Theoretical Study of $(CH\cdots C)^-$ Hydrogen Bonds in $CH_{4-n}X_n$ ($X = F, Cl$; $n = 0, 1, 2$) Systems Complexed with Their Homoconjugate and Heteroconjugate Carbanions

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This work deals with a theoretical study of the $(CH\cdots C)^-$ hydrogen bonds in CH_4, CH_3X, and CH_2X_2 ($X = F$, Cl) complexed with their homoconjugate and heteroconjugate carbanions. The properties of the complexes are calculated with the B3LYP method using the 6-311++G(d,p) or 6-311++G(2df,2p) basis sets. The deprotonation enthalpies (DPE) of the CH bond or the proton affinities of the carbanions ($PA(C^-)$) are calculated as well. All the systems with the exception of the $CH_4\cdots CHCl_2^-$ one are characterized by a double minimum potential. In some of the complexes, the $(CH_b\cdots C)^-$ hydrogen bond is linear. In other systems, such as $CH_3F\cdots CH_2F^-$ and $CH_3F\cdots CHF_2^-$, there is a large departure from linearity, the systems being stabilized by electrostatic interactions between the nonbonded H of the neutral molecule and the F atom of the carbanion. In the transition state, the $(CH_b\cdots C)^-$ bond is linear, and there is a large contraction of the intermolecular $C\cdots C$ distance. The binding energies vary within a large range, from -1.4 to -11.1 kcal mol^{-1} for the stable complexes and -8.6 to -44.1 kcal mol^{-1} for the metastable complexes. The energy barriers to proton transfer are between 5 and 20 kcal mol^{-1} for the heteroconjugate systems and between 3.8 and 8.3 kcal mol^{-1} for the homoconjugate systems. The binding energies of the linear complexes depend exponentially on $1.5DPE - PA(C^-)$, showing that the proton donor is more important than the proton acceptor in determining hydrogen bond strength. The NBO analysis indicates an important electronic reorganization in the two partners. The elongations of the CH bond resulting from the interaction with the carbanion depend on the occupation of the $\sigma^*(CH_b)$ antibonding orbitals and on the hybridization of the C bonded to H_b. The frequency shifts of the $\nu(CH)(A_1)$ stretching vibration range between 15 and 1150 cm^{-1}. They are linearly correlated to the elongation of the CH_b bond.

Introduction

Proton-transfer reactions play a basic role in chemistry and biochemistry. Proton-transfer processes involving electronegative atoms such as N or O have been the subject of numerous experimental and theoretical investigations.[1−5] In contrast, the $(CH\cdots C)^-$ hydrogen bonds have been much less investigated. It has been pointed out that proton transfer between C atoms is rather different than in other systems. The binding energies $(CH\cdots C)^-$ are generally much weaker than the binding energies in the $(OH\cdots O)^-$ or $(NH\cdots N)^-$ systems. Further, the much lower proton-transfer rates observed for C bases have led to the general conclusion that the intrinsic energy barrier for transfer between C atoms is much higher than for the electronegative atoms. For example, the barrier energy in the $CH_4\cdots CH_3^-$ complex is very large as compared with other systems, and the energy of the $(CH\cdots C)^-$ hydrogen bond formation is rather weak.[6,7] The most obvious difference between C acids and N or O acids is the much weaker proton donating ability of the former. For this reason, most of the studies of proton-transfer processes deal with carbon acids involving sp hybridization such as $R-C\equiv CH$ or in unsaturated systems such as $CH_3CH=CH_2$, $H_2C=C=CH_2$, and their derivatives which are better proton donors than C with sp^3 hybridization.[8−12] The barriers for the identity proton transfers have been studied in these systems. The geometries, charge distributions of the neutral molecule and its conjugated anion, and the same parameters in the transition states have been calculated by the MP2 method with extended basis sets.[10−12] It has also been discussed how increased s-character and unsaturation may affect intrinsic barriers and transition-state imbalances. It must be noticed that most of these studies[8−12] refer to the carbon-to-carbon identity proton-transfer reactions.

The present work deals with a theoretical investigation of the $(CH\cdots C)^-$ hydrogen bonds in the CH_4, CH_3X, and CH_2X_2 ($X = F$, Cl) molecules complexed with the deprotonate species. Homoconjugate systems where the proton is bonded to the same carbanions, as well as heteroconjugate systems where the proton is bonded to different carbanions, are investigated. It must be mentioned that the main scope of the present work is to discuss the properties of the $(CH\cdots C)^-$ hydrogen bonds such as their geometries, energies, and vibrational properties. Less attention will be paid to the properties of the transition state. Let us notice that to the best of our knowledge, no experimental data have been reported for these complexes.

The present work is arranged as follows. We will at first discuss the optimized geometries of the complexes. The second section deals with the energies of the $CH\cdots C^-$ hydrogen bonds and their correlation with the acidity of the CH proton donors. In the third section, the results of a NBO analysis, more specifically the charge on the different atoms, the charge transfer

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from one subunit to the other, the occupation of the $\sigma^*(CH)$ antibonding orbitals, and the hybridization of the C atom bonded to H are presented. The last section deals with the influence of complex formation on the frequencies and infrared intensities of the $\nu(CH)$ stretching vibrations.

Computational Methods

The geometries of the isolated molecules or carbanions and the corresponding complexes were fully optimized at the B3LYP/6-311++G(d,p) level. This method and basis set were also used for the study of homoconjugate $(OH\cdots O)^-$ systems.[13] It is also worth stressing that in recent studies on hydrogen bonds involving CH groups including the blue-shifted as well the red-shifted hydrogen bonds, the B3LYP results have been shown to parallel the MP2 data quite closely.[14] For the weak $CH\cdots O$ hydrogen bonds, the B3LYP results exhibit the same patterns as do the MP2 data.[15] The interaction energies also calculated with the more extended 6-311++G(2df, 2p) basis set were obtained as the difference in energy between the complex, on one hand, and the sum of the isolated monomers, on the other hand. These energies were corrected for the zero-point vibrational energies (ZPE) and the basis set superposition errors (BSSE) calculated by the counterpoise method.[16] Harmonic vibrational frequencies and infrared intensities of the $\nu(CH)$ stretching vibration were calculated as well. Charge individual atoms, populations of molecular orbitals, and coefficients of the hybrid orbitals were obtained by using the natural bond population scheme.[17]

The interaction between filled and vacant orbitals represents the deviation from the Lewis structure and can be used as a measure of delocalization, also called hyperconjugation. The hyperconjugative interaction energy can be calculated from the second-order perturbation theory

$$E(2) = -n_\sigma \frac{\langle \sigma|\hat{F}|\sigma^*\rangle^2}{\epsilon_\sigma{}^* - \epsilon_\sigma} = -n_\sigma \frac{F_{\sigma\sigma^*}{}^2}{\Delta E}$$

where $\langle \sigma\hat{F}|\sigma^* >$ or $F_{\sigma\sigma^*}$ is the Fock matrix element between the NBO σ and σ^* orbitals, ϵ_σ and ϵ_{σ^*} are the energies of the σ and σ^* NBO orbitals, respectively, and n_σ is the population of the donor σ orbital.

