A Theoretical Investigation of the Effects of Electronegative Substitution on the Strength of C−H···N Hydrogen Bonds

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The effects of electronegative substitution (as modeled using fluoro substituents) on the strength of C−H···N interactions, and how these effects change with hybridization or with acidity of the proton donor, are examined through the use of quantum chemistry. The binding energies (D_o) in complexes between fluorinated derivatives of acetylene, ethylene, ethane and methane (the donors) and ammonia (the acceptor) are considered. We find that fluoro substitution leads to a strengthening of the C−H···N hydrogen bonds in all cases. The effect of replacing a beta hydrogen by fluorine increases as the hybridization of the proton donor goes from sp $<$ sp^2 $<$ sp^3. This trend is the opposite of the propensity of the unsubstituted C−H donors to participate in a hydrogen bond. The magnitude of the effect of an alpha fluorine is significantly greater than that of a beta fluorine for the ethylene−ammonia complex, but the difference is much smaller for the ethane−ammonia complex. In general, the increase in the hydrogen-bond strength upon fluoro substitution of the proton donor qualitatively parallels an increase in the acidity of the donor. We find that the strength of even the most weakly bound systems (i.e., those with sp^2- and sp^3-hybridized proton donors) can be made comparable to, or larger than, that of the acetylene−ammonia complex through electronegative (fluoro) substitution.

Introduction

The classical picture of a hydrogen bond involves the interaction between an electronegative atom that has at least one lone pair of nonbonding electrons and a hydrogen atom that is covalently bound to another (highly) electronegative atom.[1−3] This definition restricts the formation of hydrogen bonds to systems such as the water dimer and $H_3N\cdots HCl$. More modern definitions[3] allow other types of donor and acceptor groups, including weak donors such as C−H, P−H and As−H bonds, or weak acceptors, such as the π-cloud of a benzene ring.

For a long time, it had been disputed whether C−H groups can be proton donors.[1−3] However, this is now well accepted and a wide variety of C−H···X hydrogen bonds have been identified.[1−4] It is recognized that the ability of a C−H group to participate in a hydrogen bond, and the strength of the resulting bond, is related to the hybridization (or acidity) of the proton donor.[1−3] Theoretical studies have shown that the C−H···X (X = NH_3, OH_2, FH, PH_3, SH_2, and ClH) hydrogen-bond strength decreases very rapidly in going from sp- to sp^2- to sp^3-hybridized carbon atoms,[4,5] and that the bonds in the last case are generally very frail.

Weak hydrogen bonds of the type C−H···N and C−H···O are of particular interest. Intramolecular and intermolecular bonds of this kind are believed to play a role in protein folding, the structure of carbohydrates and the binding between some nucleotide (or nucleoside) bases.[6] In fact, early evidence for C−H···O interactions came from studies of carbohydrates where the C−H bonds have a tendency to align toward oxygen.[2,3,6b] For this reason, both experimental and theoretical research on C−H···X hydrogen bonding initially focused on these quite weakly bound C−H···O systems.[3] Subsequent experimental studies have also identified a diverse range of C−H···N hydrogen bonds.[7]

It has been recognized that electronegative substitution strengthens C−H···X hydrogen bonds.[1−4] Recent theoretical studies have examined the effects of electronegative substitutents, such as F, NO_2, NH_2, and OH, on the complexes between methane (or sometimes ethane) and oxygen-containing acceptors, the most popular acceptor being water.[8−13] Theoretical investigations have also examined the complexes formed between a series of chloromethanes and HF or HCl.[14] A very recent study has examined the interactions between fluorinated-methanes and NH_3, CH_3NH_2 and CH_2NH.[15] These studies have revealed that the strength of hydrogen bonds involving weak C−H donors is more sensitive to changes in the donor than the acceptor group.[8,15]

In the present study, we examine in detail how C−H···N hydrogen bonds can be made stronger through electronegative substitution. We use fluoro substituents because these would be expected to lead to the largest effects and hence make identification of trends more straightforward. We focus particularly on how the substituent effect changes with hybridization of the proton donor. Complexes between acetylene, ethylene, ethane, or methane (the proton donor, Scheme 1) and ammonia (the proton acceptor) are initially investigated. Subsequently, each hydrogen atom in the proton donor that is not involved in the C−H···N bond is systematically replaced by fluorine.[16] We would hope that the present study might assist in the understanding of C−H···X hydrogen-bonds in biological systems where electronegative substituents (though less electronegative than fluorine) are generally attached to carbon.

Computational Details

All results reported in the present study were obtained using the GAUSSIAN 98,[17] MOLPRO 98[18a] or MOLPRO 2000[18b] packages.

In previous detailed studies of C−H···X hydrogen-bonded systems, we examined a large variety of methods for determin-

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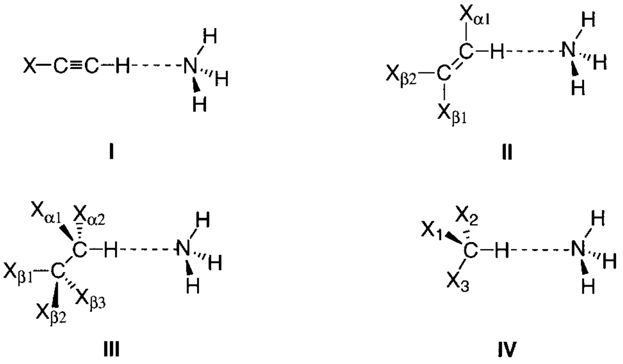
SCHEME 1: Fluorinated Complexes of Acetylene−ammonia (I), Ethylene−ammonia (II), Ethane−ammonia (III) and Methane−ammonia (IV) Considered in the Present Work. Both Staggered (s) and Eclipsed (e) Orientations about the C···N Bond Have Been Examined but, unless Otherwise Noted, Only the Results for the Lower-energy Form Are Reported



ing the geometries of such complexes.[4,19] We found that CCSD(T)/6-311+G(3df,2p) and MP2/6-311+G(3df,2p) both perform well. However, because of computational expense, the former is restricted to small systems and the latter to medium-sized systems. For larger systems, density functional theory (DFT) methods, such as B3-LYP, are more readily applicable. Although some reservations have been expressed,[20] DFT has been successfully used to study hydrogen-bonded complexes.[4,19,21,22]

In our previous work on C−H···X complexes, we found that B3-LYP/6-311+G(3df,2p) generally produces geometries in reasonable agreement with MP2/6-311+G(3df,2p).[4] The r(H···X) and r(C···X) geometrical parameters vary to the greatest extent and tend to be overestimated with B3-LYP, with the largest deviations occurring for the weakest complexes (i.e., $D_e < 1$ kJ mol^{-1}). However, the differences in binding energies obtained from high-level single-point calculations (i.e., CCSD(T)/6-311+G(3df,2p)) on the B3-LYP and MP2 geometries are small.

