Delta d \approx -0.002$ Å, $\Delta\nu \approx +30\,cm^{-1}$) show more significant blue shifts than the linear complexes ($\Delta d \approx -0.001$ Å, $\Delta\nu \approx +15\,cm^{-1}$). For the complex of F_3C—H with H—Li, the double-interaction complex ($\Delta d = -0.0004$ Å, $\Delta\nu = +9.9\,cm^{-1}$) is blue shifted whereas the linear complex is red shifted ($\Delta d = +0.0004$ Å, $\Delta\nu = -20.6\,cm^{-1}$). Finally, the double-interaction complex of F_3C—H···SiH_4 ($\Delta d = -0.0004$ Å, $\Delta\nu = +5.1\,cm^{-1}$) shows less blue shift than the bifurcated dihydrogen-bonded complex ($\Delta d = -0.0009$ Å, $\Delta\nu = +13.5\,cm^{-1}$). The interaction energies for F_3C—H···SiH_4 and F_3C—H···H—Be—X (X = H, F, or Cl) are positive after BSSE correction. Nevertheless, the interaction energies for F_3C—H···H—Li ($-29.9\,kJ\,mol^{-1}$), F_3C—H···H—Be—CH_3 ($-4.2\,kJ\,mol^{-1}$) and F_3C—H···H—Mg—X (X = H, F, Cl, or CH_3) (ca -11–$13\,kJ\,mol^{-1}$) are definitely negative. Therefore, stable blue-shifted dihydrogen bonds do exist.

For the complexes of F_3Si—H with H—BeX and H—MgX, the double-interaction complexes ($\Delta d \approx -0.006$ Å, $\Delta\nu \approx +35\,m^{-1}$) also show more significant blue shifts than the linear complexes ($\Delta d \approx -0.001$ Å, $\Delta\nu \approx +6\,cm^{-1}$). For the complex of F_3Si—H with H—Li, the double-interaction complex is not a minimum whereas the linear complex is blue shifted ($\Delta d = -0.002$ Å, $\Delta\nu = +1.8\,cm^{-1}$). Finally the double-interaction complex of F_3Si—H···SiH_4 ($\Delta d = -0.0003$ Å, $\Delta\nu = +1.8\,cm^{-1}$) shows less blue shift than the bifurcated dihydrogen bonded complex ($\Delta d = -0.0002$ Å, $\Delta\nu = +4.2\,cm^{-1}$). The interaction energies for F_3Si—H···SiH_4 and F_3Si—H···H—Be—X (X = H, F, or Cl) are positive after BSSE correction. Nevertheless, the interaction energies for F_3Si—H···H—Li ($-7.9\,kJ\,mol^{-1}$), F_3Si—H···H—Be—CH_3 ($-1.2\,kJ\,mol^{-1}$) and F_3Si—H···H—Mg—X (X = H, F, Cl, or CH_3) (ca -15–$20\,kJ\,mol^{-1}$) are definitely negative. Again, stable blue-shifted dihydrogen bonds do exist.

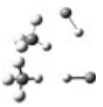
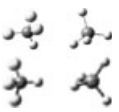
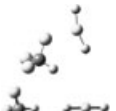
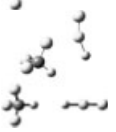
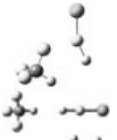
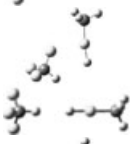
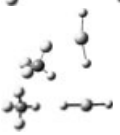
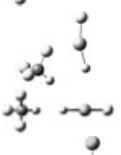
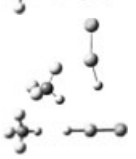
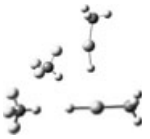
NBO analysis of dihydrogen bonding

The above results suggest that both the linear and double-interaction structures should be considered for the dihydrogen bonding complexes. In the linear complexes the major interaction is clearly the H···H interaction only as evidenced from the three-dimensional structures. On the other hand, in the double-interaction complexes we have to consider the F···metal interaction in addition to the H···H interaction. Since the linear complexes can show a blue shift, in the following mechanistic studies we shall consider the linear complexes only in order to simplify the analyses.