The GAUSSIAN 98 program was used for all calculations reported in the present work[18]

Results and Discussion

Optimized Geometries. The optimized geometry of the homoconjugate $CH_3F\cdots CH_2F^-$ system (A) and of the heteroconjugate system $CH_3F\cdots CHF_2^-$ (B) is shown in Figure 1. Table 1 provides a summary of the bond lengths and angles that are the most relevant to the questions addressed in this study, namely, the distances in the $(CH_b\cdots C)^-$ hydrogen bond and the corresponding CHC^- angle. These parameters are listed for homoconjugate systems and for heteroconjugate systems where the geometry parameters are indicated for the most stable structure and for the proton-transferred structure to the other subunit. Intra- and intermolecular distances are also reported for the transition state. It should be noticed that we could not find a transition state for the $CH_4\cdots CHCl_2^-$ system. This implies that for this complex, there exists a very shallow double minimum with a very small barrier to proton transfer.

The results show that in all the systems, the intermolecular $H_b\cdots O$ distances are shorter than the sum of the van der Waals radii and that all the CHC^- angles are larger than 90°. This clearly indicates that the molecules and the carbanions are held together by hydrogen bonds.

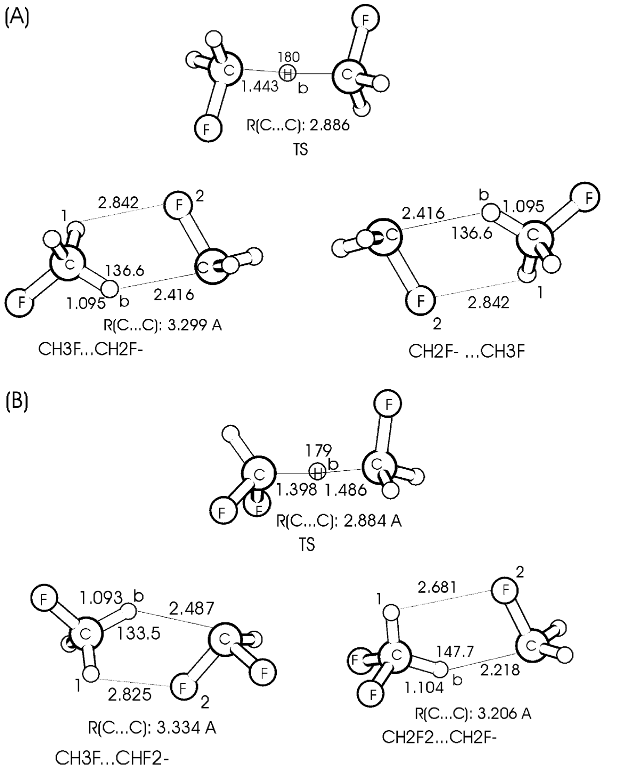

Figure 1. B3LYP/6-311++G(d,p) optimized geometries of $CH_3F\cdots CH_2F^-$ $CH_3F\cdots CHF_2^-$ (stable complex) and $CH_2F_2\cdots CH_2F^-$ (metastable complex). The geometry of the corresponding transition states (TS) is also shown.

In all the complexes, the $CH\cdots C^-$ bonds are asymmetrical, the optimized geometries indicating that the proton stays preferentially near one of the C atoms. This has been previously discussed for the $CH_4\cdots CH_3^-$ system.[6,7] In most of the systems at the exception of the CH_2Cl_2 ones, the intermolecular $H_b\cdots C$ distance is more than twice the CH_b distance. The elongation of the CH_b bond resulting from complex formation is also indicated in Table 1. Our results show that this elongation is moderate, taking a value between 0.0011 and 0.0127 Å in the CH_4 and CH_3F complexes. Largest elongations are predicted for the CH_2Cl_2 complexes. In the metastable $CH_2Cl_2\cdots CH_2F^-$ system, for example, the elongation of the CH_b bond is 0.0862 Å, which is unusual for a CH bond; in this complex, the intermolecular $H_b\cdots C$ distance is also the shortest (1.850 Å). In the transition state, the five homoconjugate complexes are symmetrical, the two $C\cdots H_b$ distances being strictly identical. These distances decrease on going from the $CH_4\cdots CH_3^-$ system (1.445 Å) to the $CH_2Cl_2\cdots CHCl_2^-$ one (1.412 Å). The heteroconjugate complexes are asymmetrical in the TS. The large contraction of the $C\cdots C$ bond in the TS is also worth noticing. This contraction amounts to 0.80−0.87 Å in the CH_4 complexes and is lower in the other ones, ca. 0.35−0.5 Å.

The angular properties of the present complexes are also worth discussing. Most of the theoretical carbon-to-carbon proton-transfer studies have been carried out in systems with sp or sp^2 C atoms. In these systems, the most stable orientation leads to a linear arrangement in which the bridging proton lies along the $C\cdots C$ internuclear bond. Our present calculations show that in the CH_4 complexes, the $CH\cdots C^-$ hydrogen bonds are nearly linear, the corresponding angle varying from 180 to ca. 184°. In other systems such as $CH_3Cl\cdots CH_3^-$, $CH_2F_2\cdots CH_3^-$, and $CH_2Cl_2\cdots CH_2Cl^-$, the deviation from linearity is ca. 10°.

