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Red-, Blue-, or No-Shift in Hydrogen Bonds: A Unified Explanation

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Abstract: We provide a simple explanation for X−H bond contraction and the associated blue shift and decrease of intensity in IR spectrum of the so-called improper hydrogen bonds. This explanation organizes hydrogen bonds (HBs) with a seemingly random relationship between the X−H bond length (and IR frequency and its intensity) to its interaction energy. The factors which affect the X−H bond in all X−H···Y HBs can be divided into two parts: (a) The electron affinity of X causes a net gain of electron density at the X−H bond region in the presence of Y and encourages an X−H bond contraction. (b) The well understood attractive interaction between the positive H and electron rich Y forces an X−H bond elongation. For electron rich, highly polar X−H bonds (proper HB donors) the latter almost always dominates and results in X−H bond elongation, whereas for less polar, electron poor X−H bonds (pro-improper HB donors) the effect of the former is noticeable if Y is not a very strong HB acceptor. Although both the above factors increase with increasing HB acceptor ability of Y, the shortening effect dominates over a range of Ys for suitable pro-improper X−Hs resulting in a surprising trend of decreasing X−H bond length with increasing HB acceptor ability. The observed frequency and intensity variations follow naturally. The possibility of HBs which do not show any IR frequency change in the X−H stretching mode also directly follows from this explanation.

Introduction

Until a few years ago a hydrogen bond (HB) between X−H and Y, where X is a more electronegative atom or group than H and Y has a lone pair of electrons or π electrons, implied an X−H bond lengthening and associated red shift and enhanced intensity in IR spectra. It is now well-established that there exist weak HBs which shorten X−H bonds, showing blue shifts having decreased intensity in IR spectra.[1−16] Such HBs were initially named as "anti HBs",[1] which was inappropriate as it evoked an idea that it is not an HB. Later it was renamed as "improper blue-shifting HBs".[2] Another type of X−H bond contractions as well as blue shifts and decrease of intensities in IR spectra have been observed for some X−Hs even if H is not involved in an interaction with Y, but some other group bonded to X is involved in HB as an HB acceptor. They are called blue-shifted bonds rather than blue shifting.[16−20]

The origin of X−H bond lengthening and the associated effects of normal or proper HB is understood as a consequence of the stabilizing interactions in the complex, namely, the electrostatic interaction.[21,22] There is also an explanation based on hyperconjugation, a concept well-known to chemists.[23] In the simplest explanation, electrostatic interaction causes X−H lengthening since negative Y pulls positive H closer to it. Y also causes polarization of the X−H bond further, which not only increases the interaction but also increases the intensity of X−H stretching band in the IR. The associated red shift occurs because of weakening of the X−H bond. The stabilization in the hyperconjugation scheme is due to the overlap of the vacant σ^* molecular orbital of the X−H bond with the filled molecular orbital of the HB acceptor (usually the lone pair).[23] Since the

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electron density from Y transfers to the X−H antibonding orbital, the bond is weakened and lengthened. These explanations suggest that a better interaction, enhanced lengthening, larger red shift and greater increase in intensity of X−H bond can be achieved by increasing the electron affinity of X and by a better HB acceptor Y. As a corollary, a lesser red shift would be expected when a less polar X−H such as a C−H involves in a HB with a weak HB acceptor such as benzene and leads to no shift at the extreme of no interaction. Within this framework, the blue shift observed in many instances—improper HBs—appeared as counterintuitive.

After having convinced that the improper HBs are a true phenomenon by a series of high level computations and systematic experiments,[1−16] researchers explored whether there are any fundamental differences between the blue shifting and the well-known red shifting HBs. A consensus has now emerged that, barring the blue shift, decrease in IR intensity, and X−H bond contraction, all energetic, magnetic (chemical shift in NMR), and topological characteristics are similar in all HBs including improper HBs but with differing magnitudes.[24−32] These similarities revealed that subtle variations of some factors could cause such a noticeable effect. At the same time, it made it difficult to attribute a single reason for the improper behavior of seemingly wide range and type of complexes.

Among the several explanations offered for the improper HBs, four gained more attention. The first one attributes the X−H bond contraction to the short-range repulsive forces faced by H in the complex while attempting stabilization.[2,25−29,33−36] The second explanation is based on the observation that electron density transfer from Y occurs mainly to atoms linked to X rather than to the X−H σ^* orbital for some of the examples of improper HBs, and the contraction of X−H bond was considered as its consequence.[7,9,37,38] Since an electric field was found to cause an X−H bond shortening for some X−H, the observed shortening was partly attributed to the effect of the electric field of the Y.[4,8,30−32,35,36,39] The fourth explanation is based on the increased percent s character in the X component of the X−H bond when Y approaches H, and the X−H bond contraction was ascribed to a weak hyperconjugation to X−H σ^* which is unable to lengthen it.[40] Though none of these explanations identify the exact origin of the improper behavior, the present trend is to propose one of the above whenever a new improper HB is identified.

In the first section below, these explanations are critically examined. Next we discuss the origin of the improper behavior. The following points are kept in mind in this analysis. The new explanation must be compatible with all the evidence and observations available so far. Despite the apparent improper nature of the blue-shifting HBs, it is similar to the well-known normal HBs. We discuss in the last section the interrelationships among X−H bond length, IR frequency and intensity, and HB energy. This leads to a revision of the general assumption that an HB necessarily affects the HB bond length. We show that HBs without any change in X−H bond lengths cannot be ruled out.

Computational Details

The objective of this work demanded frequent use of the existing literature results. To augment our arguments, we have used several potential energy (PE) scans in this study. These involved complete optimization of all parameters of the system X−H···Y except the H to Y distance; the variable used in the scan. A “tight” convergence criterion available in Gaussian package[41] was employed for all the optimization in view of the flat PE surface. All computations, unless otherwise mentioned, are at the MP2/6-31+G* level. Comparison of extensive literature in this field reveals that the trends are generally the same at other levels of theory and basis sets (Figure S1 in the Supporting Information provides additional support).

Discussion

Examination of Available Explanations. 1. Short-Range Repulsive Forces. An initial attempt to explain the X−H bond contraction was based on energy decomposition analysis which showed that dispersion energy is an important component in weak HBs.[42] For example, Hobza group reasoned that for a haloform−benzene system, molecules try to come closer to increase the dispersion interaction. This forces H to be in the short-range repulsive regime of Y, hence a shortening of C−H results.[1,2,34,43]

Weak complexes, whose main stabilizing interaction is dispersion, are known to show such forced shortenings and blue shifts. For example, blue shifts were predicted in Cl−H···O═C and Cl−H···F−B complexes[44] where the positive H is near to a positive end of a dipole. Similarly, electron rich H of Si−H contracts when it is near to another electron rich center, NH_3.[34] Other computational examples include complexes of F−H[45] and NC−H[46] with He and Ne. Strictly speaking, none of the above are coming under the definition of HBs, as either Y is not electron rich or X is not electronegative.

Unlike the above examples, improper HBs are stable even in the absence of dispersion interaction. The fact that blue shift and bond shortening of X−H are reproducible even at the Hartree−Fock(HF) level of theory, where electron correlation is taken into account poorly, is a clear indication that the dispersion effect does not have much of a role for the improper behavior.[33,35,36] This has led many authors to attribute Pauli repulsion, which is operative even at HF theory, as the cause for X−H bond contraction.[25−29,33,35,36] Though no convincing rationale was provided why some complexes indulge in such a repulsive interaction without any apparent advantage, the support

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is derived from the low positive charge of H of many improper HB donors and hence the Pauli repulsion can be larger than in the case of normal HB donors. A proof based on energy decomposition analysis is difficult as the method is necessarily arbitrary and any interpretation of small differences of each component of the interaction energy of as low a value as <4 kcal/mol is error-prone.

