C−H···X Hydrogen Bonds of Acetylene, Ethylene, and Ethane with First- and Second-Row Hydrides

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The structures and binding energies of a series of C−H···X hydrogen-bonded complexes involving acetylene, ethylene, and ethane as proton donors and the first- and second-row hydrides CH_4, NH_3, OH_2, FH, PH_3, SH_2, and ClH as proton acceptors have been determined. Geometries were optimized with both the MP2 and the B3-LYP methods in conjuction with the 6-311+G(3df,2p) basis set. In general, we note good agreement between MP2 and B3-LYP hydrogen-bonded structures. However, for some very weakly bound complexes larger differences exist, particularly in the r(H···X) distance, and in these instances the MP2 results are determined (from comparative CCSD(T) calculations) to be more reliable. The CCSD(T)/6-311+G(3df,2p) binding energies (D_e), which include corrections for basis set superposition errors, are very similar for the MP2 and B3-LYP geometries, reflecting the relative insensitivity of D_e to geometry for weakly bound complexes. The C−H···X hydrogen-bond strength (D_0) shows a considerable dependence on the acidity of the C−H donor group and on the nature of the proton-accepting group. The strongest hydrogen bonds are formed between acetylene and either NH_3 (9.2 kJ mol^{-1}) or OH_2 (7.7 kJ mol^{-1}). These values decrease significantly for the corresponding complexes between acetylene and FH, CH_4 or the second-row hydrides. The binding energies for the complexes between ethylene and either NH_3 or OH_2 (2.1 and 1.5 kJ mol^{-1}, respectively) are much smaller than those of the corresponding acetylene complexes. The complexes between ethylene and PH_3, SH_2 or ClH, as well as the complexes between ethane and NH_3 or H_2O, are more weakly bound again and have binding energies less than 1.0 kJ mol^{-1}.

Introduction

Since the early 1960s, crystallographic and spectroscopic studies have shown that (activated) C−H groups can act as proton donors in hydrogen-bonded systems.[1] In the following decade, a variety of theoretical studies based on semiempirical and ab initio molecular orbital approaches for a series of C−H···X hydrogen-bonded complexes appeared,[2] and, despite the limitations due to the computational resources at that time, they gave important insights into the nature of C−H···X hydrogen-bonded complexes. However, it was not until 1982 that the first appearance of a thorough and conclusive survey of C−H···X hydrogen bonds surfaced.[3] Since then, mainly supported by crystal correlation studies and spectroscopic examinations, increasing attention has been directed to these attractive and directional interactions. The concept of C−H···X hydrogen bonds is now well documented,[4] although not always undisputed.[5] In particular, C−H···N,[6−11] C−H···O,[12−20] and C−H···π[21−24] complexes have been the focus of a number of such investigations. Some attention has also been paid to complexes involving C−H···S,[25] C−H···Hal (Hal = F, Cl, Br),[21r,26] C−H···Se,[25f,27] and even C−H···C[28−32] interactions.

In the present study, we have carried out a detailed examination of a series of C−H···X, hydrogen-bonded complexes in which the proton donor and proton acceptor are varied systematically. The dependence of the hydrogen-bond strength on the hybridization of the donor carbon and the acidity of the donor C−H group is examined using acetylene, ethylene and ethane[33] as proton donors. The effect of proton-acceptor strength on the interaction energy is examined using the first- and second-row hydrides CH_4, NH_3, OH_2, FH, PH_3, SH_2, and ClH as proton acceptors.

In the present paper, we focus only on C−H···X hydrogen-bonded complexes. It is known that alternative structures of the general type X−H···π, in which the hydride acts as a proton donor toward the C=C or C≡C π-bonds, are energetically more favorable in, for example, the case of HC≡CH···FH,[22] HC≡CH···ClH,[23] and $H_2C{=}CH_2$···OH_2,[24] but such structures are not discussed in detail here.

Theoretical Procedures

Standard ab initio molecular orbital theory[34] and density functional theory[35] calculations were performed with GAUSSIAN 98,[36] MOLPRO 98,[37a] and MOLPRO 2000.[37b] In the present work, we have used both MP2 and B3-LYP in conjunction with the 6-311+G(3df,2p) basis set to calculate equilibrium geometries. CCSD(T)/6-311+G(3df,2p) single-point calculations on these geometries are used to evaluate the binding energies. We have recently shown that these methodologies both perform well for the description of the C−H···N hydrogen-bonded complex HC≡CH···NH_3, giving results that are of comparable quality to the CCSD(T)/6-311+G(3df,2p)//CCSD(T)/6-311+G(3df,2p) procedure.[7] The extension of this conclusion to weaker complexes will be considered in the present study (see below). All electrons were correlated in all MP2 and CCSD(T) calculations discussed in the present work.

The raw equilibrium binding energies were corrected by subtracting the basis set superposition error (BSSE), evaluated

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TABLE 1: Comparison of B3-LYP, MP2, and CCSD(T) Structures, and Dependence on Geometry of Calculated Binding Energies, of Hydrogen-Bonded Complexes[a,b]

dimer	method[c]	r(C≡C)	r(C−H)	r(H···X)	D_e[d,e]	BSSE[d]	D_e[d]
HC≡CH···NH_3[f]	B3-LYP	1.198	1.072	2.308	16.1	2.0	14.1
(C_{3v})	MP2	1.211	1.070	2.275	16.1	2.1	14.0
	CCSD(T)	1.209	1.073	2.280	16.1	2.0	14.1
H_3CH···NH_3	B3-LYP		1.088	2.969	3.2	0.6	2.6
(C_{3v})	MP2		1.085	2.814	3.3	0.7	2.6
	CCSD(T)		1.088	2.793	3.3	0.7	2.6
HC≡CH···CH_4	B3-LYP	1.196	1.063	3.131	2.5	0.4	2.1
(C_{3v})	MP2	1.209	1.062	2.724	3.2	0.8	2.4
	CCSD(T)[g]	1.206	1.065	2.725	3.3	0.8	2.5

[a] Bond lengths are given in Å, energies in kJ mol^{-1}. [b] Unless otherwise noted, geometry and energy calculations were performed with the 6-311+G(3df,2p) basis set. [c] Method used for geometry optimizations. [d] D_e and BSSE values were obtained from CCSD(T)/6-311+G(3df,2p) single-point calculations on the respective geometries. [e] D_e value without the incorporation of BSSE. [f] Ref 7. [g] The 6-311+G(2df,p) basis set was used in the CCSD(T) geometry optimization for HC≡CH···CH_4.

according to the Boys and Bernardi counterpoise method[38]

$$\mathrm{BSSE} = (E^{\mathrm{full}}_{\mathrm{H-donor}}) - (E^{\mathrm{monomer}}_{\mathrm{H-donor}}) + (E^{\mathrm{full}}_{\mathrm{H-acceptor}}) - (E^{\mathrm{monomer}}_{\mathrm{H-acceptor}}) \quad (1)$$

where $E^{\mathrm{full}}_{\mathrm{H-donor}}$ and $E^{\mathrm{full}}_{\mathrm{H-acceptor}}$ are the total energies of the monomers in their respective complex geometries using the full basis set of the complex, whereas $E^{\mathrm{monomer}}_{\mathrm{H-donor}}$ and $E^{\mathrm{monomer}}_{\mathrm{H-acceptor}}$ are the total energies of the monomers calculated at their respective complex geometries but using only the monomer basis sets. The resulting binding energies are denoted D_e.

