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Properties of the C−H···H Dihydrogen Bond: An ab Initio and Topological Analysis

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The dihydrogen-bonded complexes of methane and its fluoro and chloro derivatives with lithium hydride are analyzed using ab initio methods as well as the Bader theory. All calculations were performed using Pople's basis sets (6-311++G(d,p), 6-311++G(2df,2pd), and 6-311++G(3df,3pd)) and the Dunning bases (aug-cc-pVDZ and aug-cc-pVTZ) within the MP2 method. The results of the calculations show that the binding energy for the analyzed complexes increases with the increase of the number of fluoro or chloro substituents, up to ∼7 kcal/mol. In the same order there is an increase of the electrostatic energy term, showing that for the $CF_3H\cdots HLi$ complex the dihydrogen bond interaction is similar in nature as for the water dimer where a conventional O−H···O hydrogen bond exists, while for the $CCl_3H\cdots HLi$ dimer the exchange energy term outweighs the electrostatic energy. Hence, the other attractive energy terms are important. A topological analysis based on the Bader theory supports the results of the ab initio calculations since the electron densities at the H···H bond critical points and the other topological parameters are similar to those calculated for moderate conventional hydrogen bonds.

Introduction

During the 1990s a new type of interaction named dihydrogen bond[1] (DHB) was detected for metal organic crystal structures.[2,3] This interaction was designated as X−H···H-M, where X−H denotes the typical proton donating bond such as O−H or N−H; the second hydrogen atom possessing a negative charge and connected with M (M is the transition metal or boron) is the acceptor center. Since that time, a number of experimental and theoretical studies of dihydrogen-bonded systems have increased rapidly. Other systems were also classified as DHBs,[3c] and even C−H···H−C interactions were investigated.[4]

One of the first theoretical investigations has been connected with a simple model system, the LiH···HF complex;[5] however, early studies have also considered crystal structure systems such as molybdenum and ruthenium complexes.[6] It was pointed out that DHBs differ significantly from other unconventional H-bond interactions. C−H···Y, C−H···π, X−H···C, X−H···π, C−H···C, and C−H···π interactions are usually classified as weak or very weak H-bonds;[7] however, there are exceptions such as the NH_3^+-$CH_2^-\cdots HCCH$ complex where the binding energy calculated at the MP2/6-311++G(3d,3p) level of theory (BSSE included) amounts to −8.2 kcal/mol.[8] Contrary to other unconventional H-bonds, DHBs are usually moderate or strong interactions.[3a,6] For example, the binding energy for the LiH···HF complex calculated at the high QCISD(T)/6-311++(d,p) level of theory (counterpoise correction included) amounts to −11.9 kcal/mol.[9]

There are also studies of DHBs where the topological parameters derived from the Bader theory[10] are analyzed. Alkorta et al. were the first to apply topological analyses to DHBs.[11] They found for the sample of the following complexes, $BH_4^-\cdots HCN$, $BH_4^-\cdots CH_4$, $LiH\cdots NH_4^+$, LiH···HCN, LiH···HCCH, $BeH_2\cdots NH_4^+$, $BeH_2\cdots HCN$, and $CH_4\cdots NH_4^+$, that the electron density at the H···H bond critical point (BCP) correlates with the binding energy. Similarly, such relationships between the binding energy and the electron density at H···Y (Y designates the proton acceptor) were detected for the other samples of conventional H-bonds.[12] These relationships were detected later[9] for other samples of dihydrogen-bonded model systems, and it was found that there are similar correlations between geometrical, topological, and energetic parameters as for conventional H-bonds. For example, the H···H distance correlates with the H-bond energy. There is also the elongation of the proton donating bond due to complexation which is greater for stronger interactions.

The importance of DHBs in chemical, physical, and biochemical processes was studied. For example, the equilibrium between the neutral dihydrogen-bonded molecules and cation/H_2/anion complexes and the field effects on these systems was investigated.[13] The authors have pointed out that similar processes were observed for biological systems such as the enzyme hydrogenase in bacteria and algae which catalyzes the activation of molecular hydrogen leading to the uptake of H_2 gas. Alkorta et al. concluded that DHB interactions may be as common as typical H-bonds[14] due to their importance in physical, chemical, and biological processes.

Early studies were also concentrated on such problems as, is there a difference between DHBs and conventional H-bonds and what is the nature of these interactions?[3a,5] It is evident that for typical hydrogen bonds the proton acceptor possesses at least one free electron pair while this does not occur for DHBs. It was pointed out that the H-bond is the interaction without borders[15] since in principle there are no differences

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between van der Waals interactions and very weak H-bonds and that very strong interactions, such as resonance-assisted hydrogen bonds (RAHBs), are partly covalent in nature;[16] hence, there is no sharp border between RAHBs and covalent bonds. A similar situation occurs for DHBs. Robertson et al. have studied C−H···H−C interactions and have concluded that there is no sharp border between very weak DHBs and typical H···H contacts which are usually attributed to van der Waals contacts.[4] However, they have claimed that such a border exists if we consider strong DHBs bordering with covalent H−H bonds. Extensive ab initio studies of geometrical, energetic, IR spectroscopic, and topological properties of dihydrogen-bonded complexes have been performed,[17] and it was found that for some systems such as $LiNCH^+\cdots HLi$ and $NaNCH^+\cdots HLi$ complexes the binding energies indicate very strong H-bonds since the corresponding binding energies amount to −27.1 and −23.7 kcal/mol, respectively, for calculations performed at the MP2/aug′-cc-pVTZ level of theory (aug′-cc-pVTZ designates that there is the Dunning correlation-consistent polarized valence triple-split basis set on the H, Li, and Na atoms, and this is basis augmented with diffuse functions on the other atoms). Similar results have been obtained very recently for the $NH_4^+\cdots HBeH$ and $NF_3H^+\cdots HBeH$ complexes[18] where the MP2 binding energies extrapolated into the complete basis set from the aug-cc-pVDZ and aug-cc-pVTZ bases amount to −10.3 and −21.6 kcal/mol, respectively. Additionally for the latter case, a negative value of Laplacian was detected indicating the partly covalent nature of the interaction; the H···H distance calculated at the MP2/aug-cc-pVDZ level is equal to 1.132 Å. Hence, we may conclude that the DHB interaction is also an interaction without borders as was stated by Desiraju for the hydrogen bond.[15]