In the present study, we have chosen to obtain optimized geometries at the B3-LYP/6-311+G(3df,2p) level. We previously found this procedure to perform reasonably well for the complexes between ammonia and acetylene, ethylene, ethane, and methane.[4] For the ethane−ammonia and methane−ammonia complexes, the weakest complexes in the present study, the B3-LYP and MP2 intermolecular r(H···N) and r(C···N) distances differ by less than 10%. On the basis of our previous work, we would expect B3-LYP to perform even better for the remaining systems investigated in the present study.

The importance of high-level calculations when studying the binding energies of weakly bound complexes has been emphasized numerous times.[2] Previously, we have used CCSD(T)/6-311+G(3df,2p) single-point calculations (with all electrons correlated) to evaluate accurate binding energies.[4,19] However, due to the computational resources required for this procedure and the size of the systems investigated in the present work, a computationally less demanding method is necessary. Although B3-LYP/6-311+G(3df,2p) single-point calculations have been recommended for large, hydrogen-bonded systems,[19] we believe that higher-level ab initio calculations would be preferable for our (intermediate-sized) systems (Scheme 1). Therefore, we seek a middle ground between the accuracy obtained from CCSD(T) calculations (with all electrons correlated) and B3-LYP.

To benchmark alternative methods for single-point calculations, we have initially investigated the binding energy of the acetylene−ammonia and methane−ammonia complexes (Table 1). It is clear in the first place that neglecting core electrons in the CCSD(T) calculation (CCSD(T)(fc)) does not significantly affect the binding energy. Although this modification reduces the computation time, such calculations are still too large for some of our systems (e.g., the pentafluoroethane−ammonia complex). A practically more useful alternative to CCSD(T)/6-311+G(3df,2p) is the G3(MP2,CCSD) formalism.[23] This method combines results obtained from CCSD(T)/6-31G(d) and MP2/6-31G(d) calculations with large-basis-set MP2 calculations to effectively approximate a large-basis-set CCSD(T) result. Raw binding energies (D_e) calculated for the acetylene−ammonia and methane−ammonia complexes with G3(MP2,CCSD)[24] are in good agreement with the complete CCSD(T)/6-311+G(3df,2p) calculations (Table 1) and represent a significant improvement over B3-LYP/6-311+G(3df,2p).

TABLE 1: Binding Energies and BSSE Corrections (kJ mol^{-1}) Calculated for the Acetylene-Ammonia and Methane-Ammonia Complexes[a]

	B3-LYP[b]	CCSD(T)[b,c]	CCSD(T)(fc)[b,d]	G3(MP2,CCSD)[e]
		Acetylene−Ammonia complex		
D_e[f]	13.0	16.1	16.1	16.0
BSSE	0.4	2.0	1.7	2.6
D_e[g]	12.6	14.1	14.4	13.4
		Methane−Ammonia complex		
D_e[f]	1.2	3.2	3.3	3.3
BSSE	0.2	0.6	0.6	0.8
D_e[g]	1.1	2.6	2.8	2.5

[a] All single-point calculations performed on B3-LYP/6-311+G(3df,2p) geometries. [b] Calculations performed with the 6-311+G(3df,2p) basis set. [c] All electrons correlated. [d] Only valence electrons correlated. [e] The G3(MP2,CCSD) BSSE is evaluated for each step in the composite procedure. See Reference 27 for more details. [f] Binding energy without BSSE correction. [g] Binding energy including BSSE correction.

All binding energies were corrected by subtracting the basis set superposition error (BSSE) calculated according to the Boys and Bernardi counterpoise method.[25] The general importance of including this correction has been well-documented in the literature.[2,4,19,26] The G3(MP2,CCSD) BSSE (Table 1) is evaluated at each step in the G3(MP2,CCSD) composite procedure, and the results combined according to the same formalism.[27] The final G3(MP2,CCSD) BSSE and BSSE-corrected binding energies (D_e) are in good agreement with those obtained from complete CCSD(T)/6-311+G(3df,2p) calculations (Table 1). Once again, the G3(MP2,CCSD) results are superior to B3-LYP/6-311+G(3df,2p) and are recommended if such calculations are computationally feasible.

Binding energies at 0 K (D_o) were obtained by adding a scaled zero-point vibrational energy (ZPVE) to D_e. Scale factors for the B3-LYP/6-311+G(3df,2p) ZPVE of the monomers and complexes were obtained as described in detail in previous work.[4,19] The reference ZPVEs for ammonia, ethylene, and methane were obtained from spectroscopic constants,[28] whereas those for ethane and the fluoro-substituted hydrocarbons were taken from B3-LYP/cc-pVTZ harmonic frequency calculations using a scale factor of 0.985.[4,28] Unless otherwise noted, all binding energies in the text refer to G3(MP2,CCSD) values, with zero-point vibrational energies obtained as described above.[24]

We examined both staggered and eclipsed conformations about the C···N bond for all complexes (where applicable). Our previous high-level calculations found that such alternative conformations generally have very similar binding energies.[4] Therefore, in the discussion that follows, we generally consider only the lowest-energy conformer for each complex and focus, for the most part, on the $r(\mathrm{H}\cdots\mathrm{N})$ and $r(\mathrm{C}\cdots\mathrm{N})$ distances and the $\angle(\mathrm{C}-\mathrm{H}\cdots\mathrm{N})$ angle. However, full geometrical details are provided in the Supporting Information in the form of GAUSSIAN 98 archive entries (Tables S1 to S3). Total energies, BSSE corrections and ZPVEs are also available in the Supporting Information (Tables S4 to S7).

Results and Discussion

General Comments on the Geometries and Binding Energies of the Complexes. In general, the changes in the geometry of the proton donor upon complex formation are small. The largest changes upon complexation with ammonia involve lengthening of the acetylene C≡C and C−H bonds by up to 0.003 and 0.010 Å, respectively. In general, changes accompanying complexation in the ethylene derivatives are smaller than changes in the acetylene derivatives, and they are generally smaller still for the derivatives of ethane and methane. This trend is observed even for the sequence of perfluorinated derivatives for which the hydrogen-bond strength increases in going from the monofluoroacetylene to the trifluoroethylene to the pentafluoroethane complex.

