J. Phys. Chem. A **2001,** *105,* 10607−10612

Influence of Hybridization and Substitution on the Properties of the CH···O Hydrogen Bond

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Received: August 10, 2001; In Final Form: September 27, 2001

Ab initio calculations are used to compare the hydrogen bonding ability of acetylene and ethylene, and various derivatives, with the analogous properties of alkanes. Water is used as the universal proton acceptor and paired with HCCH, FCCH, ClCCH, and NCH as well as with ethylene, and its mono-, di-, and trifluorosubstituted derivatives. With regard to the hydrocarbons, sp-hybridized acetylene forms the strongest bond, followed by sp^2 and then sp^3. Halogenation of the proton donor strengthens each type of hydrogen bond, particularly when the substitution takes place on the C involved in the hydrogen bond. sp^3-hybridized systems are most sensitive to this substitution-induced bond strengthening, followed in order by sp^2 and sp. For each hybridization type, the length of the hydrogen bond shortens in proportion to the strengthening, with alkanes exhibiting the greatest sensitivity and alkynes the least. Whereas formation of the hydrogen bond causes the sp^3 CH bond to contract and undergo a blue shift, the opposite trend is seen in the alkynes; the CH bond length is essentially unaffected in the alkenes. All types of CH··O hydrogen bonds are weakened more gradually as the two subunits are drawn apart than are OH···O bonds. Whereas alkyne CH···O bonds behave very similarly to OH···O interactions with regard to angular distortions, the hydrogen-bond energy of alkenes is less sensitive to such nonlinearity.

Introduction

Along with the proliferation of high-resolution crystal structures in recent years has come the realization that there are a vast multitude of close contacts between a CH group and an electronegative O or N atom. Many of these contacts have the structural earmarks of a hydrogen bond, leading to a growing sense that CH···O interactions may in fact constitute a true hydrogen bond in certain circumstances.[1−3] Identification of this interaction as a hydrogen bond is supported, at least indirectly, by accumulated IR and NMR spectral data.[4,5]

The question of the potentially attractive interaction between CH and an electronegative atom is particularly important in biological systems, where such contacts are numerous indeed.[6,7] Such CH···O interactions are present in nucleic acids,[8,9] proteins,[10,11] and carbohydrates,[12] as well as protein−nucleic acid contacts[13] and DNA−drug complexes.[14]

On the other hand, this notion that the CH···O interaction amounts to a hydrogen bond has not been without criticism,[15,16] based largely on the low electronegativity of the carbon atom and its presumed weakness as a proton donor. Critics have also argued that the mere finding of a close contact is not conclusive evidence of a hydrogen bond, but could result from crystal forces pressing the CH and O groups into proximity. Moreover, IR observations of CH···O interactions over the years have led to the puzzling finding that the CH stretching frequency is on some occasions shifted to the red, which is a classic indicator of a hydrogen bond,[17] but in other instances is shifted in precisely the other direction.[18−20]

To bridge the gap that is presented by crystal structural data which cannot elucidate the nature of the force between the CH and O groups, quantum chemical calculations have been brought to bear on this problem. There seems little question that the sp hybridization of alkynes permits the ≡CH group to form an attractive interaction with a proton acceptor,[21] as can the even more acidic HCN.[22] Work related to the alkenes and alkanes is sparser,[23−25] indicating a weaker interaction, whose identification as a hydrogen bond is tenuous.

Whereas the pure hydrocarbons are weak proton donors, addition of electron-withdrawing groups strengthens them to the point where their interaction energies with proton acceptors clearly enter the range of conventional hydrogen bonds. Halogenation of the alkanes, for example, makes them into potent proton donors.[26,27] Recent calculations from this laboratory[28−30] have documented that the interactions formed by such haloalkanes with proton acceptors are genuine hydrogen bonds, not only in an energetic and geometric sense, but also in terms of electronic structure and spectroscopic markers. This work went on to demonstrate the CH bond contraction (and blue shift) observed in certain CH···O interactions[20,31,32] is not inconsistent at all with their classification as hydrogen bonds. The electron-withdrawing agent that imparts sufficient acidity to the CH group so as to permit hydrogen-bonding is not limited to halogens, but occurs as well with carboxyl,[33] hydroxyl/ether,[34−36] amine,[37] NO_2,[38] and cyano,[39] or combinations as in amides[40,41] or peptides.[42]