To gain a more detailed understanding of the nature of dihydrogen bonds, an interaction energy decomposition according to the perturbational IMPPT scheme[19] has been performed by Pecul et al. on the following complexes: $LiH\cdots H_2$, $LiH\cdots CH_4$, $LiH\cdots C_2H_6$, and $LiH\cdots C_2H_2$.[20] The authors have found that only for the LiH···HCCH complex the interaction is dihydrogen bonded; the others are van der Waals complexes since in the first case the attractive electrostatic energy term significantly outweighs the exchange energy, and hence, the Heitler-London term is negative. For the others, the exchange energy outweighs the electrostatic term, and they are van der Waals complexes. Similar results were obtained very recently for other samples of DHBs where the continuum between van der Waals interactions and DHBs was detected.[21] The nature of the border between dihydrogen bonds and H···H van der Waals interactions was studied very recently for the crystal structures of 4-((*E*)but-1-enyl)-2,6-dimethoxyphenylpyridine-3-carboxylate and 4-((*E*)pent-1-enyl)-2,6-dimethoxyphenylpyridine-3-carboxylate,[22] for styrene and its derivatives,[22] between the ortho-hydrogen atoms in planar biphenyl[23] and for 2-cyclopropyl ethenol and its derivatives.[24] It was concluded that very often such interactions partly fulfill some of the criteria for the existence of H-bonding and that their classification is often problematic.

One of the most important criterion for the existence of H-bonding is the elongation of the X−H proton donating bond due to complexation and the weakening of this bond accompanied by a decrease in the X−H stretch vibration frequency.[25,26] This shift to lower frequencies is called a red shift and is connected with the increase in intensity of the corresponding band. However, for some C−H···Y H-bonds, an atypical situation was detected where there is a shift to higher frequencies, a blue-shift.[27] The corresponding C−H···Y bonds are usually named as blue-shifting hydrogen bonds. Several studies of such systems have been performed[28] showing that practically there are no other differences between red-shifted and blue-shifted hydrogen bonds. It was shown that $C(sp^3)-H$ bonds are preferable as possible proton donors for blue-shifted H-bonds since fluoro methane derivatives often form such C−H···O H-bonds, but ethylene and ethyne fluoro derivatives do not.[29]

The aim of this study is to investigate the properties of complexes of methane and its fluoro and chloro derivatives with lithium hydride. The choice of C−H···H dihydrogen bonds where the C-atom has sp^3 hybridization for the proton donating bond is connected with trials to find blue-shifted DHBs since to our knowledge such systems have not yet been reported. Only the shortening of the accepting bond for DHBs was detected (for example for complexes with LiH).[9,17]

Computational Details

The calculations were carried out using the Gaussian 98[30] and Gaussian 03[31] programs. The complexes of methane and its fluoro and chloro derivatives with lithium hydride, $CH_4\cdots HLi$, $CFH_3\cdots HLi$, $CF_2H_2\cdots HLi$, $CF_3H\cdots HLi$, $CClH_3\cdots HLi$, $CCl_2H_2\cdots HLi$, and $CCl_3H\cdots HLi$, were fully optimized, and the geometry of the complexes corresponds to minima since no imaginary frequencies were detected. The calculations were performed using the second-order perturbation Møller−Plesset method (MP2). The Pople type basis sets were used (6-311++G(d,p), 6-311++G(2df,2pd), and 6-311++G(3df,3pd)) and also the Dunning basis sets (aug-cc-pVDZ and aug-cc-pVTZ).

To attain deeper insight concerning the nature of the investigated interactions, the variation-perturbation approach which allows the interaction energy to be decomposed was applied here.[32] This interaction energy decomposition was implemented[33] in the GAMESS program.[34] In this approach, the starting wave functions of the subsystems are obtained in the dimer-centered basis set (DCBS). Hence the total interaction energy as well as its components is free of basis set superposition error (BSSE) due to the full counterpoise correction.

The interaction energy within the variation-perturbation scheme mentioned above is decomposed in the following way. The interaction energy at the all-electron MP2 level is decomposed into a Hartree−Fock (SCF) contribution and a correlation term

$$\Delta E^{\mathrm{MP2}} = \Delta E^{\mathrm{HF}} + \Delta E^{\mathrm{CORR}} \tag{1}$$

The Hartree−Fock term is further decomposed

$$\Delta E^{\mathrm{HF}} = \epsilon_{\mathrm{el}}^{(10)} + \epsilon_{\mathrm{ex}}^{\mathrm{HL}} + E_{\mathrm{del}}^{\mathrm{HF}} \tag{2}$$

where $\epsilon_{\mathrm{el}}^{(10)}$ is the first-order electrostatic term, $\epsilon_{\mathrm{ex}}^{\mathrm{HL}}$ is the first-order Heitler-London exchange term, and $E_{\mathrm{del}}^{\mathrm{HF}}$ corresponds to a higher order delocalization term. The sum of the first-order terms constitute the Heitler-London energy term, ΔE^{HL}

$$\Delta E^{\mathrm{HL}} = \epsilon_{\mathrm{el}}^{(10)} + \epsilon_{\mathrm{ex}}^{\mathrm{HL}} \tag{3}$$

The correlation correction to the Hartree−Fock interaction energy, $\Delta E^{\mathrm{CORR}} = \epsilon_{\mathrm{MP}}^{(2)}$, is decomposed according to the equation given below

$$\Delta E^{\mathrm{CORR}} = \epsilon_{\mathrm{MP}}^{(2)} = \epsilon_{\mathrm{disp}}^{(20)} + \epsilon_{\mathrm{e,r}}^{(12)} + \Delta E_{\mathrm{EX-DEL}}^{(2)} \tag{4}$$