The binding energy D_e is further corrected to 0 K with scaled zero-point vibrational energy (ZPVE) contributions, giving D_0 values. Appropriate scale factors (sf) for the ZPVEs of monomers and complexes were derived according to

$$\mathrm{sf}_{\mathrm{H-donor}} = \frac{\mathrm{ZPVE}^{\mathrm{ref}}_{\mathrm{H-donor}}}{\mathrm{ZPVE}^{\mathrm{calc}}_{\mathrm{H-donor}}} \qquad \mathrm{sf}_{\mathrm{H-acceptor}} = \frac{\mathrm{ZPVE}^{\mathrm{ref}}_{\mathrm{H-acceptor}}}{\mathrm{ZPVE}^{\mathrm{calc}}_{\mathrm{H-acceptor}}} \quad (2)$$

$$\mathrm{sf}_{\mathrm{complex}} = \frac{\mathrm{ZPVE}^{\mathrm{ref}}_{\mathrm{H-donor}} + \mathrm{ZPVE}^{\mathrm{ref}}_{\mathrm{H-acceptor}}}{\mathrm{ZPVE}^{\mathrm{calc}}_{\mathrm{H-donor}} + \mathrm{ZPVE}^{\mathrm{calc}}_{\mathrm{H-acceptor}}} \quad (3)$$

where $\mathrm{sf}_{\mathrm{H-donor}}$ and $\mathrm{sf}_{\mathrm{H-acceptor}}$ are scale factors derived from calculated and reference ZPVEs for the monomers (i.e., the H-donor and H-acceptor), whereas $\mathrm{sf}_{\mathrm{complex}}$ is the scale factor to be applied to the calculated ZPVE of the complex. $\mathrm{ZPVE}^{\mathrm{calc}}_{\mathrm{H-donor}}$ and $\mathrm{ZPVE}^{\mathrm{calc}}_{\mathrm{H-acceptor}}$ are the ZPVEs for the monomers, obtained at either the MP2/6-311+G(3df,2p) or B3-LYP/6-311+G(3df,2p) level of theory. $\mathrm{ZPVE}^{\mathrm{ref}}_{\mathrm{H-donor}}$ and $\mathrm{ZPVE}^{\mathrm{ref}}_{\mathrm{H-acceptor}}$ represent reference ZPVEs obtained, unless otherwise noted, from spectroscopic constants or high-level calculations of the anharmonic force field.[39] We note that the scale factor for the complex derived using our approach is exact in the limit of infinitely separated monomers. The final binding energy thus derived is referred to as D_0, and corresponds to the binding energy at 0 K.

Total energies, BSSE corrections, ZPVEs and corresponding scale factors for the monomers and complexes used to calculate the binding energies D_e and D_0 are summarized in the Supporting Information (Tables S1−S4). GAUSSIAN 98 archive entries for B3-LYP and MP2 optimized structures are presented in Tables S5 and S6, respectively.

Results and Discussion

Assessment of Theoretical Procedures. In a previous study,[7] we examined the performance of a wide variety of levels of theory in describing the hydrogen-bonded complex HC≡CH···NH_3. We found that CCSD(T)/6-311+G(3df,2p)//MP2/6-311+G(3df,2p) and CCSD(T)/6-311+G(3df,2p)//B3-LYP/6-311+G(3df,2p) reproduce CCSD(T)/6-311+G(3df,2p)//CCSD(T)/6-311+G(3df,2p) results to reasonable accuracy (Table 1). However, because it is more expensive to characterize MP2 than B3-LYP potential surfaces, the latter is more suitable for application to large systems.

To verify whether the same conclusions carry over to weaker hydrogen-bonded complexes, we present additional calculations here on the C_{3v}-symmetric H_3C−H···NH_3 and HC≡CH···CH_4 complexes (Table 1). The former system is included in the assessment calculations because of its close relationship with other weakly hydrogen-bonded systems discussed in the present work, as well as the computational benefits of its small size.

We optimized the geometries of the H_3C−H···NH_3 and HC≡CH···CH_4 complexes at the CCSD(T) level in order to provide benchmark results for comparison (Table 1).[40] For both systems, the MP2 and CCSD(T) geometries are in uniformly close agreement. The B3-LYP r(C−H) distances are also in good agreement with CCSD(T). There are slightly larger differences between the B3-LYP and CCSD(T) C≡C bond lengths, and greater discrepancies exist between B3-LYP and CCSD(T) r(H···X) distances, where B3-LYP tends to overestimate the lengths. These latter discrepancies increase for weaker complexes. For example, for the weakly bound acetylene−methane complex (for which D_e is approximately 2 kJ mol^{-1}), the B3-LYP r(H···X) intermolecular distance is roughly 0.4 Å (or equivalently 15%) longer than that calculated with either CCSD(T) or MP2.

Our CCSD(T) calculations indicate that, in cases where MP2 and B3-LYP geometries differ significantly, the MP2 geometries are likely to be more reliable. This is in agreement with early findings of Del Bene and co-workers.[41] However, there is a wide range of literature which has shown the success of density functional theory (DFT) in reliably describing the geometries of hydrogen-bonded complexes (see, for example, refs 7, 16 and 42). Although cautionary remarks have been made regarding the application of DFT to hydrogen-bonded systems,[43,44] the general conclusion is that DFT, and B3-LYP in particular, is a reasonably reliable alternative to describe the geometry of large hydrogen-bonded complexes when MP2 results are unreachable.[42g] Our results support this general conclusion.

Even where there are discrepancies between B3-LYP and MP2 geometries, the CCSD(T) binding energies calculated with the B3-LYP and MP2 geometries differ only slightly, mainly because the potential surfaces in the vicinity of the minimum energy structures are extremely flat. The CCSD(T)//MP2 and CCSD(T)//CCSD(T) binding energies are in close agreement for all complexes considered in our assessment study (Table

TABLE 2: Selected MP2 and B3-LYP (in parentheses) Structural Parameters and CCSD(T) BSSEs and Binding Energies (D_e and D_0, Including BSSE) for C−H···X Hydrogen-Bonded Complexes Involving Acetylene and First- and Second-Row Hydrides[a]

	r(C−H)	r(H···X)	r(C···X)	∠(C−H···X)	symmetry	BSSE	D_e	D_0
monomer								
HC≡CH	1.061				$D_{\infty h}$			
	(1.062)							
acetylene complex								
CH_4	1.062	2.724	3.786	180.0	C_{3v}	0.8	2.4	0.3
	(1.063)	(3.131)	(4.194)	(180.0)		(0.4)	(2.1)	(1.2)
NH_3[b]	1.070	2.275	3.345	180.0	C_{3v}	2.1	14.0	9.2
	(1.072)	(2.308)	(3.380)	(180.0)		(2.0)	(14.1)	(9.3)
OH_2[c]	1.066	2.184	3.250	177.7	C_s	2.4	11.0	6.9
	(1.068)	(2.228)	(3.295)	(178.5)		(2.3)	(11.1)	(7.1)
	1.066	2.171	3.237	180.0	C_{2v}	2.3	11.1	7.7
	(1.068)	(2.221)	(3.288)	(180.0)		(2.1)	(11.2)	(8.1)
FH	1.063	2.292	3.336	166.9	C_s	1.3	6.4	3.9
	(1.065)	(2.293)	(3.340)	(167.2)		(1.3)	(6.4)	(3.9)
PH_3	1.064	2.967	4.031	180.0	C_{3v}	1.5	4.9	2.5
	(1.065)	(3.098)	(4.163)	(180.0)		(1.3)	(4.9)	(2.7)
SH_2	1.064	2.837	3.901	179.0	C_s	2.0	5.4	2.5
	(1.065)	(2.958)	(4.022)	(176.7)		(1.8)	(5.6)	(2.8)
ClH	1.062	2.807	3.839	163.8	C_s	2.3	3.4	1.6
	(1.064)	(2.991)	(4.024)	(164.1)		(2.0)	(3.6)	(1.7)

[a] Bond lengths are given in Å, energies in kJ mol^{-1}. The 6-311+G(3df,2p) basis set is used throughout. [b] Ref 7. [c] The C_s and C_{2v} structures are displayed in Figures 1c and 1d, respectively.