We analyze the problem using a series of PE scans for the complex. This is obtained by decreasing the H$\cdots$Y distance from 6.00 Å in small decrements and optimizing all the other geometric parameters at each of these points. The variation of X$-$H bond length for a given H$\cdots$Y distance shows the tendency of the X$-$H bond for lengthening or shortening during the formation of the HB. A lengthening of the X$-$H bond at a larger separation of H and Y is expected since electrostatic effects are known to lengthen the X$-$H bond, and a shortening near equilibrium distance is expected if any short-range repulsive forces are operative.[33] The C$-$H bond in the $H_3C-H\cdots$benzene complex, which has a large dispersion component,[42] shows a continuous shortening (Figure 1A) of the C$-$H bond until the total energy minimum when Y approaches H. This should not be taken in isolation to conclude that short-range repulsive interaction is the cause for the observed C$-$H bond contraction. A study of $H_3C-H\cdots NH_3$ complex, where C$-$H is elongated at equilibrium[47] is instructive. In view of the larger polarity of NH_3 in comparison with benzene, a continuous lengthening of C$-$H and a slight shortening, if at all, at near equilibrium distance is expected. Figure 1B shows an exactly opposite picture: shortening of the C$-$H bond at larger H$\cdots$Y separations as in Figure 1A, but lengthening when it approaches the equilibrium distance. In fact the X$-$H bond contraction at large H$\cdots$Y separation is a general trend for improper HBs and some proper HBs (see below). Figure 1B reveals that at near equilibrium distances, as expected from electrostatic and overlap explanations, the C$-$H bond is lengthened, but it still has been shortened at larger separation where the short-range repulsive forces are expected to be even weaker. In addition, comparison of Figure 1A and B implies that had the short-range lengthening effect caused by the better HB acceptor NH_3 not existed, it would have shown improper behavior. Conversely, in the case of $H_3C-H\cdots$benzene, benzene being a weak HB acceptor, the short-range lengthening effect is overshadowed by a (long range!) shortening effect whose origin will be deciphered below. To check this interpretation again, let us consider a complex with benzene but the HB donor is chloroform which also shows improper HB[2] (Figure 1C).

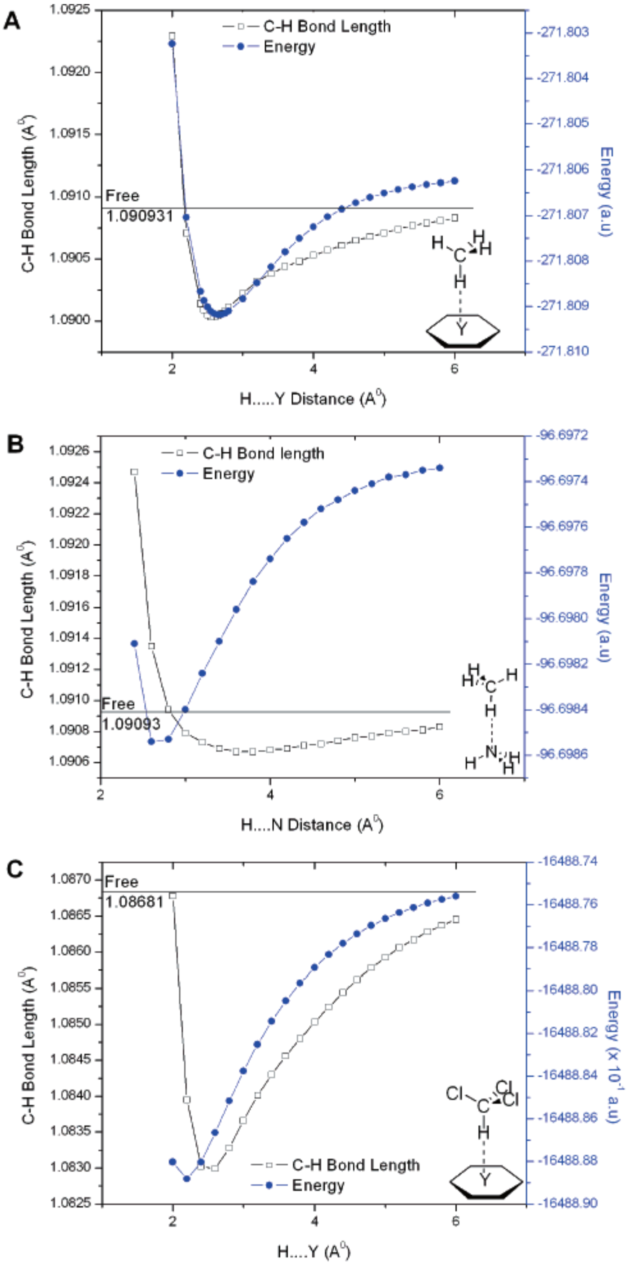

Figure 1. Variation of C$-$H bond length with total energy of the complex during the potential energy scan: (A) $H_3C-H\cdots$benzene; (B) $H_3C-H\cdots NH_3$; (C) $Cl_3C-H\cdots$benzene.

Figure 1C is similar to Figure 1B except that at equilibrium the C$-$H bond is still shorter than in the uncomplexed Cl_3C-H. The lengthening of C$-$H bond near-equilibrium distances of Figure 1B and C clearly rules out the short-range repulsive forces suggested by several authors as the main cause for X$-$H shortening for improper HBs. In other words, as in ordinary HBs, here also the bond-shortening effect of Pauli repulsion is dominated by bond-lengthening effects at around equilibrium with HB acceptors such as π system or O and N based Ys, even if it shows X$-$H bond contraction with respect to uncomplexed X$-$H bond. An elongation of the C$-$H bond at large X$\cdots$Y separation and a contraction near equilibrium distance for the $F_3C-H\cdots FH$ system was taken as an evidence for the dominance of Pauli repulsion on improper HBs.[33] However, this trend in the C$-$H bond is due to the restriction of keeping the distance X$\cdots$Y fixed during the scan. We kept the distance H$\cdots$Y fixed, which is a better description for the separation of the monomers while they approach each other and allows maximum interdependent motions of nuclei of HB donor during the optimization. Such scans for F_3C-H with Cl^-, OH_2, and NH_3 also show a similar trend as in Figure 1.[40,48] A systematic decrease of energy at a particular H$\cdots$Y, in the H$\cdots$Y scan relative to the X$\cdots$Y scan proves that the H$\cdots$Y scan is more representative for the HB situation and the X$\cdots$Y scan provides another part of the PE surface (Table S1).

The fact that the forces that control the minimum in the C$-$H bond length in Figure 1 lead to a minimum in energy not at the

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minimum of C−H bond length and that the these two minima vary from each other in the PE scans heralds the obvious. There is going to be a continuum of behaviors from lengthening to no change to shortening in the X−H bond lengths in HBs.

2. Internal Rearrangement (Redistribution of Electron Density). Hobza[7,9,37,38] identified that many improper HBs are very different from proper HBs as per NBO analysis[23] since the X−H σ^* occupancies either decrease or only slightly increase for improper HBs. A detailed analysis reveals that a considerable amount of the transferred electron density from Y goes to orbitals of other atoms bonded to X (and not to X−H σ^*) in many improper HBs. It was argued that the charge transferred to the remote part causes a geometrical rearrangement in the molecule resulting in X−H bond contraction. However, it remains unexplained why and how the NBO charges transfer differently for different X−H and how the geometrical rearrangement causes a shortening for improper HBs.

The implication of different mechanisms operative in improper and proper HBs prompted Scheiner and Kar to consider electron-density shifts. They found that at equilibrium, electron-density shifts are very much alike at the X−H region of proper and improper HBs and the geometrical rearrangement at the remote part of both classes of complexes are similar, namely, lengthening at the remote part.[49] The surprising fact in this point of view is that both type of HBs have similar electron-density shifts,[24,49] yet they show different behaviors in terms of the X−H bond length at energy minimum.

3. Electric Field Explanation. It was shown that under weak negative electric field molecules which have a negative dipole derivative along the X−H bond, such as F_3C-H and H_3C-H, exhibit X−H bond contraction and blue shift.[4,8,30−32,35,36,39] On the basis of this, the X−H bond contractions at equilibrium in improper HBs were partly attributed to the electric field of Y and the remaining part to Pauli repulsion which has been shown above as not determinative in controlling the X−H bond length. So, the extra contraction of X−H bond length at equilibrium, rather than that caused by the "electrostatic potential derived" point charges model of Y,[35,36] is due to electron-density transfer and polarization of Y which is contrary to the case of normal HBs. In addition, the fact that molecules having a positive dipole derivative (for example F_2N-H)[50] exhibit improperness (F2N−H···FH)[33,51] invalidates the universality of the underlying assumption in this formalism—the HB donor attempts stabilization in an HB by increasing its dipole moment in the same way it could increase the dipole moment in the uncomplexed form. The questions that remain to be answered are (a) why do some X−H bonds possess negative dipole derivatives while others positive dipole derivatives and (b) how do electron-density transfer and polarization of Y help to enhance X−H shortening for some complexes.