The hydrogen-bond angles ($\angle(\mathrm{C}-\mathrm{H}\cdots\mathrm{N})$) in the complexes of ammonia with substitued ethanes and ethylenes are close to linear, with the deviation in most complexes being less than 5°. The hydrogen-bond angles in the α-fluoroethylene−ammonia complex, as well as the difluoromethane−ammonia complex, deviate more significantly from linearity (each by 9.1°). We attribute the larger deviations of the C−H···N hydrogen bonds from linearity to weak H···F−N interactions. These are discussed in more detail below.

The C−H bonds involved in the C−H···N interaction generally either remain unchanged or lengthen slightly (by up to 0.01 Å) upon complexation. However, the C−H bond *contracts* in complexes between ammonia and ethane (by 0.0006 Å), α-fluoroethane (by 0.0012 Å), α,α-difluoroethane (by 0.0004 Å), α,β-difluoroethane with $X_{\alpha 1}$ and $X_{\beta 1}$ = F (by 0.0004 Å), fluoromethane (by 0.0005 Å) and difluoromethane (by 0.0003 Å). Despite the fact that these are small changes, *contraction* of the C−H bond in the proton donor upon complexation is interesting since hydrogen bonding is normally associated with elongation of this bond. Furthermore, we note that C−H bond contraction upon binding is accompanied by a small (less than 2−19 cm^{-1}) *increase* in the C−H stretching frequency for these complexes. This is contrary to the decrease in the C−H stretching frequency typically observed for hydrogen-bonded systems. For example, a decrease in the C−H stretching frequency of 107 cm^{-1} is calculated at the same level of theory for the acetylene−ammonia complex. Similar contractions of bonds and increases in the C−H stretching frequencies have been reported previously for systems involving C−H···O and C−H···π interactions,[4,29] and the interactions were termed anti-hydrogen bonds.[29] However, the interactions between fluorinated methanes and either water[8] or ammonia[15] were found to replicate many of the properties of more conventional hydrogen bonds, despite C−H bond contraction, and the term blue-shifting hydrogen bonds[30] may be more appropriate. More recent calculations of NMR chemical shieldings show some differences between the behavior of these weakly bound systems and those containing conventional hydrogen bonding.[12]

It is known that equilibrium structures of hydrogen-bonded complexes reside in wells much shallower than those of standard molecules.[2] Indeed, the B3-LYP/6-311+G(3df,2p) and G3(MP2,CCSD) potential-energy surfaces in the vicinity of the minimum energy complexes examined in the present study are extremely flat. This is most evident for very weakly bound systems where we find that the binding energy is very insensitive to the hydrogen-bond length and to deviations of the hydrogen-bond angle from linearity. The insensitivity of the binding energy to modest changes in the hydrogen-bond length and angle has been reported in previous theoretical studies of complexes between fluoro-substituted methanes and water[8,10] or ammonia.[15] In more strongly bound complexes, such as HCCH···NH$_3$, the B3-LYP, and G3(MP2,CCSD) surfaces have greater curvature. The most important conclusion from our search of the potential energy surfaces for these systems is that the binding energies reported in our study will be only slightly, if at all, affected by moderate changes in the geometry of the complex.

TABLE 2: Selected Structural Parameters (Å)[a] and Binding Energies (kJ mol^{-1})[b] for Acetylene and Fluoroacetylene Monomers and Their Complexes with Ammonia (See I, Scheme 1)

X	symmetry	$r(\mathrm{C}\equiv\mathrm{C})$	$r(\mathrm{C}-\mathrm{H})$	$r(\mathrm{H}\cdots\mathrm{N})$	$r(\mathrm{C}\cdots\mathrm{N})$	D_o[b]	ΔD_o[c]
monomer							
H	$D_{\infty h}$	1.196	1.062				
F	$C_{\infty v}$	1.191	1.061				
dimer							
H	C_{3v}	1.198	1.072	2.308	3.380	8.6	0.0
F	C_{3v}	1.193	1.071	2.284	3.355	9.8	1.2

[a] Geometries calculated at the B3-LYP/6-311+G(3df,2p) level. [b] Calculated with a modified G3(MP2,CCSD) technique which uses B3-LYP/6-311+G(3df,2p) geometries and scaled zero-point vibrational energies. [c] ΔD_o is the binding energy calculated relative to that of the acetylene−ammonia dimer.

We note that all systems in our study exhibit a stabilizing effect upon complexation (i.e., $D_o > 0$). BSSE corrections have previously been found to potentially contribute up to 40% of the raw complexation energy in weakly bound systems.[4] We also find a large contribution of the BSSE to the binding energy for our present systems. Additionally, we find that the magnitude of the BSSE increases with the number of fluoro substituents (see Supporting Information).

The remainder of this paper focuses primarily on the binding energies for complexes between fluoro-substituted C−H donors and ammonia. Our main goal is to examine the effects of electronegative substitution on the binding energy and to try to understand how these effects change with the substitution site and the hybridization or acidity of the C−H group. Our discussion will begin with the most strongly bound (C(sp)-H···N) complexes.

Acetylene and Fluoroacetylene as the Proton Donor. Several experimental studies have investigated how the proton-donating ability of an sp-hybridized C−H group is affected by electronegative substitution.[31] In the present study, the G3(MP2,CCSD) binding energy of the acetylene−ammonia complex was calculated to be 8.6 kJ mol^{-1} (Table 2), in good agreement with the best estimate from our previous high-level theoretical studies (9.3 kJ mol^{-1})[4,19] and the experimental upper bound (11.7 kJ mol^{-1}).[32] The fluoro substituent reduces the $r(\mathrm{H}\cdots\mathrm{N})$ and $r(\mathrm{C}\cdots\mathrm{N})$ distances by 0.024 and 0.025 Å, respectively, from the values in the acetylene−ammonia complex. Accordingly, the binding energy is increased by 1.2 kJ mol^{-1}. Thus, fluoro substitution in the beta position of an sp-hybridized C−H proton donor has a small strengthening effect on the C−H···N hydrogen bond.