TABLE 3: Selected MP2 and B3-LYP (in parentheses) Structural Parameters and CCSD(T) BSSEs and Binding Energies (D_e and D_0, Including BSSE) for C−H···X Hydrogen-Bonded Complexes Involving Ethylene and First- and Second-Row Hydrides[a]

		r(C−H)	r(H···X)	r(C···X)	∠(C−H···X)	symmetry	BSSE	D_e	D_0
monomer									
$H_2C{=}CH_2$		1.079				D_{2h}			
		(1.083)							
ethylene complex									
NH_3[b]	(s)	1.081	2.608	3.680	171.3	C_s	1.2	4.9	2.1
		(1.084)	(2.740)	(3.824)	(179.2)		(1.0)	(4.9)	(1.9)
	(e)	1.081	2.608	3.688	178.9	C_s	1.2	4.9	2.1
		(1.084)	(2.741)	(3.824)	(179.2)		(1.0)	(4.9)	(1.6)
OH_2		1.080	2.454	3.533	177.9	C_s	1.4	4.2	1.5
		(1.083)	(2.596)	(3.679)	(178.8)		(1.1)	(4.3)	(1.7)
PH_3[b]	(s)	1.080	3.268	4.347	177.6	C_1	1.1	2.1	0.9
		(1.083)	(3.627)	(4.704)	(179.5)		(0.8)	(2.0)	(0.4)
	(e)	1.080	3.275	4.353	176.6	C_s	1.0	2.1	0.9
		(1.083)	(3.630)	(4.713)	(178.6)		(0.8)	(2.0)	(0.7)
SH_2		1.080	3.187	4.265	177.1	C_s	1.4	2.3	0.6
		(1.083)	(3.399)	(4.482)	(178.3)		(1.2)	(2.4)	(0.1)
ClH		(1.083)	(3.423)	(4.506)	(179.3)	C_s	(1.2)	(1.5)	(0.3)

[a] Bond lengths are given in Å, energies in kJ mol^{-1}. The 6-311+G(3df,2p) basis set is used throughout. [b] (s) refers to the staggered, (e) to the eclipsed conformer with respect to the C=C double bond. See Figure 2a, 2b, 2d and 2e.

1). The D_e values calculated with CCSD(T)//B3-LYP are also generally in good agreement with the CCSD(T)//CCSD(T) results, but there are small differences for the weakest complexes. The relative insensitivity to geometry of binding energies for weak hydrogen-bonded complexes has been previously noted in studies of the binding between substituted methanes and either water[19a] or ammonia.[6p]

The general importance of including BSSE corrections in calculated binding energies has been well documented in the literature.[4e,7,45] Recent studies show that BSSE-corrected binding energies converge more smoothly and systematically toward well-defined limits compared with uncorrected binding energies.[45d,46] Additionally, more rapid convergence is obtained with the BSSE-corrected values.[7,45d,46] For example, the difference between CCSD(T)/6-31+G(d) and CCSD(T)/6-311+G-(3df,2p) binding energies for the acetylene-ammonia complex decreases from 5.2 kJ mol^{-1} to 1.5 kJ mol^{-1} upon inclusion of the BSSE correction.[7]

Here, we find improved agreement between CCSD(T) binding energies calculated with the MP2 and B3-LYP geometries once the BSSE is incorporated. For example, the difference in the CCSD(T)/6-311+G(3df,2p) binding energies obtained from B3-LYP and MP2 structures of the HC≡CH···CH_4 complex is reduced from 0.7 to 0.3 kJ mol^{-1} upon inclusion of the BSSE correction. We also note that the CCSD(T) BSSE correction is larger for MP2 geometries than for B3-LYP geometries.

To examine the generality of the above conclusions, we have optimized all complexes with both MP2 and B3-LYP (Tables 2−4). The differences between the geometries predicted by the two levels of theory are generally small, but tend to increase in relative magnitude with a decrease in the binding energy. For the majority of our complexes, the B3-LYP r(H···X) distances are less than 10% longer than the MP2 results. However, for some of the most weakly bound complexes investigated in the present study (i.e., $D_e < 1$ kJ mol^{-1}), there are discrepancies of up to 15%. In these instances, a closer examination of the potential-energy surface reveals that the B3-LYP surface is particularly flat with respect to the r(H···X) intermolecular parameter compared with the MP2 surface.

It is noteworthy that for the majority of the complexes investigated, the differences between the CCSD(T)//B3-LYP and CCSD(T)//MP2 binding energies D_e are less than 0.1 kJ mol^{-1}

TABLE 4: Selected MP2 and B3-LYP (in parentheses) Structural Parameters and CCSD(T) BSSEs and Binding Energies (D_e and D_0, Including BSSE) for the $H_3C-CH_3\cdots NH_3$ and $H_3C-CH_3\cdots OH_2$ Complexes[a]

		r(C−H)	r(H···X)	r(C···X)	∠(C−H···X)	symmetry	BSSE	D_e	D_0
monomer									
H_3C-CH_3		1.087	1.087			D_{3d}			
		(1.091)							
ethane complex									
NH_3[b]	(s)	1.087	2.809	3.896	180.0	C_s	0.9	2.6	0.9
		(1.091)	(3.076)	(4.166)	(179.0)		(0.7)	(2.5)	(0.5)
	(e)	1.087	2.798	3.884	177.1	C_1	0.9	2.6	1.0
		(1.091)	(3.030)	(4.120)	(177.7)		(0.7)	(2.5)	(0.2)
OH_2		1.087	2.667	3.738	168.3	C_s	1.3	2.1	0.3
		(1.090)	(2.892)	(3.968)	(169.2)		(1.0)	(2.1)	(0.1)

[a] Bond lengths are given in Å, energies in kJ mol-1. The 6-311+G(3df,2p) basis set is used throughout. [b] (s) refers to the staggered, (e) to the eclipsed conformer of $H_3C-CH_3\cdots NH_3$ dimer with respect to the C···N bond, see Figures 3a and 3b.

(Tables 2−4). Exceptions to this general trend include the $HC\equiv CH\cdots CH_4$, $HC\equiv CH\cdots SH_2$, and $HC\equiv CH\cdots ClH$ complexes, where the corresponding differences are 0.3, 0.2, and 0.2 kJ mol^{-1}, respectively. Furthermore, we note that the inclusion of the BSSE correction is particularly important for complexes with very weak C−H···X hydrogen bonds, for which the BSSE may contribute up to 44% of the raw complexation energy. As found also for our test systems above, the CCSD(T) BSSE corrections are generally slightly larger when calculated with MP2 geometries than with B3-LYP geometries.