TABLE 1: Geometrical Parameters (in Å) for Complexes of Methane and Its Fluoro Derivatives with LiH

level of calculations	ΔLi−H	H···H	ΔC−H
$H_3CH\cdots HLi$			
MP2/6-311++G(d,p)	−0.002	2.662	0.000
MP2/6-311++G(2df,2pd)	−0.001	2.575	0.001
MP2/6-311++G(3df,3pd)	0.000	2.511	0.001
MP2/aug-cc-pVDZ	−0.006	2.451	0.000
MP2/aug-cc-pVTZ	0.001	2.508	0.001
$H_2FCH\cdots Hli$			
MP2/6-311++G(d,p)	−0.002	2.331	−0.001
MP2/6-311++G(2df,2pd)	−0.001	2.267	0.000
MP2/6-311++G(3df,3pd)	0.000	2.252	0.000
MP2/aug-cc-pVDZ	−0.007	2.211	0.000
MP2/aug-cc-pVTZ	0.001	2.247	0.000
$HF_2CH\cdots Hli$			
MP2/6-311++G(d,p)	−0.003	2.126	−0.001
MP2/6-311++G(2df,2pd)	−0.002	2.079	0.000
MP2/6-311++G(3df,3pd)	0.000	2.079	0.000
MP2/aug-cc-pVDZ	−0.007	2.044	0.000
MP2/aug-cc-pVTZ	0.000	2.073	0.001
$F_3CH\cdots Hli$			
MP2/6-311++G(d,p)	−0.003	1.965	0.001
MP2/6-311++G(2df,2pd)	−0.003	1.931	0.002
MP2/6-311++G(3df,3pd)	−0.001	1.937	0.002
MP2/aug-cc-pVDZ	−0.009	1.907	0.003
MP2/aug-cc-pVTZ	−0.001	1.932	0.003

where $\epsilon_{\mathrm{disp}}^{(20)}$ designates dispersion energy, $\epsilon_{\mathrm{e,r}}^{(12)}$ is the second-order electrostatic correlation correction, and $\Delta E_{\mathrm{EX-DEL}}^{(2)}$ designates the exchange-delocalization second-order energy term.[19d]

The "atoms in molecules" (AIM) theory of Bader[10] was applied, and the critical points which were further analyzed in terms of electron densities and their Laplacians were found. The AIM calculations were performed with the use of the AIM2000 program.[35]

Results and Discussion

Geometries and Frequencies. One of the most important questions concerning the results presented here is that of the nature of the interactions. Are the complexes investigated connected through hydrogen bonds? The classification of the interactions to hydrogen bonds is not obvious here since the complexes are connected through C−H···H links which are usually called unconventional H-bonds, and the nature of these interactions is the subject of controversy. The analyzed species are unconventional because they are dihydrogen-bonded systems and because C−H bonds with nonelectronegative carbon atoms are proton donors.

Tables 1 and 2 show the geometrical parameters for methane and its fluoro and chloro derivatives linked with the LiH acceptor. The H···H distance for the $CH_4\cdots HLi$ complex is approximately equal to ~2.5−2.6 Å for all levels of calculations. For complexes with CFH_3, CF_2H_2, and $CClH_3$ donors, the H···H distances amount to ~2.0−2.3 Å, corresponding approximately to the sum of van der Waals radii. For the CCl_2H_2, CCl_3H, and CF_3H donors, these distances are less than 2.0 Å which may support the idea of hydrogen bonding interactions. The H···H distance decreases if the number of halogen substituents increases. It is worth mentioning that it corresponds to an increase in H-bond strength since correlations between the H···H distance and the binding energy were found for intermolecular DHBs.[9] Additionally for the CX_nH_{4-n} donors the H···H distances are smaller for X = Cl meaning that the chlorine donating moieties are stronger Lewis acids than the corresponding fluorine moieties.

TABLE 2: Geometrical Parameters (in Å) for Complexes of Chloro Derivatives of Methane with LiH

level of calculations	ΔLi−H	H···H	ΔC−H
$H_2ClCH\cdots HLi$			
MP2/6-311++G(d,p)	−0.002	2.205	0.001
MP2/6-311++G(2df,2pd)	−0.001	2.126	0.003
MP2/6-311++G(3df,3pd)	0.000	2.117	0.003
MP2/aug-cc-pVDZ	−0.007	2.081	0.002
$HCl_2CH\cdots HLi$			
MP2/6-311++G(d,p)	−0.003	1.937	0.004
MP2/6-311++G(2df,2pd)	−0.002	1.885	0.006
MP2/6-311++G(3df,3pd)	−0.001	1.882	0.006
MP2/aug-cc-pVDZ	−0.008	1.853	0.006
$Cl_3CH\cdots HLi$			
MP2/6-311++G(d,p)	−0.003	1.746	0.010
MP2/6-311++G(2df,2pd)	−0.001	1.713	0.012
MP2/6-311++G(3df,3pd)	−0.001	1.706	0.012
MP2/aug-cc-pVDZ	−0.009	1.679	0.012

For the typical red-shifted H-bonds, the elongation of the proton donating bond is often treated as strong evidence for the hydrogen bond interaction.[7] Even for C−H···O interactions, the correlation between the C−H bond length and the H···O intermolecular distance was found for homogeneous samples of amino acids.[36] For the C−H···H interactions considered here, there are only slight elongations of the C−H bonds (Tables 1 and 2). All levels of calculations show that the greatest elongation of about 0.01 Å is for the $Cl_3CH\cdots HLi$ complex for which the shortest H···H distance and the strongest H-bond were detected. For the remaining complexes, the change of the C−H donating bond due to complexation is negligible. It is worth mentioning that, at the MP2/6-311++G(d,p) level, there is a shortening of the C−H bonds for H_2FCH and HF_2CH donors of about 0.001 Å indicating that the corresponding complexes may be treated as blue-shifted dihydrogen bonds. For the other basis sets, a negligible shortening of the C−H bond length is observed only for the $H_2FCH\cdots HLi$ complex, a shortening of about $\sim 10^{-4}$ Å for the 6-311++G(2df,2pd) basis set and 2×10^{-4} Å for aug-cc-pVDZ. At the MP2/aug-cc-pVTZ level of theory, such a shortening is not observed for any of the complexes.

The dependence of the level of theory on the change of the C−H bond length due to complexation was analyzed very recently for the $F_3CH\cdots FH$ dimer.[29c] Analyzing the C−H bond length the authors detected a red shift for the Hartree−Fock method and nonsaturated basis sets and a blue shift for higher levels of theory up to MP2(full)/6-311++G(d,p). However, the more extended basis sets were not applied as was done for the complexes investigated here where for the 6-311++G(d,p) basis set blue shifts were detected but for 6-311++G(3df,3pd) and aug-cc-pVTZ blue-shifts were not detected.