The present communication concerns itself first with a quantitative assessment of how the hybridization of the C atom (sp, sp^2, and sp^3) affects the ability of the CH group to engage in a hydrogen bond. Since the addition of electron-withdrawing groups to alkanes appears capable of strengthening their hydrogen bonds, it is logical to presume that the same is true

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10.1021/jp0131267 CCC: $20.00 © 2001 American Chemical Society
Published on Web 10/31/2001

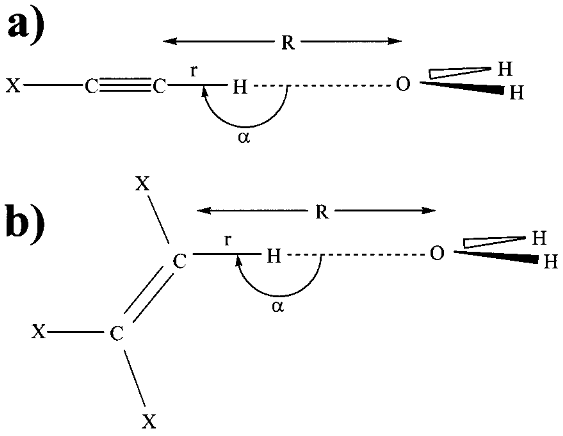

Figure 1. Geometrical parameters defined for substituted alkynes (a) and alkenes (b) in complex with water.

of alkenes and alkynes. The calculations described here are designed to measure how strongly each sort of CH···O hydrogen bond is affected by such substitutions, including how quickly these effects are weakened as the point of substitution is moved further away from the CH group in question. Another major goal of this work is the development of an understanding as to why it is that some CH bonds are lengthened and undergo a red shift in their stretching frequency upon formation of a hydrogen bond, whereas others behave in exactly the opposite fashion. Since it was found previously that the strength of an alkane (sp^3) CH···O bond decays more slowly than an OH···O bond as each is stretched,[28] which has important implications for structure and function, the present work inquires as to whether the same is true for other hybridizations of the C atom.

Methods

The systems examined here are illustrated in Figure 1, which also defines the geometrical parameters. The X designation indicates either a hydrogen or F or Cl halide atom. Ab initio calculations were carried out using the GAUSSIAN-98 set of codes[43] with its various built-in basis sets. Standard notation was used for basis sets wherein + signs indicate the presence of diffuse functions on non-hydrogen atoms (one +) or all atoms (double +); analogous meaning is attached to * signs and polarization functions. Electron correlation was included via the second-order Møller-Plesset (MP2) treatment,[44] as well as by use of the B3LYP variant of density functional theory (DFT).[45,46] NMR chemical shifts were computed using the gauge-including atomic orbital (GIAO) approach[47] at the MP2 level, which has been shown to produce rather accurate data for hydrogen bonds.[48] The electron density was analyzed via the atoms in molecules approach.[49]

Alkynes

The interaction energies of acetylene, and some of its derivatives, with water are reported in Table 1 at various levels of theory. As in our earlier work,[28] all of these values have been corrected for basis set superposition error by the counterpoise procedure.[50] As may be seen by the first column of data in Table 1, acetylene binds to water by some 2.5 kcal/mol at the SCF level. This quantity is affected very little by electron correlation as the MP2 binding energy is also around 2.5 kcal/mol. There is very little basis set sensitivity, consistent with the earlier study of the substituted methanes, and an earlier set of calculations of HCCH···OH_2.[51] The main exception is the aug-cc-pVDZ basis set, for which the SCF binding energy is about 0.3 kcal/mol smaller, and the MP2 value some 0.1 kcal/mol larger, than the results obtained with the other sets. The B3LYP binding energy is quite close to the MP2/aug-cc-pVDZ value. Hartmann et al.[25] have very recently arrived at a benchmark value for this interaction energy. Using the counterpoise-corrected CCSD(T) procedure, coupled with a 6-311+G(3df,2p) basis set, their binding energy is 2.6 kcal/mol, in good agreement with our own MP2 values computed with smaller basis sets, lending further confidence to the accuracy of our results.