Another possible source for discrepancies between results from different computational methods is the zero-point vibrational energy contribution for complex formation. We previously found that the scaled B3-LYP and MP2 ZPVE corrections for the binding energy of the acetylene-ammonia complex are in close agreement.[7] This conclusion supports the reliability of our approximate procedure to obtain suitable scaling factors. For the range of hydrogen-bonded systems investigated in the present work, the scaled MP2 and B3-LYP ZPVE corrections are also in good general agreement, with a mean absolute deviation of 0.3 kJ mol^{-1}.[47] Although B3-LYP has been found to be more reliable than MP2 for vibrational frequency (and hence ZPVE) predictions for normal molecules,[48] it is not clear whether this would carry over to weak hydrogen-bonded complexes, particularly given the better performance of MP2 in the geometry predictions. In addition, an appropriate higher-level assessment of this issue is currently computationally too demanding. Therefore, the CCSD(T) binding energies reported in the present work are corrected using the ZPVE obtained at the same level of theory (i.e., MP2 or B3-LYP) as used in the geometry optimization procedure.

For simplicity, unless otherwise noted, results within the remainder of the text are those based on MP2 geometries, whereas the B3-LYP data are included in the tables for comparative purposes.

Structures and Energies of the Complexes: General Comments. The effect of complex formation on the structures of the monomers is found to be relatively small (Tables 2−4). The largest changes occur for the bond lengths of the donor C−H group (r(C−H) is lengthened by up to 0.009 Å) and for the acetylene C≡C triple bond (r(C≡C) is lengthened by up to 0.002 Å), and are found for complexes of acetylene with either NH_3 or OH_2 acting as the proton acceptor. Very small changes in the intramolecular parameters of the hydrogen-bond donors are calculated for the weaker complexes between acetylene and, for example CH_4 or ClH, they are further reduced for the complexes between ethylene and the various acceptors, especially with second-row hydrides, and they are negligible for the ethane complexes. The parameters of the proton-acceptor groups do not change significantly in any of the complexes.[49]

Attention in the following discussion is focused on the intermolecular contact distance r(H···X) between hydrogen and the proton acceptor X and the r(C···X) distance between the donor carbon and the acceptor X. The r(C−H) distance and the ∠(C−H···X) angle, which represents a measure of the linearity or nonlinearity of the hydrogen bond, will also be discussed where appropriate. Complete details regarding the geometries obtained for the monomers and complexes examined in our work are presented in the Supporting Information (Tables S5−S6).

D_e values obtained for the various complexes, including the BSSE correction, lie in the range 2.1 to 14.0 kJ mol^{-1}. Further consideration of ZPVE contributions leads to D_0 values between 0.3 and 9.2 kJ mol^{-1}. Although these binding energies fall away quickly with less acidic proton donors and second-row hydrides, all of the complexes examined show an attractive interaction.

HC≡CH as the Proton Donor. Selected structural parameters and binding energies of C−H···X hydrogen-bonded complexes of the general type HC≡CH···X, where X = CH_4, NH_3, OH_2, FH, PH_3, SH_2, and ClH (Figure 1), are summarized in Table 2. Our calculations indicate that the intermolecular contact distances r(H···X) are either significantly smaller than (X = NH_3, OH_2, FH) or very close to (X = CH_4, PH_3, SH_2, ClH) the sum of the van der Waals radii of hydrogen and the proton acceptor.[50] However, comparison of the C···X separations[51] leads to a less clear-cut picture in this regard, the calculated distances r(C···X) being very close to (X = NH_3, OH_2, FH) or even larger than (X = CH_4, PH_3, SH_2, ClH) the sum of the corresponding van der Waals radii.[50]

Another interesting feature, which was emphasized 30 years ago by Schuster[52] for hydrogen bonds in general and by Bonchev and Cremaschi[2b] for C−H···X hydrogen bonds in particular, is the absence of a relationship between the contact distance r(H···X) and the binding energies D_e and D_0. Our calculations show that within a row of proton acceptors (i.e., X = NH_3, OH_2, FH or PH_3, SH_2, ClH), the shortest contact distance does not necessarily result in the greatest binding energy.

Our results support the view that an assignment of the existence of a hydrogen bond that relies only on estimated geometrical cutoff criteria like van der Waals radii or is solely focused on intermolecular contact distances is not sufficient and somewhat misleading.[53] On the other hand, we find that the lengthening of the donor C−H bond correlates nicely with the binding energies, at least in the HC≡CH···X systems.

$HC\equiv CH\cdots CH_4$. Because of the lack of a lone pair of electrons, it might seem somewhat unusual to consider CH_4 as a potential proton acceptor involved in hydrogen bonds. However, previous spectroscopic and theoretical examinations clearly show that, provided the acidity of the proton donor is sufficiently high, there is a definite propensity of CH_4 in

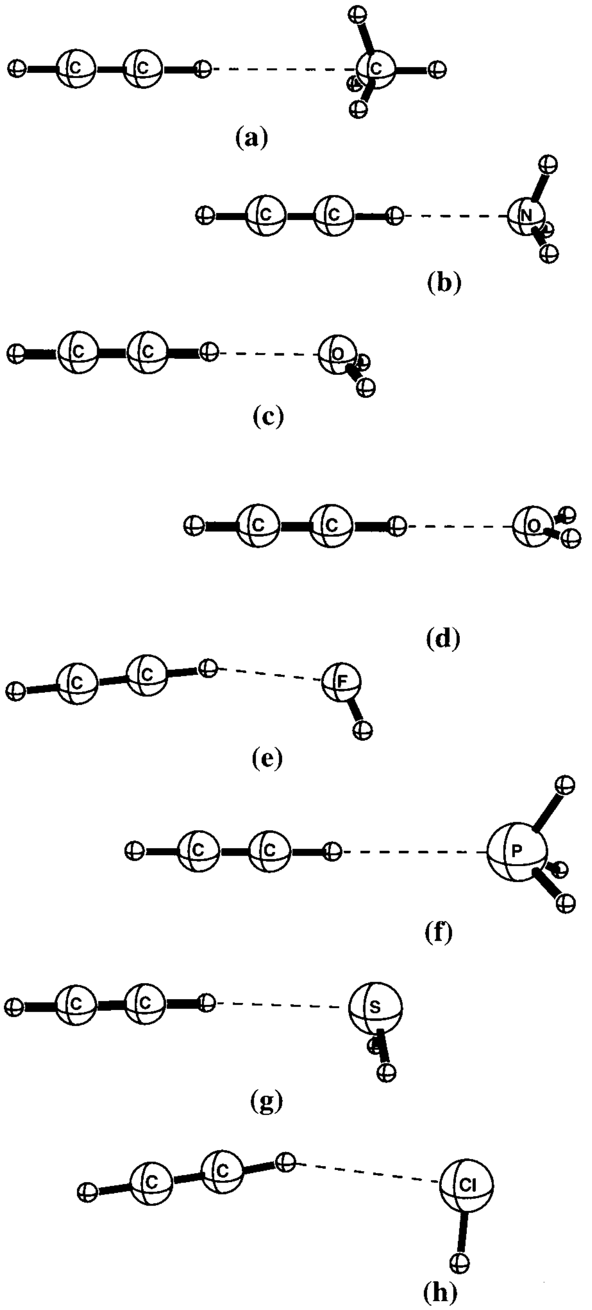

Figure 1. Structures obtained at the MP2/6-311+G(3df,2p) level of theory for C−H···X hydrogen-bonded dimers of the general type HC≡CH···X, where X = CH_4, NH_3, OH_2, FH, PH_3, SH_2, and ClH.

particular,[29,30] as well as sp^3-hybridized carbon in general,[31,32] to act as a proton acceptor in such situations.

