

Sensitivity of Noncovalent Bonds to Intermolecular Separation:
Hydrogen, Halogen, Chalcogen, and Pnicogen Bonds

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Abstract

It is well known that noncovalent bonds are weakened when stretched from their equilibrium intermolecular separation. Quantum chemical calculations are used to examine and compare the sensitivity to stretches of hydrogen, halogen, chalcogen, and pnicogen bonds. NH_3 was taken as the universal electron donor, paired with HOH and FH in H-bonds, as well as with FPH_2 , FSH, and FCl. Even though the binding energies span a wide range, stretching the intermolecular separation by 1 Å cuts this quantity by the same proportion, roughly in half, for each system. Taking the sum of van der Waals radii as an arbitrary cutoff, the H-bond energy in $\text{FH}\cdots\text{NH}_3$ remains at 5.5 kcal/mol while the binding energy of the other three bond types is only slightly smaller at 4.5-4.7 kcal/mol.

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INTRODUCTION

The hydrogen bond has a long and venerated history^{1,2}. From the standpoint of vibrational spectroscopy, the stretching frequency of the AH bond most commonly shifts to the red upon engaging in a AH...D interaction with an electron donor D. This shift is often accompanied by an intensification and broadening of the band. The NMR spectrum is affected as well, most notably a downfield shift of the signal of the bridging proton. Within a structural context, the AH...D arrangement strives toward linearity, and the separation between the H and D atoms is short, frequently described as smaller than the sum of the van der Waals radii of these two atoms. The A-H bond is elongated to a certain degree by the H-bond, and this bond lengthening correlates with the energetic strength of the interaction. The latter weakening of this bond is commonly attributed to the accumulation of charge in the A-H σ^* antibonding orbital.

While perhaps a somewhat later development than the H-bond, the halogen bond has undergone a great deal of scrutiny from both experimental and theoretical directions³⁻⁹. The replacement of the bridging H atom by a halogen X results in a number of parallels, but there are also significant differences. Like the H-bond, the A-X...D arrangement prefers a linear configuration, and the attraction between the two subunits results in a short contact distance between X and D, again less than the van der Waals radii sum. The tendency toward linearity is attributed to various factors. There is a decreased repulsive wall in this direction³. The A-X bond induces a nonspherical shape of the electrostatic potential around the halogen atom, wherein a ring of negative charge surrounds a crown of positive charge directly opposite the A-X bond, an effect sometimes referred to as a σ -hole¹⁰⁻¹³. The resulting electrostatic attraction to an incoming electron donor, is supplemented by other factors¹⁴⁻¹⁶ such as polarization/ charge-transfer effects^{3,17-20}, as well as dispersion²¹⁻²³. A transfer from the D lone pair to the A-X σ^* antibonding orbital, lengthens the A-X bond²⁴⁻²⁶. As in the case of H-bonds, this lp $\rightarrow\sigma^*$ shift can be overridden by other factors, so not all halogen bonds result in a lengthening of the C-X bond²⁷⁻³⁰. Whether a H or X bond, the presence of electron-withdrawing substituents on the electron-acceptor enhances the binding³¹⁻³³, a direct parallel to what is seen in H-bonds. There is a clear pattern wherein the strength of a halogen bond increases in the order F < Cl < Br < I^{34,35}, and further that a halogen bonded to a sp³-hybridized C forms a weaker bond than does one involving sp, with sp² intermediate³⁶. Halogen bonding energies can reach, and even surpass, the strengths of comparable H-bonds^{37,38}.

Evidence has accumulated that H and X bonds are not alone. Work over the years has implicated chalcogen atoms such as O and S as potential replacements for halogens as bridging atoms³⁹⁻⁴¹ and that nucleophiles tend to approach along extensions of the covalent bond by which the chalcogen is bound^{42,43}. Also like halogen bonds, this bonding has been attributed at least in part to charge transfer into a σ^* antibonding orbital⁴⁴⁻⁴⁷, again supplemented by electrostatic attraction^{48,49}, with an additional attraction supplied by dispersion⁵⁰. There is evidence that like X bonds, chalcogen bonds also strengthen as the bridging atom moves down the pertinent column of the periodic table^{27,51-54}.

