Nature of X−H$^{+\delta}\cdots{}^{-\delta}$H−Y Dihydrogen Bonds and X−H···σ Interactions

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Ab initio studies of complexes HCCH···H_2, FCCH···H_2, HCCH···HLi, FCCH···HLi, HCCH···HBeH, FCCH···HBeH, HCCH···HBeF, and FCCH···HBeF with H···H intermolecular binding contacts were carried out up to the MP2/6-311++G(3df,3pd)/MP2/aug-cc-pVQZ level of theory. Binding energies extrapolated to the complete basis set (CBS) limit indicate that the results obtained at the MP2/6-311++G(3df,3pd) level of theory are almost saturated. An analysis of the geometrical and energetic parameters was performed, indicating that the more strongly bonded complexes could be classified as X−H$^{+\delta}\cdots{}^{-\delta}$H−Y dihydrogen bonds, whereas the weaker ones may belong to the X−H···σ category. In the first case, the electrostatic and exchange contributions are the most important energetic terms, whereas in the second case, the correlation term also makes a sizable contribution to the overall dimer stability. The atoms in molecules (AIM) theory was also applied to explain the nature of all of the complexes. A complete analysis of the different parameters of the complexes shows that the stronger complexes may be classified as H bonded and that the weaker complexes my be classified as van der Waals complexes. However, there is no evident borderline between them, which indicates the ambiguous nature of dihydrogen-bonded complexes or the arbitrary character of the definitions used to categorize the molecular complexes.

Introduction

In the middle of the 1990s, a new kind of molecular complex was described as being related to the hydrogen bond in nature. It was designated as X−H···H−E, where X−H is the typical proton-donating bond (such as O−H or N−H) and E designates a transition metal or boron.[1] This type of interaction was termed a dihydrogen bond (DHB)[2] because the link between the molecules within the complex is realized through the H···H contact. In early work on dihydrogen bonds, authors tried to identify the unique features of this kind of interaction in comparison with those of typical hydrogen bonding.[3] It was pointed out that a H atom acting as the proton acceptor differs from typical acceptors such as oxygen and nitrogen atoms where the lone electron pairs are responsible for the existence of H bonding. Such acceptor H atoms should be negatively charged, and this situation occurs for some of the transition-metal hydrides that exist in metalloorganic crystal structures. The negatively charged hydrogens are also typical for hydrides of the first and second groups of the periodic table of elements. Hence, model ab initio calculations of dihydrogen-bonded complexes with LiH, BeH_2, and other simple molecules as proton acceptors have been performed. One of the first theoretical investigations of the dihydrogen-bonded FH···HLi complex was carried out by Liu and Hoffman.[4] The binding energy predicted at the HF/6-31G* level of theory is equal to −9.21 kcal/mol, which is greater than the binding energy of the water dimer for which the typical O−H··O hydrogen bond exists. Additional calculations performed at higher levels of theory have confirmed the finding that the dihydrogen bonds are not necessarily weak.[5] For example, the binding energy for the aforementioned FH···HLi dimer calculated at the QCISD(T)/6-311++G(d,p) level of theory and corrected for BSSE amounts was found to equal −11.9 kcal/mol.[6]

An interesting study of X−H···H−E systems was presented by Crabtree and co-workers,[2] who performed the search of N−H···H−B contacts in the Cambridge Structural Database (CSD).[7] Twenty-six such systems with short H···H contacts (<2.2 Å) were found in 18 X-ray crystal structures. They found that the H···H distances are usually in the range of 1.7−2.2 Å and that the N−H···H angle tends to be more linear than bent, being in the range of 150−170°. The B−H···H angle tends to be more bent than linear, with the majority of the angle's data points in the range of 95−115°. They claim that the predominance of the bent B−H···H angles in the CSD may be better if one considers the interaction between the N−H proton-donating bond and the B−H bond as a whole. Hence, the concept of hydrogen bonding may be extended from the typical X−H···Y (Y contains at least one lone pair of electrons) to X−H···π (π electrons) and further to X−H···σ (σ bond) interactions usually named as dihydrogen bonds. They also claim that the strength of the H bonds range from −6 to −8 kcal/mol for the conventional N−H···lone pair H bonds, from −1 to −2 kcal/mol for the N−H···π bonds, and from −4 to −6 kcal/mol for N−H···σ, as was calculated earlier for the NH_3−BH_3 boroamine dimer.[3b] Hence, this phenomenon of a negatively charged hydrogen atom acting as the proton acceptor for DHBs or the possibility of forming σ bonds is addressed in the present study.

In earlier work, similarities between the conventional H-bonds and dihydrogen bonds were also observed. Ab initio calculations of the DHBs with hydrogen fluoride as the proton donor and

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the simple hydrides of the first and second groups as acceptors have been carried out up to the MP4(SDQ)/6-311++G(d,p) and QCISD(T)/6-311++(d,p) levels of theory.[6] The results of the calculations of DHBs have shown similar relationships to those that are known for conventional H bonds. The HF proton-donating bond is elongated because of complexation, and the elongation correlates well with the H-bond energy.[8] Such a relationship is well known for O−H⋯O bonds and other conventional H bonds.[9] Other correlations were also observed for DHBs, such as between the H⋯H distance and the H-bond energy, and were found to be similar to the most often observed relationships between the H⋯Y distance (Y is the proton acceptor for the X−H⋯Y system) and the H-bond energy. These geometrical and energetic dependencies are reflected in other features of dihydrogen-bonded complexes.[10] Complexation induces changes in the vibrational frequencies: shifts of X−H bands and increases in their intensities, similar to those of conventional H bonds,[11] changes in the magnetic resonance shielding constants,[12] and changes in the topological parameters derived from the Bader theory and others.[13]