Ethylene and Its Fluoro-Substituted Derivatives as the Proton Donor. The G3(MP2,CCSD) binding energy of the ethylene−ammonia complex is calculated to be 1.7 kJ mol^{-1} (Table 3), which reflects the much smaller tendency of an sp^2-

TABLE 3: Selected Structural Parameters (Å)[a] and Binding Energies (kJ mol^{-1})[b] for Ethylene and Fluorinated Ethylene Monomers and Their Complexes with Ammonia[c] (See II, Scheme 1)

$X_{\alpha1}$	$X_{\beta1}$	$X_{\beta2}$	symmetry	r(C−H)	r(H···N)	r(C···N)	∠(C−H···N)	D_o[b]	ΔD_o[d]
					monomer				
H	H	H	D_{2h}	1.083					
F	H	H	C_s	1.081					
H	F	H	C_s	1.080					
H	H	F	C_s	1.079					
H	F	F	C_{2v}	1.077					
F	F	H	C_{2h}	1.080					
F	H	F	C_{2v}	1.079					
F	F	F	C_s	1.077					
					dimer				
H	H	H	C_s (s)	1.084	2.740	3.824	179.2	1.7	0.0
F	H	H	C_1 (s)	1.083	2.493	3.567	170.9	6.3	4.6
H	F	H	C_1 (e)	1.083	2.592	3.673	176.1	4.2	2.5
H	H	F	C_1 (s)	1.082	2.611	3.692	178.8	4.4	2.7
H	F	F	C_1 (e)	1.081	2.516	3.597	178.6	6.1	4.4
F	F	H	C_1 (e)	1.084	2.409	3.493	179.2	8.1	6.4
F	H	F	C_1 (s)	1.083	2.435	3.517	177.5	8.6	6.9
F	F	F	C_1 (s)	1.082	2.371	3.453	177.5	10.1	8.4

[a] Geometries calculated at the B3-LYP/6-311+G(3df,2p) level. [b] Calculated with a modified G3(MP2,CCSD) technique which uses B3-LYP/6-311+G(3df,2p) geometries and scaled zero-point vibrational energies. [c] Eclipsed (e) and staggered (s) configurations about the C···N bond. [d] ΔD_o is the binding energy calculated relative to that of the unsubstituted ethylene−ammonia dimer.

hybridized C−H group to participate in a hydrogen bond compared with an sp-hybridized C−H group, and compares reasonably with our previous high-level theoretical estimate of 2.1 kJ mol^{-1}.[4] Substitution of hydrogen by fluorine at the alpha position in ethylene ($X_{\alpha1}$, Scheme 1) leads to a decrease in the hydrogen-bond length by 0.247 Å and the r(C···N) distance by 0.257 Å. The corresponding increase in D_o is 4.6 kJ mol^{-1}. Replacing the hydrogen in either beta position ($X_{\beta1}$ or $X_{\beta2}$) results in a smaller increase in the binding energy of only 2.5−2.7 kJ mol^{-1}.

Difluoro substitution leads to a further increase in the binding energy and a further shortening of the r(H···N) and r(C···N) distances in the corresponding complex with ammonia. If only the beta positions are occupied by fluorine, then the binding energy increases by 4.4 kJ mol^{-1} with respect to ethylene as the proton donor. Alternatively, if fluorine resides in the alpha position and either beta position, then D_o increases by 6.4−6.9 kJ mol^{-1}. Trifluoro substitution in ethylene leads to an increase in the binding energy of 8.4 kJ mol^{-1}. Correspondingly, the intermolecular r(H···N) and r(C···N) distances decrease by 0.369 and 0.371 Å, respectively, relative to the unsubstituted complex.

Our results indicate that the effect of a fluorine atom in an alpha position on the binding energy is nearly two times greater than the effect of a fluorine atom in a beta position for an sp^2-hybridized C−H donor. Furthermore, the effects of α,β-difluorosubstitution are slightly less than the sum of the individual effects of monosubstitution. We note, however, that the hydrogen-bond angle in the α-fluoroethylene−ammonia complex deviates significantly from linearity relative to the angle in other complexes due to additional weak F···H−N interactions. If the hydrogen-bond angle in the α-fluoroethylene−ammonia complex is constrained to be linear, then the binding energy is decreased to 5.7 kJ mol^{-1} and the corresponding increase in D_o relative to the ethylene−ammonia complex is 4.0 kJ mol^{-1}. Thus, if the benefits of the additional F···H−N interactions are removed, then the effect of a fluorine atom in an alpha position is 1.5 times greater than the effect of a fluorine in a beta position and the effects of α,β-difluorosubstitution are now nearly additive.

The effects of substitution at the beta position on the hydrogen-bond strength involving an sp^2-hybridized C−H donor are approximately double those for an sp-hybridized C−H donor. Although the effect of trifluoro substitution (8.4 kJ mol^{-1}) is slightly less than the sum of the individual effects of monosubstitution ($X_{\alpha1} = 4.6$; $X_{\beta1} = 2.5$; $X_{\beta2} = 2.7$ kJ mol^{-1}; total = 9.8 kJ mol^{-1}), the binding energy of the trifluoroethylene−ammonia complex is 1.5 kJ mol^{-1} greater than that calculated for the acetylene−ammonia complex. A bond strength comparable to that of the acetylene−ammonia complex can be achieved through α,β-disubstitution by fluorine, with substitution at the beta position anti to the hydrogen bond ($X_{\beta2}$). Thus, although the C−H···N hydrogen-bond strength decreases very rapidly in going from sp- to sp^2-hybridized carbon atoms, appropriate electronegative substitution in sp^2-hybridized donors can result in hydrogen bonds as strong as, or stronger than, those involving sp-hybridized donors.

Ethane and Its Fluoro-Substituted Derivatives as the Proton Donor. The G3(MP2,CCSD) binding energy for the ethane−ammonia complex is only 0.5 kJ mol^{-1}, reflecting the weak propensity of an sp^3-hybridized C−H bond to partake in a hydrogen bond, although a positive attraction does exist. We recently calculated a binding energy of 1.0 kJ mol^{-1} at the CCSD(T)/6-311+G(3df,2p) level.[4] Mono-α-fluoro substitution increases the binding energy of the ethane−ammonia complex by 3.6 kJ mol^{-1}. We note that there is a slight variation in the calculated binding energy depending on whether the $X_{\beta1}$ or $X_{\beta2}$ (or equivalently $X_{\beta3}$) position (Scheme 1) is occupied by fluorine in the ethane−ammonia complex. Substitution at the position anti to the hydrogen bond ($X_{\beta1}$) leads to a stronger hydrogen bond ($D_o = 3.6$ kJ mol^{-1}) than replacement at $X_{\beta2}$ ($D_o = 3.3$ kJ mol^{-1}). This trend may be attributed to the weakened (longer) C−H bond located anti with respect to fluorine (i.e., $X_{\beta1}$) in the monomer of the proton donor.

Interestingly, mono-β-fluoro substitution in ethane results in only a slightly smaller increase in D_o (2.8−3.1 kJ mol^{-1}) than mono-α-fluoro substitution (3.6 kJ mol^{-1}). We noted a larger difference in the corresponding effects for the ethylene−ammonia complex, though part of this was attributed to F···H−N bonding. The magnitude of the increase in D_o with α-fluoro substitution in ethane is slightly less than the increase for ethylene, while the effect of β-fluoro substitution is slightly greater.