Given the ability of atoms of Groups VII and VI to engage in interactions with a nucleophile, it should come as no surprise that the pnictogen (also sometimes referred to as pnictogen or pnigogen) family can do so as well. Most of the evidence for pnictogen bonds arose earliest from crystal structure analyses⁵⁵⁻⁵⁹, but were latter bolstered by computational support^{53,60-63}. There are strong parallels with the halogen and chalcogen bonds, particularly in terms of the preference for a nucleophile to approach the pnictogen atom along an extension of one of its covalent bonds. Recent work from this laboratory⁶⁴⁻⁶⁸ has emphasized the importance of charge transfer from the lone pair of the approaching nucleophile into the PB σ^* antibonding orbital (where B represents the atom bonded to P that is turned away from the nucleophile), and that the strengths of pnictogen bonds are comparable to those of H, X, and chalcogen bonds. Other sets of calculations^{63,69,70} have confirmed these findings, and in particular the ability of electron-withdrawing substituents to enhance the bond. In contrast to a preponderance of findings that confirm the importance of charge transfer in these sorts of noncovalent bonds^{43,69,71-78}, there are others that assert a dominating role of electrostatic phenomena⁷⁹.

In addition to H-bonds, halogen bonds have also been recognized as important structural components in biological and non-biological macromolecules alike^{8-10,80-82}, self assembly^{83,84}, liquid crystal formation^{85,86}, nonlinear optical properties^{87,88}, or for recognition processes^{89,90}. Their potential to be incorporated as design elements in pharmaceuticals^{91,92} or crystal^{93,94} engineering is also well established. Can the same be said of chalcogen and pnictogen bonds? Perhaps the first issue revolves around the recognition of these interactions when they are present. It is thus important to establish the geometric criteria that are associated with such bonds. A second and related question has to do with the strength of each such noncovalent bond. How much energy can they contribute to a given structure? And how does this maximal contribution diminish if these bonds are distorted from their optimal arrangement due to other

structural restraints within the entire crystal? Is there a set of cutoffs that can be recommended for halogen and other noncovalent bonds, in the same manner as has been done previously for H-bonds? The goal of the present communication is to try to provide answers to these questions, via quantum chemical calculations.

METHODS

Small model chemical systems are chosen by which to simulate H, halogen, chalcogen, and pnictogen bonds. In order to maximize the similarities, all binary complexes incorporate a common electron donor molecule, NH_3 in this case. The five complexes considered are illustrated in Fig 1. The Gaussian 09 package⁹⁵ was used to perform all calculations. Geometries were optimized at the ab initio MP2/aug-cc-pVDZ level which has been shown to be of high accuracy, especially for weak intermolecular interactions of the type of interest here^{96,97} where the data are in close accord with CCSD(T) values with larger basis sets^{22,65,98} and in excellent agreement with experimental energetics⁹⁹. Binding energies were computed as the difference in energy between the dimer, and the sum of the optimized energies of the isolated monomers, corrected for basis set superposition error by the counterpoise procedure.

RESULTS

HOH and HF form H-bonds, with total binding energies of 5.81 and 11.64 kcal/mol, respectively, as indicated by the blue numbers below each structure in Fig 1. The second-row atoms P, S, and Cl were chosen to study the pnictogen, chalcogen, and halogen bonds, respectively, as first-row atoms are reluctant participants in such interactions. The other three complexes thus involve electron acceptors H_2FP , HFS , and FCl . The fluorosubstituted molecules were selected as they have been found to form strong noncovalent bonds, more easily visible via crystal structures, and also as they facilitate comparison with the H-bonds, as documented below.