TABLE 1: Binding Energies (kcal/mol) of Acetylene Derivatives with Water, Calculated with Counterpoise Correction of Basis Set Superposition Error[a]

		HCCH	FCCH	ClCCH	NCH
SCF	6-31G*	2.53	2.86	3.15	5.60
	6-31+G*	2.44	2.65	2.82	5.08
	6-31+G**	2.51	2.71	2.88	5.13
	6-31++G**	2.50	2.68	2.86	5.12
	6-311++G**	2.51	2.67	2.83	5.07
	aug-cc-pVDZ	2.22	2.40	2.54	4.62
MP2	6-31G*	2.69	3.03	3.23	5.75
	6-31+G*	2.55	2.90	2.92	5.07
	6-31+G**	2.51	2.82	2.81	4.91
	6-31++G**	2.50	2.80	2.80	4.90
	6-311++G**	2.48	2.61	2.64	4.67
	aug-cc-pVDZ	2.62	2.81	2.87	4.69
B3LYP	6-311++G**	2.65	2.78	2.86	5.26

[a] All C_{2v} geometries fully optimized at the level indicated.

Replacement of the nonparticipatory hydrogen atom of HCCH by the electronegative F and Cl atoms lead to the binding energies displayed in the next two columns of Table 1. These substitutions can be expected to enhance the acidity of the alkyne, and in fact increase the binding energies. At the SCF level, the chlorosubstitution has a larger effect than F, but this difference is largely washed out when electron correlation is added. The MP2 binding energy of FCCH with water is only marginally smaller than for ClCCH; both are larger than the values for the unsubstituted acetylene by 0.1−0.5 kcal/mol. A 0.2−0.3 kcal/mol increment is probably the best guess from the computed data. It is interesting that this increment is considerably smaller than the corresponding increase of 1 kcal/mol in the binding energy of methane with water as F atoms are added to the alkane.[28] The discrepancy is likely due at least in part to the greater physical separation between the F and bridging H atoms in acetylene (two C atoms) as compared to methane (one C atom); see further discussion below.

A far greater enhancement of the interaction energy arises from replacement of HCCH by the much more acidic HCN in the last column of Table 1. The binding of the latter with water is in the neighborhood of 5 kcal/mol, perhaps even a little stronger than the conventional OH···O hydrogen bond in the water dimer.

It is typically the case that increasing strength of a hydrogen bond is connected with a closer association between the two subunits. The intermolecular separations optimized for the various complexes presented in Table 2 confirm this expectation. The SCF distances for the HCCH···OH_2 complex in the first column are about 3.34 Å, shortened by about 0.07 Å at the MP2 level to roughly 3.27 Å. This correlation-induced bond shortening is observed in the other complexes of Table 2 as well. As in the case of binding energies, the FCCH and ClCCH proton donors lead to much the same intersubunit separation, roughly 3.25 Å, only slightly shorter than in HCCH···OH_2. A more substantial contraction to 3.14 Å occurs for the stronger hydrogen bond in NCH···OH_2.

It is evident that the computed information is relatively insensitive to the particulars of the basis set, consistent with

TABLE 2: Optimized Intermolecular C···O Distances (Å)

		HCCH	FCCH	ClCCH	NCH
SCF	6-31G*	3.323	3.292	3.277	3.143
	6-31+G*	3.296	3.282	3.273	3.162
	6-31+G**	3.316	3.304	3.296	3.177
	6-31++G**	3.315	3.304	3.294	3.178
	6-311++G**	3.338	3.322	3.312	3.185
	aug-cc-pVDZ	3.381	3.358	3.350	3.216
MP2	6-31G*	3.251	3.215	3.210	3.093
	6-31+G*	3.217	3.193	3.192	3.116
	6-31+G**	3.238	3.214	3.215	3.130
	6-31++G**	3.234	3.212	3.211	3.128
	6-311++G**	3.268	3.250	3.247	3.142
	aug-cc-pVDZ	3.254	3.225	3.228	3.134
B3LYP	6-311++G**	3.239	3.221	3.219	3.100

TABLE 3: Changes in Properties of Proton Donor Molecules Caused by Complexation with Water[a]

	HCCH	FCCH	ClCCH	NCH
		Δr^b, mÅ		
SCF	4.3	4.7	4.7	6.8
MP2	4.8	6.0	6.0	7.3
		$\Delta\nu^c$, cm^{-1}		
SCF	−31	−55	−56	−88
MP2	−40	−75	−76	−104
		$I/I_o{}^d$		
SCF	2.1	2.4	2.7	3.5
MP2	2.6	3.1	3.5	4.4
		$\Delta\sigma^e$, ppm		
isotropic	−1.9	−2.1	−2.0	−2.1
anisotropic	7.5	7.9	7.7	8.5

[a] Computed with 6-311++G** basis set. [b] Elongation of CH bond length. [c] Shift in frequency of CH bond stretch. [d] Magnification of intensity of CH bond stretch. [e] Changes in NMR chemical shifts of bridging H caused by complexation, computed by MP2(FC)/GIAO using 6-31+G** basis set.