The effect of each additional electronegative substituent at a particular position is smaller than the effect of the first substituent at the same position. Thus, the replacement of one alpha hydrogen with fluorine increases the binding energy by 3.6 kJ mol^{-1} while further substitution at the second alpha position leads to a slightly smaller increase (3.1 kJ mol^{-1}). Similarly, replacement of hydrogen at $X_{\beta2}$ increases D_o by 2.8 kJ mol^{-1}, while further substitutions at $X_{\beta3}$ and $X_{\beta1}$ increase D_o by an additional 1.8 kJ mol^{-1} for each substitution. However, if fluorine occupies both alpha and beta positions, then the increase in D_o depends on the substitution pattern. For example, the increase in D_o is slightly greater than the sum of the increases for the individual alpha and beta substitutions for α,β-difluoro (by 0.3 kJ mol^{-1}) and pentafluoro (by 0.2 kJ mol^{-1}) substitutions, but the effect on D_o is less than the sum of the individual effects for α,α,β-trifluoro (by 0.6 kJ mol^{-1}) and α,α,β,β-tetrafluoro (by 0.7 kJ mol^{-1}) substitutions.

The binding energies calculated for the ethane−ammonia complex with various degrees of fluoro substitution at the donor provide valuable insight into the design of stronger C−H···N hydrogen bonds involving sp^3 carbon atoms. The hydrogen-bond strength for the ethane−ammonia complex (0.5 kJ mol^{-1}) can be increased beyond the strength of the ethylene−ammonia complex (1.7 kJ mol^{-1}) through mono-fluoro substitution, even at the beta position ($D_o \approx 3-4$ kJ mol^{-1}). α,α-difluoro substitution in the ethane−ammonia complex results in a bond strength (7.2 kJ mol^{-1}) almost as large as that of the acetylene−ammonia complex (8.6 kJ mol^{-1}), while α,α,*β*-trifluoro substitution leads to a binding energy (9.4 kJ mol^{-1}) slightly larger than that of the acetylene−ammonia complex. Thus, C(sp^3)-H···N hydrogen-bond strengths equivalent to those involving sp- or sp^2-hybridized carbon atoms can be achieved through suitable electronegative substitution at the proton donor.

Methane and Its Fluoro-Substituted Derivatives as the Proton Donor. The C−H···N hydrogen bond with methane acting as the proton donor is perhaps the best studied of weak C−H···X bonds.[2,3] In fact, some of the first evidence for the participation of C−H groups in hydrogen bonds came from studies of the complexes between substituted methanes and ammonia.[2,8] An early theoretical study predicted that CF_3H could be a proton donor to NH_3.[33] This was later verified by an experimental study,[34] which speculated that the strength of this hydrogen bond is nearly equal to that in the acetylene−ammonia complex. Since these investigations, many theoretical studies have appeared which examined the strength of the bond formed between methanes, substituted usually by either Cl[35] or F,[8−10,12] and oxygen-containing acceptors (such as water, methanol, or formaldehyde). The binding energies in complexes between chloromethanes and HF or HCl have also been investigated.[14] More recently, the ability of ammonia to act as a proton acceptor in a C−H···N interaction[15,36] and the effects of changes to the acceptor[15] and electronegative substitution in the donor[15] on these interactions have been studied. To complement the examination of our other systems, we have also investigated the effects of systematic replacement of hydrogen with fluorine in the methane−ammonia complex.

Interestingly, the only minimum located on the potential energy surface for the fluoromethane−ammonia complex with C−H···N interactions also possesses F···H−N interactions, despite the fact that fluorine in organic molecules is only a weak hydrogen-bond acceptor[37] and, therefore, has a significantly bent C−H···N angle (121.7°). To focus on structures displaying predominantly C−H···N interactions, we constrain the hydrogen-bond angle in the fluoromethane−ammonia complex to be 180°.[38] This restriction has been previously employed in computational studies of complexes between substituted methanes and water[8] or ammonia.[15] We find that the changes in the binding energy of the difluoromethane−ammonia complex, as well as D_o for the substituted-ethylene−ammonia and substituted-ethane−ammonia complexes, are negligible when the constraint of a linear hydrogen bond is imposed on these systems. More specifically, the binding energy for the difluoromethane−ammonia complex changes by only 0.1 kJ mol^{-1} when the C−H···N hydrogen bond is constrained to be linear. For the series of complexes between ammonia and substituted ethanes and ethylenes, we find a mean absolute deviation of 0.2 kJ mol^{-1} between the total binding energy (D_o) of the true minima that we discuss in the present study (Tables 3 and 4) and the D_o obtained from geometries with constrained linear hydrogen bonds. We note that examination of the constrained linear C−H···N form of the fluoromethane−ammonia complex extends the applicability of our study to the understanding of C−H···N hydrogen bonds in cases where F···H−N interactions are not possible (for example, when trimethylamine is the proton acceptor).

TABLE 4: Selected Structural Parameters (Å)[a] and Binding Energies (kJ mol^{-1})[b] for Ethane and Fluorinated Ethane and Their Complexes with Ammonia[c] (See III, Scheme 1)

$X_{\alpha1}$	$X_{\alpha2}$	$X_{\beta1}$	$X_{\beta2}$	$X_{\beta3}$	symmetry	*r* (C−H)	*r* (H···N)	*r* (C···N)	∠ (C−H···N)	D_o[b]	ΔD_o[d]
						monomer					
H	H	H	H	H	D_{3d}	1.091					
F	H	H	H	H	C_s	1.091					
H	H	H	F	H	C_s	1.090					
H	H	F	H	H	C_s	1.092					
H	H	H	F	F	C_s	1.089					
F	H	F	H	H	C_1	1.093					
F	F	H	H	H	C_s	1.092					
H	H	F	F	F	C_{3v}	1.087					
F	F	H	F	H	C_1	1.091					
F	F	H	F	F	C_{2h}	1.091					
F	F	F	F	F	C_s	1.091					
						dimer					
H	H	H	H	H	C_s (s)	1.091	3.076	4.166	179.0	0.5	0.0
F	H	H	H	H	C_1 (e)	1.090	2.684	3.773	177.0	4.1	3.6
H	H	H	F	H	C_1 (s)	1.090	2.773	3.860	175.0	3.3	2.8
H	H	F	H	H	C_1 (e)	1.092	2.796	3.887	177.2	3.6	3.1
H	H	H	F	F	C_1 (s)	1.090	2.613	3.702	175.8	5.1	4.6
F	H	F	H	H	C_1 (s)	1.093	2.574	3.666	178.3	7.5	7.0
F	F	H	H	H	C_1 (e)	1.091	2.499	3.589	178.3	7.2	6.7
H	H	F	F	F	C_1 (e)	1.090	2.542	3.632	179.4	6.9	6.4
F	F	H	F	H	C_1 (e)	1.092	2.414	3.505	178.9	9.4	8.9
F	F	H	F	F	C_1 (e)	1.093	2.343	3.436	179.0	11.1	10.6
F	F	F	F	F	C_s (e)	1.094	2.308	3.401	177.0	13.9	13.4

[a] Geometries calculated at the B3-LYP/6-311+G(3df,2p) level. [b] Calculated with a modified G3(MP2,CCSD) technique which uses B3-LYP/6-311+G(3df,2p) geometries and scaled zero-point vibrational energies. [c] Eclipsed (e) and staggered (s) configurations about the C···N bond. [d] ΔD_o is the binding energy calculated relative to that of the unsubstituted ethane−ammonia dimer.