TABLE 1: B3LYP/6-311++G(d,p) Optimized Geometry Parameters of the (CH···C)- Bonds in Complexes between CH_4, CH_3X, CH_2X_2 (X = F, Cl), and Their Corresponding Anions in the Ground and Transition States[a]

system[b]	CH_b	$H_b\cdots C$	$C\cdots C$	$\Delta r(CHb)$[c]	$-CH_bC$
$CH_4\cdots CH_3^{-d}$	1.1036	2.656	3.760	0.0127	180.0
TS	1.445	1.445	2.890		180.0
$CH_4\cdots CH_2F^-$	1.1030	2.546	3.645	0.0121	184.4
TS	1.462	1.436	2.897		181.4
$CH_3F\cdots CH_3^-$	1.1020	2.483	3.515	0.0104	167.6
$CH_4\cdots CH_2Cl^-$	1.1011	2.543	3.644	0.0102	180.1
TS	1.534	1.348	2.870		190.2
$CH_3Cl\cdots CH_3^-$	1.0868	2.288	3.359	0.0259	160.9
$CH_4\cdots CHF_2^-$	1.1008	2.622	3.722	0.0099	182.1
TS	1.385	1.516	2.901		180.6
$CH_4\cdots CHCl_2^-$	1.0969	2.554	3.651	0.0060	180.8
no TS					
$CH_3F\cdots CH_2F^-$	1.0951	2.416	3.299	0.0035	136.6
TS	1.443	1.443	2.886		180
$CH_3F\cdots CH_2Cl^-$	1.0971	2.409	3.398	0.0055	142.5
TS	1.512	1.369	2.875		180.9
$CH_3Cl\cdots CH_2F^-$	1.1705	1.850	2.990	0.0144	163.4
$CH_3F\cdots CHF_2^-$	1.0927	2.487	3.334	0.0011	133.6
TS	1.398	1.486	2.884		180.9
$CH_2F_2\cdots CH_2F^-$	1.1041	2.318	3.206	0.0127	147.7
$CH_3F\cdots CHCl_2^-$	1.0927	2.462	3.395	0.0011	149.2
TS	1.711	1.226	2.921		184.4
$CH_2Cl_2\cdots CH_2F^-$	1.1705	1.850	2.990	0.0862	163.4
$CH_3Cl\cdots CH_2Cl^-$	1.1033	2.254	3.279	0.0165	153.5
TS	1.430	1.430	2.860		179.9
$CH_3Cl\cdots CHF_2^-$	1.1012	2.272	3.230	0.0144	145.0
TS	1.458	1.411	2.867		184.1
$CH_2F_2\cdots CH_2Cl^-$	1.1049	2.221	3.278	0.0055	159.3
$CH_3Cl\cdots CHCl_2^-$	1.0962	2.297	3.302	0.0094	152.1
TS	1.308	1.552	2.858		181.6
$CH_2Cl_2\cdots CH_2Cl^-$	1.1339	1.972	3.084	0.0496	186.9
$CH_2F_2\cdots CHF_2^-$	1.1004	2.262	3.236	0.0090	146.3
TS	1.439	1.439	2.877		180.0
$CH_2F_2\cdots CHCl_2^-$	1.0980	2.267	3.296	0.0066	155.2
TS	1.292	1.588	2.875		183.0
$CH_2Cl_2\cdots CHF_2^-$	1.1416	1.985	3.084	0.0573	165.6
$CH_2Cl_2\cdots CHCl_2^-$	1.1106	2.093	3.166	0.0263	161.5
TS	1.412	1.412	2.840		176.3

[a] Distances are in angstroms, and angles are in degrees. [b] By convention, the proton is bonded to the left molecule. [c] The CH distances in isolated CH_4, CH_3F, CH_3Cl, CH_2F_2, and CH_2Cl_2 are equal to 1.0909, 1.0916, 1.0868, 1.0914, and 1.0843 Å, respectively. The use of four digits for the CH_b bond length is justified by the small elongation of the CH bond in some of the investigated complexes.[d] The $CH_4\cdots CH_3^-$ system has been studied in previous works.[6,7] The calculations indicate a double minimum potential with a high barrier. The optimized geometries are different. At the SCF level with lower basis sets, the C···C distance is 4.542 Å (2.902 Å in the TS). The predicted elongation of the CH_b bond is small (0.001 Å).[7]

The other complexes have a five-membered ring structure where two CH groups of CH_3X or CH_2X_2 are acting as proton donors. In these complexes, the largest departures from linearity are predicted for the $CH_3F\cdots CH_2F^-$ and $CH_3F\cdots CHF_2^-$ complexes where the CHC^- angles are equal to 136.6 and 133.6°, respectively. In these two complexes, the distances between the H atom of the first subunit and the F atom of the second one are relatively short. In the homoconjugate system $CH_3F\cdots CH_2F^-$, the intermolecular H1···F2 distance is 2.842 Å, and in the heteroconjugate complex $CH_3F\cdots CHF_2^-$, the H1···F2 distance is 2.825 Å when the proton lies to the left side and 2.681 Å when the proton is transferred to the left side. The $C^-\cdots H_b$ distances are also markedly different, being equal to 2.487 Å in the most stable configuration and 2.681 Å in the proton-transferred structure (Figure 1). The H1···F2 distances are too long to be classified as true hydrogen bonds; our results suggest that the bent structures are stabilized by electrostatic interactions between the nonbonded H1 and F2 atoms. Weak interactions between the nonbonded atoms also exist in complexes involving CH_3Cl and CH_2Cl. For example, in the $CH_3F\cdots CH_2Cl^-$ system where the $CH\cdots C^-$ hydrogen bond shows a large departure from linearity ($CH\cdots C^-$ angle = 142.5°), the intermolecular H1···Cl2 distance is relatively short (3.446 Å) suggesting a weak interaction between these two nonbonded atoms. It is worth mentioning that the H1···F2 or H1···Cl2 interaction can be explained by the large negative charge on the halogen atoms in the CH_2X^- and CHX_2^- carbanions. This will be discussed more in detail in the third section.

TABLE 2: Experimental and Calculated DPE (B3LYP/6-311++G(d,p) of the CH Bond in CH_4, CH_3X, and CH_2X_2 (X = F, Cl) Molecules (kcal mol^{-1})

compound	DPE^{calc}	$DPE^{exp\,a}$
CH_4	416.7[b]	418.8 ± 0.7
CH_3F	407.6	408.9 ± 4.1
CH_3Cl	395.6	396.0 ± 0.3
CH_2F_2	394.3	389.1 ± 3.6
CH_2Cl_2	374.1	374.5 ± 3.1

[a] Ref 20. [b] Recent values calculated with the MP2 or B3LYP methods and the 6-311+G(2df, 2p) basis sets are 418.1 and 415.8 kcal mol^{-1}, respectively.[11]

It is also worth mentioning that in the heterodimers between neutral molecules such as $CH_4\cdots CH_2F_2$ or $CH_3F\cdots CHF_3$, the optimized geometries do not reveal simple CH···F interactions. Recent calculations have shown that two or more H atoms are acting as a bridge, as in the present complexes. In these neutral heterodimers, the intermolecular distances are also too long to be classified as true hydrogen bonds.[19]

Binding Energies and Deprotonation Enthalpies. In this section, we discuss the correlation between the hydrogen bond strength and the acidity/basicity of the two subunits. The deprotonation enthalpies calculated at the B3LYP/6-311++G-(d,p) level are reported in Table 2. There is a good correspondence between the experimental and the calculated values, taking into account the fact that the experimental errors are on the order of magnitude of 3−4 kcal mol^{-1} for CH_3F and CH_2F_2 .[20] This justifies our computational method and level.