Firstly, the natural bond orbital (NBO) partitioning technique developed by Reed *et al.*[19] was used to analyze the dihydrogen bonding involved in linear F_3C—H···H—Li and F_3C—H···H—Be—H complexes (Fig. 1). The MP2/6–311++G(d,p) method was used in the NBO analyses.

The NBO analysis results for the monomers suggest that in F_3C—H the H atom carries a certain amount of positive charge. On the other hand, in both H—Li and H—Be—H the H atoms carry a significant amount of negative charge. Therefore, hydridic-to-protonic interaction should take place in both F_3C—H···H—Li and F_3C—H···H—Be—H. This means that the non-covalent interaction involved in F_3C—H···H—Li and F_3C—H···H—Be—H can be defined as dihydrogen bonding.

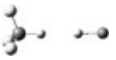
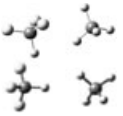
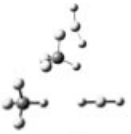
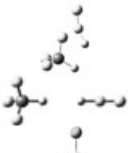
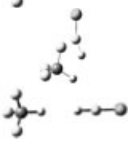
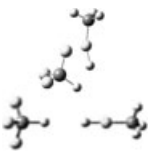
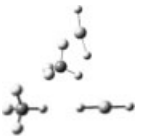
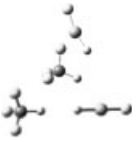
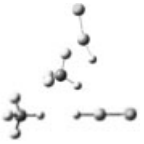
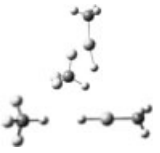
Table 2. Blue-shifted dihydrogen bonds between F_3C—H and various types of hydrogen-centered proton acceptors predicted by the MP2/6–311++G(d,p) method

Proton acceptor	Structure	$d_{C—H}$ (Å)	$\Delta d_{C—H}$ (Å)	$\nu_{C—H}$ (cm^{-1})	$\Delta\nu_{C—H}$ (cm^{-1})	ΔE ($kJ\,mol^{-1}$)
F_3C—H		1.0877	—	3223.3	—	—
H—Li		1.0873 1.0881	−0.0004 +0.0004	3233.2 3202.7	+9.9 −20.6	−29.9 −19.9
SiH_4		1.0873 1.0868	−0.0004 −0.0009	3228.4 3236.8	+5.1 +13.5	+0.5 +0.9
H—Be—H		1.0857 1.0865	−0.0020 −0.0012	3255.2 3239.4	+31.9 +16.1	+7.1 +1.7
H—Be—F		1.0861 1.0865	−0.0016 −0.0012	3250.6 3238.9	+27.3 +15.6	+3.2 +2.3
H—Be—Cl		1.0859 1.0865	−0.0018 −0.0012	3253.9 3239.0	+30.6 +15.7	+5.4 +1.3
H—Be—CH_3		1.0864 1.0863	−0.0013 −0.0014	3244.1 3241.6	+20.8 +18.3	−2.4 −4.2
H—Mg—H		1.0860 1.0866	−0.0017 −0.0011	3250.8 3234.1	+27.5 +10.8	−11.3 −4.4
H—Mg—F		1.0863 1.0866	−0.0014 −0.0011	3249.3 3235.7	+26.0 +12.4	−13.7 −2.2
H—Mg—Cl		1.0864 1.0865	−0.0013 −0.0012	3248.7 3235.8	+25.4 +12.5	−13.4 −2.7
H—Mg—CH_3		1.0861 1.0866	−0.0016 −0.0011	3250.3 3233.5	+27.0 +10.2	−12.0 −8.2

Further analyses suggest that charges transfer should occur from the proton acceptor to the proton donor in both F_3C—H···H—Li and F_3C—H···H—Be—H. In the linear F_3C—H···H—Li complex the positive charge carried by the H—Li moiety amounts to +0.02 e. In the linear F_3C—H···H—Be—H complex the positive charge carried by the H—Be—H is +0.004 e. A similar magnitude of charge transfer has also been found in other C—H···H dihydrogen-bonded systems such as HCCH···H—Li ($\Delta q = 0.014$ e) and NCH···H—Li ($\Delta q = 0.033$ e).[20]