The binding energies of these molecules with NH_3 enlarge from 6.18 kcal/mol for $\text{H}_2\text{FP}\cdots\text{NH}_3$ up to 10.37 kcal/mol for the halogen bond, as indicated in Fig 1. Note that these three values are bracketed by the two H-bonding energies. It might also be noted that the H-bond lengths are quite a bit shorter than the others, due largely to the small size of the bridging H atom. As the strengths of the $\text{A}\cdots\text{N}$ bonds grow, so do the intermolecular distances shrink, from 2.62 Å for $\text{H}_2\text{FP}\cdots\text{NH}_3$ down to 2.27 Å for $\text{FCl}\cdots\text{NH}_3$.

The effects of stretching each sort of bond on the binding energy is illustrated in Fig 2. The horizontal axis refers to the elongation of the intermolecular separation relative to the fully

optimized complex. This separation was increased in uniform increments, and for each new distance, the remainder of the geometry of each complex was fully optimized. For all five systems, one may note a sharp rise in energy as the bond begins to stretch from its equilibrium distance. Each curve begins to flatten as the stretch continues, as it approaches its asymptote of zero interaction energy for very long distances.

Any differences between the various curves are fairly subtle. For example, the $\text{FH}\cdots\text{NH}_3$ H-bond energy remains stronger than any of the other complexes for all stretches. It seems to maintain its separation throughout, suggesting that this H-bond is of longer range than the other noncovalent bonds. This distinction is likely due to the high proportion of electrostatic attraction as a contributing factor to this bond, most notably the dipole-dipole attraction which is distinguished by a perfect alignment of the two molecular dipoles. In contrast, the energy of $\text{FCl}\cdots\text{NH}_3$ appears to rise a bit more sharply than do the other complexes, suggesting that halogen bonds are perhaps a bit more sensitive to stretching than are the other noncovalent bonds considered here.

One might introduce an arbitrary quantitative measure of the steepness of each curve, ρ , the stretch required to reduce the interaction energy to half its maximal value. All five of the systems considered here have values of ρ between 0.9 and 1.1 Å, as reported in Table 1. In other words, stretching the intermolecular separation by some 1 Å cuts the binding energy of each system roughly in half. This required stretch ρ is smallest for $\text{FCl}\cdots\text{NH}_3$, making this the system most sensitive to bond stretch, while $\text{FH}_2\text{P}\cdots\text{NH}_3$ is the least sensitive. But again, there is not a large difference of ρ from one system to the next, all within the range of 0.9-1.1 Å.

What might be considered the cutoff or threshold? That is, after how much of a stretch can one say that a H or other noncovalent bond is “broken”? This is a question that has laid at the heart of many discussions of H-bonds¹⁰⁰. The answer clearly depends upon one’s definition of a bond. A criterion of an attractive force, even if a small one, is probably unsatisfactory as the attraction persists to even very long distances. A threshold of a particular bond energy would lead to the idea that the stronger interactions may be stretched a greater amount. Taking 4 kcal/mol as a sample cutoff, the $\text{FH}\cdots\text{NH}_3$ H-bond may be stretched by 1.3 Å, while the allowed stretch in $\text{FH}_2\text{P}\cdots\text{NH}_3$ is only 0.8 Å. Still another view might envision the stretch required to reduce the binding energy to half its maximal value, in which case all the systems can sustain a stretch of some 1.0 ± 0.1 Å.

It might be instructive to consider how particular choices of a bond distance cutoff correlate with binding energy. In the strongly H-bonded $\text{FH}\cdots\text{NH}_3$ complex, the equilibrium $\text{R}(\text{H}\cdots\text{N})$ distance is 1.69 Å. Adding in the $r(\text{FH})$ bond length of 0.96 Å, the $\text{R}(\text{F}\cdots\text{N})$ distance is 2.65 Å. If one were to assert a $\text{R}(\text{F}\cdots\text{N})$ cutoff of 3.02 Å, the sum of $r_{\text{F}} + r_{\text{N}}$ van der Waals radii¹⁰¹, the stretch of 0.37 Å would leave a residual H-bond energy of 10 kcal/mol. Even taking the longer cutoff of 3.2 Å would correspond to a value of 8.5 kcal/mol. A $\text{R}(\text{H}\cdots\text{N})$ distance of 2.75 Å, corresponding to the sum of $r_{\text{H}} + r_{\text{N}}$ van der Waals radii, and representing a stretch of 1.06 Å, is still associated with a rather strong interaction, of some 5.5 kcal/mol. One of the longer H-bond threshold values proposed in the literature sets the $\text{R}(\text{F}\cdots\text{N})$ distance at 4 Å¹⁰², which would reduce the interaction energy to 1.0 kcal/mol.