The lowest energy configuration found for the HC≡CH···CH_4 complex has C_{3v} symmetry (Figure 1a). The intermolecular distances r(H···C) and r(C···C) are 2.724 and 3.786 Å, respectively. The latter distance is slightly longer (by approximately 0.02−0.05 Å) than the corresponding values reported for the closely related N≡CH···CH_4 complex.[29,30] As noted above, the B3-LYP hydrogen-bond length for HC≡CH···CH_4 differs from the MP2 value by more than 0.4 Å. Our calculated binding energy D_0 is just 0.3 kJ mol^{-1}. Nguyen et al. reported D_0 values for the N≡CH···CH_4 complex that varied between 3 and 4 kJ mol^{-1} (without BSSE corrections), depending on the level of theory used.[30] The greater binding energy in the latter is consistent with the greater acidity of HC≡N compared with HC≡CH.

HC≡CH···NH_3. We have reported detailed results for this complex in a study of the levels of theory required to reliably describe hydrogen-bonded systems.[7] The most stable equilibrium geometry for the HC≡CH···NH_3 complex has C_{3v} symmetry (Figure 1b). Our MP2/6-311+G(3df,2p) calculations predict the intermolecular distances r(H···N) and r(C···N) to be 2.275 and 3.345 Å, respectively. On the basis of microwave spectra, Klemperer et al.[8] reported a vibrationally averaged value of 2.333 Å, which is in reasonable agreement with our calculated value, as is a previous high-level theoretical estimate of 2.301 Å.[9] The observed infrared photodissociation of the HC≡CH···NH_3 complex suggested that the binding energy D_0 is less than 11.7 kJ mol^{-1}.[10] Our estimate of 9.2 kJ mol^{-1} is consistent with this upper limit. Frisch, Pople, and Del Bene[11] reported a binding energy from their ab initio calculations of 15.1 kJ mol^{-1}. They also predicted that the use of larger basis sets in their calculations will lower this binding energy to 12.6 kJ mol^{-1}, which is still somewhat higher than our present result.

HC≡CH···OH_2. We have examined two C−H···O hydrogen-bonded structures of the HC≡CH···OH_2 complex, corresponding to nonplanar C_s- and planar C_{2v}-symmetric forms.[54] At the CCSD(T)/6-311+G(3df,2p)//MP2/6-311+G(3df,2p) level, these two structures are very close in energy.[55] We find that inclusion of the ZPVE correction can alter the energetic ordering of these systems, preferentially favoring the C_{2v} structure. Likewise, Turi and Dannenberg[14] have reported that the potential minima with and without the BSSE correction can be different on a flat potential energy surface.[56] In accord with previous studies,[14,15] we take the planar C_{2v}-symmetric structure as the more suitable description.[57] The binding energy D_0 of this HC≡CH···OH_2 complex is 7.7 kJ mol^{-1}, which is consistent with previously computed binding energies,[14−16] but falls slightly below the experimentally estimated range of 8.4 to 12.6 kJ mol^{-1}.[17]

HC≡CH···FH. The spectroscopically observed structure of the complex between HC≡CH and HF is T-shaped, with HF acting as a proton donor toward the C≡C triple bond.[22] Although no experimental evidence for the corresponding C−H···F hydrogen-bonded complex is available, it is of interest to examine this complex for comparative reasons to help establish characteristic trends among C−H···X hydrogen-bonded complexes between acetylene and first-row hydrides. The structure thus obtained (Figure 1e) has C_s symmetry and represents a local minimum on the potential energy surface.[58] The intermolecular r(H···F) and r(C···F) distances are 2.292 and 3.336 Å, respectively. We note that the angle between the C−H bond in the donor and the H···F hydrogen bond in this complex (166.9°) deviates significantly from collinearity. The binding energy D_0 is 3.9 kJ mol^{-1}, which is significantly less than the D_0 values for the analogous complexes involving NH_3 and H_2O, indicating a decreased tendency to form C−H···X hydrogen bonds along this series of first-row hydrides. This trend correlates nicely with the relative proton affinities of the acceptor groups.

HC≡CH···PH_3. The structure for the HC≡CH···PH_3 complex is shown in Figure 1f. It has C_{3v} symmetry and intermolecular distances r(H···P) and r(C···P) of 2.967 and 4.031 Å, respectively. The binding energy D_0 for HC≡CH···PH_3 is 2.5 kJ mol^{-1}, which is considerably smaller than for the corresponding complexes involving the first-row hydrides NH_3, H_2O, or HF as proton acceptors. In this respect, it is interesting to note that although the proton affinity of PH_3 is greater than the proton affinities of H_2O or HF,[59] this does not translate here to a stronger hydrogen bond.[60]

HC≡CH···SH$_2$. The energetically most favorable structure found for the HC≡CH···SH$_2$ complex has C_s symmetry (Figure 1g). The structure is distorted from planarity significantly more (by approximately 45°) than the HC≡CH···OH$_2$ complex, as expected on the basis of the narrower bond angles and greater degree of pyramidality at the trivalent sulfur. The intermolecular distances r(H···S) and r(C···S) are 2.837 and 3.901 Å, respectively, which are slightly shorter than the corresponding values found for HC≡CH···PH$_3$ (2.967 and 4.031 Å), but the D_0 value is virtually the same as that for HC≡CH···PH$_3$. We note, however, that the binding energy without ZPVE contributions (D_e) is 0.5 kJ mol^{-1} greater for HC≡CH···SH$_2$ than for HC≡CH···PH$_3$.

HC≡CH···ClH. There is no experimental evidence for the existence of a C−H···Cl hydrogen-bonded complex of the type HC≡CH···ClH, and experimental observations have only been reported for a C_{2v}-symmetric, T-shaped Cl−H···π complex.[23] The C−H···Cl complex (Figure 1 h) nevertheless represents a local minimum on the potential surface.[61] It has C_s symmetry and intermolecular distances r(H···Cl) and r(C···Cl) of 2.807 and 3.839 Å, respectively. As is the case for HC≡CH···FH, the angle between the C−H and H···Cl bonds deviates significantly (by 16.2°) from a collinear arrangement. The weak nature of the C−H···Cl interaction is reflected in the binding energies D_e and D_0, which are calculated to be 3.4 and 1.6 kJ mol^{-1}, respectively. These values are smaller than the corresponding values obtained for the analogous complex involving HF, in contrast to the respective proton affinities.

H$_2$C=CH$_2$ as the Proton Donor. Changing the proton donor from an acetylenic sp-hybridized C−H bond to an ethylenic sp^2-hydridized C−H bond results in significantly reduced binding energies and longer intermolecular r(H···X) and r(C···X) distances. The results obtained for complexes of the general type H$_2$C=CH$_2$···X, where X = NH$_3$, OH$_2$, FH, PH$_3$, SH$_2$ and ClH (Figure 2) are shown in Table 3. The trends observed for the hydrogen-bonded complexes involving acetylene generally also hold for the complexes involving ethylene as the proton donor. Thus, the lengthening of the donor C−H bonds upon complex formation correlates with the binding energy, and the shortest r(H···X) and r(C···X) distances within a row are observed for complexes involving group VIA elements as proton acceptors. However, the effects are less pronounced for C−H···X hydrogen bonds having ethylene as the donor than they are for complexes involving acetylene due to the relative magnitudes of the binding energies. The intermolecular contact distances r(H···X) are very close to the corresponding sums of the van der Waals radii, whereas the r(C···X) separations are significantly larger.[50]

H$_2$C=CH$_2$···NH$_3$. The energetically most favorable structures found for the H$_2$C=CH$_2$···NH$_3$ complex have C_s symmetry (Figures 2a and 2b). They correspond to staggered (Figure 2a) and eclipsed (Figure 2b) orientations of the N−H bonds of NH$_3$ with respect to the C=C double bond. The energy difference between the two conformers is, however, negligible, as are the differences in the structural parameters. We therefore focus our discussion only on the staggered conformer. The intermolecular distances r(H···N) and r(C···N) are 2.608 and 3.680 Å, respectively, considerably larger than the corresponding values obtained for the analogous acetylene complex (2.275 and 3.345 Å). The binding energy D_0 is calculated to be only 2.1 kJ mol^{-1}, which is considerably lower than the binding energy of HC≡CH···NH$_3$ by 7.1 kJ mol^{-1}. This reflects the strong dependence of the hydrogen-bond strength on the nature of the C−H donor group.