The energy decomposition allows deeper insight into the physical nature of the stabilization energy to be obtained. Such an approach was applied to the dihydrogen bonds of H_3BNH_3, H_2BNH_2, and NH_3 molecules[14] using the Kitaura and Morokuma[15] energy decomposition scheme. They pointed out that the main difference between DHB systems and conventional H-bonded systems is the significant contribution from polarization, charge transfer, correlation, and higher-order components of the total interaction energy in the former case. The energy decomposition was also recently applied to other dihydrogen-bonded systems including LiH⋯H_2, LiH⋯CH_4, LiH⋯C_2H_6, and LiH⋯C_2H_2.[12] Using the perturbational IMPPT scheme,[16] they found that the components of the interaction energy of the LiH⋯C_2H_2 complex are very similar to those of the water dimer; the main binding-energy contributions come from the electrostatic energy, followed by the induction and dispersion energies. A different partitioning pattern was found for the other three complexes, where the large repulsive exchange term outweighs the attractive electrostatic term, and hence the Heitler−London interaction energy is positive. The main attractive term is the dispersion energy, and there is also the meaningful induction energy term. It is worth mentioning that for the LiH⋯HCCH complex the binding energy amounts to −4.1 kcal/mol and for the remaining complexes the binding energies are <1 kcal/mol. (This means that the arbitrary values are > −1 kcal/mol.) These values were obtained at the MP2/aug-cc-pVTZ/CCSD(T)/aug-cc-pVTZ level of theory with the inclusion of the vibrational contribution to the interaction energy. They concluded that the first complex is H bonded and that the others are van der Waals complexes. Recently, Del Bene et al.[17] studied theoretically modeled dihydrogen-bonded systems ranging from weak to strong; for example, the binding energy for the $LiNCH^+$⋯HLi complex calculated at the MP2/aug′-cc-pVTZ level of theory (aug′ means that the basis set is augmented with diffuse functions on C and N atoms but not for other atoms) is equal to −27.1 kcal/mol.

It is worth mentioning that the range of H⋯H contacts that may be classified as DHBs is broader than that which was pointed out in the first studies of such types of interactions. There are not only H−E (E is the transition metal) or H−B proton acceptors, but the other bonds may also play the role of acceptors. The studies of C−H⋯H−C interactions in organoammonium tetraphenylborates are one of the recent examples.[18] They applied the Bader theory[19] after multipole refinement of the crystal structures,[20] and they claim that the transition from nonshared (closed-shell) X−H⋯H−Y interactions to covalent (shared-shell) X⋯H−H⋯Y interactions is discontinuous. However, the transition from H⋯H contacts within DHBs to H⋯H in typical van der Waals complexes is not sharp, and there is no evident borderline between these categories. A similar problem was investigated 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,[21] where intramolecular H⋯H contacts were found. An analysis of such interactions using the Bader theory shows that they may be classified as hydrogen bonds similar to the H⋯H intramolecular contacts in the related styrene compound and its simple fluoro derivatives.[21] A more detailed topological analysis of H⋯H intramolecular interactions was performed by Matta et al.[22] They concluded that the H⋯H interaction makes a stabilizing contribution of ≤10 kcal/mol to the energy of the molecule in which it occurs; however, this interaction is distinct from dihydrogen bonding.

The aim of the present study is to analyze H⋯H interactions for a wider spectrum of model dihydrogen-bonded complexes. This study is based on the high level ab initio theories and additionally verified by comparison with complete basis set (CBS) estimates. In addition, the Bader theory has also been applied. The energy decomposition scheme is applied to gain more detailed insight into the nature of the interactions. One of the aims of this study is to answer the following questions: Is there a borderline between the dihydrogen-bonded complexes classified as hydrogen bonded and van der Waals interactions? Are there any sharply defined differences in the physical nature of these compexes? These questions are very important because there are numerous H⋯H intra- and intermolecular contacts for various organic and metalloorganic compounds that may contribute to the corresponding crystal cohesion energy. Hence, it is interesting to evaluate the influence of H⋯H interactions on the arrangement of molecules in crystals, which could be essential for crystal structure engineering.[23]

Computational Details

The calculations were carried out with the Gaussian 98[24] and Gaussian 03[25] sets of codes. Complexes HCCH⋯H_2, FCCH⋯H_2, HCCH⋯HLi, FCCH⋯HLi, HCCH⋯HBeH, FCCH⋯HBeH, HCCH⋯HBeF, and FCCH⋯HBeF with H⋯H intermolecular contacts were considered. The calculations were performed using the second-order perturbation Møller−Plesset method (MP2).[26] The following Pople basis sets[27−30] were used: 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3d,3p), and 6-311++G(3df,3pd). Also, the following Dunning-type basis sets[31,32] were used: cc-pVDZ, cc-pVTZ, cc-pVQZ, aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ and, for some systems, cc-pV5Z and aug-cc-pV5Z. Full optimizations have been performed using Pople-type basis sets up to the MP2/6-311++G(3df,3pd) level. Single-point MP2 calculations have been carried out with the Dunning basis sets for the reference geometry, as optimized at the MP2/6-311++G(3df,3pd) level of theory.