4. Rehybridization. Rehybridization at X of an X−H bond was considered as a cause for X−H bond contraction by Alabugin et al.[40] The reasoning was based on Bent's rule[52] which states that the percent s character of A in the A−B bond increases when a more electropositive atom replaces B. An analogous increase of the percent s character in X when H becomes increasingly positive in a HB was attributed as causing the X−H shortening in the absence of a strong hyperconjugation.[40]

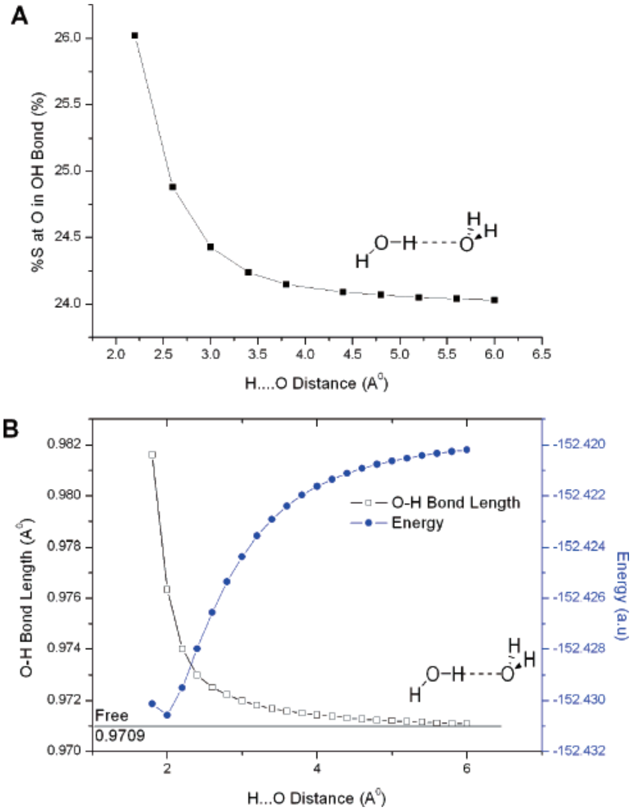

Figure 2. Variation of (A) percent s character at O and (B) O−H bond length of water molecule at various separation of $Y = OH_2$, $\angle O-H\cdots O = 180°$.

It must be emphasized that the NBO orbitals are being generated from the final electron density of the complex. Therefore, two examples having the same density distributions give the same NBO data even if their origins are different, and hence the above explanation can at best be considered as a description. Besides, an increase in the percent s character of one atom in a bond alone cannot explain the bond length. This is clear from Figure 2; for water dimer also there is an increase in percent s character similar to that seen in the scan of F_3C-H with OH_2 reported in ref 40, but the O−H is being continuously lengthened even before the hyperconjugation becomes operative, whereas, for F_3C-H, C−H is being continuously shortened at larger separation (Figure S2).

A Unified Explanation for Improper Hydrogen Bond. 1. Classification of HB Donors. Throughout the following discussion we concentrate mainly on the variation in the X−H bond length, as it is known that there is an approximate linear relationship for bond shortening with blue shift and bond lengthening with red shift.[33,35,36,53,54] Most of our studies are based on PE scans, and immediately we face a problem with the current definition of improper HBs. We note that some HB

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Table 1. Examples of Proper and Pro-improper HB Donors

Based on Equilibrium Geometry	
proper (red shift, bond lengthening)	improper (blue shift, bond shortening)
$HO-H$, H_2N-H, $F-H$, $Cl-H$, etc., with all HB acceptors.[22]	F_3C-H with FH, ClH, OH_2, SH_2, and with π electron donors such as enzene, acetylene, etc.[1,33,40]
	F_2ClC-H, FCl_2C-H with oxygen-based HB acceptors.[10]
$HCC-H$, NC-H with OH_2,[29] π electron donors, etc.[2]	Cl_3C-H with benzene, fluorobenzene, etc.[14]
	H_3C-H with π electron donors,[2] with OH_2, OHMe, OCH_2.[25]
F_3C-H with electron donors like Cl^-, F^-, $N(CH_3)_3$, $NH(CH_3)_2$.[33,40]	Benzene dimer.[2]
	$X-Ng-H$ with OC, N_2, CO, OH_2, etc. (X = F, Cl, OH; Ng = noble gas).[55−57]
Cl_3C-H with $O(CH_3)_2$.[8]	F_3Si-H with various HB acceptors.[33,47]
	F_2N-H with FH.[33, 51] $ON-H$ with CO.[50]
H_3C-H with Cl^-.[9]	F_4P-H dimer.[58]
Based on HB Donor	
proper (red shift, bond lengthening)	pro-improper (blue/red shift, bond shortening/lengthening)
H_2O, FOH, HF, NH_3, HCl, HF, etc.	alkanes, alkenes, aldehydes, CH_xF_{4-x}, CH_xCl_{4-x}, C_6H_6
$F_2C{=}CH_2$	F_3SiH, F_2NH, HNO, F_2PH, F_4PH
$HCC-H$, $NC-H$, $FCC-H$	$X-Ng-H$, (X = F, Cl, OH; Ng = noble gas)

donors which do not form improper HBs do not show an X−H contraction at larger H···Y separation, whereas others which are known to exhibit proper or improper HBs, depending on Y, show a shortening at larger separation with many common Ys. It is clear, therefore, that the proton donor plays a decisive role on whether it would show improper behavior. The molecules, whose X−H bond continuously lengthens in a potential energy scan of the H···Y distance, independent of Y, show proper HB at equilibrium and may be classified as proper HB donors. We call the other class as pro-improper X−H in the following discussion, as this could form proper or improper HBs depending on Y. Table 1 shows many of the examples known (Figure S3 shows the detailed basis of this new classification). Since all pro-improper X−H shorten and all proper X−H lengthen its X−H bond at large separation of monomers, this characteristic may be used to easily determine in which category a particular molecule belongs by a single calculation (optimization).

Table 1 reveals a few characteristics of a pro-improper X−H: (1) The X−H bond is relatively less polar; (2) electronegative atoms such as fluorine enable some of the proper X−H to change into pro-improper (inclined to be improper) X−H (e.g., from H_2N-H to F_2N-H), while in other cases it converts pro-improper to proper (e.g., from $H_2C{=}CH-H$ to $F_2C{=}CH-H$). These facts need to be accounted.

It may be noted that a comparison of PE scans of proper and improper HBs of a pro-improper X−H cannot reveal much information since they are more similar than their equilibrium geometries suggest. Similarly, a comparison of proper HBs of proper and pro-improper HB donors at equilibrium is not representative as in both cases the X−H bond lengthens at equilibrium. A better comparison would be between a proper X−H and a pro-improper X−H throughout the scan. An explanation on the origin of the initial shortening of pro-improper X−H is expected to throw light onto the equilibrium situation since a lengthening at nearby equilibrium is anticipated from the known explanations of HB.

Why does the X−H bond contract at large H···Y separation for the pro-improper X−H? F_3C-H is widely studied (Figure S2) and is a representative example for pro-improper X−H; we relate it to a proper X−H, HO−H (Figure 2B). At large H···Y separation, say 6 Å, there cannot be any orbital interaction, so shortening due to exchange repulsion can be ruled out. Since there cannot be any charge transfer as well, one can assume that this shortening is due to the electrostatic interaction, which is a long range interaction, with Y. As mentioned earlier it was shown that an electric field can produce such a shortening[39] for H_3C-H while producing a lengthening for HCC−H and HO−H so that this shortening is caused by the electric field effect of Y. A shortening effect of electric field/charge on a negatively charged H, say H_3Si-H, is understandable, as a negative field pushes electron density to bond. In the case of F_3C-H, H is considerably positive and such an argument is unreasonable.

2. Electron Density Reorganizations. Figure 3 shows the evolution of electron density difference of X−H···Y when Y approaches H. The similarities between (A) HO−H···OH_2, (B) $F_3C-H\cdots OH_2$, and (C) $F_3C-H\cdots NH_3$ is in accordance with already alluded topological similarities of all HBs.[24]

We identify that there is loss of electron density around the H nucleus, especially on the opposite side of X (on the right-hand side of H as drawn in Figure 3) and conjecture that this depletion is not due to the forced shift of electron density by electron rich Y, but due to the favorable pull by X in the presence of Y. The electron density distribution in the isolated X−H is decided by a balance of forces. The electron density is certainly shifted from H to X because of more electron affinity of X. Any further shift is resisted by the increased positive charge generated at H by the depletion of electron density. In the presence of Y, however, X can withdraw electron density further. Qualitatively, the role of electron density in the right-hand side (rhs) of H is now served by Y with its electrons. This withdrawal of electron density by X is manifested in the increasingly negative X and increasingly positive H when Y approaches H. For example, as Y approaches H of F_3C-H, the positive charge of H and the negative charges of F and C increase continuously (Figure S4[40]). This explanation accounts for the charge redistribution in the HB donor in an electric field[35,36] and in the presence of a dipole.[33] A net loss of electron density at the rhs of H and a net gain by X in the X−H region, as evidenced by the electron density difference maps and NBO charge evolution, causes H to move to the left-hand side (lhs)