TABLE 4: Properties of Electron Density (au) in Complexes with Water at H···O Bond Critical Point[a]

	HCCH	FCCH	ClCCH	NCH	HOH
			ρ		
SCF	0.011	0.011	0.011	0.015	0.017
MP2	0.014	0.014	0.014	0.018	0.023
			Laplacian		
SCF	0.044	0.046	0.047	0.065	0.075
MP2	0.052	0.054	0.055	0.071	0.091

[a] Computed with 6-311++G** basis set.

TABLE 5: Calculated Properties of Various Alkene Proton Donors Associated with Water[a]

	H_2CCH_2	$FHCCH_2$	F_2CCH_2	H_2CCFH	F_2CCFH
$-\Delta E$, kcal/mol	0.86	1.67	1.91	2.10	3.11
R(C···O), Å	3.458	3.385	3.337	3.339	3.263
Δr,[b] mÅ	−0.3	0.8	1.7	0.0	1.7
$\Delta\nu$,[c] cm^{-1}	0	−4	−12	10	−16
$\Delta\sigma_{iso}$,[e] ppm	−1.2	−1.5	−1.7	−1.3	−1.8
$\Delta\sigma_{an}$,[e] ppm	3.0	4.8	6.0	4.4	2.5

[a] Computed at MP2/6-31+G** level. The C atom forming the CH···O interaction is the second. [b] Elongation of CH bond length.[c] Shift in frequency of CH bond stretch. [d] Magnification of intensity of CH bond stretch. [e] NMR chemical shifts of bridging H computed by MP2(FC)/GIAO.

findings in similar systems.[25,28] For this reason, and in the interest of conserving space, the remaining structural and spectroscopic data are reported only for the 6-311++G** basis set. Examination of the full set of data indeed confirms no significant deviations from the trends observed in Tables 1 and 2.

Another parameter that is usually closely associated with the strength of a hydrogen bond is the stretch that the formation of this bond causes in the X−H bond of the proton donor molecule. These stretches are reported, in mÅ, in the first two rows of Table 3, where the expected correlation is in fact observed. Correlation adds to the bond stretch, just as it causes the hydrogen-bond energy to increase and its length to contract. The CH bond of acetylene stretches by 5 mÅ when bound to water, identical to the value obtained at the CCSD(T)/6-311+G(3df,2p) level.[25] This stretch increases by 1 mÅ for FCCH and ClCCH, and by a further 1.3 mÅ for HCN. The B3LYP stretches (not listed in Table 3) appear to be somewhat overestimated.

Along with the stretch in the equilibrium length of the CH bond, one can expect a red shift of the stretching frequency associated with this bond in an alkyne.[52] These red shifts are listed in the next two rows of Table 3, and a clear correlation with the other properties is evident. That is, the greater the degree of CH bond stretch, the larger is the magnitude of the red shift. The best estimates of this property are around −40 cm^{-1} for $HCCH\cdots OH_2$, increasing to −75 cm^{-1} for the fluoro- and chlorosubstituted species, and as high as −104 cm^{-1} for $NCH\cdots OH_2$. Last, concerning this particular stretching mode, the magnification of the intensity of this band is reported in the succeeding two rows of Table 3 where it may be seen to follow the same patterns. The magnification of this intensity varies from 2.6 for $HCCH\cdots OH_2$ up to a high of 4.4 for $NCH\cdots OH_2$.

The last two rows of Table 3 list the isotropic and anisotropic chemical shifts of the bridging hydrogen, compared to the same quantities in the isolated proton donor molecule. The negative change in the isotropic shift is consistent with prior computations in related CH···O and other hydrogen bonds,[30,42] as is the larger magnitude positive value for the anisotropic shift. The former quantity typically becomes slightly more negative with increased hydrogen-bond strength, a phenomenon which is seen here as well. One can also discern a pattern wherein the changes in the anisotropic shift are roughly proportional to hydrogen-bond strength.