Starting from the free species, namely, the neutral molecule and the carbanion, one can consider the reaction paths a and b

$$C_1H\cdots C_2^- \leftarrow C_1^- + H^+ + C_2^- \rightarrow C_1^-\cdots HC_2 \qquad (1)$$

Association via path a takes place when the basicity of C_1^- is higher than that of C_2^- ($\Delta DPE < O$); association via path b leads to a metastable complex where the proton is bonded to the anion having the largest DPE ($\Delta DPE > 0$).

Table 3 reports the binding energies ($-E_{HB}$) including the ZPE corrections calculated with the 6-311++G(d,p) and 6-311++G(2df,2p) basis sets for all the complexes investigated in this work. The BSSE have been calculated at both levels. It should be noticed that the BSSE corrections seem unrealistic at least for the complexes of CH_4 that are linear or nearly so.

Indeed, the binding energies of these complexes are expected to be ordered according to the basicity of the carbanion that is as follows (Table 2): $CH_3^- > CH_2F^- > CH_2Cl^- > CHF_2^- > CHCl_2^-$.

The BSSE corrected binding energies calculated at the 6-311++G(d,p) and 6-311++G(2df,2p) levels do not follow this order. As discussed in refs 21 and 22, the CP method is ambiguous in the case of the interaction between charged and neutral species and in the case of symmetrically charged species. Therefore, the hydrogen bond energies were obtained, as recommended by some authors[23] with 50% BSSE correction. It should also be mentioned that the values calculated with the

TABLE 3: Binding Energies Including ZPE Corrections Calculated at the B3LYP/6-311++G(d,p) and 6-311++G(2df,2p) Levels, Transition State Energies, and Energy Barriers to Proton Transfer (kcal mol^{-1}) in Systems of CH_4, CH_3X, and CH_2X_2 (X= F, Cl) Complexed with the Carbanions[a]

system	$-E_{HB}$[b] (6-311++G(d,p))	$-E_{HB}$[b] (6-311++G(2df,2p))	E^*[b]	E_{PT}[b]
$\mathit{CH_4\cdots CH_3^-}$	3.27 (2.55)	2.94 (2.36)	4.87 (5.78)	8.14 (8.33)[c]
$CH_4\cdots CH_2F^-$	3.06 (2.57)	2.83 (2.47)	6.12 (7.02)	9.18 (9.59)
$CH_4\cdots CH_2Cl^-$	2.42 (2.07)	2.16 (1.98)	10.36(11.01)	12.78 (13.08)
$CH_4\cdots CHF_2^-$	2.35 (2.11)	2.09 (1.91)	10.44 (11.30)	12.79 (13.41)
$CH_4\cdots CHCl_2^-$	1.81 (1.43)	1.44 (1.25)	no TS	
$\mathbf{CH_3F\cdots CH_3^-}$	9.25 (8.56)	8.43 (7.85)	−3.03 (−2.13)	6.22 (6.43)
$\mathit{CH_3F\cdots CH_2F^-}$	10.32 (9.91)	9.72 (9.33)	−2.28 (−1.36)	8.05 (8.55)
$CH_3F\cdots CH_2Cl^-$	9.20 (8.88)	8.39 (8.15)	2.07 (−1.36)	11.20 (11.68)
$CH_3F\cdots CHF_2^-$	8.98 (8.73)	8.67 (8.40)	1.94 (2.80)	10.8 (11.53)
$CH_3F\cdots CHCl_2^-$	7.64 (7.31)	7.03 (6.76)	11.75 (12.67))	19.39 (19.98)
$CH_3Cl\cdots CH_3^-$	12.36 (11.54)	11.49 (10.86)	−10.85 (−12.67)	1.51 (1.34)
$CH_3Cl\cdots CH_2F^-$	12.37 (12.09)	11.77 (11.32)	−9.99 (−10.20)	2.38 (3.12)
$\mathit{CH_3Cl\cdots CH_2Cl^-}$	11.10 (10.66)	10.23 (9.98)	−5.75 (−4.99)	5.35 (5.67)
$CH_3Cl\cdots CHF_2^-$	10.67 (10.34)	10.39 (10.10)	−5.98 (−5.23)	4.69 (5.11)
$CH_3Cl\cdots CHCl_2^-$	9.02 (8.54)	8.22 (7.92)	2.89 (3.73)	11.91 (12.27)
$\mathbf{CH_2F_2\cdots CH_3^-}$	14.33 (13.56)	13.02 (12.50)	−12.10 (−11.25)	2.23 (2.31)
$\mathbf{CH_2F_2\cdots CH_2F^-}$	15.42 (14.90)	14.29 (13.91)	−11.45 (−10.57)	3.97 (4.33)
$\mathbf{CH_2F_2\cdots CH_2Cl^-}$	14.10 (13.71)	12.90 (12.70)	−7.30 (−6.56)	6.90 (7.15)
$\mathit{CH_2F_2\cdots CHF_2^-}$	13.50 (13.24)	12.75 (12.50)	−7.36 (−6.68)	6.14 (6.56)
$CH_2F_2\cdots CHCl_2^-$	11.54 (11.11)	10.41 (10.18)	1.76 (2.50)	13.30 (13.61)
$\mathbf{CH_2Cl_2\cdots CH_3^-}$	44.25 (44.07)	42.81 (42.62)	no TS	
$\mathbf{CH_2Cl_2\cdots CH_2F^-}$	20.85 (19.99)	19.33 (18.1)	−21.95 (−21.03)	−1.10 (−1.04)
$\mathbf{CH_2Cl_2\cdots CH_2Cl^-}$	17.95 (17.31)	16.53 (16.20)	−18.75 (−17.91)	−0.80 (−0.60)
$\mathbf{CH_2Cl_2\cdots CHF_2^-}$	17.54 (17.05)	16.92 (16.51)	−18.54 (−17.80)	−1.00 (−0.75)
$\mathit{CH_2Cl_2\cdots CHCl_2^-}$	13.66 (12.96)	12.29 (4.92)	−10.22 (−9.13)	3.44 (3.83)