Turning next to the pnictogen bond in Fig 1c, a threshold of 3.0 Å for the $\text{R}(\text{P}\cdots\text{N})$ separation corresponds to a stretch of 0.38 Å from its equilibrium value, reducing the bond energy by only 0.6 kcal/mol, from 6.2 down to 5.6. Taking the sum of van der Waals radii¹⁰¹ for this pair of atoms, 3.35 Å, as the threshold leaves a remaining noncovalent bond energy of 4.5 kcal/mol, still quite strong. (The binding energies of the halogen and chalcogen bonds are quite similar, 4.6 and 4.7 kcal/mol, respectively, when the molecules are separated by the sum of van der Waals radii.) Indeed, even a stretch of the intermolecular distance up to 4.0 Å provides a bond energy in excess of 2 kcal/mol. Note that the latter represents a stronger interaction than a H-bond of only 1 kcal/mol with a similar $\text{R}(\text{F}\cdots\text{N})$ distance. One of the longer thresholds in the literature for interactions of this sort is a value of 4.5 Å¹⁰³. At this very long distance, the interaction energy remains at roughly 1.5 kcal/mol.

The slow die-off of these interaction energies suggests that there is perhaps a heavy element of electrostatic attraction. And indeed, previous work⁶⁴⁻⁶⁸ from this laboratory has confirmed that electrostatics, along with induction, is a strong contributor to such noncovalent bonds. The electrostatic and induction energies are similar in magnitude to one another, and both correlate very closely with the total interaction energy in pnictogen, chalcogen, and halogen bonds. In the case of H-bonds, electrostatic attraction plays an even more important role, not only in the ground, but also in excited states¹⁰⁴⁻¹⁰⁶.

Of course, the systems discussed above may indeed be stretched but all are undistorted in an angular sense. In other words, the two molecules are allowed to adopt their most favorable relative orientations. The proton in $\text{FH}\cdots\text{NH}_3$ lies directly along the $\text{F}\cdots\text{N}$ axis, for example, and the F atom in $\text{H}_2\text{FP}\cdots\text{NH}_3$ is turned 167° away from the N atom. But just as crystal forces induce

stretches in these noncovalent bonds, so too are bends quite common. The effects of such misalignments were examined earlier¹⁰⁷ in the same systems illustrated in Fig 1, as well as several others. The calculations showed that pnictogen, as well as chalcogen and halogen bonds, are more sensitive to misorientations than are H-bonds. The dependence of the energy upon the bending angle, $\Delta\theta$, was very close to a parabola, so that it was possible to closely fit the energy to a quadratic function of the form $E = \frac{1}{2} k(\Delta\theta)^2$.

The force constants, k , computed for bending the two H-bonded systems, $\text{FH}\cdots\text{NH}_3$ and $\text{HOH}\cdots\text{NH}_3$, were 15.8 and 10.5 kcal mol⁻¹ rad⁻², respectively. These same quantities were several times greater, between 61 and 70 kcal mol⁻¹ rad⁻², for the pnictogen, chalcogen, and halogen bonded systems incorporating H_2FP , HFS , and FCl . From another perspective, the H-bond energy of $\text{FH}\cdots\text{NH}_3$ can withstand a bend of some 40° and still maintain half its optimal value, as listed as τ in the last column of Table 1; the $\text{HOH}\cdots\text{NH}_3$ system is even more flexible with a value of τ of 45°. These same quantities are greatly reduced in the pnictogen, chalcogen, and halogen-bonded systems, which lose half of their binding energy when bent by only 15-20°. One can conclude that any thresholds imposed on angular features of these types of bonds might be quite different than those applied to H-bonds, and should take into account their lesser flexibility.