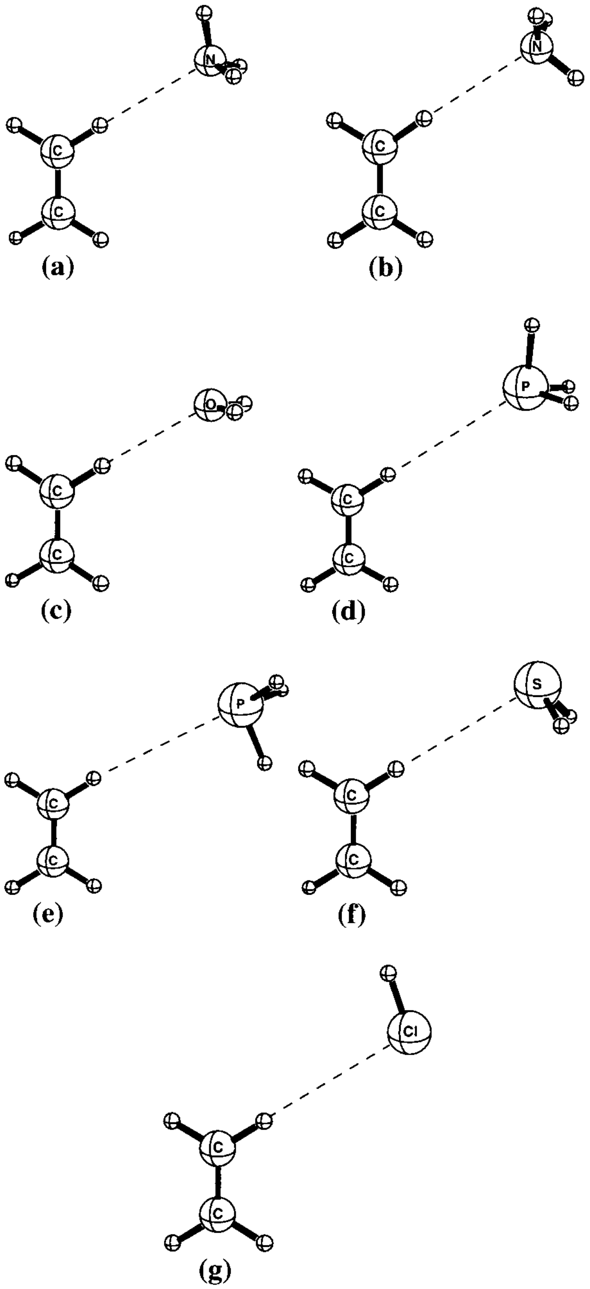

Figure 2. Structures obtained at the MP2/6-311+G(3df,2p) level of theory for C−H···X hydrogen-bonded dimers of the general type H$_2$C=CH$_2$···X, where X = NH$_3$, OH$_2$, PH$_3$, and SH$_2$, and at the B3-LYP/6-311+G(3df,2p) level of theory for H$_2$C=CH$_2$···ClH.

H$_2$C=CH$_2$···OH$_2$. Although the only experimentally observed complex is a T-shaped O−H···π hydrogen-bonded complex,[24] we consider the corresponding C−H···O hydrogen-bonded species (Figure 2c) for comparative reasons.[62] The separations r(H···O) and r(C···O) between the monomers are 2.454 and 3.533 Å, which are shorter (by approximately 0.15 Å) than the corresponding distances in H$_2$C=CH$_2$···NH$_3$. The binding energy D_0 for the H$_2$C=CH$_2$···OH$_2$ complex is 1.5 kJ mol^{-1}. The shortening of r(H···X), and the decrease in the binding energies (by 0.6 kJ mol^{-1}), on going from H$_2$C=CH$_2$···NH$_3$ to H$_2$C=CH$_2$···OH$_2$ are consistent with the trends observed for the corresponding acetylene complexes.

H$_2$C=CH$_2$···FH. We were not able to locate a local minimum on the potential energy surface corresponding to a C−H···F hydrogen-bonded H$_2$C=CH$_2$···FH complex. Although structures of this type were found, they invariably turned out to represent transition structures (first-order saddle points). The unique imaginary frequencies for these structures are non-negligible and the eigenvectors associated with these vibrational modes lead to the more favorable π-complex in which FH acts as a proton donor and the acetylenic triple-bond as a proton-acceptor.[63]

$H_2C{=}CH_2{\cdots}X$, where X = PH_3, SH_2, and ClH. All the complexes involved in this series (Figure 2d−2g) have binding energies D_0 of less than 1.0 kJ mol^{-1}. Because of the weak nature of the binding in these systems, they show some of the largest deviations between the MP2 and B3-LYP potential-energy surfaces. For example, the intermolecular distances r(H$\cdots$P) and r(C$\cdots$P) for both the staggered and the eclipsed conformers of the $H_2C{=}CH_2{\cdots}PH_3$ complex are calculated to be roughly 0.35 Å longer with B3-LYP than with MP2. This is analogous to the situation discussed for the $HC{\equiv}CH{\cdots}CH_4$ complex (see above), for which comparisons with CCSD(T) results suggest that the MP2 geometry is likely to be more accurate.

The B3-LYP and MP2 geometries for the $H_2C{=}CH_2{\cdots}SH_2$ complex lie closer together than for the $H_2C{=}CH_2{\cdots}PH_3$ complex. The B3-LYP r(H$\cdots$X) distance is approximately 6% longer than the MP2 result in the former compared with a 12% difference in the latter. Importantly, the trends found when PH_3 is replaced by SH_2 as the proton acceptor are consistent at both levels of theory. More specifically, the $H_2C{=}CH_2{\cdots}SH_2$ complex has shorter r(H$\cdots$X) and r(C$\cdots$X) distances but also a smaller binding energy (by 0.3 kJ mol^{-1}).

In a manner similar to the $H_2C{=}CH_2{\cdots}FH$ situation, we were not able to locate a local minimum on the MP2 potential-energy surface corresponding to a C−H$\cdots$Cl hydrogen-bonded $H_2C{=}CH_2{\cdots}ClH$ complex.[64] Interestingly, in contrast to the MP2 surface for $H_2C{=}CH_2{\cdots}ClH$ and both the MP2 and the B3-LYP results for the lighter homologue $H_2C{=}CH_2{\cdots}FH$, a local minimum can be located on the B3-LYP potential energy surface for $H_2C{=}CH_2{\cdots}ClH$ that has a C−H$\cdots$Cl interaction. The intermolecular r(H$\cdots$Cl) and r(C$\cdot\cdot$Cl) distances for this B3-LYP complex are 3.423 and 4.506 Å, and the binding energy is 0.3 kJ mol^{-1}. The difference in behavior between MP2 and B3-LYP for this system is associated with a change in the nature of the lowest-energy vibrational mode at the B3-LYP level compared with MP2.[65]

The differences that we find between the MP2 and B3-LYP surfaces illustrate the delicate nature of C−H$\cdots$X interactions. Furthermore, the results emphasize that caution must be exercised when MP2 and B3-LYP differ significantly. Although B3-LYP appears to work well for most hydrogen-bonded systems, and even for some very weak interactions, complications can arise in the description of extremely weakly bound complexes (i.e., $D_0 < 1$ kJ mol^{-1}).