The conclusions based on the changes of C−H bond length due to the process of complexation are supported here by vibrational spectra analysis. It is well-known that for the mediate and strong H-bonds the frequency associated with the X−H stretch (X−H is the proton donating bond) is usually red-shifted and its intensity is enhanced upon formation of hydrogen bonding.[25,29a] For example, for the water dimer, the MP2/6-31+G(d,p) calculations led to a decrease of the OH bond stretching frequency by 31 cm^{-1} and an increase of the corresponding mode intensity since I/I_0 is equal to 1.89 (I corresponds to the intensity within the complex while I_0 to the intensity for the monomer).[29a] The results of Table 3 present the frequency shifts and intensity changes due to complexation for the dihydrogen bonded systems considered here. For the $H_3CH\cdots HLi$, $FH_2CH\cdots HLi$, and $F_2HCH\cdots HLi$ complexes, there

TABLE 3: Shift in Frequency and Intensity of C−H Stretch Caused by Complexation (MP2 Results)[a]

basis set	CH_4	CFH_3	CF_2H_2	CF_3H
6-311++G(d,p)	−1.6	**7.0**	**2.0**	−24.8
	0.08	**0.15**	**0.34**	0.48
6-311++G(2df,2pd)	−7.4	**0.3**	−4.1	−37.4
	0.01	**0.17**	0.48	1.08
6-311++G(3df,3pd)	−9.3	−1.8	−4.3	−35.1
	0.01	0.19	0.51	1.18
aug-cc-pVDZ	−1.7	**1.1**	−7.2	−50.7
	0.01	**0.19**	0.63	2.10
aug-cc-pVTZ	−10.4	−3.3	−7.6	−45.5
	0.01	0.21	0.58	1.48

[a] LiH is the proton acceptor; the proton donors are designated; upper values correspond to $n - n_0$ (in cm^{-1}) and lower to I/I_0; subscript 0 corresponds to the monomer not involved in the H-bond interaction; blue-shifted systems are in bold.

is a reduction in intensity due to complexation; the I/I_0 values are smaller than unity. For the CH_4···HLi dimer, one can observe a decrease of the CH stretching frequency (red-shift) for all levels of theory. There is a blue-shift for the H_2FCH···HLi complex for the 6-311++G(d,p), 6-311++G(2df,2pd) and aug-cc-pVDZ basis sets, whereas for 6-311++G(3df,3pd) and aug-cc-pVTZ, small red-shifting is observed. Blue-shifting for the F_2HCH···HLi dimer is observed only for the 6-311++G(d,p) basis set. For the F_3CH···HLi dimer all results show red-shifting and an increase in intensity as for typical mediate or strong H-bonds except at the MP2/6-311++G(d,p) level of theory where a decrease in intensity is observed (I/I_0 is equal to 0.48). One can see that the vibrational spectra results, as one would expect, correspond to the geometrical ones given in Table 1 and described earlier. The vibrational results for chlorine species are not presented here since for all of them an elongation of the C−H proton donating bond is observed (Table 2), and there is a corresponding red-shift. However the frequency results for fluorine species show (similar to the geometrical results) that one should be careful classifying H-bonds as being red- or blue-shifting since such classification depends on the level of theory applied, especially for slight changes due to the process of complexation as were found here. For the complexes analyzed here, the greatest blue shift of 7 cm^{-1} occurs for H_2FCH···HLi (MP2/6-311++G(d,p) level), whereas for example for F_3CH···O (CH_3OH as an accepting molecule), a blue shift of 47 cm^{-1} was found at the MP2/6-31+G(d,p) level.[29a]

Tables 1 and 2 also show the effect of the shortening of the LiH accepting bond observed earlier for the other DHBs.[9,17] However, for some of fluoro derivatives of methane as proton donors, the effect of shortening the Li−H bonds disappears at the MP2/aug-cc-pVTZ level, and a negligible elongation of the LiH bond is observable. For chloro derivatives, all levels show a shortening of the Li−H bond, but there are no MP2/aug-cc-pVTZ results in this case since convergence was not achieved.

Decomposition of the Interaction Energy for Dihydrogen-Bonded Complexes. Tables 4 and 5 present the binding energies (ΔE^{MP2}**)** and their terms obtained within the decomposition scheme for fluorine and chlorine donating molecules, respectively. The binding energies were calculated according to the supermolecular approach where the interaction energy of two systems A and B is calculated as the difference between the energy of the dimer E_{AB} (here ΔE^{MP2}) and the energies of the monomers E_A and E_B, each calculated for a given nuclear configuration.[19d]

There are the following tendencies for the binding energy (ΔE^{MP2}) for complexes analyzed here (Tables 4 and 5): an increase of energies according to the increase in the size of the Pople type basis set. In the case of the Dunning basis sets, the differences in binding energies are practically negligible. One can also see systematic changes according to the change in the size of the basis set for components of energy. The SCF energy (ΔE^{HF}) is greater for the Pople basis set of smaller size, but its components ($\epsilon_{el}^{(10)}$, ϵ_{ex}^{HL}, and E_{del}^{HF}) are greater for larger Pople type basis sets.

For all levels of calculations applied here, one can observe that for complexes with methane the absolute values of binding energies are less than 1 kcal/mol; for CXH_3 they are approximately ∼2−3 kcal/mol, for CX_2H_2 approximately ∼4−5 kcal/mol, and for CX_3H approximately ∼6−7 kcal/mol. For the latter, the hydrogen bonds are stronger than for the trans-linear water dimer (4.5−5.0 kcal/mol) and may be classified as moderate H-bonds. Also there is the same observation here as for H···H distances that chlorine derivatives are stronger donors than the fluorine derivatives since for the former the binding energies are greater by about 1 kcal/mol. Figure 1 shows the relationship between the H···H distance and the binding energy; the linear correlation coefficient for this dependence amounts to 0.98.

If one concentrates on the fluorine complexes (Table 4), then the following findings may be pointed out. There is an increase in the first-order electrostatic interaction energy ($\epsilon_{el}^{(10)}$) if the number of F-substituents increases, and one can observe that this term is in principle the most important attractive term. The CH_4···HLi complex is an exception since here the other attractive terms are comparable; for example, for the aug-cc-pVTZ basis set, the dispersion energy term $\epsilon_{disp}^{(20)}$ amounts to −1.04 kcal/mol, whereas the electrostatic term amounts to −0.80 kcal/mol. The Heitler-London first-order energy (the sum of the first-order exchange and electrostatic energy terms) is positive for the methane complex at all levels of calculations. This indicates that the exchange energy term (ϵ_{ex}^{HL}) outweighs the electrostatic term. For the H_2FCH···HLi complex the electrostatic and exchange energy terms are approximately equivalent with the electrostatic value being slightly greater; hence, the first-order Heitler-London energy is negative. The attractive delocalization higher order energy term (E_{del}^{HF}) increases with an increase in the number of F-substituents but not as rapidly as the $\epsilon_{el}^{(10)}$ term. For the CH_4···HLi complex, E_{del}^{HF} amounts to 78% of $\epsilon_{el}^{(10)}$; for H_2FCH···HLi it is 31%; for HF_2CH···HLi it is 28%; and for F_3CH···HLi it is 27% (aug-cc-pVTZ).