Hence both the H($\delta+$)···H($\delta-$) electrostatic interaction and the charge transfer from the proton acceptor to proton donor should be important driving forces for the formation of the dihydrogen bond. However, it is worth mentioning that the H($\delta+$)···H($\delta-$) electrostatic

Table 3. Blue-shifted dihydrogen bonds between F_3Si—H and various types of hydrogen-centered proton acceptors predicted by the MP2/6–311++G(d,p) method

Proton acceptor	Structure	$d_{Si—H}$ (Å)	$\Delta d_{Si—H}$ (Å)	$\nu_{Si—H}$ (cm^{-1})	$\Delta\nu_{Si—H}$ (cm^{-1})	ΔE ($kJ\,mol^{-1}$)
F_3Si—H		1.4489	—	2456.2	—	—
H—Li		1.4469	−0.0020	2458.0	+1.8	−7.9
SiH_4		1.4486 1.4487	−0.0003 −0.0002	2458.0 2460.4	+1.8 +4.2	+0.7 +0.7
H—Be—H		1.4428 1.4481	−0.0061 −0.0008	2491.3 2462.3	+35.1 +6.1	+7.1 +4.2
H—Be—F		1.4440 1.4485	−0.0049 −0.0004	2485.6 2460.4	+29.4 +4.2	+2.7 +3.5
H—Be—Cl		1.4434 1.4484	−0.0055 −0.0005	2489.0 2461.1	+32.8 +4.9	+4.1 +2.8
H—Be—CH_3		1.4434 1.4479	−0.0055 −0.0010	2487.9 2463.4	+31.7 +7.2	+4.3 −1.2
H—Mg—H		1.4423 1.4476	−0.0066 −0.0013	2493.8 2462.9	+37.6 +6.7	−15.4 +1.8
H—Mg—F		1.4439 1.4478	−0.0050 −0.0011	2486.8 2462.6	+30.6 +6.4	−20.7 +1.5
H—Mg—Cl		1.4439 1.4481	−0.0050 −0.0008	2486.4 2461.1	+30.2 +4.9	−20.4 +1.7
H—Mg—CH_3		1.4420 1.4475	−0.0069 −0.0014	2494.8 2463.1	+38.6 +6.9	−15.3 −2.4

interaction should weaken the C—H bond by pulling the H($\delta+$) atom from the C atom to the H($\delta-$) atom.[21] In addition, the charge transfer from the proton acceptor to proton donor should also weaken the C—H bond because the transferred charge goes to the C—H antibonding σ^* orbital.[22] Therefore, both the electrostatic interaction and charge transfer effect can only increase the C—H bond length and red shift the C—H stretching frequency.

Physical origin of the blue shift

In order to understand the physical origin of the blue-shifted dihydrogen bonds, we studied two linear dihydrogen-bonded complexes: F_3C—H···H—Li and F_3C—H···H—Be—H. The former complex has a red shift whereas the latter has a blue shift. By fixing the C···H distances in F_3C—H···H—Li and F_3C—H···H—