$H_3C{-}CH_3$ as the Proton Donor. Selected structural parameters and binding energies for the complexes of the general type $H_3C{-}CH_3{\cdots}X$, where X = NH_3 or OH_2, are summarized in Table 4. The calculated structures of the most stable conformers are displayed in Figure 3. Previous ab initio studies of C−H$\cdots$X hydrogen-bonded complexes involving sp^3-hybridized carbon as the hydrogen donor have shown BSSE-corrected equilibrium binding energies D_e between 1.2 and 3.5 kJ mol^{-1}.[18−20] The present results also indicate that an sp^3-hybridized C−H bond can act as a proton donor in appropriate C−H$\cdots$X hydrogen-bonded species. We also note the continuing significant decrease in D_0 as we go from complexes with acetylene, to those with ethylene and ethane.

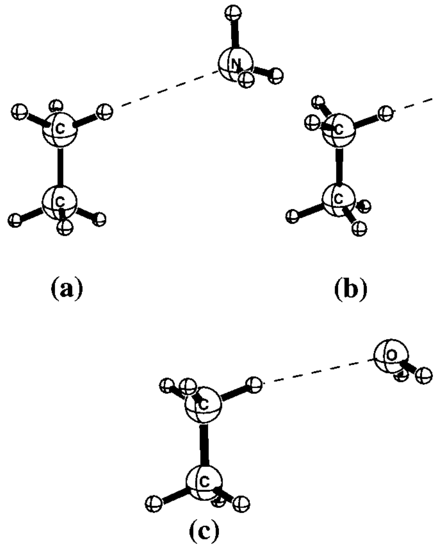

Figure 3. Structures obtained at the MP2/6-311+G(3df,2p) level of theory for the C−H$\cdots$X hydrogen-bonded dimers $H_3C{-}CH_3{\cdots}NH_3$ and $H_3C{-}CH_3{\cdots}OH_2$.

An intriguing result for the ethane complexes is that the change in the r(C−H) bond length is negative in sign, that is, there is a very small *contraction* in the C−H bond of the donor group as a result of complex formation. A larger contraction is calculated for the ethane complex with OH_2 (0.0005 Å at MP2 and 0.0007 Å at B3-LYP) than the complex with NH_3 (0.0001 Å at MP2 and 0.0006 Å at B3-LYP for both the staggered and the eclipsed conformers). We also note that the contraction is calculated to be larger with B3-LYP than MP2. Although the bond length contractions are extremely small, it is nevertheless surprising that the bond lengths shorten at all given that hydrogen bonding is normally associated with an elongation of the bond to hydrogen in the proton-donor molecule. Similar contractions in the C−H bond length in other C−H$\cdots$O and also C−H$\cdots\pi$ hydrogen-bonded systems have been observed recently by Hobza et al.,[66] who referred to the phenomenon as "anti-hydrogen bonding". However, Scheiner et al. in two very thorough studies of $F_nH_{3-n}C{-}H{\cdots}O$[19a] and $F_nH_{3-n}C{-}H{\cdots}N$[6p] (n = 1−3) systems conclude that there is no fundamental distinction between such C−H$\cdots$X hydrogen-bonded systems and conventional hydrogen-bonded systems. Therefore, on the basis of a variety of features including geometries, energetics, vibrational spectra, and charge redistributions, Scheiner et al. categorized these as true hydrogen bonds.[6p,19a] However, more recent calculations of NMR chemical shieldings by the same group are less conclusive.[19b]

$H_3C{-}CH_3{\cdots}NH_3$. Two conformers of the ethane−ammonia complex, representing staggered and eclipsed conformers with respect to the C−C bond, were investigated in the present work (Figure 3a and 3b, respectively). The calculated contact distances r(H$\cdots$N) of the two subunits are 2.809 and 2.798 Å, respectively. The r(C$\cdots$N) distances are 3.896 and 3.884 Å, respectively. The binding energies D_0 for the two conformers are calculated to be just 0.9 and 1.0 kJ mol^{-1}, which is in accord with the general trends for the stability of C−H$\cdots$X hydrogen-bonded complexes studied in this work.

$H_3C{-}CH_3{\cdots}OH_2$. The energetically most favorable structure for the $H_3C{-}CH_3{\cdots}OH_2$ complex is shown in Figure 3c. It has C_s symmetry and intermolecular r(H$\cdots$O) and r(C$\cdots$O) distances of 2.667 and 3.738 Å, respectively. These separations are approximately 5% shorter than the corresponding values for the $H_3C{-}CH_3{\cdots}NH_3$ conformers and consistent with the trends found earlier for the analogous acetylene and ethylene complexes. Our estimate for the binding energy D_0 of the $H_3C-CH_3 \cdots OH_2$ complex is very small (0.3 kJ mol^{-1}). The decrease in the binding energy with ethane when NH_3 is replaced by OH_2 as the proton acceptor (0.6−0.7 kJ mol^{-1}) parallels the reductions found for the corresponding ethylene complexes (0.6 kJ mol^{-1}) and acetylene complexes (1.5 kJ mol^{-1}).

Concluding Remarks

We have investigated the relative binding energies for a series of C−H···X hydrogen-bonded complexes involving acetylene, ethylene, and ethane as proton donors and the first- and second-row hydrides as proton acceptors. The CCSD(T) binding energies obtained using MP2 and B3-LYP geometries are in reasonable agreement for all structures. However, we note that discrepancies between the two geometries can arise for particularly weakly bound systems (i.e., $D_e < 1$ kJ mol^{-1}). CCSD(T) data for the $HC{\equiv}CH \cdots CH_4$ complex suggest that in instances where significant differences arise between the MP2 and B3-LYP (intermolecular) parameters, the MP2 geometries are likely to be more reliable. Nevertheless, the performance of MP2 and B3-LYP is comparable for most complexes in the present study, including some weakly bound systems. Therefore, we conclude that B3-LYP would generally be a suitable alternative to MP2 for large hydrogen-bonded systems.

The CCSD(T) binding energies are relatively insensitive to the intermolecular geometrical parameters due to the flat potential energy surfaces associated with these complexes. They, therefore, do not generally change significantly in going from MP2 to B3-LYP geometries. However, we note that in order to estimate reasonable binding energies, incorporation of BSSE corrections is important. In this respect, even the differences between CCSD(T)//B3-LYP and CCSD(T)//MP2 binding energies are reduced upon inclusion of the BSSE correction. The BSSE is particularly important for weakly bound complexes where it can contribute a significant proportion of the overall binding energy.

Our calculations show that the C−H···X hydrogen-bond strength depends significantly on the nature of the proton-donor group. As expected, the strongest hydrogen bonds are formed with acetylene as the proton donor, those with ethylene are much weaker and those with ethane weaker still. The dependence of the binding energies on the proton-acceptor group is also significant, with NH_3 and OH_2 being considerably better proton acceptors than FH, CH_4 or any of the second-row hydrides.