CONCLUSIONS

Halogen, chalcogen, and pnictogen bonds all exhibit a reduction in binding energy upon stretching that is fairly similar to H-bonds, even though the systems considered covered a wide range of interaction energy at equilibrium. As a general rule, a stretch of 1 Å from equilibrium reduces the binding energy by a factor of one half for all systems. When the two molecules are separated by the sum of their van der Waals atomic radii, the binding energies of the halogen, chalcogen, and pnictogen bonds are all 4.6 ± 0.1 kcal/mol. In contrast to similarities in terms of stretching, the H-bonds are considerably less sensitive to angular distortions than are the other bond types.

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Table 1. Distortions that result in reduction of maximal binding energy, BE, by a factor of one half

	BE, kcal/mol	ρ^a , Å	τ^b , degs
FH ₂ P	6.18	1.10	15
FHS	7.92	1.05	20
FCI	10.37	0.90	20
FH	11.64	0.95	40
HOH	5.81	1.00	45

^a ρ = stretch required to reduce the interaction energy to half its maximal value.

^b τ = bend required to reduce the interaction energy to half its maximal value.

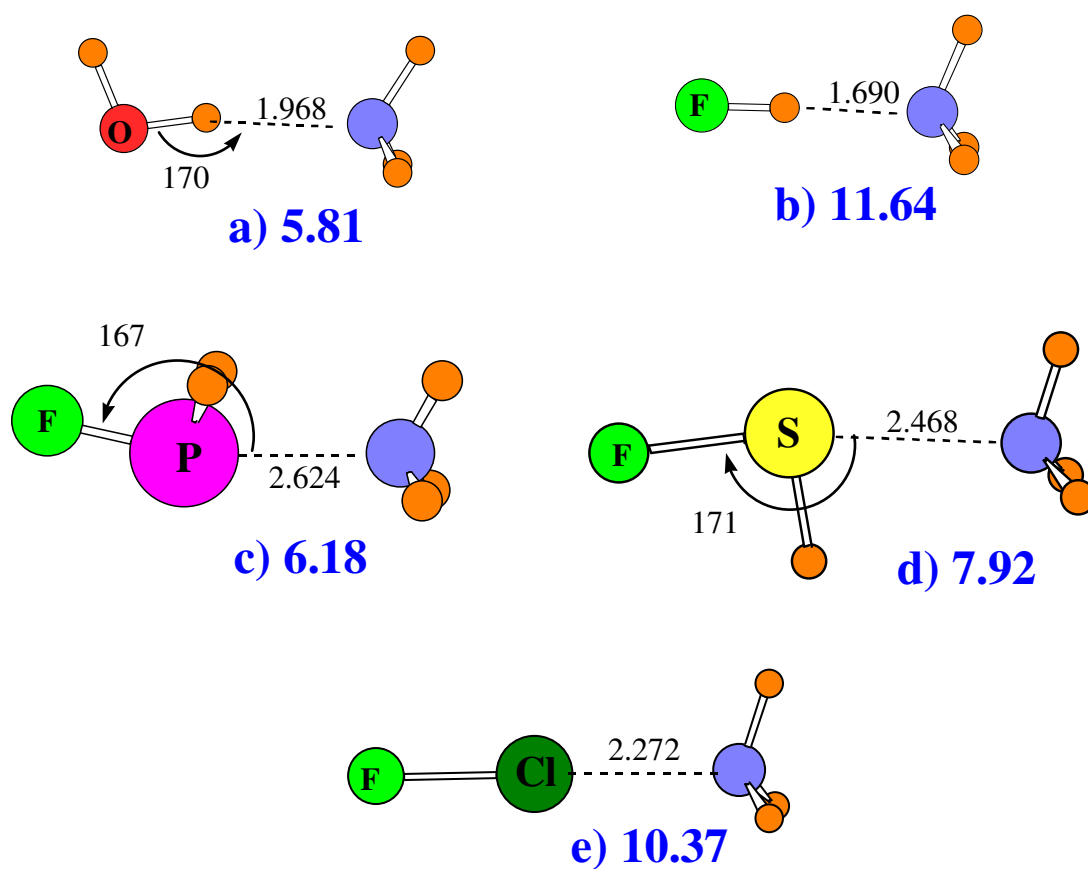


Fig 1. Optimized geometries of various complexes, all involving NH_3 as electron donor. Acceptors are a) HOH , b) FH , c) H_2FP , d) HFS , and e) FCl . Distance in Å and angles in degs. Large blue numbers indicate counterpoise-corrected binding energies in kcal/mol.