The atoms in molecules (AIM) perspective[49] of the binding interaction focuses directly on the electron density. After locating the bond critical point between the two subunits, both the electron density at that point, and its Laplacian, provide an indicator of the hydrogen-bond strength. These two properties are listed in Table 4, and the data conform to the patterns gleaned from energetic, structural, and spectroscopic features above. In particular, addition of electron correlation adds a small amount to the SCF values in each case. More importantly, one can note a pattern wherein the replacement of the nonparticipating H atom of HCCH by F or Cl adds only a very small increment to the density properties, whereas a much larger increment occurs for HCN. The electron density properties of the most strongly bound $NCH\cdots OH_2$ complex approach fairly closely the corresponding quantities in the water dimer, reported in the final column of Table 4.

Alkenes and Comparisons

The geometrical parameters of the analogous alkenes and their complex with water are illustrated in Figure 1b. The various nonparticipating H atoms, indicated by X in the figure, were progressively replaced by F as a strongly electron-withdrawing agent. A summary of corresponding data for the alkene complexes is displayed in Table 5, all computed using the 6-31+G** basis set.

In the case of unsubstituted ethylene, the interaction energy is slightly below 1 kcal/mol, intermediate between the extremes of 0.3 kcal/mol for methane[28] or ethane and 2.5 kcal/mol for acetylene. Our MP2/6-31+G** value of 0.9 kcal/mol is quite close to Hartmann et al.'s much higher level CCSD(T)/6-311+G(3df,2p) binding energy of 1.0 kcal/mol,[25] as well as a MP2/6-31+G(2d,2p) estimate of 0.96 kcal/mol.[53] The attractive nature of the interaction, on the borderline of true hydrogen bonds, buttresses structural and spectroscopic evidence that alkenes can act as proton donor in a hydrogen bond.[11,52]

The various fluorosubstitutions of ethylene make it a progressively stronger proton donor, and thus enhance its binding energy with water. Placing an F atom on the C atom that is not involved in the hydrogen bond ($FHCCH_2$) nearly doubles the binding energy to 1.7 kcal/mol. Replacing both H atoms on the same C atom (F_2CCH_2) adds a small additional increment of 0.2 kcal/mol. The 0.8 kcal/mol increment in the binding energy of ethylene that arises from monofluorosubstitution of the nonparticipating C atom compares with only 0.3 kcal/mol in the alkyne analogue. That is, the binding energy of HCCH to water is increased by only 0.3 kcal/mol when the acetylene is replaced by FCCH. A corresponding calculation for the alkanes (CH_2FCH_3 vs CH_3CH_3), also at the MP2/6-31+G** level, reveals an increment of 1.0 kcal/mol from 0.26 to 1.25 kcal/mol. Hence, the changing hybridization in the proton donor from sp to sp^2 to sp^3 corresponds to an increasing sensitivity of the hydrogen-bond energy (0.3 to 0.8 to 1.0 kcal/mol) to fluorosubstitution on the C atom adjacent to the donor CH.

The effect of fluorosubstitution is larger if the F atom is located on the C atom which participates directly in the hydrogen bond. Compared to ethylene's binding energy of 0.9 kcal/mol, the same quantity for H_2CCFH is 2.1 kcal/mol, more than twice as large. This increment of 1.2 kcal/mol is similar to the increase in binding energy (also 1.2 kcal/mol) that occurs in the alkane···water complexes when a H of the participating C atom of ethane is replaced by F. Nonetheless, the hydrogen-bond energy of $H_2C{=}CFH\cdots OH_2$ is smaller than the binding energy of either unsubstituted sp-hybridized acetylene or sp^3 difluoromethane with water (both 2.5 kcal/mol). As may be seen in the last column of Table 5, replacement of all three nonparticipating H atoms of ethylene by fluorine results in a binding energy of 3.1 kcal/mol, greater than the corresponding quantity for HC≡CH or even FC≡CH.

The equilibrium hydrogen-bond lengths are reported in the second row of Table 5 which shows a clear connection between a stronger hydrogen bond and a shorter internuclear distance. To elaborate on this correlation, the R(C···O) distances are plotted against hydrogen-bond energy in Figure 2. The line drawn through the alkene data points is associated with a correlation coefficient of 0.98. Similar straight lines accurately represent the substituted alkynes and alkanes[28] (all using MP2/6-31+G** data), both of which correspond to a correlation coefficient of 0.99. The slopes of these lines vary in a predictable way, from 0.043 for the alkynes, to 0.087 for the alkenes, and 0.101 for the alkanes (all in units of Å/kcal mol^{-1}). In other words, the alkanes exhibit the greatest sensitivity of the intermolecular distance to the strength of the hydrogen bond, and the alkynes the least. Note also from Figure 2 that for a given hydrogen-bond energy, the alkanes will have the longest hydrogen bond and the alkynes the shortest. Taking 3 kcal/mol as an example, the −CH···O distance will be about 3.30 Å, as compared to 3.26 Å for =CH···O, and 3.21 Å for ≡CH···O. The figure indicates further that this discrepancy in hydrogen-bond length diminishes as the hydrogen bond is strengthened, and is projected to disappear entirely in the neighborhood of 4−5 kcal/mol where the three lines intersect. This sort of relationship between hydrogen-bond length and strength is consistent with prior crystal studies[54] where the C···O distance diminished by as much as 0.27 Å as a result of trihalogenation of the proton donor molecule.