The change in the donor C−H bond length upon complexation is found generally to correlate nicely with the bond strength. However, shorter contact r(H···X) distances do not necessarily result in larger binding energies. Furthermore, the use of threshold values for the assignment of C−H···X hydrogen bonds is not recommended as we find that C···X and H···X separations can be larger than the sum of their van der Waals radii. We also find that although the binding energies for complexes between acetylene and the first-row hydrides NH_3, OH_2, and FH change in accord with the relative proton affinity, this trend does not always hold when comparing complexes of different rows of the periodic table.

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Supporting Information Available: Total energies, BSSE corrections, ZPVEs, and corresponding scale factors used to calculate the binding energies D_e and D_0 (Tables S1 to S4), and GAUSSIAN 98 archive entries for the B3-LYP/6-311+G(3df,2p) (Table S5) and MP2/6-311+G(3df,2p) optimizations (Table S6) (27 pages).

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(54) A T-shaped complex (C_s symmetry) with water acting as the proton donor and involving an $O-H\cdots\pi$ rather than a $C-H\cdots O$ interaction was found to be slightly less stable than the nonplanar hydrogen-bonded complex by 3.4 kJ mol^{-1} on the BSSE-corrected CCSD(T)/6-311+G(3df,2p)//MP2/6-311+G(3df,2p) surface. The intermolecular contact distance between the donor hydrogen and the midpoint of the acetylenic triple bond is calculated to be 2.334 Å. The conversion of the $O-H\cdots\pi$ complex to the $C-H\cdots O$ complex is determined to be almost barrierless. These results are in accord with the very flat potential surface in this region (see also refs 11 and 15).

(55) The C_s-symmetric structure (Figure 1c), which has a nearly linear hydrogen bond ($\angle(C-H\cdots O) = 177.7°$), is slightly more stable (by 0.1 kJ mol^{-1}) at the CCSD(T)/6-311+G(3df,2p)//MP2/6-311+G(3df,2p) level than the planar C_{2v}-symmetric arrangement (Figure 1d).

(56) Other examples where the inclusion of BSSE has led to modified global minima have also been presented in the literature. (See, for example: (a) Hobza, P.; Havlas, Z. *Collect. Czech. Chem. Commun.* **1998**, *63*, 1343−1354 and (b) Sadlej, J.; Mazurek, P. *J. Mol. Struct.* **1995**, *337*, 129−138.) In fact, it has been shown that both the location of potential minima and the vibrational frequencies can be dependent on the inclusion of BSSE. (See, for example: (c) Bouteiller, Y.; Behrouz, H. *J. Chem. Phys.* **1992**, *96*, 6033−6038.)

(57) Although the C_{2v} form is characterized at MP2 (and B3-LYP) as a transition structure (first-order saddle point) that connects two equivalent C_s structures, after consideration of BSSE corrections the apparently higher-lying planar transition structure is stabilized to the extent that it lies 0.1 kJ mol^{-1} below the nonplanar geometry. Due to the well-documented importance of BSSE corrections, we can feel confident that the BSSE-corrected geometries are more reliable (see also refs 14 and 15). For examples of improved agreement with experiment when the BSSE-corrected potential energy surface is considered, see (a) Hobza, P.; Bludsky, O.; Suhai, S. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3073−3078 and ref 56b.

(58) The corresponding C_{2v}-symmetric T-shaped $H-F\cdots\pi$ complex is lower in energy than the C_s-symmetric $C-H\cdots F$ hydrogen-bonded complex by 5.4 kJ mol^{-1} on the BSSE-corrected surface. The bond distance between the donor hydrogen and the midpoint of the acetylenic triple bond is calculated to be 2.115 Å. The conversion of the $C-H\cdots F$ hydrogen-bonded complex into the T-shaped $H-F\cdots\pi$ complex is found to be almost barrierless.

(59) Lias, S. G.; Bartmess, J. E.; Liebman. J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data Suppl. 1* **1988**, 17.

(60) This contrasts with the binding energies for complexes involving acetylene and the first-row hydrides NH_3, H_2O, and HF, which correlate nicely with the proton affinities of the proton acceptor.

(61) The corresponding T-shaped $Cl-H\cdots\pi$ complex with C_{2v} symmetry is lower in energy than the $C-H\cdots Cl$ hydrogen-bonded complex discussed in the text by 3.0 kJ mol^{-1} on the BSSE-corrected surface. The bond distance between chlorine and the midpoint of the acetylenic triple bond is calculated to be 3.573 Å, compared with an experimental value of 3.699 Å.[23] On both the MP2/6-311+G(3df,2p) and the B3-LYP/6-311+G(3df,2p) surfaces, the conversion of the $C-H\cdots Cl$ hydrogen-bonded complex into the $Cl-H\cdots\pi$ complex is almost barrierless. Refined CCSD(T)/6-311+G(3df,2p) energy calculations predict the transition structure to lie lower in energy than the $C-H\cdots Cl$ form, suggesting again a barrierless transformation to the $Cl-H\cdots\pi$ complex.

(62) The T-shaped $O-H\cdots\pi$ complex has C_s symmetry and is lower in energy than the $C-H\cdots O$ hydrogen-bonded complex discussed in the text by 1.6 kJ mol^{-1} on the BSSE-corrected surface. The CCSD(T) binding energy for the $O-H\cdots\pi$ complex (3.1 kJ mol^{-1}) is smaller than the value estimated from experiment (6−8 kJ mol^{-1}).[24a] The bond distance between the donor hydrogen and the midpoint of the ethylenic double bond is calculated to be 2.376 Å, compared with an experimental value of 2.48 Å.

(63) The binding energy D_0 of the $F-H\cdots\pi$ complex is 9.3 kJ mol^{-1}. This complex is more stable than the transition structures that resemble $C-H\cdots F$ hydrogen-bonded complexes by approximately 11−12 kJ mol^{-1}.

(64) The CCSD(T)/6-311+G(3df,2p)//MP2/6-311+G(3df,2p) binding energy D_0 of the $Cl-H\cdots\pi$ complex is 1.2 kJ mol^{-1}. This complex is more stable than the transition structures that resemble $C-H\cdots Cl$ hydrogen-bonded complexes by approximately 5 kJ mol^{-1}. A similar energy difference between the complexes containing $Cl-H\cdots\pi$ and $C-H\cdots Cl$ interactions is obtained with CCSD(T)/6-311+G(3df,2p)//B3-LYP/6-311+G(3df,2p) (5.4 kJ mol^{-1}). However, both structures represent local minima on the B3−LYP surface.

(65) The lowest energy vibrational mode for the $H_2C{=}CH_2\cdots ClH$ complex on the B3-LYP surface is an in-plane motion dominated by changes in the $C-H\cdots Cl$ hydrogen-bond angle. In contrast, the lowest energy vibrational mode on the MP2 surface of $H_2C{=}CH_2\cdots ClH$, as well as on the MP2 and B3-LYP surfaces of $H_2C{=}CH_2\cdots FH$, are dominated by the displacement of hydrogen in the proton acceptor out of the molecular plane.

(66) (a) Hobza, P.; Spirko, V.; Selzle, H. L.; Schlag, E. W. *J. Phys. Chem. A* **1998**, *102*, 2501−2504. (b) Hobza, P.; Spirko, V.; Havlas, Z.; Buchhold, K.; Reimann, B.; Barth, H.-D.; Brutschy, B. *Chem. Phys. Lett.* **1999**, *299*, 180−186. (c) Cubero, E.; Orozco, M.; Hobza, P.; Luque, F. J. *J. Phys. Chem. A* **1999**, *103*, 6394−6401. (d) Hobza, P.; Havlas, Z. *Chem. Phys. Lett.* **1999**, *303*, 447−452.