For the Pople type basis set, 6-311++G(3df,3pd), and for the Dunning basis sets, the HF energy for the CH_4···HLi complex is positive indicating that if one does not take into account the correlation effects then improper results concerning stability may be obtained since the interaction energy calculated at the MP2 level is negative for this dimer.

There are similar observations for the dispersion effects ($\epsilon_{disp}^{(20)}$) as for the delocalization term; $\epsilon_{disp}^{(20)}$ increases from 1.0 kcal/mol to 1.5, from 2.1 to 2.5 kcal/mol (absolute values are given) when fluorine substituents are added (aug-cc-pVTZ). It is worth mentioning that the correlation correction to the RHF energy ($\epsilon_{MP}^{(2)}$) is practically constant changing only slightly from −0.8 to −1.1 kcal/mol for the aug-cc-pVTZ basis set. However, two other energy terms, the second-order electrostatic correlation correction term and the second-order exchange-delocalization term, are repulsive and increase if the number of F-substituents increases. Except for the CH_4···HLi dimer, the partitioning of the interaction energy for DHBs considered here is similar to typical H-bonds. It was found earlier that for

TABLE 4: Decomposition of the Interaction Energy for Complexes of Methane and Its Fluoro Derivatives With Lithium Hydride[a]

	ΔE^{HF}	$\epsilon_{el}^{(10)}$	ϵ_{ex}^{HL}	E_{del}^{HF}	ΔE^{MP2}	$\epsilon_{MP}^{(2)}$	$\epsilon_{e,r}^{(12)}$	$\epsilon_{disp}^{(20)}$	$\Delta E_{EX-DEL}^{(2)}$
$H_3CH\cdots HLi$[b]	−0.11	−0.73	1.08	−0.46	−0.49	−0.38	0.00	−0.51	0.12
$H_3CH\cdots HLi$[c]	−0.05	−0.82	1.29	−0.52	−0.64	−0.59	−0.01	−0.74	0.15
$H_3CH\cdots HLi$[d]	0.04	−0.96	1.60	−0.61	−0.73	−0.76	−0.01	−0.96	0.22
$H_3CH\cdots HLi$[e]	0.10	−1.12	1.92	−0.70	−0.69	−0.79	−0.02	−1.05	0.28
$H_3CH\cdots HLi$[f]	0.05	−0.80	1.64	−0.62	−0.77	−0.82	−0.02	−1.04	0.23
$H_2FCH\cdots HLi$[b]	−1.65	−3.34	2.62	−0.93	−2.03	−0.38	0.25	−0.89	0.26
$H_2FCH\cdots HLi$[c]	−1.41	−3.49	3.13	−1.06	−2.20	−0.79	0.21	−1.32	0.31
$H_2FCH\cdots HLi$[d]	−1.36	−3.53	3.27	−1.10	−2.29	−0.93	0.19	−1.49	0.37
$H_2FCH\cdots HLi$[e]	−1.45	−3.84	3.60	−1.22	−2.30	−0.85	0.22	−1.51	0.44
$H_2FCH\cdots HLi$[f]	−1.37	−3.55	3.30	−1.11	−2.37	−1.00	0.19	−1.54	0.38
$HF_2CH\cdots HLi$[b]	−3.42	−6.33	4.48	−1.57	−3.72	−0.30	0.56	−1.28	0.41
$HF_2CH\cdots HLi$[c]	−3.04	−6.43	5.12	−1.73	−3.91	−0.87	0.48	−1.83	0.47
$HF_2CH\cdots HLi$[d]	−2.99	−6.37	5.12	−1.74	−4.00	−1.01	0.44	−1.95	0.51
$HF_2CH\cdots HLi$[e]	−3.25	−6.87	5.55	−1.93	−4.09	−0.85	0.49	−1.95	0.61
$HF_2CH\cdots HLi$[f]	−3.00	−6.43	5.20	−1.77	−4.11	−1.11	0.44	−2.07	0.53
$F_3CH\cdots HLi$[b]	−5.58	−9.79	6.72	−2.51	−5.74	−0.16	0.93	−1.70	0.61
$F_3CH\cdots HLi$[c]	−5.04	−9.77	7.39	−2.67	−5.95	−0.90	0.79	−2.33	0.64
$F_3CH\cdots HLi$[d]	−5.01	−9.62	7.25	−2.64	−6.05	−1.04	0.73	−2.42	0.65
$F_3CH\cdots HLi$[e]	−5.41	−10.32	7.88	−2.97	−6.22	−0.80	0.81	−2.41	0.80
$F_3CH\cdots HLi$[f]	−5.04	−9.65	7.26	−2.65	−6.17	−1.13	0.73	−2.52	0.67

[a] All energy terms are in kcal/mol. ΔE^{HF}, interaction energy calculated at the restricted Hartree−Fock; $\epsilon_{el}^{(10)}$, first-order electrostatic interaction energy; ϵ_{ex}^{HL}, Heitler-London exchange effects; ΔE^{HL}, Heitler-London energy (as a sum $\epsilon_{el}^{(10)} + \epsilon_{ex}^{HL}$ and is not included in the table); E_{del}^{HF}, delocalization effects; ΔE^{MP2}, interaction energy calculated at the MP2 level of theory; $\epsilon_{MP}^{(2)}$, correlation correction to the RHF interaction energy; $\epsilon_{disp}^{(20)}$, dispersion effects; $\epsilon_{e,r}^{(12)}$, the second-order electrostatic correlation correction; $\Delta E_{EX-DEL}^{(2)}$, the exchange-delocalization second-order energy term. [b] MP2/6-311++G(d,p). [c] MP2/6-311++G(2df,2pd). [d] MP2/6-311++G(3df,3pd). [e] MP2/aug-cc-pVDZ. [f] MP2/aug-cc-pTZ.