Because the basis sets applied are not saturated, the basis set extension effects were checked using the extrapolation formula

$$E(X) = E(\mathrm{CBS}) + A/X^3 \qquad (1)$$

where CBS designates the complete basis set[33] and X is the cardinal number of the basis set (cc-pVXZ and aug-cc-pVXZ).

TABLE 1: Optimized H···H Distances (Å) for Dihydrogen-Bonded Complexes, $C_2H_2\cdots H_2$ and FCCH···H_2[a]

basis set	$C_2H_2\cdots$HLi	FCCH···HLi	$C_2H_2\cdots$HBeH	FCCH···HBeH	$C_2H_2\cdots$HBeF	FCCH···HBeF	$C_2H_2\cdots\sigma(H_2)$	FCCH···$\sigma(H_2)$
6-311++G(d,p)	2.0499	2.0165	2.2934	2.2620	2.2989	2.2756	2.6006	2.5959
6-311++G(2d,2p)	1.9953	1.9630	2.2253	2.1921	2.2393	2.2093	2.6016	2.5948
6-311++G(3d,3p)	1.9906	1.9616	2.1963	2.1764	2.2113	2.1886	2.6001	2.5935
6-311++G(3df,3pd)	1.9818	1.9593	2.1936	2.1721	2.1965	2.1729	2.5997	2.5920

[a] The distance between the proton of the donating bond and the middle of the H_2 bond (BCP) is taken into account.

The binding energies for the analyzed complexes have been computed as the difference between the total energy of the complex and the energies of the isolated monomers, and they have been corrected for the basis set superposition error (BSSE) via the standard counterpoise method.[34] Much deeper insight into the characteristic features of various types of molecular complexes could be obtained by the inspection of various interaction-energy components. The rigorous symmetry adapted perturbation theory (SAPT)[35,36] yields the most comprehensive insight into the physical nature of the intermolecular interactions, but it also requires very intensive computational effort. Therefore, we decided to apply here the less-resource-demanding variation−perturbation approach,[37] reproducing the first-order SAPT interaction energy components for the benchmark He_2 and $(H_2O)_2$[38] systems at the Hartree−Fock limit.[39]

In the variation−perturbation approach mentioned above, the starting wave functions of the subsystems are obtained in the dimer-centered basis set (DCBS).[34] Hence, the total interaction energy and all of its components are free of BSSE owing to the full counterpoise correction.[16a,34,40]

The interaction energy can be decomposed in the following way:

$$\Delta E = \Delta E_{EL}{}^{(1)} + \Delta E_{EX}{}^{(1)} + \Delta E_{DEL}{}^{(R)} + \Delta E_{CORR} \qquad (2)$$

where $\Delta E_{EL}{}^{(1)}$ is the first-order electrostatic term, $\Delta E_{EX}{}^{(1)}$ is the first-order exchange component, and $\Delta E_{DEL}{}^{(R)}$ and ΔE_{CORR} correspond to higher-order delocalization and correlation terms, respectively. Such interaction energy partitioning defines the entire hierarchy of theoretical models from the most complete MP2 or coupled cluster, Hartree−Fock, and Heitler−London to the simplest electrostatic theory level.

The electrostatic term $\Delta E_{EL}{}^{(1)}$ could be further decomposed into the long-range multipole $\Delta E_{EL-MTP}{}^{(1)}$ component and the short-range penetration term $\Delta E_{EL-PEN}{}^{(1)}$.

$$\Delta E_{EL}{}^{(1)} = \Delta E_{EL-MTP}{}^{(1)} + \Delta E_{EL-PEN}{}^{(1)} \qquad (3)$$

For the sake of comparison, the classical Kitaura−Morokuma[15] interaction energy decomposition as implemented in the GAMESS program[41] has also been applied, although some terms are contaminated with the BSSE.

The atoms in molecules (AIM) theory of Bader[19] was applied to find the critical points[42,43] and to analyze them in terms of electron densities and their Laplacians. The AIM calculations were carried out using the AIM2000 program.[44]

Results and Discussion

Geometrical and Energetic Results. There are different ways of detecting hydrogen bonding. One of the most often used is the application of the geometrical criteria for the existence of H bonds, which is applied particularly by crystallographers. Among the geometrical criteria, one states that the H···Y distance should be less than the corresponding sum of the van der Waals radii.[45] However, the van der Waals cutoff is strongly criticized because the hydrogen bonding is electrostatic in nature and acts far beyond this distance.[46] Hence, this criterion does not act properly, especially for weaker C−H···Y H bonds, where the H···Y distances are close to or greater than the sum mentioned above.[46,47]

Table 1 presents the H···H distances for the complexes analyzed here. The complexes were optimized at different levels of theory. Because the H···H sum of the van der Waals radii amounts to 2.2−2.4 Å, the investigated sample may be divided into three cases. For the first group, there are complexes with H···H distances $\lesssim$2.0 Å: HCCH···HLi and FCCH···HLi. The first of these complexes was investigated previously[9,12] and has been included here only for comparison to other results using the same level of theory. Applying the geometrical criterion mentioned above, one may conclude that these complexes are H bonded. For the second group, with the BeH_2 and BeFH molecules as proton acceptors, the H···H distances are approximately within the 2.2−2.4-Å range mentioned above, which corresponds to the sum of van der Waals radii, or are slightly below this range. In this case, it is difficult to classify these dimers as H bonded or as van der Waals complexes. For the third group, where the H_2 molecule is an acceptor, the T-shaped conformations are observed: HCCH and FCCH molecules are perpendicular to H_2, and the H···H distances are greater than the sum of the van der Waals radii.