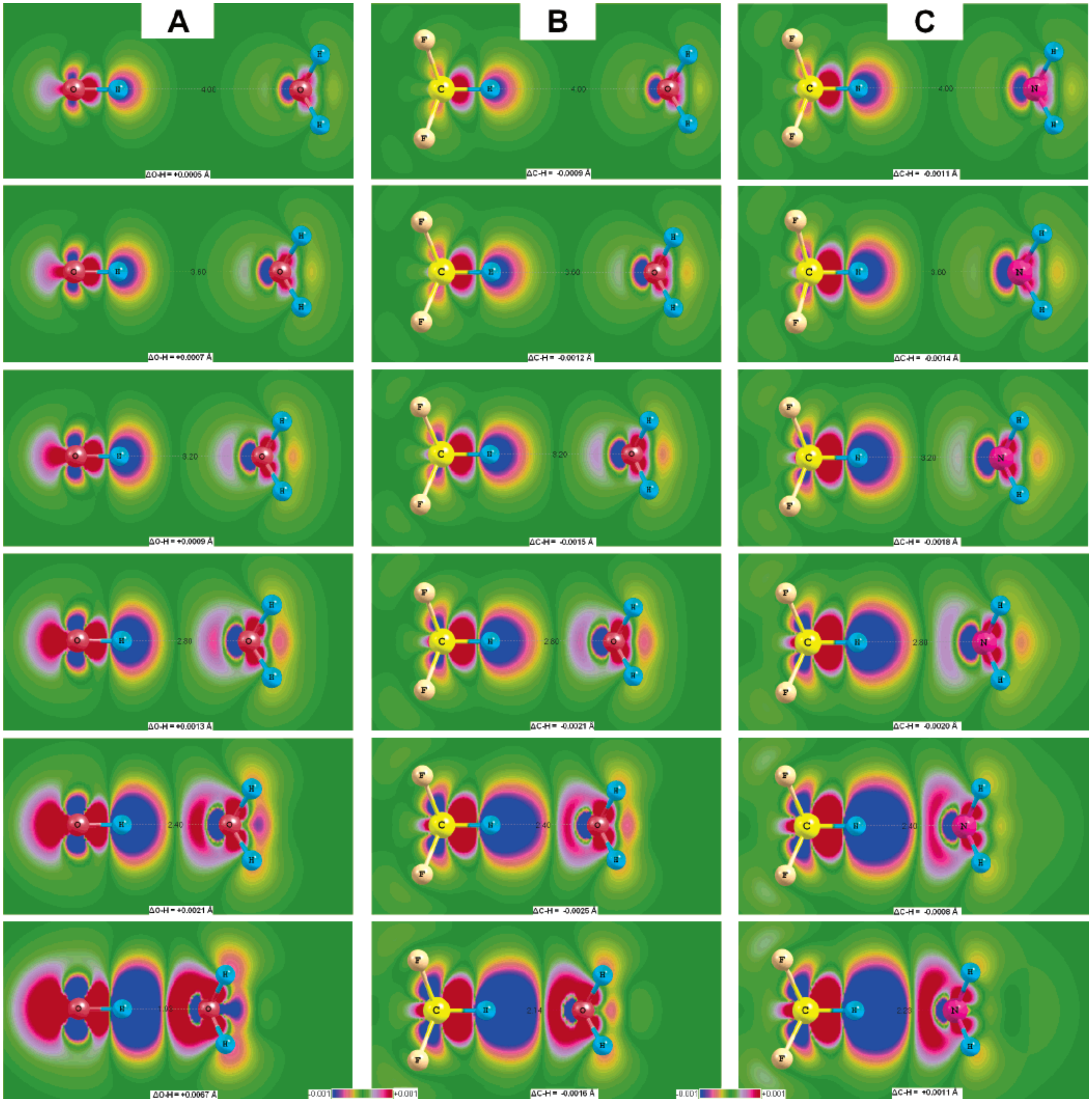

Figure 3. Electron density difference map of (A) HO−H···OH_2, (B) F_3C−H···OH_2, and (C) F_3C−H···NH_3. The last row corresponds to H···Y equilibrium separation. All the bond lengths and bond angles are of optimized monomers. The colors change from −0.001 e/$Å^3$ (blue) to +0.001 e/$Å^3$ (red). The plots were generated using the ChemCraft program.

(in the scan where H is fixed, the X to move to the rhs, instead)—the contraction of the X−H bond. In other words, increased attraction between increasingly negative X and increasingly positive H cause an X−H bond contraction.[59] But, as is clear from Figure 3, the contraction manifested only for situation B and C, while this should have happened in A as well. This is because we tacitly ignored the attractive interaction between positive H and negative Y, by no means a less important factor. This is the second factor which controls the X−H bond length. If the latter dominates then the X−H bond elongates. If the former dominates then the X−H bond contracts.

Let us now dwell more on the relative importance of both of the above opposing factors, starting with the HB donor. The more polar the X−H bond is, the better it is as an HB donor. For very polar X−H bonds such as F−H, HO−H, and H_2N−H, the attraction between H and Y is very strong owing to the large positive charge of H, and so the lengthening effect is overwhelming. In addition, the contracting ability is weak. The strong electron withdrawing effect of X makes the X−H bond electron rich and hence already very short in the uncomplexed

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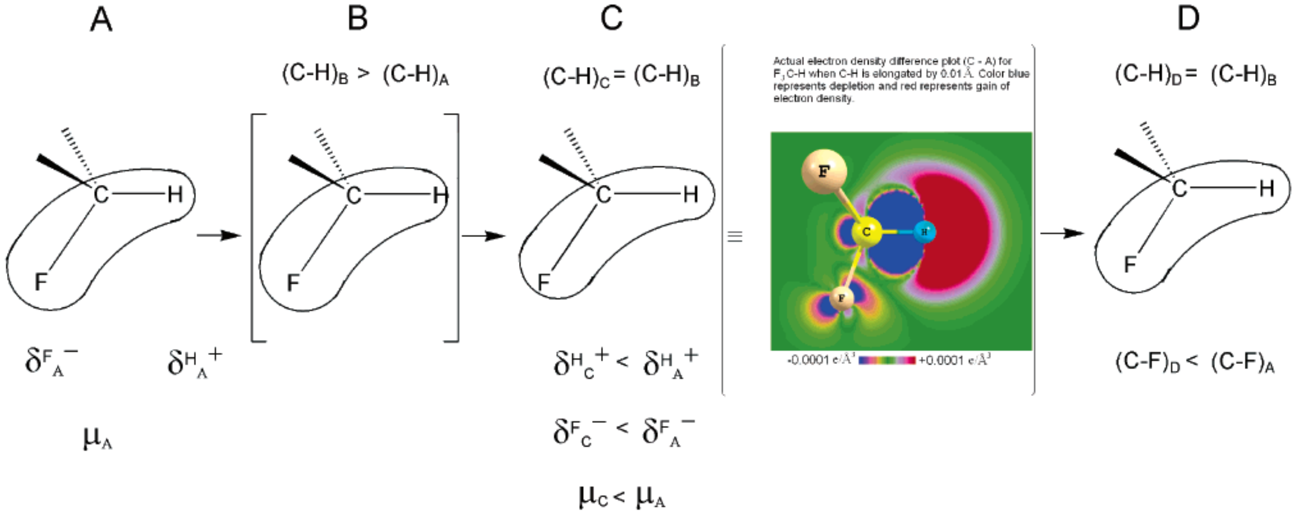
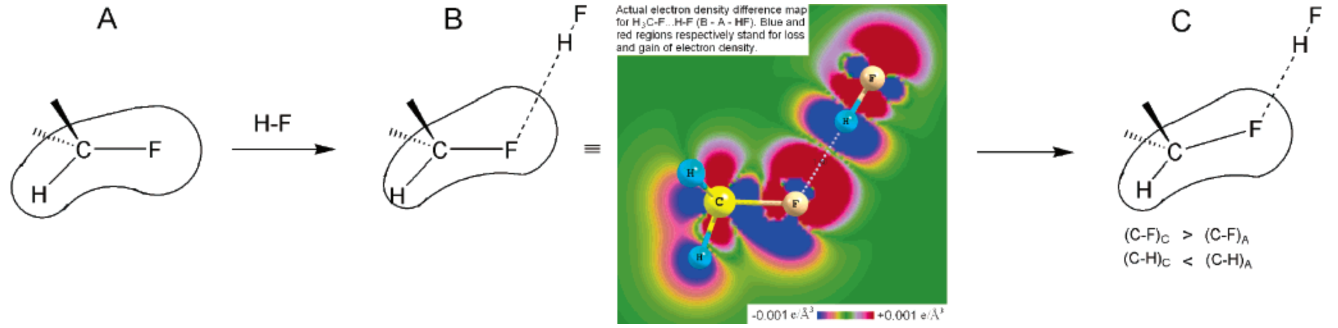
(59) There is no need to invoke that the extra charge on F is somehow shortening the C−H bond.[37,38] Similarly, a charge gain in F means lengthening of the C−F bond as there is more of an increase of electron density on the periphery of F than in the monomer. This shift in electron density towards C from H would come in NBO analysis as increasing percent s character of C in the C−H bond.