TABLE 5: Decomposition of the Interaction Energy for Complexes of Chloro Derivatives of Methane with Lithium Hydride[a]

	ΔE^{HF}	$\epsilon_{el}^{(10)}$	ϵ_{ex}^{HL}	E_{del}^{HF}	ΔE^{MP2}	$\epsilon_{MP}^{(2)}$	$\epsilon_{e,r}^{(12)}$	$\epsilon_{disp}^{(20)}$	$\Delta E_{EX-DEL}^{(2)}$
$H_2ClCH\cdots HLi$[b]	−1.87	−4.15	3.59	−1.31	−2.42	−0.56	0.33	−1.25	0.36
$H_2ClCH\cdots HLi$[c]	−1.60	−4.50	4.47	−1.57	−2.80	−1.20	0.26	−1.92	0.46
$H_2ClCH\cdots HLi$[d]	−1.56	−4.52	4.57	−1.61	−2.93	−1.37	0.22	−2.10	0.51
$H_2ClCH\cdots HLi$[e]	−1.65	−4.88	5.00	−1.77	−2.93	−1.28	0.24	−2.12	0.61
$HCl_2CH\cdots HLi$[b]	−3.52	−7.98	7.18	−2.72	−4.43	−0.91	0.65	−2.25	0.69
$HCl_2CH\cdots HLi$[c]	−3.09	−8.29	8.28	−3.08	−5.00	−1.91	0.53	−3.23	0.80
$HCl_2CH\cdots HLi$[d]	−3.02	−8.25	8.34	−3.11	−5.14	−2.11	0.47	−3.43	0.85
$HCl_2CH\cdots HLi$[e]	−3.26	−8.79	8.92	−3.40	−5.18	−1.92	0.47	−3.38	0.99
$Cl_3CH\cdots HLi$[b]	−4.91	−11.88	11.71	−4.74	−6.44	−1.53	0.89	−3.54	1.12
$Cl_3CH\cdots HLi$[c]	−4.34	−12.01	12.79	−5.12	−7.17	−2.83	0.75	−4.78	1.18
$Cl_3CH\cdots HLi$[d]	−4.22	−12.05	13.04	−5.21	−7.31	−3.09	0.70	−5.05	1.26
$Cl_3CH\cdots HLi$[e]	−4.38	−12.71	13.83	−5.70	−7.38	−2.80	0.67	−4.92	1.45

[a] All energy terms are in kcal/mol. All designations of levels of computations and energy terms are the same as for Table 4.

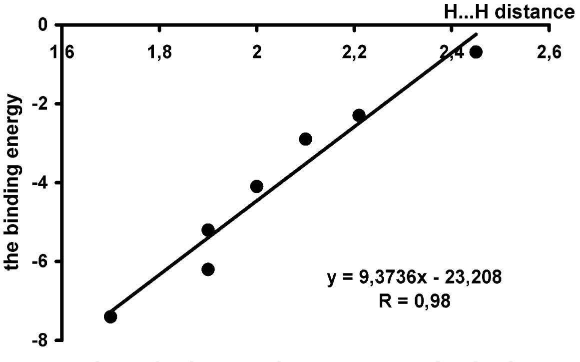

Figure 1. Relationship between the H···H intermolecular distance (in Å) and the binding energy (in kcal/mol).

stronger dihydrogen bonds, such as $HCCH\cdots HLi$, the first-order Heitler-London energy term is negative as for the water dimer.[20,21] Such partitioning of the interaction energy occurs here for the $F_3CH\cdots HLi$ dimer where red-shifting hydrogen bonding occurs.

Table 5 presents the results for chlorine complexes. Only approximately similar observations as for fluorine derivatives may be pointed out here. The most important difference is that for chlorine derivatives there is practically an equivalent increase of the first order energy terms, the exchange energy term and the electrostatic term. Hence the Heitler-London energy term is repulsive for larger basis sets and only slightly attractive for smaller ones; even for the $Cl_3CH\cdots HLi$ complex, the ΔE^{HL} energy value is positive despite the fact that the binding energy shows the existence of a stronger H-bond than for the water dimer (about 5 kcal/mol for water). One can observe the greater importance of the delocalization energy for chlorine species than for fluorine species. For chlorine derivatives, despite the approximate equivalence of the first-order energy terms, the SCF energy is negative due to the importance of the delocalization energy term. One can also observe that the correlation energy $\epsilon_{MP}^{(2)}$ is more sensitive to the number of Cl substituents and more significantly contributes in attraction interactions than fluorine species. Particularly, one can observe this for the $CCl_3H\cdots HLi$ complex. The dispersion energy also significantly contributes to the binding energy for the chlorine species. Hence one can conclude that in the case of fluorine complexes the most important attractive term is the electrostatic term, while for chlorine derivatives the electrostatic energy term is compensated by the exchange term; hence, the delocaliztion and the dispersion are responsible for their stabilization.

TABLE 6: Topological Parameters (in au) of the Bond Critical Point at the H···H Contact[a]