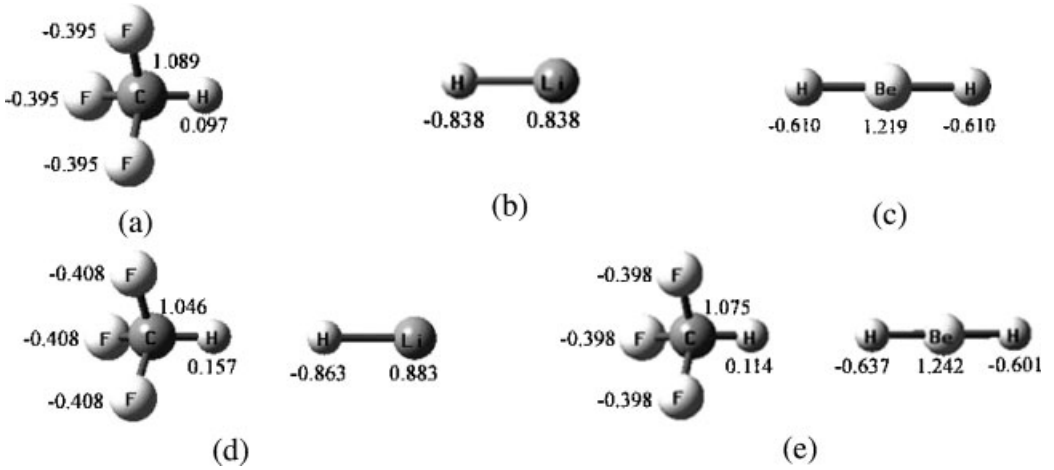


Figure 1. NBO charge distributions in (a) F_3C—H, (b) H—Li, (c) H—Be—H, (d) F_3C—H···H—Li (C_{3v}, linear) and (e) F_3C—H···H—BeH (C_{3v}, linear)

Be—H and by optimizing the remaining coordinates of the complexes, we obtained curves of the interaction energies (not corrected with BSSE) and the optimized C—H bond lengths as functions of the C···H distance (Fig. 2).

The potential energy curves of the two complexes are very similar in shape, regardless of whether the hydrogen bond is blue-shifted or red-shifted. At long distances, the interaction energy becomes more negative as the C···H distance decreases. This behavior is undoubtedly caused