Upon systematic replacement of hydrogen by fluorine in methane, the *r*(H···N) and *r*(C···N) distances shorten. The C−H bond in the proton donor involved in the C−H···N interaction contracts upon complex formation between ammonia and monofluoromethane or difluoromethane but lengthens in the trifluoromethane−ammonia complex. These results suggest that trifluoro substitution leads to C−H···X interactions that are more similar to conventional hydrogen bonds, presumably because of the associated increase in the binding energy.

The binding energy D_o, which includes both BSSE and ZPVE corrections, is calculated to be 0.5 kJ mol^{-1} for the methane−ammonia complex, the same as that calculated for the ethane−ammonia complex. The binding energy increases by approximately 3.5 kJ mol^{-1} for both the first and second substitutions.[39] This contrasts with the situation for the corresponding α,α-disubstituted ethane−ammonia complex, where the effect decreases with increasing substitution. Replacing the final hydrogen by fluorine increases D_o to a greater extent (4.8 kJ mol^{-1}) than the first two substitutions, which leads to a hydrogen-bond strength of 12.2 kJ mol^{-1}. Thus, the net increase in D_o for the trifluoromethane−ammonia complex relative to the methane−ammonia complex (11.7 kJ mol^{-1}) is slightly greater than the sum of the individual effects of three fluorines (i.e., roughly 10.5 kJ mol^{-1}).

The D_o values calculated for the complexes between ammonia and methane or ethane are similar. The binding energies of these complexes reflect the very weak tendency for sp^3-hybridized C−H groups to participate in hydrogen bonding, as well as the negligible effects of a relatively inert substituent (CH_3) on D_o, as noted in a previous study.[9] The very small influence of the methyl group is further supported by the similar changes in the

TABLE 5: Selected Structural Parameters (Å)[a] and Binding Energies (kJ mol^{-1})[b] for Methane and Fluorinated Methane Monomers and Their Complexes with Ammonia[c] (See IV, Scheme 1)

			symmetry	r(C−H)	r(H···N)	r(C···N)	∠(C−H···N)	D_o[b]	ΔD_o[d]
					monomer				
H	H	H	T_d	1.088					
F	H	H	C_{3v}	1.089					
F	F	H	C_{2v}	1.090					
F	F	F	C_{3v}	1.089					
					dimer				
H	H	H	$C_{3v\,(s)}$	1.089	2.970	4.059	180.0	0.5	0.0
F	H	H	C_1 (e)	1.089	2.656	3.745	180.0[c]	3.9	3.4
F	F	H	C_1 (e)	1.090	2.472	3.562	170.9	7.5	7.0
F	F	F	C_{3v} (e)	1.091	2.326	3.417	180.0	12.2	11.7

[a] Geometries calculated at the B3-LYP/6-311+G(3df,2p) level. [b] Calculated with a modified G3(MP2,CCSD) technique which uses B3-LYP/6-311+G(3df,2p) geometries and scaled zero-point vibrational energies. [c] The geometries of the complex between ammonia and fluoromethane was obtained with the restriction of a linear hydrogen bond. [d] The binding energy calculated relative to that of the unsubstituted methane−ammonia dimer.

hydrogen-bond length and binding energy upon fluoro-substitution of methane and ethane in the complexes with ammonia. It is interesting that the binding energy in the trifluoromethane−ammonia complex is 1.6 kJ mol^{-1} smaller than the binding energy in the pentafluoroethane−ammonia complex, indicating that the CF_3 substituent has a larger effect than the (third) fluoro substituent. The larger effect on D_o of a CF_3 substituent compared with a fluoro substituent can also be seen by comparing the binding energies of the complexes between ammonia and monofluoromethane (3.9 kJ mol^{-1}) and the β,β,β-trifluoro-substituted ethane (6.9 kJ mol^{-1}).

There has been speculation that the interactions between ammonia and CF_3H or HC≡CH are similar.[34,40] Our calculations predict that the strength of the $CF_3H\cdots NH_3$ hydrogen bond (12.2 kJ mol^{-1}) actually exceeds the strength of the acetylene−ammonia hydrogen bond (8.6 kJ mol^{-1}). Even the difluoromethane−ammonia complex has a binding energy (7.4 kJ mol^{-1}) close to that of the acetylene−ammonia complex.

The Effect of Electronegative Substitution on the Acidity of the Proton Donor. It has been noted previously that both the hydrogen-bond strength and the acidity of a C−H proton donor increase as the hybridization of the donor goes from $sp^3 < sp^2 < sp$.[1−5] It is therefore of interest to investigate first how electronegative substitution affects the acidity of the proton donor, and second how the increase in the hydrogen-bond strength upon electronegative substitution relates, if at all, to changes in the acidity of the proton donor.

Gas-phase acidities at 0 and 298 K (Table 6) were calculated at the G3(MP2,CCSD)[24] level as the enthalpy change in the reaction:

$$HA \rightarrow H^+ + A^-$$

A decrease in the enthalpy change corresponds to an increase in the HA acidity. Experimentally determined acidities obtained from a variety of methods, and under different conditions, are also included in Table 6.[41] The reliability of some of the experimental numbers is uncertain and is reflected in the large quoted error bars. In most cases, there is reasonable agreement between our calculated values and the experimental data. However, our results suggest that reexamination of the experimental acidities for trifluoroethylene and difluoromethane would be in order. Our calculated acidities are in close agreement with previously reported results obtained for some of the present systems from G2[42] and G3[43] calculations. For simplicity, we will restrict our subsequent discussion to our calculated 0 K gas-phase acidities.