[a] The $-E_{HB}$ and E^* values are calculated with respect to the isolated molecules and the considered carbanions. By convention, in all the systems, the proton is bonded to the left molecule. The energy barriers to proton transfer are the sum of ($-E_{HB}$ + E^*) values. The homoconjugate systems are in italics and the metastable systems are in bold. [b] The numbers in parentheses are the binding energies, energies of the transition state and proton-transfer barriers with 50% BSSE-corrections. [c] The E_{PT} values calculated with much smaller basis sets give much higher values of 22.3 and 15 kcal mol^{-1}.[6,7] The barrier to proton transfer is 8.1 (12.1) kcal mol^{-1} at the MP2/ 6-311+G(d,p) level and 6.7 (7.9) kcal mol^{-1} at the B3LYP/ 6-311+G(d,p) level.[11]

more extended basis set are smaller by 0.3−1.5 kcal/mol. A further extension of the basis set to the 6-311++G(3df, 2pd) level does not change the energies by more than 0.05 kcal mol^{-1}. In the next discussion, we will consider the energetic parameters calculated at the 6-311++G(d,p) level including the 50% BSSE correction.

Inspection of the results of Table 3 indicates that the binding energies of the neutral molecules with the carbanions are roughly ordered according to the proton donor ability of the CH bonds: $CH_4 < CH_3F < CH_3Cl < CH_2F_2 < CH_2Cl_2$.

It is, however, important to notice that the binding energies of the $CH_3F\cdots CH_2F^-$ and $CH_2Cl_2\cdots CH_2F^-$ complexes are by ca. 1 kcal mol^{-1} larger than the binding energies of the $CH_3F\cdots CH_3^-$ and $CH_2Cl_2\cdots CH_3^-$ complexes. This may be accounted for by the large deviation from linearity of the $CH\cdots C^-$ hydrogen bonds in these last systems where the calculated CHC^- angles are 136.7 and 147.7°, respectively (Table 1). Owing to the dependence of the hydrogen bond strength on the internuclear angle,[24,25] we will consider in the next discussion the systems where the $CH\cdots C^-$ hydrogen bonds have only a departure from linearity of 10° or less, namely, the CH_4 complexes, the $CH_2Cl_2\cdots CHCl_2^-$ complex, and the proton-transferred systems of CH_3^- complexed with CH_2F_2, CH_3Cl, and CH_2Cl_2.

The correlations between hydrogen bond strengths and DPE of the proton donor or proton affinities (PA) of the proton acceptor have been discussed in numerous papers.[26−34] Briefly summarizing, the correlations established for the OHO^+, NHO^+, NHN^+, and SHO^+ systems are only approximately linear, and the deviation from linearity increases when the hydrogen donor and acceptor abilities become very different.[35−41] Much less quantitative data are available for $CH\cdots C^-$ hydrogen bonds. For a limited set of homoconjugate complexes involving CH groups in acetylene, ethylene, and propane, the binding energies have been shown to be correlated to the DPE of the CH bonds.[12,41]

The hydrogen bond energies of a given proton donor with a series of proton acceptors depend on the PAs of the bases. For the linear CH_4 complexes ($n = 5$) investigated in this work, the following correlation holds:

$$-E_{HB} = -9.05 + 0.028\ \mathrm{PA}\ (C^-)\ (r = 0.9737) \qquad (2)$$

It must be noticed that the slope of eq 2 strongly depends on the system. For the complexes between vinyl alcohols and substituted vinyl alcoholates, where the $(OH\cdots O)^-$ hydrogen bond is almost linear, the slope calculated from the data of ref 13 is equal to 0.30. Thus, the slope and intercept of the correlation between the hydrogen bond strength and the acidity/basicity of the interacting molecules is a general feature of the hydrogen bond and will not be discussed hereafter. We now express the $CH\cdots C^-$ binding energies as a function of both the proton donor and the proton acceptor abilities of the two partners.

The fact that in the homoconjugate systems the binding energies markedly increase from CH_4 (2.55 kcal mol^{-1}) to CH_2Cl_2 (12.96 kcal mol^{-1}) indicates that the energies are not simply correlated to ΔPA, the difference in proton affinities of the proton donor and proton acceptor. A relatively good correlation is found when taking different coefficients for DPE and PA. The best correlation coefficient is calculated for the exponential expression

$$-E_{HB} = 4330\mathrm{e}^{-0.0333\,[(1.5\,\mathrm{DPE(CH)}-\mathrm{PA(C-)}]}\ (r = 0.9818) \qquad (3)$$

This correlation is illustrated in Figure 2. We must mention that the intercept and slope of eq 3 calculated with the more

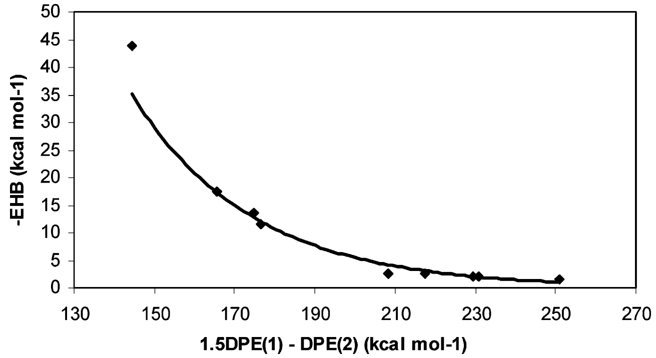

Figure 2. $-E_{HB}$ (kcal mol^{-1}) as a function of 1.5 DPE (CH) − PA (C$^-$) for complexes with CH···C$^-$ angles between 170 and 190°.

extended basis set (6-31++G(2df,2p)) are slightly different (4403 and −0.0338, respectively), giving the same hydrogen bond pattern. Eq 3 demonstrates that the proton donor is more important than the proton acceptor in hydrogen bond formation, and this can be anticipated for every level of theory. The predominance of the proton donor has also been established for the linear (OH···O)$^-$ hydrogen bonds in vinyl alcohol−vinyl alcoholate systems.[13] As discussed in a recent work,[43] this predominance seems to be a general feature of the hydrogen bond.