Scheme 1. Origin of Negative Dipole Derivative for X−H Bond and Intramolecular Negative Response[16−20,48] for Vicinal Bonds for a Pro-improper HB Donor



Actual electron density difference plot (C - A) for F_3C-H when C-H is elongated by 0.01 Å. Color blue represents depletion and red represents gain of electron density.

Scheme 2. Origin of Blue-Shifted C−H Bond Even in the Absence of C−H···Y Interaction



Actual electron density difference map for H_3C-F...H-F (B - A - HF). Blue and red regions respectively stand for loss and gain of electron density.

state. So the electron density shift from the rhs of H to the bond has less effect in reducing the X−H bond length than in the case of an electron poor, lengthier bond such as C−H. So an electron rich, highly polar bond almost always shows X−H lengthening, whatever be the HB acceptor, and belongs under proper HB donor in Table 1. Increasing polarity of X−H is, therefore, a direct way for making an HB donor proper. This explains why the bond shortening is decreased in the order $sp^3 > sp^2 > sp$ for C−H.[29] Indeed sp hybridized HCC−H, FCC−H, NC−H, and MeCC−H are all proper HB donors (see Table 1).

Analogously, electron poor, less polar X−H bonds constitute pro-improper HB donors. Here the tendency for shortening dominates over the tendency for lengthening ability at larger separation of H···Y, because the former effect is caused by the attraction of a closer X and the latter is acting on a H whose positive charge is not very large. In these examples the nature of Y is very important in dictating whether the X−H bond is longer or shorter at equilibrium. Unlike the effect of increasing the polarity of the X−H bond, the increasing HB acceptor ability of Y helps the cause of both the shortening and the lengthening effects. The reason for the enhanced shortening effect is clear from Figure 3B and C. A better donor, NH_3, allows F and C to withdraw more electron density from H. As the H···Y separation decreases, the better lengthening ability of NH_3 over OH_2 causes the C−H bond to lengthen more in Figure 3C. So at equilibrium $F_3C-H\cdots NH_3$ becomes proper ($\Delta C-H = +0.0011$ Å), while $F_3C-H\cdots OH_2$ remains improper ($\Delta C-H = -0.0016$ Å).

Now we explain why and how the above-described pro-improper HB donors generally have a negative dipole derivative, $\partial\mu/\partial r_{XH}$ along the X−H stretch[35,36] and a negative intramolecular response for vicinal bonds.[16−20,48] In fact, improper HBs, negative dipole derivatives, and negative intramolecular responses are manifestations of the characteristic electron distribution of the pro-improper HB donors determined by the relative electron affinities of constituent atoms. No one of them is an explanation for the other. At the boarder ranges of proper and pro-improper HB donors all the three factors need not be present collectively. Let us consider the example of F_3C-H (Scheme 1**)**. An elongation of C−H bond (B) disturbs the equilibrium electron distribution shown in part A. Consequently, the H pulls more electron density from the C and Fs resulting in part C, where the F lost some electron density from its periphery. This argument is reversed when the C−H bond is compressed. The situation in Scheme 1C may be qualitatively described as a decrease of charge in the dipole, leading to a decrease in the dipole moment despite a lengthening of the dipole. The redistributed electron density necessitates the F to move closer to C, shortening of C−F bond—negative intramolecular coupling of C−H and C−F bonds (part D, Scheme 1). (Conversely, if the F−C bond is stretched from part A, F effectively acts as more electron demanding to C and H, which give up some electron density, a net loss of electron density at the periphery of the H and hence a contraction of the C−H bond.) To make these argumentsin a more quantitative footing, eq 1, which is a reasonable approximation for $\partial\mu/\partial r_{XH}$ may be used.[60]

$$\frac{\partial \mu}{\partial r_{XH}} \approx q_H^0 + r_{XH}^0\left(\frac{\partial q_H}{\partial r_{XH}}\right) \qquad (1)$$

Here q_H^0 is the charge of H, r_{XH}^0 is the X−H bond length of the monomer at equilibrium, and $\partial q_H/\partial r_{XH}$ is the charge flux on H owing to the X−H stretch.[61] Obviously, a negative $\partial \mu/\partial r_{XH}$ results if q_H^0, the atomic charge of H, is smaller than the second term which is always negative for a covalent protic H. Now, a less electron demanding X not only decreases the positive charge of H but increases the charge flux also. Besides, X−H bond is long for such an X.[61] These factors result in a negative dipole moment derivative for a less polar X−H bond. This negative dipole moment derivative decreases with increase in electronegativity of X and eventually reverses sign when X becomes more electronegative and/or when the bond length is short. This explains the tendency of polar X−H bonds in general to have a positive dipole moment derivative. Qualitatively, the increase of dipole moment upon stretching of a polar X−H bond is due to the lengthening of the dipole (despite the small decrease of charge of the dipole).

Recently there have been several studies on noble gas molecules, X−Ng−H, where X is an electronegative atom/group (F, Cl, OH, etc.) and Ng is a noble gas atom. These molecules form HBs with weak Ys such as N_2 and CO. Some of these complexes show Ng−H bond contractions besides showing other characteristics of improper HBs.[55−57] Results revealed that complexes with a heavier Ng atom in the periodic table are more prone to Ng−H bond contraction.[57] This is now easily explainable; the low polarizablity of He and Ne cause a large positive charge on H, whereas the more polarizable Ar and Kr allow H to be less positive. In the presence of Y, H faces a stronger pull from Y in the former case than in the latter case; besides, the electron density shift from H is larger for the latter. It was reported that F−Kr−H shows X−H bond contraction with N_2, CO, P_2, and OH_2, whereas F−He−H shows the contraction only with N_2, but elongation with CO, P_2, and OH_2.[57]

If the above arguments are correct it is also possible that there is no appreciable change in the X−H bond length at a large H···Y separation during a scan for some X−H which lies in the boarder areas of proper and pro-improper regime, because in such molecules both the shortening and lengthening effects can be balanced. Figure 4 shows two such examples: fluoroethene and difluoroethene are in border areas for Y = OH_2 at MP2/6-31+G* theory. Note that, although there is little change in bond length at a larger separation of monomers, for fluoroethene the bond is still slightly shorter and for difluroethene it is slightly longer than a free molecule. Here fluorines convert pro-improper ethylene to a proper one.

That the withdrawal of electron density from H can indeed shorten a C−H bond is also supported by C−H bond lengths of isolated molecules. For example, the following bond lengths obtained at MP2/6-31+G* may be noted: CH_4 and CHF_3, 1.0909 and 1.0876 Å; $H_2C{=}CH_2$, $FHC{=}CH_2$, $F_2C{=}CH_2$, and $F_2C{=}CFH$, 1.0859, 1.0834 (average), 1.0803, and 1.0801 Å, respectively. The corresponding distances for MeCCH, HCCH, and FCCH are 1.0678, 1.0677, and 1.0660 Å, respectively. But such a substitution of an electron-withdrawing atom is not expected to shorten a highly polar bond. Highly polar bonds are already at a very short length because of being electron rich, and H is already too polarized to give away much electron density. Therefore fluorine substitution would pull electron density from the bond/X and hence the X−H bond lengthens, for example, H_2O versus FOH, 0.9709 versus 0.9813 Å, and NH_3 versus NF_2H, 1.0169 versus 1.0293 Å. In the language of electrostatic interaction, these lengthenings are due to the decrease in the negative charge of X and is also a reason for the lengthening of the bonds in HB acceptors (for example, N−H bond in X−H···NH_3) when it involves in an HB. This is also the explanation for the positive coupling of N−F and N−H bonds of F_2NH.[20] Similarly, protonation of NH_3 (NH_4^+) results in an elongation of N−H from 1.0169 to 1.0287 Å as there is a removal of electron density from the bonds. All four bonds are "electron deficient" in relation to the N−H bond in NH_3. We therefore expect that the effect of the electron-density shift from H to N would be noticeable in all N−H bonds when Y interacts with the N−H. As is clear from Figure 5A, all N−H bonds shorten when a Y (=NH_3) approaches the N−H bond of NH_4^+; the more shortened is the directly interacting N−H bond. Again, when Y becomes closer, the interacting N−H lengthen as is expected since the lengthening ability of Y is appreciable, but the gained electron density enables other N−H bonds to replenish further, and it shows enhanced shortening.