From a geometrical point of view, the complexes with BeH_2 and BFH as acceptors are between those with LiH and H_2 acceptors. This feature is not connected only with the H···H distances presented in Table 1. For the HCCH···H_2 and FCCH···H_2 complexes, the molecules are perpendicular, whereas for complexes with LiH acceptors, the systems are linear. For the (F)HCCH···HBeH(F) complexes, the C−H···H angle is in the 173−175° range, whereas the Be−H···H angle is in the 168−170° range. This is partially in line with previous investigations of the N−H···H−B systems found in CSD.[2] As was mentioned in the Introduction, the N−H···H angles are closer to linear, whereas the B−H···H angles are more bent, which could be evidence of the σ bond as a proton acceptor.

Table 2 shows the binding energies of the investigated complexes. Different levels of theory were applied up to MP2/6-311++G(3df,3pd), similar to that for the geometry optimization. Again, the three subranges may be pointed out if one considers the energetic results. For the first subrange, there is the LiH acceptor, and the binding energies are > -4 kcal/mol (arbitrary values are lower). For the second subrange, with the BeH_2 and BFH molecules as proton acceptors, the binding energy is ~ -1 kcal/mol or slightly less. For the third subrange, with the H_2 as the proton acceptor, the binding energy amounts to ~ -0.3 kcal/mol.

Table 2 also presents the binding energies obtained from the extrapolations to the CBS limits. All binding energies were calculated as differences between the energies of complexes and the energies of monomers; all energies were obtained for fully optimized minimum species. For the results up to the MP2/6-311++G(3df,3pd) level, the BSSE correction was taken into account. The energies for the CBS were obtained after the application of eq 1. The first limit estimate was obtained after

TABLE 2: Binding Energies (kcal/mol) of the Dihydrogen-Bonded Complexes Analyzed Here[a]

basis set	$C_2H_2\cdots HLi$	$FCCH\cdots HLi$	$C_2H_2\cdots HBeH$	$FCCH\cdots HBeH$	$C_2H_2\cdots HBeF$	$FCCH\cdots HBeF$	$C_2H_2\cdots\sigma(H_2)$	$FCCH\cdots\sigma(H_2)$
6-311++G(d,p)	−3.65	−3.97	−0.91	−0.95	−0.61	−0.63	−0.15	−0.17
6-311++G(2d,2p)	−3.97	−4.32	−1.02	−1.08	−0.73	−0.76	−0.23	−0.24
6-311++G(3d,3p)	−4.10	−4.44	−1.08	−1.14	−0.78	−0.81	−0.27	−0.28
6-311++G(3df,3pd)	−4.17	−4.46	−1.09	−1.14	−0.79	−0.81	−0.28	−0.29
CBS[b]	−4.37	−4.71	−1.07	−1.13	−0.74	−0.78	−0.35	−0.37
CBS[c]	−4.35	−4.66	−1.09	−1.13	−0.76	−0.77	−0.36	−0.36

[a] Calculations performed within the MP2 theory; BSSE correction is included [b] Basis set limit achieved via the extrapolation formula applied for cc-pVTZ and cc-pVQZ. [c] Basis set limit achieved via the extrapolation formula applied for aug-cc-pVTZ and aug-cc-pVQZ.

TABLE 3: Changes in Properties of Proton Donor Molecules Caused by Complexation (at the MP2/6-311++G(3df,3pd) Level of Theory)

$C_2H_2\cdots HLi$	$FCCH\cdots HLi$	$C_2H_2\cdots HBeH$	$FCCH\cdots HBeH$	$C_2H_2\cdots HBeF$	$FCCH\cdots HBeF$	$C_2H_2\cdots\sigma(H_2)$	$FCCH\cdots\sigma(H_2)$
			Δr (mÅ)				
11.4	12.7	1.8	2.3	1.2	1.7	0	0.3
			$\Delta\nu$ (cm^{-1})				
−128	−180	−13	−28.3	−7.7	−21	1.5	−3.7
			I/I_0				
4.36	5.55	1.80	2.15	1.68	1.99	1.21	1.30

the use of the cc-pVXZ basis sets, and the second one, after the use of the aug-cc-pVXZ bases. The extrapolations were performed for cardinal numbers $X = 3$ and 4. It is worth mentioning that eq 1 was applied for all species investigated (complexes and monomers), and from the obtained results, the binding energies included in Table 2 were calculated. There are no meaningful differences between the binding energies obtained from the extrapolations done for the cc-pVXZ and aug-cc-pVXZ basis sets. This is not surprising because the differences between the values of both limits for all species are ≤1 mhartree. The binding energies for the CBS calculations are free of BSSE. The BSSE decreases for larger basis sets and disappears for CBSs. This is well documented for the $HCCH\cdots H_2$ and $FCCH\cdots H_2$ complexes analyzed here. The BSSE corrections for them are ~0.2 kcal/mol for the 6-311++G(d,p), cc-pVDZ, and aug-cc-pVDZ basis sets, decreasing with the extension of the bases, and ~0.02−0.04 kcal/mol for the aug-cc-pVQZ basis set.

The results of Table 2 show that the use of the cc-pVXZ basis sets is sufficient to evaluate the CBS limit, and more time-consuming aug-cc-pVXZ calculations are not needed. The proper choice of extrapolation formulas is also studied here. For the H_2, C_2H_2, and C_2FH molecules and for the $HCCH\cdots H_2$ and $FCCH\cdots H_2$ complexes, the calculations have been performed up to $X = 5$ (the cc-pV5Z and aug-cc-pV5Z basis sets). However, convergence was not achieved in this case because for both CBS limits the lower energies were obtained for all mentioned species.