The hydrogen bond energies in the cyclic complexes are the sum of two contributions, the CH$_b$···C$^-$ and the CH$_1$···X$_2$ (Figure 1). In the cyclic complexes between nucleobases and water[44−46] or hydrogen peroxide,[47] we have shown that the energy of the hydrogen bond in the six-membered ring depends mainly on the acidity of the groups involved in the formation of the closed structure. In this case, the atoms are held together by conventional OH···O and NH···O hydrogen bonds. Such a correlation could not be deduced for the present complexes. Indeed, in the nonlinear structures, two H atoms bonded to the same C atom are acting as proton donors. This leads to an anticooperative structure defined by the theory of Huyskens.[48] It is also interesting to notice that in the dimers of fluoromethanes, bifurcated hydrogen bonds where two or three CH groups are bonded to the F atoms of the other molecules are stable structures.[19] In this case also, the different contributions to the total binding energy cannot be separated.

Table 3 also reports the energy of the transition state (E^*) taken with respect to the isolated molecules and the proton-transfer energy barrier (E_{PT}). As mentioned in the first section, the C···C distance is considerably smaller in the transition state. It has been shown that in the CH$_4$···CH$_3^-$ system, the amount of hydrogen bond contraction is related to the height of the barrier.[6] Our data show that the hydrogen bond contraction is the largest for the CH$_4$ complexes (0.75−0.87 Å) and the smallest for the CH$_2$Cl$_2$ complexes (0.20−0.34 Å). As expected, the E_{PT} values tend to increase with decreasing hydrogen bond strength. Owing to the angular characteristics of the hydrogen bonds, no general correlation could be established between these two parameters.

NBO Analysis. Complex formation results in a marked electronic reorganization in both the proton donor and the proton acceptor molecules. We will consider these changes in the stable CH$_3$F···CHF$_2^-$ complex shown in Figure 1.[49] Our calculations show that the CT taking place from the carbanion to the neutral entity is 0.047 e. The charge transfer occurs at the expense of the C atom of CHF$_2^-$ that loses 0.020 e but also at the expense of the H atom that loses a nonnegligible amount of 0.014 e. The existence of an interaction between the H$_1$ and the F$_2$ atoms is shown by the fact that the F$_2$ atom of CHF$_2^-$ loses 0.014 e, and the charge on the other F atom of CHF$_2^-$ remains almost unchanged. There is also a marked electronic reorganization in all atoms of the proton donor molecule (increase of the polarity of the CH$_b$ bond, increase of the charge on the F atom (0.035 e), and decrease of the charge on the external H atom (0.012 e). The marked change of the occupation of the σ^*(CH$_b$) orbital that increases from 0.016 e and the increase of the s-character of the CH$_b$ bond (2.85%) on going from isolated CH$_3$F to its complex with CHF$_2^-$ is also worth noticing. Smaller perturbations are predicted for the nonbonded CH bond of CH$_3$F, its s-character increasing by ca. 1%. In contrast, the s-character of the C bonded to F decreases by more than 6%.

Table 4 provides a summary of the parameters that are the most relevant to the present study, namely, the NBO charges on the C and H$_b$ atoms, the overall charge transfer from the carbanion to the neutral molecule, the occupation of the σ^*(CH$_b$) antibonding orbitals, the percentage of s-character of the CH$_b$ bond, and the hyperconjugative charge-transfer energies from the lone pair of the C$^-$ to CH$_b$ (C$^-$ → CH$_b$).

In all the systems, the interaction between the CH donor and the carbanion results in an increase of the negative charge on the C atom (or a decrease of the positive charge in the CH$_3$Cl and CH$_2$F$_2$ systems) and an increase of the positive charge on the H$_b$ atom, indicating an increase of the C−H$_b$ polarity. This a general feature of the hydrogen bonds that has been predicted even in blue-shifted hydrogen bonds involving methylhalides and hydrogen peroxide.[47] The charge transfer from the carbanion to the neutral molecule remains moderate, ranging from 0.018 e (CH$_4$···CHCl$_2^-$) to 0.078 e (CH$_3$Cl···CHF$_2^-$). The charge transfer is larger in the metastable complexes, taking the largest value of 0.223 e in the CH$_2$Cl$_2$···CH$_2$F$^-$ system. The hyperconjugative energies C$^-$ → CH$_b$ are also the largest in the CH$_2$Cl$_2$ systems and the smallest in the CH$_4$ systems. They are very roughly correlated to the binding energies and will not be discussed here. Correlation between CH bond lengths and hyperconjugative energies has been found for complexes involving a constant proton donor (CHF$_3$) and a variety of proton acceptors.[15] As shown in a previous work,[50] the occupation of the σ^*(CH) orbital is a more relevant parameter for discussing the CH bond length in different proton donors.

We want to discuss further the characteristics of the CH$_b$ bonds, more specifically, the occupation of the σ^*(CH$_b$) orbitals and the hybridization of the C bonded to H$_b$. In complexes involving hydrogen-bonded OH groups such as hydrogen peroxide complexed with methylhalides[50] or with nucleobases,[47] we have shown that the lengthening of the OH bond resulting from the interaction is linearly correlated to the occupation of the σ^*(OH) orbital. We failed to find a similar correlation for the present systems. A closer inspection of the data indicates that complex formation results in a marked increase of the s-character of C bonded to H$_b$, the largest increase being predicted for the CH$_2$Cl$_2$···CH$_2$F$^-$ system, the s-character increasing from 27.9 to 38.1% on going from the isolated CH$_2$Cl$_2$ molecule to the complex. It is also worth noticing that this system is characterized by the largest elongation of the CH$_b$ bond (0.086 Å) and the largest occupation of the σ^*(CHb) orbital (0.183e). As pointed out by Alabugin et al.,[14] the magnitude of the hyperconjugative interaction to the σ^*(CH) is the most important factor in defining the CH bond length, and in the present case, the anionic lone pair can be considered as a good electron donor. A second effect acts in opposite direction; it is the decrease of effective electronegativity of H in the CH bond that leads to an increase in the s-character of the C hybrid orbital. In the present systems, both effects are operating. Because the