We calculate that a β-fluoro substituent increases the gas-phase acidity of acetylene by 19.9 kJ mol^{-1}. β-fluoro subsitution has a larger effect on the acidity of ethylene, where the acidity increases by 60.6 or 66.3 kJ mol^{-1} depending on the substitution site. The effect of α-substitution in ethylene is slightly greater than β-substitution (by 5.7−11.4 kJ mol^{-1}). Successive fluoro substitution in ethylene leads to decreasing effects. For example, one α-fluoro substituent increases the acidity of ethylene by 72 kJ mol^{-1}, an additional β-fluoro substituent leads to a further increase of roughly 36 kJ mol^{-1}, whereas a second β-fluoro substituent leads to an increase in the acidity of only 24 kJ mol^{-1}.

The calculation of the acidities of fluorinated ethanes is complicated by the fact that several of the substituted anions are unstable. In particular, substituted ethyl anions with one or two beta fluorines in combination with one or less alpha fluorines dissociate into a fluoride anion and the relevant (substituted) ethylene. Anions containing three beta fluorines, two alpha fluorines or only alpha fluorines are stable with respect to the loss of a fluoride anion. This dissociation has been previously noted in the literature.[42,44] To handle this difficulty, for the mono-β-fluoroethyl, β,β-difluoroethyl and α,β-difluoroethyl anions, we have estimated the energy of the anion as the sum of the energies of the fully separated products, i.e., F^- plus the appropriate substituted ethylene. However, it is not clear whether this leads to meaningful estimates of the acidities.

Mono-α-fluoro substitution increases the acidity of ethane (35.5 kJ mol^{-1}) much less than ethylene (72.0 kJ mol^{-1}). A second α-substitutent raises the acidity of ethane by a greater amount (53.6 kJ mol^{-1}) than the first substituent. In contrast to the effects calculated for ethylene, α-fluoro substitution in ethane results in a much smaller increase in the acidity than β-fluoro substitution. The calculated effect of electronegative substitution at the beta position is erratic, which is perhaps associated with the noted difficulties (because of F^- loss) in calculating the acidities for some of these species. Among the well-behaved systems, we note that the acidity of ethane is increased by 191.7 kJ mol^{-1} through pentafluoro substitution, which is smaller than the sum of the effects of β,β,β-trifluoro and α,α-difluoro substitution (225.8 kJ mol^{-1}).

The acidity of methane is calculated to increase by 28.0 kJ mol^{-1} upon monofluoro subsitution. We calculate that a second fluorine increases the acidity by a further 47.8 kJ mol^{-1} and a third fluorine leads to an increase by an additional 80.8 kJ mol^{-1}. Previous theoretical studies,[43,45,46] have also reported that the acidity of methane increases to a greater degree with successive electronegative substitution.

The Correlation Between Hydrogen-Bond Strength and the Acidity of the Proton Donor. In the previous section, we discussed changes in the acidity of acetylene, ethylene, ethane, and methane that accompany successive fluoro substitution. In the present section, we consider how these changes relate to changes in the hydrogen-bond strength in the corresponding complexes with ammonia.

In general, we find that the greater the increase in the acidity of the proton donor upon electronegative substitution, the greater the increase in the hydrogen-bond strength in the complex with ammonia. Therefore, the majority of the changes in the hydrogen-bond strength of the ammonia complexes upon successive substitution in the proton donors can be explained by alterations to the acidity of the donor. For example,

TABLE 6: Calculated Gas-Phase Acidities (kJ mol^{-1})^{a}for Acetylene, Ethylene, Ethane, Methane and Their Fluorinated Counterparts (see Scheme 1)^{a}

					acidity (0 K)	ΔAcidity^{b} (0 K)	acidity (298 K)	experiment^{c}
					Acetylene			
X								
H					1574.9	0.0	1581.0	1581.6 ± 2.9, 1589.1 ± 2.1 1576 ± 8.8
F					1555.0	19.9	1561.1	< 1540 ± 79
					Ethylene			
$X_{\alpha1}$	$X_{\beta1}$	$X_{\beta2}$						
H	H	H			1703.0	0.0	1709.1	1712.9 ± 2.5, 1703 ± 13 1705 ± 8.4, 1699 ± 8.4
F	H	H			1631.0	72.0	1637.4	1618 ± 17
H	F	H			1642.4	60.6	1648.6	
H	H	F			1636.7	66.3	1643.3	
F	F	H			1595.4	107.6	1601.8	
F	H	F			1595.2	107.8	1601.7	
H	F	F			1611.9	91.0	1618.2	
F	F	F			1571.2	131.7	1577.7	1630 ± 24
					Ethane			
$X_{\alpha1}$	$X_{\alpha2}$	$X_{\beta1}$	$X_{\beta2}$	$X_{\beta3}$				
H	H	H	H	H	1750.3	0.0	1756.7	1758 ± 8.4, 1761 ± 8.4
F	H	H	H	H	1714.8	35.5	1721.2	
H	H	H	F	H	1598.5^{d}	151.8^{d}	1602.5	
H	H	F	H	H	1598.5^{d}	151.8^{d}	1602.5	
H	H	H	F	F	1636.0^{e}	114.3^{e}	1639.6	
F	H	F	H	H	1581.6^{e}	168.7^{e}	1585.2	
F	F	H	H	H	1661.2	89.1	1667.8	
H	H	F	F	F	1613.6	136.7	1620.6	
F	F	H	F	H	1621.0	129.3	1627.6	
F	F	H	F	F	1586.0	164.2	1580.1	
F	F	F	F	F	1558.6	191.7	1565.1	1567 ± 14
					Methane			
X_1	X_2	X_3						
H	H	H			1742.1	0.0	1748.4	1743.5 ± 3.3, 1749 ± 15
F	H	H			1714.0	28.0	1720.4	1711 ± 17
F	F	H			1666.2	75.8	1672.9	1628 ± 15
F	F	F			1585.5	156.6	1591.7	1577 ± 8.8, 1573 ± 19

[a] A modified G3(MP2,CCSD) technique was used which implements B3-LYP/6-311+G(3df,2p) geometries and scaled (0.9806) zero-point vibrational energy. [b] ΔAcidity is the relative acidity calculated with respect to the unsubstituted monomer. [c] ref 41. [d] The energy of the anion was approximated as the sum of the energy of the F^- anion plus ethylene. [e] The energy of the anion was approximated as the sum of the energy of the F^- anion plus fluoroethylene.