The MP2/CBS binding energies are approximately in agreement with the MP2/6-311++G(3df,3pd) results; the greatest differences are observed (Table 2) for the complexes with LiH and H_2 molecules as proton acceptors.

Table 3 shows the changes in the proton-donating bond parameters appearing in the process of complexation. It is well known that the proton-donating bond X−H is elongated because of the H-bond formation, and hence, the frequency associated with such a mode is red shifted and at the same time its intensity is enhanced.[47,48] The results in Table 3 also indicate the existence of the three classes mentioned above. For complexes with the LiH acceptor, there is the X−H bond elongation of about 0.01 Å, the red shift in frequency of 10^2 cm^{-1}, and the increase of the corresponding band intensity. For the BeH_2 and BeFH acceptors, the elongation of C−H is about 0.001−0.002 Å, with a shift toward the red of about 10 cm^{-1}. For the H_2 acceptor, the changes are negligible. For the $HCCH\cdots H_2$ complex, there is a slight shortening of the C−H donating bond connected with a shift toward the blue of 1.5 cm^{-1}. The shortening of the C−H bond and the blue shift are slightly greater for the lower levels of theory applied here (MP2/6-311++G(3d,3p) and MP2/6-311++G(2d,2p)) but are still negligible. The blue-shifted H bonds were described in detail previously by Hobza[49].

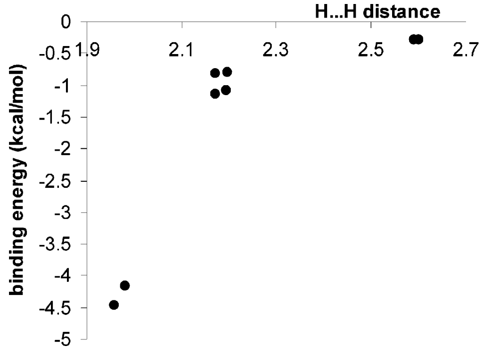

Figure 1. Dependence between the H⋯H distance (Å) and the binding energy (kcal/mol) for the complexes analyzed here.

Figure 1 shows the relationship between the H⋯H distance and the binding energy. Both parameters are often applied as measures of H-bond strength, and both are often correlated. However, such a correlation is fulfilled for the homogeneous group of the H-bonded complexes.[50] Figure 1 shows the three groups of complexes described above; those with the LiH acceptor are the most stable and may be without any doubt classified as H bonded. There is no linear correlation here; the polynomial regression of the second order is hardly satisfied. The lack of a stronger correlation may be the result of the heterogeneity of the sample considered. This heterogeneity is the reflection of the variety of acceptors: ionic, partially ionic, and σ bonds.

This finding is in line with the previous investigations of conventional and unconventional H bonds,[9] where statistical factor analysis was applied.[51] Different indicators of H-bonding strength were considered for different samples of complexes. For all samples, only one factor was retained. However, for the sample of DHBs, one factor accounted for the smallest part of the variance, −84.2%. For the other samples, seemingly consisting of less-related complexes, this value was greater, ≤92.1%. One of the explanations of such a situation is the greatest heterogeneity of the DHBs considered in comparison

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

basis set	$C_2H_2\cdots HLi$	$FCCH\cdots HLi$	$C_2H_2\cdots HBeH$	$FCCH\cdots HBeH$	$C_2H_2\cdots HBeF$	$FCCH\cdots HBeF$	$C_2H_2\cdots\sigma(H_2)$	$FCCH\cdots\sigma(H_2)$
				electron density				
6-311++G(d,p)	0.0112	0.0118	0.0056	0.0059	0.0054	0.0056	0.0033	0.0033
6-311++G(2d,2p)	0.0128	0.0136	0.0064	0.0069	0.0061	0.0065	0.0033	0.0033
6-311++G(3d,3p)	0.0128	0.0134	0.0069	0.0071	0.0065	0.0068	0.0034	0.0034
6-311++G(3df,3pd)	0.0131	0.0137	0.0069	0.0072	0.0067	0.0070	0.0034	0.0034
				Laplacian				
6-311++G(d,p)	0.0254	0.0268	0.0151	0.0161	0.0148	0.0153	0.0115	0.0115
6-311++G(2d,2p)	0.0281	0.0295	0.0190	0.0202	0.0182	0.0192	0.0125	0.0126
6-311++G(3d,3p)	0.0297	0.0312	0.0195	0.0201	0.0185	0.0194	0.0119	0.0120
6-311++G(3df,3pd)	0.0305	0.0314	0.0203	0.0212	0.0200	0.0208	0.0124	0.0126

[a] Wave functions obtained at the MP2 level of theory

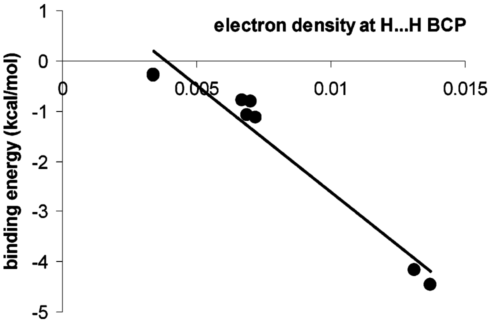

Figure 2. Dependence between the electron density at the H···H bond critical point and the binding energy (kcal/mol) for systems analyzed here.