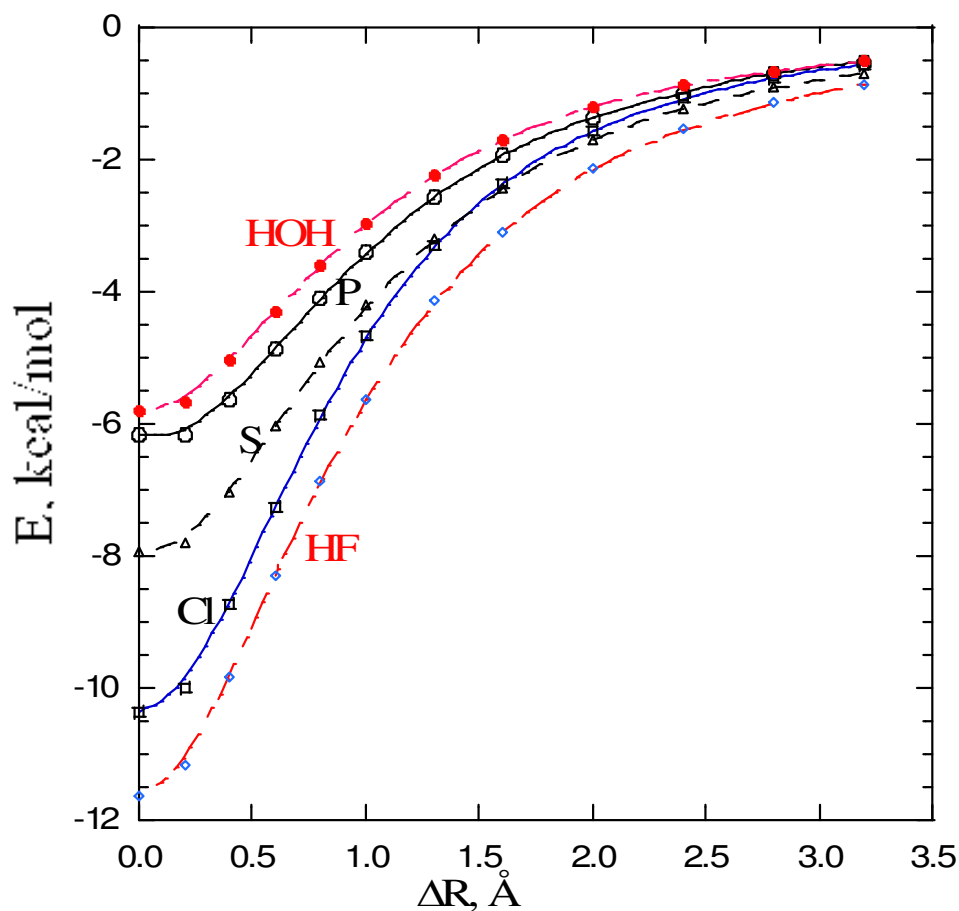


Fig 2. Weakening of binding energy of various complexes, all involving NH_3 as electron donor, as intermolecular distance is stretched. HF and HOH form H-bonds with NH_3 . P label indicates $\text{H}_2\text{FP}\cdots\text{NH}_3$ complex, S refers to $\text{HFS}\cdots\text{NH}_3$, and Cl to $\text{FCl}\cdots\text{NH}_3$. The zero of energy in each case refers to fully separated monomers. Optimized equilibrium distance in each complex (see Fig 2) is taken as $\Delta R=0$.