dimer	$\rho_{H\cdots H}$	$\nabla^2\rho_{H\cdots H}$	G_C	V_C	H_C	$Q_{H(C)}\Omega$	$Q_{H(Li)}\Omega$
$H_3CH\cdots HLi^b$	0.0040	0.0097	0.00207	−0.00173	0.00034	0.0348	−0.7679
$H_3CH\cdots HLi^c$	0.0042	0.0117	0.00236	−0.00183	0.00053	0.0249	−0.7682
$H_3CH\cdots HLi^d$	0.0050	0.0130	0.00272	−0.00215	0.00002	0.0141	−0.7676
$H_3CH\cdots HLi^e$	0.0056	0.0153	0.00315	−0.00248	0.00067	0.0184	−0.7747
$H_3CH\cdots HLi^f$	0.0051	0.0133	0.00274	−0.00215	0.00059	0.0364	−0.7649
$H_2FCH\cdots HLi^b$	0.0072	0.0160	0.00360	−0.00319	0.00041	0.0826	−0.7702
$H_2FCH\cdots HLi^c$	0.0078	0.0207	0.00434	−0.00351	0.00083	0.0743	−0.7696
$H_2FCH\cdots HLi^d$	0.0082	0.0204	0.00444	−0.00377	0.00067	0.0568	−0.7686
$H_2FCH\cdots HLi^e$	0.0088	0.0214	0.00489	−0.00443	0.00046	0.0641	−0.7711
$H_2FCH\cdots HLi^f$	0.0083	0.0206	0.00452	−0.00388	0.00064	0.0845	−0.7700
$HF_2CH\cdots HLi^b$	0.0103	0.0229	0.00515	−0.00458	0.00057	0.1382	−0.7683
$HF_2CH\cdots HLi^c$	0.0113	0.0282	0.00635	−0.00563	0.00072	0.1254	−0.7695
$HF_2CH\cdots HLi^d$	0.0113	0.0275	0.00620	−0.00552	0.00068	0.1053	−0.7680
$HF_2CH\cdots HLi^e$	0.0121	0.0266	0.00653	−0.00642	0.00011	0.1394	−0.7710
$HF_2CH\cdots HLi^f$	0.0115	0.0273	0.00629	−0.00574	0.00055	0.1345	−0.7703
$F_3CH\cdots HLi^b$	0.0136	0.0308	0.00696	−0.00620	0.00076	0.2057	−0.7681
$F_3CH\cdots HLi^c$	0.0148	0.0351	0.00845	−0.00814	0.00031	0.1904	−0.7698
$F_3CH\cdots HLi^d$	0.0146	0.0348	0.00815	−0.00761	0.00053	0.1683	−0.7685
$F_3CH\cdots HLi^e$	0.0156	0.0320	0.00828	−0.00856	−0.00028	0.2303	−0.7700
$F_3CH\cdots HLi^f$	0.0150	0.0346	0.00834	−0.00804	0.00030	0.2009	−0.7292
$H_2ClCH\cdots HLi^b$	0.0089	0.0197	0.00445	−0.00396	0.00049	0.1096	−0.7686
$H_2ClCH\cdots HLi^c$	0.0102	0.0259	0.00571	−0.00494	0.00077	0.1040	−0.7691
$H_2ClCH\cdots HLi^d$	0.0105	0.0256	0.00570	−0.00500	0.00070	0.0871	−0.7684
$H_2ClCH\cdots HLi^e$	0.0112	0.0254	0.00613	−0.00591	0.00021	0.0970	−0.7699
$HCl_2CH\cdots HLi^b$	0.0145	0.0322	0.00738	−0.00670	0.00068	0.1788	−0.7667
$HCl_2CH\cdots HLi^c$	0.0164	0.0375	0.00922	−0.00908	0.00014	0.1722	−0.7638
$HCl_2CH\cdots HLi^d$	0.0165	0.0381	0.00913	−0.00875	0.00038	0.1531	−0.7655
$HCl_2CH\cdots HLi^e$	0.0174	0.0345	0.00918	−0.00973	−0.00055	0.1909	−0.7664
$Cl_3CH\cdots HLi^b$	0.0211	0.0454	0.01106	−0.01078	0.00028	0.2373	−0.7647
$Cl_3CH\cdots HLi^c$	0.0233	0.0462	0.01293	−0.01430	−0.00137	0.2301	−0.7610
$Cl_3CH\cdots HLi^d$	0.0236	0.0488	0.01322	−0.01422	−0.00100	0.2105	−0.7595
$Cl_3CH\cdots HLi^e$	0.0247	0.0439	0.01273	−0.014470	−0.00197	0.2712	−0.7613

[a] $\rho_{H...H}$ is the electron density; $\nabla^2\rho_{H...H}$ is the laplacian of the electron density; H_C is the electron energy density; G_C is the electron kinetic energy density; V_C is the electron potential energy density; $Q_{H(C)}\Omega$ is the integrated H(C)-atom charge; and $Q_{H(Li)}\Omega$ is the integrated H(Li)-atom charge. [b] MP2/6-311++G(d.p). [c] MP2/6-311++G(2df.2pd). [d] MP2/6-311++G(3df.3pd). [e] MP2/aug-cc-pVDZ. [f] MP2/aug-cc-pVTZ.

Topological Parameters. An analysis of the characteristics of the critical points of electron densities derived from the wave functions was performed in this study. The electron densities at the critical points as well as their Laplacians were considered for complexes analyzed here since these topological parameters may characterize the type of interaction. Eight topological criteria for the existence of hydrogen bonding interactions were indicated by Koch and Popelier.[37] Among them are three that are most often applied. The electron density and its Laplacian for the H···Y contact within the X−H···Y H-bond should have a relatively high value. Both parameters for closed-shell interactions as H-bonds are positive and should be within the following ranges: 0.002−0.04 au for the electron density and 0.02−0.15 au for its Laplacian. It is worth mentioning that very strong H-bonds are often partly covalent interactions and that for such systems as for the other shared-shell interactions the values of Laplacians of the electron density at BCPs are negative.[38,39] This was observed for very strong resonance-assisted hydrogen bonds (RAHBs)[38] and very recently also for strong dihydrogen bonds for the $NF_3H^+\cdots HBeH$ complex.[18] For the complexes analyzed here, all electron densities at the H···H BCPs and all Laplacians are positive since the corresponding interactions belong to moderate or weak H-bonds (Table 6). One can see that all electron density values for all levels of calculations are within the range proposed by Koch and Popelier for H-bond interactions. The situation is different for Laplacian values; for the $CH_4\cdots HLi$ complex, the Laplacians of electron densities at H···H BCPs are below the lower limit. For complexes with H_2FCH, HF_2CH, and H_2ClCH donors, the Laplacian values are equal to ~0.02−0.03 au, approximately at the lower limit. Hence, concerning the topological parameters for some of the complexes it is equivocal to classify the interactions as H-bonds. However the topological parameters are good descriptors of hydrogen bonding strength since they correlate well with the binding energy. Figure 2 shows the linear relationship between the electron density and the binding energy at the MP2/6-311++G(3df,3pd) level of theory. The linear correlation coefficient for this dependence amounts to 0.96, whereas this coefficient for the relationship between the Laplacian of electron density and the binding energy is equal to 0.97.

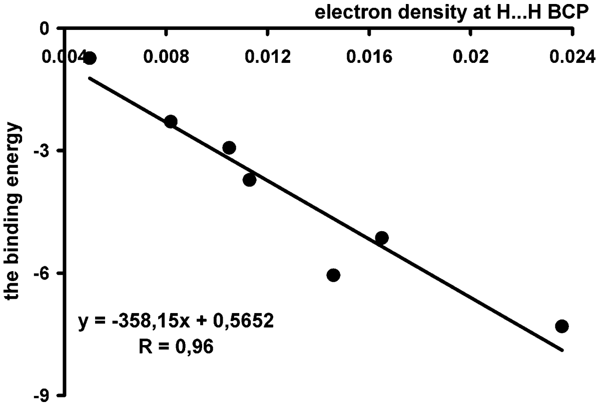

Figure 2. Dependence between the electron density at H···H BCP (in au) and the binding energy (in kcal/mol).