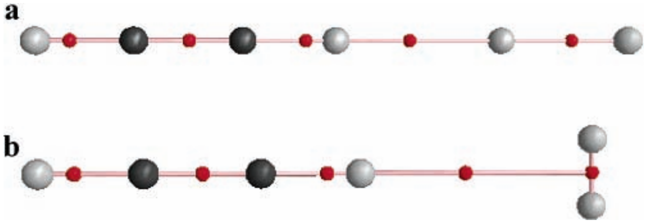

Figure 3. (a) Molecular graph of the HCCH···HLi complex; attractors are attributed to the positions of atoms (large circles), and bond paths and critical points (small circles) are shown. (b) Molecular graph of the HCCH···H_2 complex.

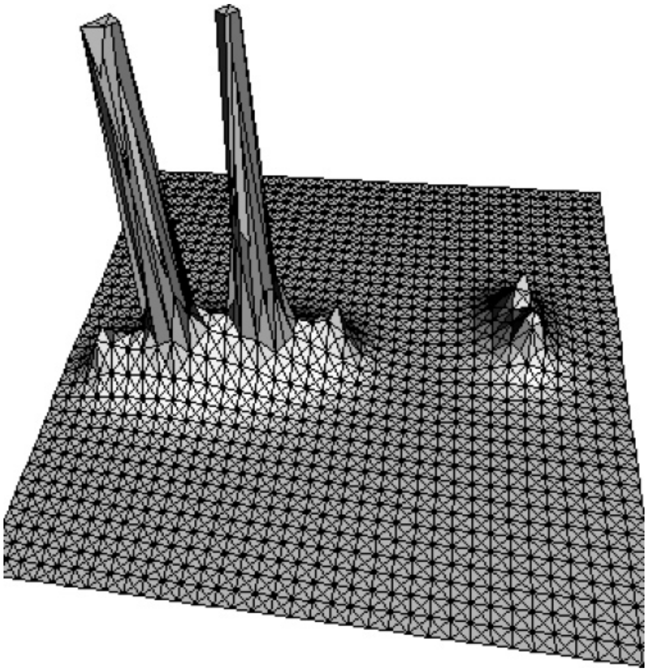

Figure 4. Relief map of the electron density for the HCCH···H_2 complex.

to that of the other samples. The sample of DHBs consisted of complexes with hydrogen fluoride as a proton donor and with hydrides of elements of the first and second groups of the periodic table as acceptors. For some of the hydrides, there are typical ionic bonds (LiH and NaH); for others, which are mostly covalent (BeH_2) and because of the diversity of the acceptors, the sample is not homogeneous.

Analysis of Topological Parameters. The topological parameters are derived from the Bader theory are often used as descriptors of H-bond strength.[9] It was pointed out that the electron density and its Laplacian at the H···Y bond critical point, the $\rho_{H\cdots Y}$ and $\nabla^2\rho_{H\cdots Y}$ values, respectively, correlate well with the H-bond energy.[52−54] Similar relationships were observed for DHBs[5a,6,8] and are also observed for the sample analyzed here. Figure 2 presents the correlation between the binding energy and the electron density at the H···H bond critical point for the MP2/6-311++G(3df,3pd) level results. The linear correlation coefficient is equal to 0.970. For the same level of theory, the linear correlation coefficient for the relationship between the binding energy and the Laplacian $\nabla^2\rho_{H\cdots H}$ is equal to 0.937.

The topological criteria are also useful in detecting the existence of H-bond interactions.[55,56] Three of them are most often applied. The first criterion states that the bond path with the bond critical point between the proton and proton acceptor should exist. Such paths for H···H contacts are observed for all complexes analyzed here. Figure 3 presents the molecular graphs of two selected complexes: HCCH···HLi and HCCH···H_2. The first graph depicts the meaningful binding energy and H···H distance that is less than the sum of the van der Waals radii, and the second graph depicts which H···H distances are greater than this cutoff; the binding energy is similar to the binding energies of the other van der Waals complexes. For the HCCH···HLi complex, there is the bond path between the hydrogen atoms, and for HCCH···H_2, the bond path connects the H atom of acetylene and the σ bond of the H_2 molecule (the middle of H_2 corresponding to the position of BCP). The last case is in line with the previous statements that the X−H···σ hydrogen bonds exist. A similar molecular graph exists for the FCCH···H_2 complex.

Two other topological criteria require that the topological parameters at H···Y BCP be within the proper range of 0.002−0.04 au for the electron density and 0.02−0.15 au for its Laplacian. Table 4 shows the electron densities and their Laplacians for H···H contacts of the complexes analyzed here. One can see that the Laplacian values for HCCH···H_2 and FCCH···H_2 are not within the proposed range; also some values of the Laplacians for BeH_2 and BeFH as acceptors do not fulfill this criterion for the existence of H bonding. But all values of the electron density do fulfill the criterion proposed by Koch and Popelier.[55] However, one should be careful in interpreting