TABLE 4: NBO Analysis of the Complexes. NBO Charges on the C and H_b Atoms (e), CT (e), Occupation of the $\sigma^*(CH_b)$ Orbital (e), Percentage s-Character of the CH_b Bond, and Hyperconjugative Energies $C^- \rightarrow CH_b$ (kcal mol^{-1})

systems	charge (C)	charge (H_b)	CT	$\sigma^*(CH_b)$	%s (CH_b)	$C^- \rightarrow CH_b$
CH_4	−0.809	0.202		0.0004	25.0	
$CH_4\cdots CH_3^-$	−0.856	0.279	0.103	0.033	28.59	5.06
$CH_4\cdots CH_2F^-$	−0.846	0.271	0.073	0.029	28.47	4.77
$CH_4\cdots CH_2Cl^-$	−0.838	0.279	0.035	0.025	28.22	4.66
$CH_4\cdots CHF_2^-$	−0.839	0.260	0.059	0.026	28.07	3.34
$CH_4\cdots CHCl_2^-$	−0.826	0.267	0.018	0.012	27.52	2.90
CH_3F	−0.075	0.157		0.016	26.63	
$CH_3F\cdots CH_3^-$	−0.118	0.244	0.053	0.046	31.0	7.93
$CH_3F\cdots CH_2F^-$	−0.106	0.219	0.073	0.037	30.14	5.63
$CH_3F\cdots CH_2Cl^-$	−0.106	0.233	0.035	0.033	30.28	6.91
$CH_3F\cdots CHF_2^-$	−0.098	0.203	0.047	0.032	29.48	3.56
$CH_3F\cdots CHCl_2^-$	−0.094	0.217	0.019	0.023	29.32	3.70
CH_3Cl	−0.529	0.204		0.013	26.67	
$CH_3Cl\cdots CH_3^-$	−0.564	0.292	0.131	0.070	32.86	13.78
$CH_3Cl\cdots CH_2F^-$	−0.531	0.271	0.084	0.061	32.08	11.52
$CH_3Cl\cdots CH_2Cl^-$	−0.529	0.283	0.055	0.047	31.80	11.58
$CH_3Cl\cdots CHF_2^-$	−0.530	0.257	0.078	0.054	31.38	8.83
$CH_3Cl\cdots CHCl_2^-$	−0.538	0.270	0.031	0.031	30.57	7.11
CH_2F_2	0.488	0.129		0.033	28.45	
$CH_2F_2\cdots CH_3^-$	0.424	0.235	0.089	0.092	34.46	21.53
$CH_2F_2\cdots CH_2F^-$	0.439	0.208	0.042	0.074	33.15	14.71
$CH_2F_2\cdots CH_2Cl^-$	0.441	0.221	0.052	0.064	33.25	15.7
$CH_2F_2\cdots CHF_2^-$	0.447	0.190	0.046	0.070	32.61	11.18
$CH_2F_2\cdots CHCl_2^-$	0.457	0.206	0.032	0.047	32.3	9.44
CH_2Cl_2	−0.378	0.207		0.028	27.92	
$CH_2Cl_2\cdots CH_2F^-$	−0.420	0.277	0.223	0.183	38.08	53.02
$CH_2Cl_2\cdots CH_2Cl^-$	−0.401	0.303	0.125	0.113	36.38	34.40
$CH_2Cl_2\cdots CHF_2^-$	−0.410	0.267	0.183	0.149	36.75	35.99
$CH_2Cl_2\cdots CHCl_2^-$	−0.381	0.291	0.067	0.067	34.15	18.14

CH distances are different in the isolated neutral molecules, we consider the elongation of the CH bonds and the change resulting from the complex formation of the two mentioned parameters. We have obtained the following equation:

$$\Delta r(CH_b) = 0.003 + 0.161[(4\,\Delta\sigma^*(CH_b) - 0.010\,\Delta\%s(CH_b)]\ (r = 0.9720) \quad (4)$$

The correlation coefficient of the equation is only 0.9720, and deviations are observed for CH_2Cl_2 complexed with $CHCl_2^-$ and CH_2Cl^- . However, the data of Table 4 indicate that the occupation of the $\sigma^*(CH_b)$ orbital is slightly predominant (by a factor of 1−2) for small elongations and predominates (by a factor of 5−6) for larger elongations. As a matter of fact, a very small increase of the s-character of the CH_b bond in the $CH_3F\cdots CHCl_2^-$ and $CH_3F\cdots CHF_2^-$ complexes should lead to a contraction of the CH_b bond and a blue shift of the corresponding stretching vibrations. For these two systems, the shifts are small, being 16 and 19 cm^{-1}, respectively. This will be discussed in the last section.

It is also interesting to note that for the blue-shifted hydrogen bonds involving CH_2X_2 and CHX_3 complexed with hydrogen peroxide, we have obtained a correlation where the coefficients of $\Delta\sigma^*$ and percents are, respectively, 4 and 0.011, very similar to those found in the present work; the slope of the equation is, however, different (0.10).[51]

Finally, it should be mentioned that in each set of complexes, the energy barrier to proton transfer increases with decreasing s-character of C bonded to H_b. As shown for the identity proton-transfer reactions,[10−12] the greater s-character of acidic carbons allows for more efficient hydrogen bonding stabilization of the transition state.

Frequencies and IR Intensities of the CH_b Stretching Vibrations. Table 5 reports the harmonic frequencies of the $\nu(A_1)$ stretching vibrations in the isolated neutral molecules and in their complexes with the carbanions. The transition states are characterized by negative frequencies that show a tendency to decrease on going from the CH_4 to the CH_2Cl_2 complexes. They are, for example, −1450 cm^{-1} in the $CH_4\cdots CH_3^-$ system

TABLE 5: Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km mol^{-1} between Parentheses) of the ν(CH) (A_1) Vibration in Isolated CH_4, CH_3X, and CH_2X_2 (X = F, Cl) (ν^ϕ)^a

system	ν^ϕ(CH) (A_1)	$\Delta\nu$ (ΔI)
CH_4	3025 (0)	
$CH_4\cdots CH_3^-$		149 (498)
$CH_4\cdots CH_2F^-$		137 (322)
$CH_4\cdots CH_2Cl^-$		110 (238)
$CH_4\cdots CHF_2^-$		107 (238)
$CH_4\cdots CHCl_2^-$		60 (116)
CH_3F	3034 (33)	
$CH_3F\cdots CH_3^-$		130 (-8)
$CH_3F\cdots CH_2F^-$		49 (65)
$CH_3F\cdots CH_2Cl^-$		67 (57)
$CH_3F\cdots CHF_2^-$		19 (8)
$CH_3F\cdots CHCl_2^-$		16 (−7)
CH_3Cl	3073 (25)	
$CH_3Cl\cdots CH_3^-$		323 (590)
$CH_3Cl\cdots CH_2F^-$		188 (245)
$CH_3Cl\cdots CH_2Cl^-$		202 (615)
$CH_3Cl\cdots CHF_2^-$		166 (300)
$CH_3Cl\cdots CHCl_2^-$		104 (210)
CH_2F_2	3060 (45)	
$CH_2F_2\cdots CH_3^-$		369 (505)
$CH_2F_2\cdots CH_2F^-$		179 (150)
$CH_2F_2\cdots CH_2Cl^-$		191 (305)
$CH_2F_2\cdots CHF_2^-$		123 (100)
$CH_2F_2\cdots CHCl_2^-$		94 (145)
CH_2Cl_2	3123 (10)	
$CH_2Cl_2\cdots CH_3^-$		158 (105)
$CH_2Cl_2\cdots CH_2F^-$		1150 ((1950)
$CH_2Cl_2\cdots CH_2Cl^-$		691 (1635)
$CH_2Cl_2\cdots CHF_2^-$		784 (1445)
$CH_2Cl_2\cdots CHCl_2^-$		355 (920)

[a] Frequency shifts ($\Delta\nu$) and intensity inrease (ΔI) of the ν(CH) (A_1) vibration resulting from complex formation.