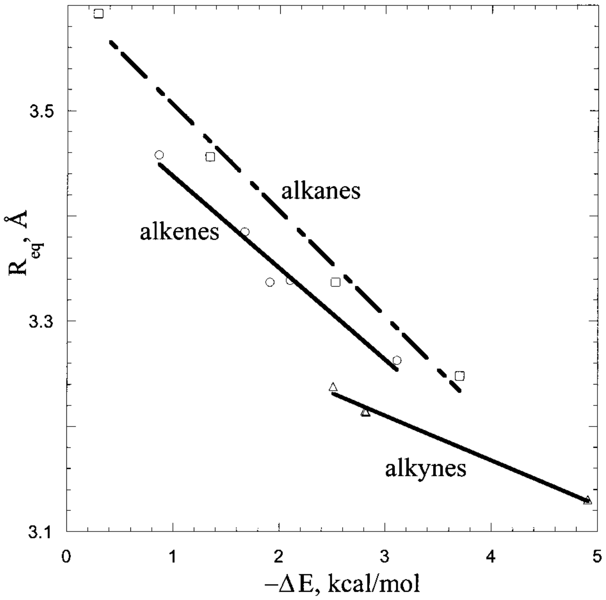

Figure 2. Interdependence of equilibrium intermolecular R(C···O) distance and interaction energy for substituted hydrocarbons. Proton acceptor is H_2O in all cases.

Whereas the alkynes conform to conventional hydrogen bonds in that their C−H bond elongates upon complexation, alkanes behave in just the opposite fashion.[25,28,29,32,55,56] As may be seen in the third row of Table 5, the situation is intermediate between these two extremes for the alkenes. Specifically, there is very little change in r(CH) as a result of complexation, less than 2 mÅ in all cases. There is a very small contraction of 0.3 mÅ for ethylene, but this value is too small to be truly indicative. Indeed, there are elongations in some of the F-containing alkenes. However, the data computed for Δr are not conclusive concerning either a contraction or stretch; one may say only that the changes in this bond length are very small indeed. A similar statement applies to the shift in the stretching frequency of this bond. Some of the values of $\Delta\nu$ in the next row of Table 5 are positive, some negative. One can detect a correlation in that the red shifts are associated with stretches of the bond, as would be expected.

Turning to the changes in the NMR chemical shifts of the bridging H in the last two rows of Table 5, the isotropic values are all negative, ranging between 1.2 and 1.8 in magnitude. This range is somewhat smaller than that presented in Table 3 above, consistent with the weaker hydrogen-bonding formed by the alkenes as compared to alkynes. In comparison, the same quantity was calculated to be about −1.2 ppm for the alkanes,[30] in accord with their weaker hydrogen bonds. There would appear to be a general correlation between the magnitude of $\Delta\sigma_{iso}$ and the strength of the hydrogen bond, as unsubstituted ethylene has associated with it the smallest value of −1.2 ppm and F_2CCFH the largest at −1.8 ppm. There is no such correlation in evidence for the anisotropic shifts in the last row of Table 5, where $\Delta\sigma_{an}$ spans the range between 2.5 and 6.0 ppm. This lack of a correlation with hydrogen-bond strength was found to be typical also of the alkanes.[30]

It was reported earlier[28] that the CH···O bond energies involving the substituted methanes have a different dependence upon intermolecular distance than do conventional OH···O