TABLE 5: Interaction Energy Terms (kcal/mol) for Complexes Analyzed in This Study

energy component[a]	$C_2H_2\cdots HLi$	$FCCH\cdots HLi$	$C_2H_2\cdots HBeH$	$FCCH\cdots HBeH$	$C_2H_2\cdots HBeF$	$FCCH\cdots HBeF$	$C_2H_2\cdots\sigma(H_2)$	$FCCH\cdots\sigma(H_2)$
$\Delta E^{(1)}$	−0.642	−0.908	−0.053	−0.057	0.255	0.294	0.093	0.087
$\Delta E_{EL}{}^{(1)}$	−6.751	−7.354	−1.562	−1.661	−1.135	−1.188	−0.303	−0.312
$\Delta E_{EL-MTP}{}^{(1)}$	−5.499	−5.873	−1.179	−1.295	−0.668	−0.680	−0.251	−0.277
$\Delta E_{EL-PEN}{}^{(1)}$	−1.252	−1.481	−0.383	−0.366	−0.467	−0.508	−0.051	−0.035
$\Delta E_{EX}{}^{(1)}$	6.109	6.446	1.509	1.604	1.391	1.482	0.396	0.398
$\Delta E_{DEL}{}^{(R)}$	−2.471	−2.632	−0.435	−0.479	−0.380	−0.423	−0.097	−0.104
ΔE_{SCF}	−3.113	−3.540	−0.488	−0.536	−0.124	−0.129	−0.004	−0.018
ΔE_{CORR}	−1.129	−1.035	−0.608	−0.605	−0.668	−0.687	−0.277	−0.277
ΔE_{MP2}	−4.241	−4.574	−1.096	−1.141	−0.792	−0.815	−0.281	−0.295

[a] $\Delta E_{MP2} = \Delta E_{SCF} + \Delta E_{CORR}$; $\Delta E^{(1)} = \Delta E_{EL}{}^{(1)} + \Delta E_{EX}{}^{(1)}$.

TABLE 6: Interaction Energy Terms Obtained within the Morokuma Scheme (kcal/mol) for Complexes Analyzed in This Study

energy component[a]	$FCCH\cdots HLi$	$C_2H_2\cdots HBeH$	$FCCH\cdots HBeH$	$C_2H_2\cdots HBeF$	$C_2H_2\cdots\sigma(H_2)$	$FCCH\cdots\sigma(H_2)$
ES	−7.39	−1.58	−1.68	−1.16	−0.31	−0.32
EX	6.50	1.53	1.63	1.41	0.39	0.40
PL	−2.6	−0.33	−0.37	−0.28	−0.05	−0.05
CT	−2.94	−0.47	−0.53	−0.45	−0.10	−0.11
MIX	2.81	0.32	0.36	0.27	0.04	0.05
ΔE_{SCF}	−3.62	−0.53	−0.59	−0.21	−0.02	−0.04
ΔE_{CORR}	−1.19	−0.78	−0.79	−0.96	−0.32	−0.32
ΔE_{MP2}	−4.81	−1.31	−1.38	−1.17	−0.34	−0.36

[a] $\Delta E_{MP2} = \Delta E_{SCF} + \Delta E_{CORR}$.

the topological criteria mentioned above. For example, there is a bond path and a BCP for the $H\cdots\sigma$ contact for the $HCCH\cdots H_2$ and $FCCH\cdots H_2$ complexes. Figure 4 presents the relief map of the electron density of the first complex. There is the rather flat area between acetylene and the hydrogen molecules that does not indicate H-bonding formation. Of course from a mathematical point of view, there is BCP in this area with electron density >0.002 au. This is the reason that different tools and criteria should be applied to analyze the nature of interactions.

Decomposition of the Energy. The decomposition of the interaction energy was performed according to eqs 2 and 3 described in the previous section. The results for the complexes analyzed here are given in Table 5. For the two complexes with the greatest binding energies, $HCCH\cdots HLi$ and $FCCH\cdots Hli$, the first-order Heitler−London energy component is negative. This is because the first-order electrostatic energy component slightly outweighs the first-order exchange energy component. Hence, these complexes could be classified as H bonded similarly to what was pointed out in the previous sections. However, in typical hydrogen-bonded complexes, the absolute value of the exchange term is usually considerably smaller (even 50%) than the electrostatic contribution. Various definitions of H bonding state that this interaction is mainly electrostatic in nature,[46,57] whereas the remaining terms (i.e., $\Delta E_{EX}{}^{(1)}$, $\Delta E_{DEL}{}^{(R)}$, and ΔE_{CORR}) tend to cancel each other to a significant extent.

For complexes with the BeH_2-and BeFH-accepting molecules, similar relative proportions of interaction energy contributions can be noted. The correlation energy terms are approximately equal, as are the attractive delocalization energy terms. However, for complexes with the BeH_2 acceptor, the first-order electrostatic energy term is slightly greater than that of the repulsive exchange term, and for the BeFH acceptor, the exchange energy term slightly outweighs the electrostatic term. The total binding energies are similar. For the first case of complexes with the BeH_2 acceptor, the total binding energies are ∼ −1.1 kcal/mol. For the second case with the BeFH acceptor, the total binding energies are ∼ −0.8 kcal/mol. For the remaining complexes with H_2 as an acceptor, the first-order energy term is positive, and the complexes are energetically stable because of the interplay of the electrostatic, exchange, and correlation terms. This resembles the results for van der Waals complexes where the correlation effects are more dominant.

Similar observations for four dihydrogen-bonded complexes have been pointed out by Cybulski et al.[12] They, after applying the partitioning of the interaction energy and the analysis of infrared and magnetic resonance spectroscopic parameters, concluded that only one of the complexes investigated is H bonded. The results for the complexes analyzed here demonstrate that there is no evident borderline between van der Waals complexes and H-bonded systems.