β-monofluoro substitution increases the hydrogen-bond strength relative to that of the complex between the unsubstituted donor and ammonia in the order acetylene (1.2 kJ mol^{-1}) < ethylene (2.5−2.7 kJ mol^{-1}) < ethane (2.8−3.1 kJ mol^{-1}), while the acidity of the donor is also increased according to acetylene (19.9 kJ mol^{-1}) < ethylene (60.6−66.3 kJ mol^{-1}) < ethane (151.8 kJ mol^{-1}). Similarly, the greater effect of α- vs β-monofluoro substitution in ethylene, α-monofluoro substitution in ethane vs ethylene, and the effect of a fluoro vs a CF_3 substituent show parallel behavior for the acidities and hydrogen-bond strengths.

We note, however, that there are instances where the qualitative correlation between an increase in the donor acidity and an increase in the hydrogen-bond strength of the corresponding complex with ammonia does not reflect the full picture. For example, although the effect on D_o of α-fluoro substitution is nearly twice that of β-fluoro substitution for an sp^2-hybridized proton donor (Table 3), the increase in the acidity of the C−H bond due to α-fluoro substitution (72.0 kJ mol^{-1}) is only slightly greater than the increase arising from β-fluoro substitution (60.6−66.3 kJ mol^{-1}). Additionally, although the binding energy of the methane−ammonia complex increases by a roughly 3.5 kJ mol^{-1} increment for each of the first and second fluoro substituents in methane, the acidity increases to a greater extent with each substitution (by 28.0 kJ mol^{-1} for the first fluorine and 47.8 kJ mol^{-1} for the second fluorine).

We also note that even the qualitative trend of increasing hydrogen-bond strength with increasing acidity of the proton donor is not always satisfied, though there are possible immediate explanations for such deviations. For example, for the series of ethylene derivatives, the hydrogen-bond strengths of the complexes between ammonia and α-fluoroethylene or β,β-difluoroethylene do not parallel the acidities of the proton donor. However, this discrepancy disappears when the additional F···H−N interaction in the α-fluoroethylene−ammonia complex is prevented from contributing to the binding energy, since a fixed linear hydrogen bond decreases the binding energy of the α-fluoroethylene−ammonia complex to 5.7 kJ mol^{-1}. As another example, the correlation between D_o and the acidity of the proton donor is erratic for the ethane systems, especially when comparing α- and β-substitutions. However, this is likely to be related to difficulties in defining the acidities of some of the β-fluorosubstituted ethanes because of the instability of the conjugate bases.

We find that an 8−25 kJ mol^{-1} increase in the acidity of the proton donor upon fluoro substitution corresponds to a 1 kJ mol^{-1} increase in the binding energy of the associated complex with ammonia for most of the systems investigated in our work. We have not included systems in which the conjugate base undergoes fragmentation in this correlation. In general, the larger ratios are observed when fluoro substitution occurs at a beta position, whereas the smaller ratios correspond to fluoro substitution at an alpha position, i.e., alpha substitution translates more effectively from an increase in acidity to an increase in hydrogen-bond strength than does beta substitution.

Conclusions

The present work investigates the effects of electronegative substitution on the strength of C−H···N hydrogen bonds. By using fluorinated derivatives of acetylene, ethylene, ethane and methane as proton donors, and ammonia as the proton acceptor, we estimate how the effects of electronegative substitution change with hybridization or with acidity of the proton donor. Our calculations show a monotonic progression toward stronger bonds with successive fluoro substitution in the donor in all cases.

The effect of fluoro substitution on the strength of a C−H···N hydrogen bond involving an sp-hybridized carbon atom is small (approximately 1 kJ mol^{-1}). This minimal effect is approximately doubled if substitution is considered at the beta position of an sp^2-hybridized carbon atom. Furthermore, for an sp^2-hybridized proton donor, the effect of an alpha fluoro substitutent is roughly twice that of a beta substituent. Thus, despite the fact that the binding energy of the ethylene−ammonia complex is small (1.7 kJ mol^{-1}), it can be increased to values (8.1−8.6 kJ mol^{-1}) comparable to that calculated for the acetylene−ammonia complex (8.6 kJ mol^{-1}) by α,β-difluoro substitution in ethylene.

For ethane, we find that the effect of each additional electronegative substitution at a particular position is smaller than the effect of the first substituent. If both the alpha and beta positions are occupied, then the relative magnitude of the increase in D_o compared with the increases due to individual substitutions depends on the substitution pattern. Monofluoro- and difluoro-substitution in methane result in roughly the same increase in the binding energy of the methane−ammonia complex, while trifluoro substitution leads to a larger effect. Negligible effects are observed for substituents such as a methyl group that do not have a strong electronic effect.

Interestingly, the effect of fluoro substituents on the binding energy of the hydrogen-bonded complexes increases with respect to hybridization of the proton donor in a direction (sp < sp^2 < sp^3) opposite to the propensity of the unsubstituted donor to partake in a hydrogen bond. As a consequence, C−H···N hydrogen-bond strengths equivalent to those involving sp- and sp^2-hybridized proton donors can be obtained through fluorine substitution in sp^3-hybridized donors. Replacement of any hydrogen with fluorine in the donor of the ethane−ammonia complex will result in a binding energy greater than that of the ethylene−ammonia complex. Furthermore, α,α,β-trifluoro substitution in ethane or trifluoro substitution in methane increases the strength of the C−H···N hydrogen bond to a value larger than that in the acetylene−ammonia complex.

For most systems in the present work, we find that an 8−25 kJ mol^{-1} increase in the acidity of the proton donor upon fluoro substitution corresponds to a 1 kJ mol^{-1} increase in the binding energy of the corresponding complex with ammonia. We also find that the binding energy of the complex with ammonia is affected proportionally more than the acidity of the donor when fluoro substition occurs at an alpha position compared with a beta position. In general, the larger the effect on the acidity of the proton donor of a particular fluoro substitution pattern, the greater the strengthening of the hydrogen bond with ammonia. Some of the minor deviations in the correlation between acidity and hydrogen-bond energy are associated with additional F···H−N interactions contributing to the latter, while other discrepancies may arise because of difficulties in calculating meaningful acidities due to dissociation of some substituted ethyl anions.

Our present study complements previous investigations of the effects of electronegative substituents on the binding energy of complexes by examining the problem systematically, including a consideration of the effects of alpha vs beta substitution and of the hybridization and acidity of the proton donor. Our study is a step toward understanding C−H···X hydrogen bonding in biological systems, where electronegative groups (though less electronegative than fluorine) are often attached to carbon.

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Supporting Information Available: GAUSSIAN 98 archive entries for the MP2/G3MP2large//B3-LYP/6-311+G(3df,2p) calculations for all relevant structures (Table S1−S3), CCSD(T)/6-31G(d), MP2/G3MP2large and MP2/6-31G(d) total energies (Table S4 and S5) and B3-LYP/6-311+G(3df,2p) ZPVEs and scale factors (Tables S6 − S7) (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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