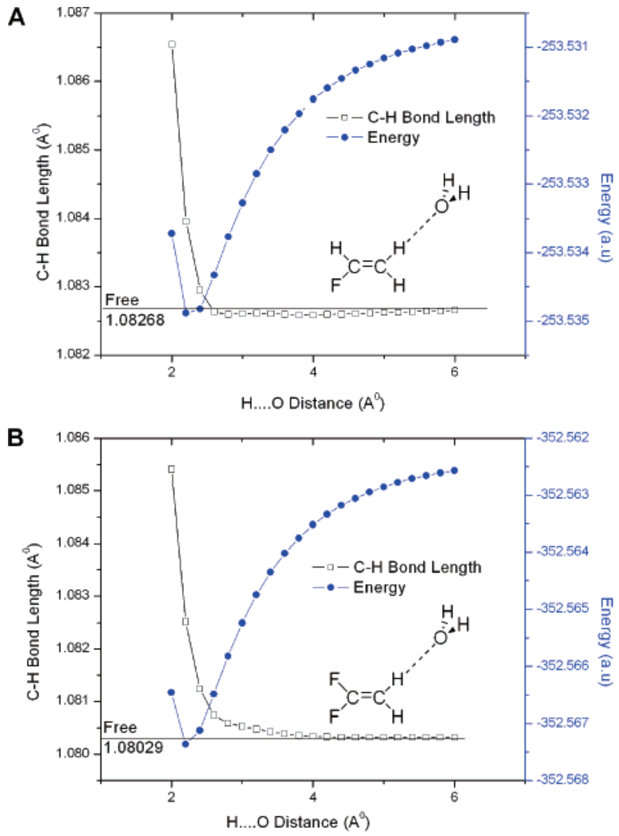


Figure 4. Potential energy scans for (A) fluoroethene and (B) difluoroethene with water. ∠C−H···O = 180°.

The above explanations also suggest that if somehow we can increase the electron withdrawing effect at X, we can achieve

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(60) Gussoni, M.; Castiglioni, C. *J. Mol. Struct.* **2000**, *521*, 1.

(61) Here it is assumed that the charge flux happens solely from X. For molecules like F_3C−H, Cl−Kr−H, etc., a part of it comes from F and Cl as well, so the X may better be considered here as the center of a negative charged region.

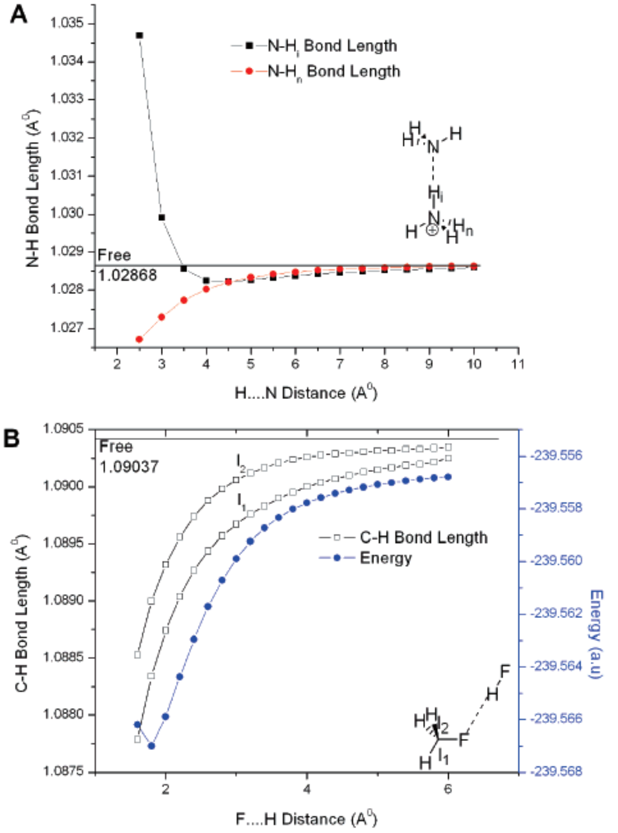

Figure 5. (A) Variation of N−H bond lengths during a scan for H_3N^+−H···NH_3 system; (B) variation of C−H bond lengths when F is involved in hydrogen bonding for H_3CF···H−F system, ∠F···H−F = 180°.

a bond shortening of C−H, say, for FH_2C−H. One way for this is F to act as an HB acceptor for another HB donor such as H−F. As shown in Scheme 2 B, this would result in polarization of electron density at F toward H (of H−F, and hence an elongation of C−F (part C)). This in turn would cause H of FH_2C−H to lose electron density, and hence shortening occurs as was observed by Kryachko and Karpfen.[16−20] It was indeed found that such HBs, where X−H is not interacting with any electron rich center, exhibits X−H bond contractions (examples: F_3CH,[17] F_3SiH,[18] HCHO,[19] F_2PH, F_2AsH,[20] dimethyl ether,[7,62] DMSO,[63] and 2-butoxyethanol[64]). The X−H contraction can be further enhanced if we allow a weak Y to interact with X−H. This too was observed when F_3CH, F_3SiH, HCHO, etc. involved in two HB interactions: F/O act as HB acceptor and X−H acts as HB donor.[17−20] To prove conclusively the effect of the electron withdrawing group, we scanned H_3C−F···H−F as shown in Figure 5B. As can be seen, all the three C−H bonds shorten when HF approaches F, the more when they are closer. Note again that the C−H bond anti to HF shortens more, clearly indicating the movement of electron density is more there, as expected.

So far we mainly concentrated at the larger H···Y separation of monomers. It is well-known that electron-density transfer from Y to HB donor occurs at near equilibrium. This transferred electron density can also go to X as before, for the same reason, and it further encourages X−H shortening. An added effect of charge transfer from Y is that it decreases the lengthening ability of Y more than the case of no charge transfer. This is why electric field and point charge model failed to predict the observed shortening at the equilibrium H···Y distance, because in such a model the polarization in Y and charge transfer from Y were not taken into account. In an NBO scheme, the continuous depletion of electron density on H would appear as a decrease in occupancy of X−H σ^*. Such decreases were reported at equilibrium for F_3C−H and Cl_3C−H complexes with water (at the B3LYP/6-311++G** level), for example.[34]

No X is an infinite sink for electron density for this mechanism to operate indefinitely. After “saturation”, it can no longer accept electron density favorably. Then there will be a build up of electron density around H as well, which would cause an X−H bond lengthening. Besides, the ever increasing lengthening effect of Y—as Y is closer to H—will be noticed more as the contracting effect subsides (Figure 6). This explains why there is an X−H lengthening at near equilibrium from a preshortened form. At this regime NBO analysis shows σ^* occupation.

In summary, the X−H bonds of all proper HB donors are relatively highly polar, electron rich, and short. Electrostatically, it can only lengthen with all reasonable Ys. The pro-improper X−H bond can shorten in the presence of Y since the X−H bond is relatively less polar, electron deficient (even a fluorine substitution does not make the C−H bond much more electron rich and polar, since F makes C also more positive in the same way it makes the H more positive), and long. Then it reaches a maximum shortened state similar to a proper HB donor in its “free” state. From this preshortened form it can only lengthen (see Figure 6).

Correlation between Properties of X−H Bond and Interaction Energy. Now we explain some of the observations from the literature that appear to defy general trends.

1. Effect of Substitution on X. With a particular Y, X−H shortening and blue shift are expected to increase if we increase the electron withdrawing ability of a pro-improper HB donor, since it helps to withdraw more electron density from H in the presence of Y. Although one cannot strictly compare the magnitude of blue shifts of different X−Hs, it is known that with Y = OH_2 the blue shifts decrease in the following order F_3C−H > Cl_3C−H > Br_3C−H > I_3C−H; the latter two are red-shifted.[9] Experimental observations of decreasing blue shift of C−H in the following order for F_3C−H > F_2ClC−H > FCl_2C−H > Cl_3C−H with dimethylether,[7,8] acetone, and oxirane[10] are in tune with the ability of electron withdrawing atoms to increase the blue shift.

As discussed earlier, a substitution of F cause an X−H bond contraction for a less polar bond by removing electron density from H. The increased positive charge on H, however, encourages an elongation, while the electron withdrawing F further tries to contract the X−H bond in the presence of Y. For alkanes, owing to less charge of H (less acidity because of sp^3 hybrid C), the elongating ability of Y is less and results in the above trend. But for alkynes it is exactly opposite. Fluorine substitution here enhances red shift.[29] For alkenes, as seen in Figure 4, the lengthening and contracting forces are very balanced. Fluorine substitutions indeed convert them from pro-improper to proper.

The electron rich, highly polar and very short O−H bond in HO−H and N−H bond in H_2N−H are proper. A way to decrease the electron density of this bond is a substitution of H

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(62) Karpfen, A.; Kryachko, E. S. *Chem. Phys. Lett.* **2006**, *431*, 428.
(63) Mrazkova, E.; Hobza, P. *J. Phys. Chem. A* **2003**, *107*, 1032.
(64) Katsumoto, Y.; Komastu, H.; Ohno, K. *J. Am. Chem. Soc.* **2006**, *128*, 9278.