Similar conclusions may be drawn if one applies the Morokuma partitioning energy scheme.[15] The results of such a partitioning are included here because this scheme is frequently used in similar studies. The results are given in Table 6. The meanings of the exchange and electrostatic first-order energy terms are similar to those described for the variation−perturbation scheme applied here.[37] The electrostatic (ES) term represents the Coulombic interaction between the charge distribution of the two subunits, and the exchange energy term (EX) approximately corresponds to the steric repulsion between the two charge clouds. The polarization term (PL) corresponds to the internal redistribution of the charge clouds of the complex components; the charge transfer (CT) is connected with the density shifts from one molecule to the other, and the MIX term represents the higher-order repulsive interactions. The electron correlation term (CORR) is calculated as the difference between the MP2 energy and the SCF energy (without removing the nonphysical BSSE). Two of the systems studied here are not included in Table 6 because of the difficulties connected with the convergence of the decomposition within the Morokuma scheme. However, there are results for each of the three groups indicated previously. For the $FCCH\cdots HLi$ complex, the electrostatic energy term outweighs the exchange term, and the higher-order attractive terms are very important. For H_2 and HBeF acceptors, the exchange terms outweigh the electrostatic terms, and the complexes are stable because of the small increments from attractive higher-order terms. A difference is observed in the complexes where the BeH_2 molecule is an acceptor. The electrostatic terms are slightly greater here than the exchange terms, but they are approximately equal. The decomposition of the other terms is similar for complexes with BeFH and H_2 acceptors. Generally, the conclusions are the same as those obtained from the analysis based on the other partitioning applied here because of the use of relatively extended basis sets where the BSSEs are negligible.

One can claim that for the $X-H\cdots\sigma$ interaction analyzed here the binding energy of -0.3 kcal/mol is too small to be able to designate them as H bonded. However, there are other examples of these interactions analyzed in previous work. Ab initio calculations of $NH_4^+(H_2)_n$ complexes ($n = 1-8$) were performed[58] up to the MP2/aug-cc-pVTZ level of theory. For $NH_4^+\cdots H_2$, it was confirmed that the H_2 molecule is perpendicular to the N−H proton-donating bond and that the $H\cdots\sigma$ distance (the middle of the H_2 molecule) is equal to 1.98 Å. The binding energy for such a complex is -2.5 kcal/mol, and the decomposition of the energy is divided as follows (the same scheme of decomposition as that applied for the results of Table 5): electrostatic (-1.62 kcal/mol), exchange (2.75 kcal/mol), delocalization (-2.62 kcal/mol), and correlation energies (-1.0 kcal/mol). One can see that the nature of the $NH_4^+\cdots H_2$ interaction is similar to that of the $HCCH\cdots\cdot H_2$ and $FCCH\cdots\cdot H_2$ complexes analyzed here despite the ionic character of the proton-donating NH_4^+ species. All geometrical and energetic parameters for $NH_4^+\cdots H_2$ show that this species may be considered to be H bonded; even the N−H donating bond is slightly elongated (1.028 Å) in comparison to the other N−H bonds (1.024 Å) of the NH_4^+ ion. These results also indicate the existence of two extreme types of interactions, $X-H^{+\delta}\cdots{}^{-\delta}H-Y$ and $X-H\cdots\sigma$. However, there is no evident borderline between them indicating the ambiguous nature of dihydrogen-bonded complexes or the arbitrary character of the definitions used to categorize the molecular complexes.

Conclusions

Different dihydrogen-bonded complexes involving $H\cdot\cdot H$ contacts were analyzed here. The results of our study indicate that there is no evident borderline between species resembling the hydrogen bond category and those resembling van der Waals complexes. The studied systems include complexes for which some of the features are typical for hydrogen bonds, but the other features are typical for van der Waals complexes.

These conclusions are in line with the recent investigations of Cameron et al.,[18] where different dependencies between energetic, geometrical, topological, and charge parameters have been analyzed, showing that there is a sharp border between the covalent bond of H_2 and the dihydrogen bond but not between the latter and van der Waals interactions.

The results presented here have also shown that the $X-H\cdots\sigma$ hydrogen bonds predicted earlier[2] are possible. However, an analysis of the $HCCH\cdots H_2$ and $FCCH\cdots H_2$ complexes indicates that some of the parameters may support the existence of H bonding and that some are van der Waals complexes. We conclude that two kinds of complexes, $X-H^{+\delta}\cdots{}^{-\delta}H-Y$ and $X-H\cdots\sigma$, are extreme cases, indicating great diversity between various dihydrogen-bonded complexes. $HCCH\cdots HLi$ is an example of the first group, those that resemble hydrogen-bonded dimers, and $HCCH\cdots H_2$ is an example of the second type, those that are close to van der Waals complexes. The main difference between these typical representatives is in the relative magnitude of the interaction energy components. For $X-H^{+\delta}\cdots{}^{-\delta}H-Y$, the electrostatic term is the most important among the attractive terms and slightly outweighs the exchange repulsive term; for $X-H\cdots\sigma$, the electrostatic, exchange, and correlation terms are the most important.

The conclusions on DHBs are in line with the more general findings on hydrogen bonds. It was pointed out that hydrogen bridges are interactions without borders[59] because in the limit the weak hydrogen bonds have considerable dispersive-repulsive character and merge into van der Waals interactions. However, very strong H bonds are partially covalent in nature,[59] as found for the resonance-assisted H bonds.[60] It is worth mentioning that very strong dihydrogen bonds were analyzed very recently, and for systems such as $NH_4^+\cdots HBeH$ and $NFH_3^+\cdots HBeH$, the covalent character of such interactions was detected.[61]

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