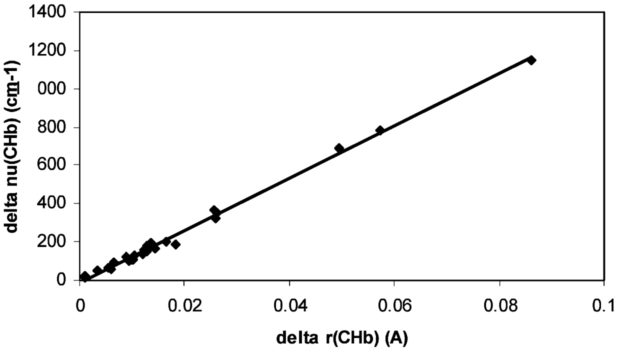

Figure 3. $\Delta\nu(CH_b)$ (cm^{-1}) as a function of $\Delta r(CH_b)$ (Å).

and -850 cm^{-1} in the $CH_2Cl_2\cdots CHF_2^-$ system. These frequencies correspond to the CH_b stretching vibration.

The $\nu(CH)A_1$ vibrations are the most sensitive to the interaction. However, it must be noticed that other CH stretching vibrations are also sensitive to interaction with the carbanion. This is the case for the triply degenerate T_2 vibration in CH_4, the doubly degenerate E vibration in CH_3F or CH_3Cl, and the B_2 vibration in CH_3F or CH_3Cl. For example, in CH_4, the T_2 vibration is calculated at 3130 cm^{-1} with an IR intensity of 26 km mol^{-1}. In the $CH_4\cdots CH_3^-$ complex where CH_4 has the local C_{3v} symmetry, the E vibration is predicted at 3074 cm^{-1} with an IR intensity of 54 km mol^{-1}. The largest frequency shift and IR intensity enhancement are calculated for the A_1 vibration. In free CH_4, this vibration that is IR inactive is calculated at 2856 cm^{-1}. This vibration shifts from 149 cm^{-1} with respect to isolated CH_4, and its IR intensity increases by 498 km mol^{-1}.

The data reported in Table 5 indicate that the $\nu(A_1)$ vibrations are red-shifted in all the complexes. As mentioned in the previous section, the shift is small for the $CH_3F\cdots CHCl_2$ complex (16 cm^{-1}). In the metastable $CH_2Cl_2\cdots CH_2F^-$ complex, the $\nu(CH)$ vibration is predicted at a low frequency, 1973 cm^{-1}, that is quite unusual for a $\nu(CH)$ vibration. The corresponding IR intensity of 1960 km mol^{-1} is also worth noticing. We do not think that these results are an artifact of calculations due to the metastable structure of this complex. Indeed, the geometrical and vibrational properties of the molecular cage of the *in*-bicyclo-1-tetradecyl cation have been reported recently.[52] The calculations carried out at the B3LYP/6-31G(d,p) level have predicted a $\nu(CH)$ stretching frequency of 2034 cm^{-1}, showing that even in this stable entity, the stretching vibration can be shifted by a very large amount.

A comparison of the data reported in Tables 1 and 5 allows us to deduce a correlation between the elongations of the CH_b bond and the frequency shifts of the $\nu(CH)$ (A_1) vibration

$$\Delta\nu(CH_b) = -12.3 + 13.66 \times 10^3\ \Delta r(CH_b)\ (r = 0.9976) \tag{5}$$

This correlation is illustrated in Figure 3. Similar equations have been established for the elongations of the OH and NH bonds and the corresponding shifts of the stretching vibrations. The OH and NH bonds are considered as better σ-acceptors. Nevertheless, the slope of eq 5 is between the slope calculated for OH bonds (10×10^3 cm^{-1}/Å) and NH bonds (18×10^3 cm^{-1}/Å).[47]

Conclusion

The calculations reported in this work indicate that the $(CH\cdots C)^-$ hydrogen bonds formed between CH_4, CH_3X, and CH_2X_2 (X = F, Cl) and their corresponding anions are strongly asymmetrical and in most of the cases show a departure from linearity. In the transition state, the $(CH\cdots C)^-$ bonds are linear and symmetrical in the homoconjugate systems. In all the systems, complex formation results in a lengthening of the CH bond, which is moderate for the stable complexes and much larger for the metastable complexes. Thus, the systems investigated in the present work can be categorized as red-shifting hydrogen bonds. The hydrogen bond energies vary within a broad range and are shown to depend more on the acidity of the CH proton donor than on the basicity of the carbanion. NBO analysis shows significant electronic reorganization upon hydrogen bond formation. In these $(CH\cdots C)^-$ hydrogen bonds, the elongation of the CH bond can be mainly accounted for by the increase of the occupation of the corresponding $\sigma^*(CH)$ orbital that outweighs the change of hybridization of the C bonded to the H. These results are in contrast with the blue-shifted hydrogen bonds where the contraction of the CH bond is mainly determined by the change of hybridization of the C bonded to H.

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(42) For identity, in carbon-to-carbon proton-transfer reactions involving acetylenic and olefinic hydrogens and propane, the CH···C$^-$ hydrogen bond is linear. The data of ref 12 allow us to deduce the following correlations: $-E_{HB} = 54.1 - 0.120$ DPE ($r = 0.9673$); the correlation coefficient for the exponential expression $-E_{HB} = 15.89e^{-0.0197\ \mathrm{DPE}}$ ($r = 0.9766$) is somewhat higher. This correlation only holds for closely related molecules, namely, aliphatic CH donors; the aromatic CH proton donor shows a departure from this correlation. Very poor correlation exists between the barrier to proton transfer and DPE.

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