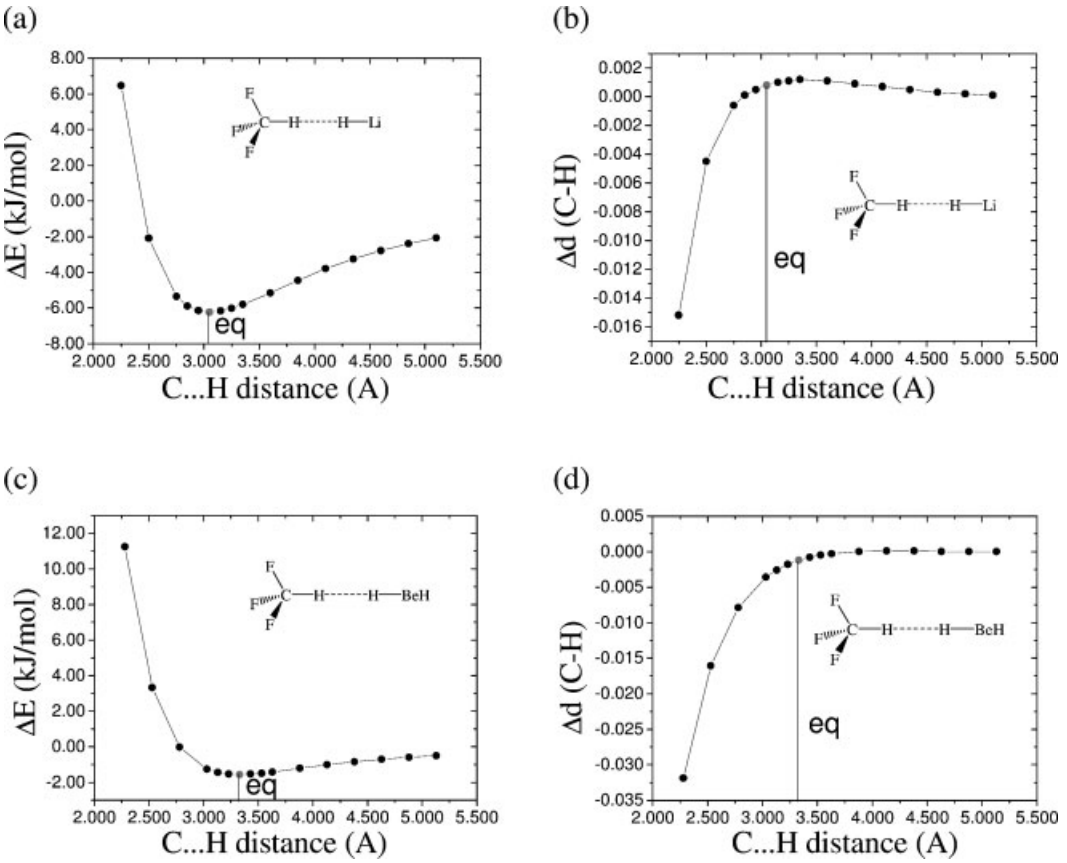


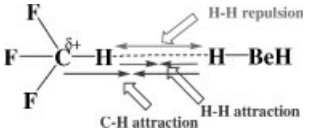
Figure 2. Interaction energy (ΔE) and change of C—H bond length (Δd) as a function of the distance between the proton donor and acceptor: (a) and (b) F_3C—H···H—Li (C_{3v}, linear), (c) and (d) F_3C—H···H—Be—H (C_{3v}, linear) (equilibrium C···H distances are indicated by the line labeled 'eq')

by the electrostatic interaction between the proton donor and acceptor. On the other hand, at short distances the interaction energy becomes less and less negative as the C···H distance decreases. This behavior is clearly due to the Pauli and nuclei–nuclei repulsions between the proton donor and acceptor, which are significant only when the proton donor and acceptor are sufficiently close to each other.

The curves for the change of C—H bond length as a function of the distance between the proton donor and acceptor are also very similar in shape for the two complexes. At long distances, the C—H bond is elongated for both F_3C—H···H—Li and F_3C—H···H—Be—H. This elongation can only be explained by either electrostatic attractions or orbital interactions (i.e. charge-transfer interactions). On the other hand, the C—H bond is shortened for both F_3C—H···H—Li and F_3C—H···H—Be—H at very short C···H distances. The contraction can only be explained as a result of Pauli and nuclei–nuclei repulsions.

Nevertheless, the equilibrium position (i.e. the position where the interaction energy is the most negative) for F_3C—H···H—Li is in the elongation region of the curve so that F_3C—H···H—Li is red shifted. In comparison, the equilibrium position for F_3C—H···H—Be—H is in the contraction region and consequently, F_3C—H···H—Be—H is blue shifted. Therefore, the difference between blue and red-shifted dihydrogen bonds is simple. For the blue-shifted bonds, the bond shortening effect is greater than the bond lengthening effect when the energy reaches a minimum. On the other hand, for the red-shifted dihydrogen bonds, there is an additional bond lengthening effect due to orbital interactions that is not overcome by the modest bond compression resulting from the repulsive interactions.

At this point, one may wonder why there is strong Pauli and nuclei–nuclei repulsion (i.e. bond shortening effect) at the energy minimum of a blue-shifted dihydrogen bond. For F_3C—H···H—Be—H we suggest that this bond shortening effect stems from the electrostatic attraction between the positively charged carbon in F_3C—H and the negatively charged hydrogen in H—Be—H (see Scheme 1). Because of this C···H attraction, the H···H distance in the complex is so short that H···H repulsion is significant. Although the energetic effect of this H···H repulsion is completely compensated by that of the H···H and C···H attraction resulting in a stable complex, the H···H repulsion forces the C—H bond to contract upon the complex formation.



Scheme 1

CONCLUSION

There are two valuable outcomes of this study. First, blue-shifted dihydrogen bonds, including some conventional linear ones and some unconventional double-interacting ones, were predicted to be present in a variety of non-covalent complexes including F_3C—H···H—Be—X, F_3C—H···H—Mg—X, F_3C—H···H_4Si, F_3Si—H···H—Li, F_3Si—H···H—Be—X, F_3Si—H···H—Mg—X and F_3Si—H···H_4Si (X = H, F, Cl, and CH_3). Second, on the basis of state-of-art NBO analyses and potential energy surface analyses, it was demonstrated that Pauli and nuclei–nuclei repulsions between the protonic hydrogen and hydridic hydrogen are the cause of the blue shift.

Acknowledgements

We thank NSFC for the financial support. We also thank one of the referees for the suggestion of the existence of the 'double-interaction' complexes.

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