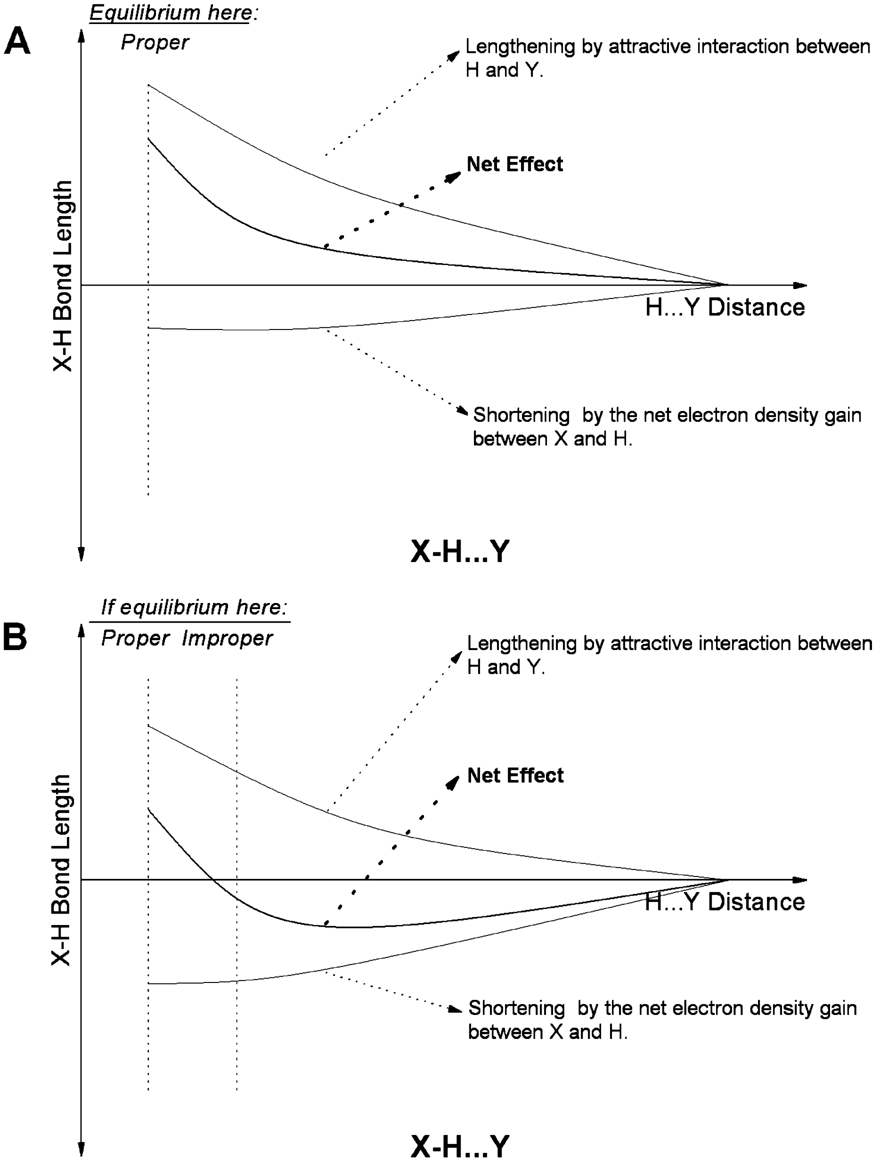

Figure 6. A schematic summary of the mechanism operative in HBs: (A) for proper X−H; (B) for pro-improper X−H.

by an electron demanding atom such as F. Such a substitution increases the O−H and N−H bond length, instead of the decrease observed for less polar bonds such as C−H (vide supra). Now there is a chance for both O−H and N−H to be shortened by a weak Y because the electron-density shift from H to the X−H bond will have a more noticeable effect. Nevertheless, FO−H still behaves "properly" as the elongating effect of Y dominates, whereas F_2N-H becomes pro-improper. Blue-shifted HB of F_2N-H is known with FH being a weak HB acceptor.[33,51] We emphasize again that all "proper" X−H behave properly because for all practical Y the lengthening effect of Y dominates as shown in Figure 6. For example, with F^-, a very strong HB acceptor, N−H in F_2N-H lengthens even at a separation of 10 Å (at MP2/6-31+G*), showing how weak pro-improper F_2N-H is.

2. **Effect of variation of Y.** For a particular X−H what would be the effect of different Ys? One would expect from the forgoing discussion that a plot of HB acceptor ability versus X−H bond length and its frequency at equilibrium would look as in Figure 7. Here the *x*-axis represents HB energy and the *y*-axis represents parameters of equilibrium HB structures such as X−H bond length, stretching vibrational frequency, and intensity with respect to the isolated HB donor. A very weak Y neither provides enough field to allow the molecule to pull electron density from H at its best nor transfers enough electron density until the saturation. A strong Y not only does both the above, but it pulls the H strongly too. An intermediate Y, therefore, causes a maximum X−H bond contraction. Such a trend was identified by Schlegel et al. for $F_3C-H\cdots NR_nH_{3-n}$ who used the proton affinity of Y as a measure of its HB acceptor ability (Table S2).[33] A remarkable study from this point of view was carried out by Fan et al.[54] They fine-tuned the electronics in $Y = D-C_6H_4-Z$ by varying Z, where D is the HB acceptor atom/group which is interacting with X−H. In effect, by changing Z the HB acceptor ability of Y was varied. Their study on the effect of substitution (Z = NH_2, CH_3, OH, H, F, Cl, CN, NO_2) on the C−H bond length and its stretching vibration for F_3C-H showed the then surprising result that the electron-donating substituent not only increases the interaction energy but also increases the blue shift with $Y = HO-C_6H_4-$

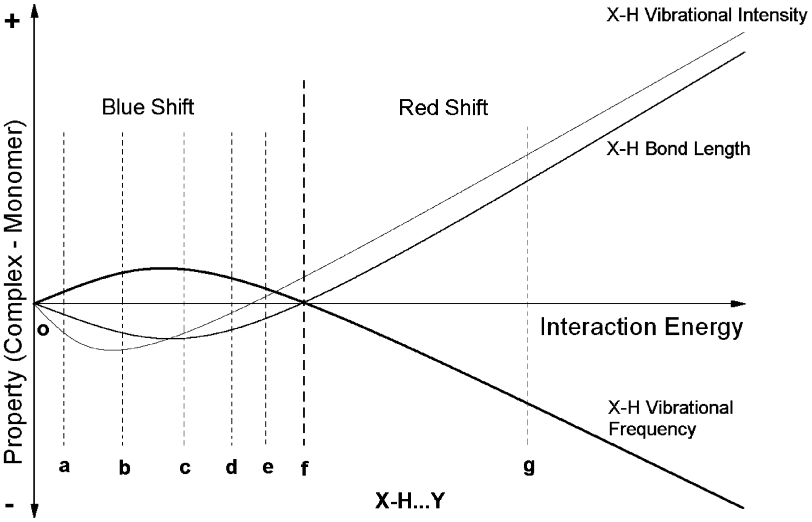

Figure 7. A qualitative trend for X−H bond length, vibrational frequency, and IR intensity with HB energy for a pro-improper X−H donor with several similar Ys.

Z, $H_2N{-}C_6H_4{-}Z$, and $F{-}C_6H_4{-}Z$. But when the D becomes O^-(phenoxide) the electron-donating group increases the interaction energy as well as red shift (the conventional trend, as interaction energy increases red shift increases[65]). We now attribute the first case to the left-hand side (regions o−c) and the second case to the right-hand side (regions c−g) of the Figure 7. Similarly, theoretical studies on Cl−Kr−H complexes with N_2, CO, and FH showed that the Kr−H contraction increases with increasing interaction energy.[56] The experimental results that fluoroform and chloroform exhibit lower blue shift with fluorobenzene than with benzene[14] can now be understood. Hobza's recent report[66] of increasing blue shift in the T shaped C−H···π interaction of benzene with interaction energy when Y = benzene, anthracene, and ovalene can also be assigned as belonging to the regions o−c.

Region f of Figure 7 suggests that there is a possibility of HBs that cannot be detected by IR spectroscopy from a frequency shift of the X−H stretching mode as there would not be any shift, but other vibrational frequencies would differ as in familiar HBs. Such an interaction can be detected by other techniques such as NMR, since the electron-density shift makes the H more downfield. Theoretically, the $H_3C{-}H{\cdots}NH_3$ complex[26] and the $H_2C{=}CH{-}H{\cdots}OH_2$ complex[29] were reported with zero shift of IR frequency at MP2/6-31+G** level. Because of the known limitation of computational predictions with actual experiments the above examples may show some frequency shifts which can be in either direction. Nevertheless, the shift would be small in magnitude. One such zero-shifted HB is already characterized in the dimer of cyclohexenon with the help of theory.[67]

Around the region f (Figure 7), it is also possible to have a blue shift with X−H lengthening or red shift with X−H contraction. Although this may seem, in isolation, as against the conventional belief of the "approximate" proportionality of X−H bond length to frequency shift,[44] it is perfectly reasonable when we consider region f along the path of regions d−g. Similarly, we should not be surprised if different methods predict different outcomes (blue or red shift)[68] when the HB is at or around region f.