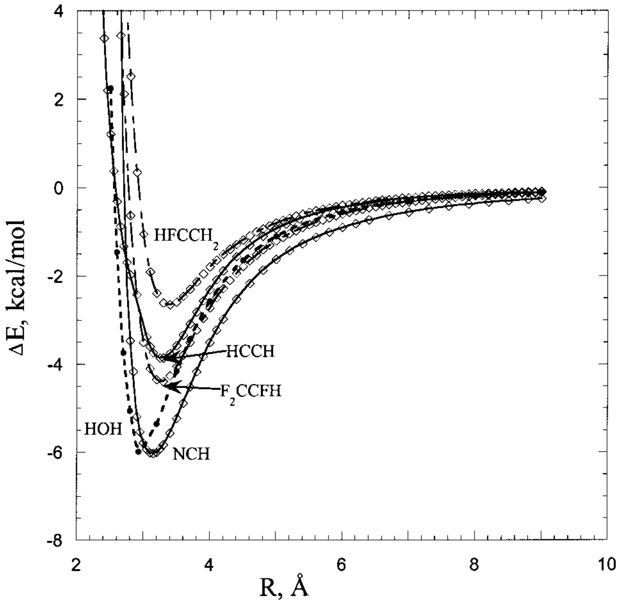

Figure 3. Variation of interaction energy with R(C···O) for complexes involving water as proton acceptor and the indicated proton donor. Broken line refers to HOH···OH$_2$, in which case R represents R(O···O). Energies uncorrected for BSSE.

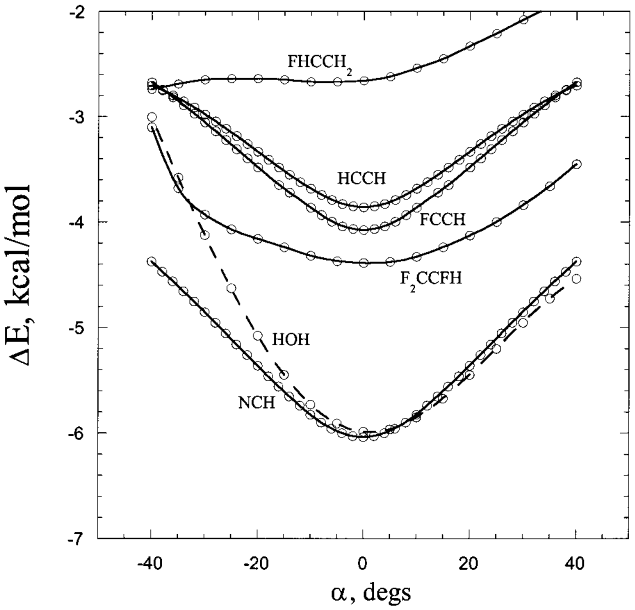

Figure 4. Variation of interaction energy with angular distortion angle α for complexes involving water as proton acceptor and the indicated substituted alkyne or alkene proton donor. Broken line refers to HOH···OH$_2$. Intermolecular separation was held fixed at its optimum value for each system. Energies uncorrected for BSSE.

interactions. Specifically, the weaker CH···O bonds die off more slowly with distance than do OH···O. The behavior of various sorts of CH···O bonds, including both sp and sp^2 hybridizations, are illustrated in Figure 4, along with the standard water dimer, denoted by the broken curve. The first and most obvious comparison is between NCH···OH$_2$ and the water dimer, which have nearly identical minima in their potentials, although they occur at slightly different hydrogen-bond lengths, 3.15 and 2.93 Å, respectively. The potential representing the CH···O bond would also appear to be broader than the curve for the OH···O interaction. As a result, the hydrogen bond of the former system is stronger than that of the water dimer for all intermolecular distances greater than 3.0 Å, where the two curves cross. In what is perhaps a more dramatic observation, even though the water dimer has a much greater maximal strength than does the alkene in F$_2$C=CFH···OH$_2$, the stretching of the former leaves it with a hydrogen-bond energy weaker than that of the latter for intermolecular distances in excess of about 3.5 Å. One can thus conclude that the slower decay of hydrogen-bond energy in the CH···O bond as compared to OH···O is characteristic of CH in general, and not only of sp^3-hybridized systems.