It is worth mentioning that, despite these correlations, the topological and energetic results do not correspond to the other noninterrelated systems. Let us consider the MP2/6-311++G-(d,p) results. For the linear-trans water dimer the binding energy is equal to −4.45 kcal/mol; the electron density at H···O BCP amounts to 0.023 au; and its Laplacian amounts to 0.091 au.[39] For the $Cl_3CH\cdots HLi$ and $F_3CH\cdots HLi$ complexes, the electron densities at H···H BCP are equal to 0.021 and 0.014 au; their Laplacians amount to 0.045 and 0.031 au (Table 6); and their binding energies amount to −6.44 and −5.74 kcal/mol, respectively (Tables 4 and 5). It seems that this inconsistency appears since there is the H···O contact for the water dimer and the H···H contacts for the systems investigated here.

There are also the other properties of the BCP which allow a deeper insight into the nature of interactions to be obtained. It is the electronic energy density H_C of the charge distribution[40] which may be expressed as

$$H_C = G_C + V_C \tag{5}$$

G_C is a local one-electron kinetic energy density, and V_C is the local potential energy density. The relation between the Laplacian and the components of the local energy density H_C is given by the equation[40]

$$(1/4)\ \nabla^2\rho(r_{BCP}) = 2G_C + V_C \tag{6}$$

The sign of Laplacian at a point determines whether the negative potential energy or the positive kinetic energy is in excess of the virial ratio amounting to 2. In negative regions of Laplacian the potential energy dominates, while in the positive regions there is the domination of the kinetic energy. It was pointed out that in bonds with any degree of covalent character $|V_C|$ is greater than G_C, and H_C is less than 0. Bonds in which this condition holds and where $|V_C|$ is less than $2G_C$ have been attributed to being partially covalent, whereas $H_C > 0$ corresponds to purely closed shell interactions.[41] Rozas et al. have introduced a new classification of hydrogen bonds according to their strength.[42] Weak hydrogen bonds show both $\nabla^2\rho(r_{BCP})$ and H_C values as being positive. For medium H-bonds, $\nabla^2\rho(r_{BCP})$ is greater than 0 and H_C is less than 0. For strong hydrogen bonds the Laplacian value as well as the electron energy density at BCP are negative.

For the complexes investigated here all Laplacians of electron density at H···H BCP are positive as was mentioned, and only in a few cases the energy density H_C at this BCP is negative. There is the negative value for the $CF_3H\cdots HLi$ dimer calculated at the MP2/aug-cc-pVDZ level; for other levels it is positive, including MP2/aug-cc-pVTZ. The negative value of H_C was also obtained for $HCl_2CH\cdots HLi$ at the MP2/aug-cc-pVDZ level and for $Cl_3CH\cdots HLi$ at all levels except MP2/6-311++G(d,p). However for chlorine species the MP2/aug-cc-pVTZ results are not available. This means that only in a few cases one can expect a partially covalent nature for the dihydrogen bonds. Also, the Laplacian values as well as energetic values (G_C, H_C, and V_C) are very sensitive to the level of theory applied. Table 6 shows that they change significantly for different basis sets. However, the electron density at H···H BCP is rather insensitive; for the given complex, the differences between the results obtained for the different basis sets are usually less than 0.001 au. The 6-311++G(d,p) basis set is an exception since the corresponding results differ significantly from the others.

Table 6 also presents integrated atomic charges for hydrogen atoms being within the intermolecular (C)H···H(Li) contact, $Q_{H(C)}(\Omega)$ and $Q_{H(Li)}(\Omega)$, respectively. Generally, in dihydrogen bonds, the charge of the H-atom of the C−H proton donating bond is positive and the charge of the H(Li) atom is negative. Practically there are only slight changes for the H(Li) charge when one compares different complexes and when the comparison is connected with different basis sets. For all complexes and all basis sets, the H(Li) charge approximately amounts to −0.77 (au). The situation is different for H(C) charges because of the influence of F and Cl electronegative atoms. Analyzing the MP2/6-311++G(3df, 3pd) results, one can see the following H(C) charges for the donating molecules: CH_4 at 0.014, H_2FCH at 0.057, HF_2CH at 0.105, F_3CH at 0.168, H_2ClCH at 0.087, HCl_2CH at 0.153, and Cl_3CH at 0.210. One can see that the positive charge on the H(C) atom increases when the number of electronegative substituents is greater. This effect is stronger for chlorine than for fluorine atoms in accordance with the fact that chlorine derivatives form stronger H-bonds than fluorine derivatives.

Summary

The complexes of methane and its fluoro and chloro derivatives with lithium hydride were investigated. The MP2 calculations were performed with the use of the Pople type basis sets up to 6-311++G(3df,3pd) and with the Dunning aug-cc-pVDZ and aug-cc-pVTZ basis sets. For all complexes, the H···H intermolecular contact exists which may suggest the existence of dihydrogen bonds. For complexes with methane the analysis of geometrical, energetic and topological parameters indicates that they may be classified as van der Waals complexes. For the remaining complexes, dihydrogen bond interactions exist. For $X_3CH\cdots HLi$ (X = Cl and F) there is no doubt that they are dihydrogen-bonded systems since all parameters analyzed show that the criteria for the existence of hydrogen bonding are fulfilled. H···H contacts are significantly shorter than the corresponding sum of van der Waals radii. The binding energies amount to ∼6−7 kcal/mol, and the topological parameters are in the ranges proposed by Koch and Popelier as those for which typical H-bonds exist.

Additionally the decomposition interaction energy was performed showing that for fluorine complexes the most important attractive is the electrostatic energy term. This is the same as for the other typical H-bonded complexes where the electrostatic interaction is dominant. For chlorine complexes the other attractive energy terms are also important.

Analysis of the properties of the donating bond show that one should be careful in classifying systems as blue-shifting H-bonds if shortening of the proton donating bond is observed. For the complexes analyzed here, for some of the species, a slight shortening is observed for the unsaturated but often applied 6-311++G(d,p) basis set, but this effect disappears for larger basis sets.

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