3. Effect of Variation of Y for IR Intensity. The intensity of an IR band is determined by the dipole moment derivative with respect to that mode of vibration.[8,30,56] Since we know that q_H^0 increases and $\partial q_H/\partial r_{XH}$ decreases in a HB, the approximate eq 1 enables us to make useful prediction on intensity of X−H stretching mode. As Y becomes a stronger HB acceptor, a decrease of negative $\partial\mu/\partial r_{XH}$, and its eventual conversion into positive are apparent from eq 1. So we expect a trend for intensity as shown in Figure 7 for a pro-improper X−H having a negative $\partial\mu/\partial r_{XH}$ in the isolated form. The effect of contraction of r_{XH}^0 helps further decreasing the intensity in the range of regions o−b (Figure 7), while its effect in regions c−g would be overcome easily by the more dominant terms in eq 1, similar to the normal HBs.[69−70]So a least intense band would occur when the blue shift (contraction) approaches the maximum. This is because all factors help to decrease the negative dipole derivative and its eventual conversion to positive dipole derivative in the region o−b. There is less data available for a suitable comparison (where the Ys are similar and the X−H mode is pure) with the above prediction. The limited data available agree. Increasing blue shift with decreasing intensity was reported in the following systems when n increases: for $HO{-}Xe{-}H{\cdots}(H_2O)_n$, $n = 1{-}4$;[55] for $F_3C{-}H{\cdots}(HF)_n$,[17] $F_3Si{-}H{\cdots}(HF)_n$,[18] and for the asymmetric stretch of $H_2CO{\cdots}(HF)_n$,[19] $n = 1{-}3$. These complexes can be identified as belonging to the o−b range . Similarly, a parallel relationship with blue shift and decrease in intensity for $F_3C{-}H$ with oxygen HB acceptors was reported.[25] One of the important consequence of the trend shown in Figure 7 is that the two cases, region a and region c,

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(65) See for example: Kryachko. E. S.; Zeegers-Huyskens, T. *J. Phys. Chem. A* **2002**, *106*, 6832.

(66) Spirko, V.; Hobza, P. *Chem. Phys. Chem.* **2006**, *7*, 640.

(67) Nolasco, M. M.; Riberio-Claro, P. J. A. *Chem. Phys. Chem.* **2005**, *6*, 496.

(68) Lu, P.; Liu, G.; Li, J. *THEOCHEM* **2005**, *723*, *95*.

(69) When the effective r_{XH}^0 is large as in the case of inert gas complexes, it will have an important role and may result in red shift with decreased intensity. A sole computational example, $F{-}Ar{-}H{\cdots}P_2$, was reported in McDowell, S. A. C. *Phys. Chem. Chem. Phys.* **2003**, *5*, 808.

(70) The sign of the dipole derivative of the X−H vibration mode was determined using GaussView. Dennington, R., II; Keith, T.; Millam, J.; Eppinnett, K.; Hovell, W. L.; Gilliland, R. *GaussView, version 2.1*; Semichem Inc.: Shawnee Mission, KS, 2003.

Table 2. Correlation of C−H Bond Length, Vibrational Frequency and IR Intensity of $F_3C{-}H$ (**A**) with Various Similar Ys at Equilibrium, and during Scans with (**B**) OH_2, (**C**) NH_3 and (**D**) F^-

	monomer	X–H bond length, r (Å)	X–H frequency ω (cm^{-1})	intensity I (kM/mol)	sign of dipole derivative[70]
	$F_3C{-}H$	1.0876	3254.8	22.8	−
	complex	**Δr (mÅ)**	**$\Delta\omega$ (cm^{-1})**	**ΔI (kM/mol)**	**sign of dipole derivative[70]**
A	$F_3C{-}H\cdots NF_3$[a,b]	−0.5	+9.9	−9.7	−
	$F_3C{-}H\cdots NCl_3$[a,b]	−0.6	+12.1	−22.2	+
	$F_3C{-}H\cdots NH_3$[a,b]	+1.1	−13.6	+6.1	+
	$F_3C{-}H\cdots NMe_3$[a,b]	+3.8	−61.4	+34.3	+
	$F_3C{-}H\cdots OH_2$[c]				
	H···O distance (Å)				
B	4.0000	−0.9	+11.2	−8.3	−
	3.6000	−1.2	+14.2	−11.0	−
	3.2000	−1.5	+18.3	−14.5	−
	2.8000	−2.1	+24.6	−18.9	−
	2.4000	−2.5	+34.3	−22.8	0
	2.1426[a]	−1.6	+37.2	−15.4	+
	$F_3C{-}H\cdots NH_3$[b]				
	H···N distance (Å)				
C	4.0000	−1.1	+13.3	−10.6	−
	3.6000	−1.4	+16.7	−14.3	−
	3.2000	−1.8	+19.7	−18.6	−
	2.8000	−2.0	+20.3	−22.6	−
	2.4000	−0.8	+6.9	−14.3	+
	2.2324[a]	+1.1	−13.6	+6.1	+
	$F_3C{-}H\cdots F^-$				
	H···F$^-$ distance (Å)				
D	6.0000	−1.4	+21.1	−14.8	−
	5.0000	−2.0	+28.8	−18.7	−
	4.0000	−2.8	+38.3	−22.6	−
	3.0000	−3.3	+35.9	−13.2	+
	2.0000	+6.8	−136.3	+190.2	+
	1.5832[a]	+40.3	−584.4	+763.3	+

[a] Equilibrium geometry. [b] These are all C_{3v} eclipsed for a suitable comparison with the minima of $F_3C{-}H\cdots NH_3$ whose staggered conformation has one imaginary frequency. [c] Angle C−H···O held at 180.0° at C_s symmetry.

can have a comparable decrease in intensities even if the interaction energies are different; region c has stronger HBs. At region a, however, the dipole derivative is negative but at region c it is positive. Such a situation is possible with X−H bond length and frequency as well (cf. regions b and d of Figure 7).

For HB donors such as $F_2N{-}H$, $Cl_3C{-}H$, and $Cl_2FC{-}H$ whose dipole derivatives are either positive or near zero, even the weakest Y can increase $\partial\mu/\partial r_{XH}$ and hence increase its intensities. In fact blue shifts with increased intensities are known experimentally for $Cl_3C{-}H$ with acetone and oxirane,[10] and for $Cl_2FC{-}H$ with acetone, oxirane,[10] and dimethy ether.[8] C−H···O interactions of some amino acids also show increased intensity with blue shift.[28] These examples can be considered as belonging to region e.

To lend more support to Figure 7, we calculated HBs of $F_3C{-}H$ with nitrogen based Ys which are shown in Table 2A. In accordance with Figure 7, C−H bond length and intensity pass through a minimum and frequency passes through a maximum when the strength of Y increases. The same trend prevails in the scans (Table 2B, C, and D) where different H···Y distances imitate different HB acceptor ability. A situation with a short H···Y distance is similar to a strong Y at equilibrium.

Conclusion

Despite the vast literature on improper HBs there was no unified explanation for all the known examples. In this article we explain how the improper behavior forms a part of the continuum of well-known normal HBs by extending it further. Instead of considering all improper HBs as exceptions and attributing different reasons for their origin, we consider them as directly related to the normal HBs by the simple explanation provided here: All X−H bonds, while they are involved in HBs, face opposing contracting and lengthening forces. The contracting force is due to the electron affinity of X, which causes a net gain of electron density at the X−H bond region in the presence of Y. The lengthening force is due to the well understood attractive interaction between the positively polarized H and the electron rich Y. For electron rich, highly polar X−H bonds, the latter almost always dominates and results in X−H elongation, whereas for the less polar, electron poor X−H bonds, the effect of the former is noticeable if Y is not a very strong HB acceptor. In other words, the nature of the electron density distribution resulting from the electron affinity of atoms involved in the HB donor predetermines it toward proper or improper HBs. Our explanation allows qualitative judgment of the strength of the interaction of improper HBs based on frequency shift, but the interpretation is more complex in comparison to conventional HBs, since there is a maximum in the plot of frequency with respect to HB energy (Figure 7). Our analysis will prompt further exploration of the consequences and significances of the X−H bond shortening and strengthening in chemistry and biology; for example, better force-fields may be parametrized to reproduce the structure and dynamics of biological molecules where weak X−H···Y interactions are important.

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Supporting Information Available: Complete ref 41; Figures S1−S4 and Tables S1 and S2 mentioned in the text and Cartesian coordinates of all geometries in Table 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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