Earlier work with substituted methane[28] had concluded that the corresponding CH···O interaction energy was less sensitive to angular distortions of the CH proton donor from the C···O hydrogen-bond axis than is the case in the OH···O bond. The sensitivity of the interaction energy for the analogous alkenes and alkynes are exhibited in Figure 4, along with the water dimer as the broken curve for purposes of comparison. Note first the tendency of all systems toward $\alpha = 0°$, i.e., linearity of the CH···O atoms. This computational result is in agreement with surveys of crystal structures involving alkynes and alkenes.[57]

Again beginning the comparison between NCH···OH$_2$ and the water dimer, the two corresponding curves are rather similar for positive values of α, while the water dimer curve climbs more rapidly when α is negative. The curves corresponding to the two alkynes, HCCH and FCCH, are generally similar to that for NCH, with the qualification that the curves become less steep for weaker interactions. The most profound differences arise between the alkynes and the alkenes, represented by FHCCH$_2$ and F$_2$CCFH. The latter systems display a much weaker sensitivity to angular distortions than do the triply bonded CH donors. Indeed, the interaction energy of FHCCH$_2$···OH$_2$ is nearly constant over the 50° range of α between $-40°$ and $+10°$. In that respect, the alkenes resemble the alkanes more than they do the alkynes.

Summary and Conclusions

As anticipated on the basis of simple chemical arguments based on hybridization and acidity, the alkynes form stronger hydrogen bonds with a proton acceptor than do alkenes, which are followed by alkanes. The binding energy of acetylene with water is computed to be 2.5 kcal/mol, as compared with 0.9 for ethylene, and 0.3 for methane and ethane. The binding of all of these molecules is enhanced by the substitution by electronegative atoms such as F. The hydrogen-bond energy is increased by 1.2 kcal/mol for the replacement of each H atom located on the C atom that is directly involved in the CH···O bond of ethane or ethylene. The effect is smaller when the fluorosubstitution occurs on an adjacent C atom, raising the binding energy for the alkane by 1.0 kcal/mol, as compared to 0.8 and 0.3 kcal/mol for ethylene and acetylene, respectively. Hence the sensitivity of the binding energy to this sort of remote substitution is greatest for sp^3, followed in order by sp^2 and then sp. The change from an alkene to a cyano group (HC≡CH to N≡CH) adds a great deal to the hydrogen-bonding propensity; NCH forms hydrogen bonds as strong as those in which water is proton donor.

Equilibrium hydrogen-bond lengths bear a strong correlation with the interaction energies, a very nearly linear relationship for each class of hydrocarbon. The length of the alkyne hydrogen bond is least sensitive to the bond strength whereas the sp^3-hybridized molecules exhibit the greatest sensitivity. For any given hydrogen-bond energy, one can expect the interaction involving the alkyne to be shortest, and that with the alkane the longest.

An interesting finding of recent years is the bond shortening and blue shift that are sometimes observed in CH···O bonds. Whereas such unusual phenomena may occur in CH bonds with sp^3 hybridization, sp alkynes mirror what is seen in conventional hydrogen bonds of the OH···O type: formation of the hydrogen bond stretches the CH bond which undergoes a simultaneous red shift and intensification in its stretching frequency. This dramatic discrepancy between sp- and sp^3-hybridized CH groups is consistent with earlier calculations of one system or the other.[55,58,59] Moreover, the magnitudes of these effects are roughly proportional to the strength of the hydrogen bond. The situation in alkenes is intermediate between these two extremes in that the CH bond length is essentially unaffected by its participation in a hydrogen bond, nor is it sensitive to the strength of this bond.

The isotropic components of the NMR chemical shifts of the bridging proton obey a predictable pattern, consistent with conventional hydrogen bonds. This quantity is downshifted by some 1.2 ppm for alkanes, and is insensitive to the strength of the interaction. The downshift is larger for the alkenes, varying between 1.2 and 1.8 ppm as the hydrogen bond is strengthened. In the case of sp-hybridized donors, the shift caused by complexation is larger, approximately 2 ppm. These magnitudes of shifts are directly in line with experimental observations of such hydrogen bonds.[60−62] The anisotropic shifts are positive for all three sorts of CH bonds. They lie in the range of 3−6 ppm for the alkanes, 2−6 ppm for alkenes, and 7−8 ppm for the alkynes, and do not follow any simple dependence upon the strength of the hydrogen bond.

CH···O bonds, whether they involve sp, sp^2, or sp^3 hybridization, lose their strength more slowly as the two subunits are drawn apart than do conventional OH···O bonds. Thus, one can anticipate that the nominally weaker CH···O bond may in fact be stronger than its OH···O counterpart when both are equally stretched from their equilibrium separation. Whereas the CH···O bond involving alkynes exhibits a functional dependence upon nonlinearity comparable to OH···O bonds, the interaction energy for alkenes is considerably less sensitive to angular distortions. In this respect, the sp^2-hybridized systems resemble their sp^3 correlates.

Acknowledgment. This work was supported by NIH Grant GM57936.

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