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High-Level Ab Initio Calculations of Dihydrogen-Bonded Complexes

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High-level ab initio calculations have been performed on dihydrogen-bonded complexes with hydrogen fluoride (HF) as a proton-donating molecule and simple molecules as proton-acceptors (CH_4, SiH_4, BeH_2, MgH_2, LiH, and NaH). MP4(SDQ)/6-311++G** and QCISD(T)/6-311++G** results show that H-bond energies for such systems are significant. For example, the H-bond energy is −11.9 kcal/mol for the LiH···HF complex at the QCISD(T)/6-311++G** level of theory; the basis set superposition error (BSSE) was included, and the geometry of the complex was optimized at the QCISD/6-311++G** level. The relationships between the geometrical parameters of these complexes are in good agreement with those obtained from the bond valence model. The BSSE is taken into account in all levels of calculations. A comparison of the results of the calculations shows that the MP2/6-311++G** level of theory is sufficient for a description of dihydrogen-bonded complexes. Additionally, Bader's theory is included in the analysis of the investigated systems.

Introduction

There has been increasing interest in unconventional hydrogen bonds in recent years.[1−5] Four kinds of unconventional H-bonds can be defined, namely, those with unconventional donors (particularly C−H bonds),[6] those with unconventional acceptors (π-bonded systems or C-atoms),[7] C−H···C or C−H···π bonds with unconventional donors and acceptors,[3,8] and dihydrogen bonds.[9−11]

The last case is connected with B−H and M−H (M designates transition metal) σ bonds acting as unexpectedly efficient hydrogen-bond acceptors toward proton donors such as O−H and N−H bonds. The resulting dihydrogen bonds (A−H···H−B, designated as DHB) have close H···H contacts (1.75−1.9 Å), as is known from X-ray and neutron diffraction studies.[9−11] Spectroscopic studies have indicated substantial heats of interaction for DHBs (3−7 kcal/mol), which lie in the range of those for conventional hydrogen bonds.

Dihydrogen bonds have also been optimized using ab initio and other theoretical techniques. For example, the B−H···H−N system was modeled[12] in PCI-80/B3LYP studies[13] by looking at the mutual interaction of two H_3BNH_3 fragments in the gas-phase dimer $[H_3BNH_3]_2$. Liu and Hoffman studied the intramolecular H···H interaction in iridium complexes using the EHT method.[14] Theoretical calculations on DHBs have been performed not only for systems with B−H and M−H bonds as proton acceptors[14,15] but also for other simple DHB systems.[14,16−18]

Investigations of fields effects on dihydrogen-bonded systems show that the transfer of hydrogen atoms is possible within a crystal because of internal forces.[19] This means that a DHB complex may develop into two molecules coordinated to a H_2 molecule.

Results of calculations at the MP2/6-311++G** level of theory on simple DHBs[18] are in agreement with the bond valence model[20] that is often applied in many chemical problems.[20−23] The DHBs were also characterized[17] using a topological analysis of the electronic charge density known as Bader's theory.[24]

The aim of this paper is to study the simple dihydrogen-bonded systems using different theoretical approaches, specifically, high-level ab initio calculations, the bond valence model for $H^{-\delta}\cdots{}^{+\delta}H-F$ triatomic systems, and Bader's theory.

Ab initio and density functional theory calculations on simple DHBs were performed previously,[18] showing the strongest H-bonds, i.e., the shortest H···H distances and the greatest H-bond energies, for ionic proton-accepting molecules and for transition metal−hydrogen proton-accepting bonds. For example, for the NaH···HF dimer, the H-bond energy and H···H distance are −13.8 kcal/mol (BSSE correction included) and 1.37 Å, respectively, at the MP2/6-311++G** level. For the CrH_2···HF dimer, the hydrogen-bond energy and H···H distance are −10.6 kcal/mol and 1.39 Å, respectively, at the B3LYP/Lanl2DZ level of theory. Thus, it is evident that the H-bond energies of DHBs can lie in the range of strong conventional H-bonded dimers. Quantum chemical calculations were also performed for larger systems known from experimental studies.[15] However, accurate computations on large complexes containing transition metal atoms presented a computational problem. Hence, the calculations were performed using density functional theory (DFT) methods and the Lanl2DZ double-ξ basis set.[15] Such a choice of computational level is connected with the earlier observations[25] that DFT results for complexes of transition metal compounds are in good agreement with experimental data and with second-order Møller−Plesset perturbation (MP2) calculations. For example, it was found that, for the $Mo(CO)_2(NO)(PH_3)_2H$···HF complex,[15a] the H-bond energy through the H···H contact is in the 11−13 kcal/mol range for different DFT methods (the basis set superposition error was not corrected at these levels of calculations).

Because correlations for simple DHB complexes were found[18] at the MP2/6-31G** and MP2/6-311++G** levels of theory, it is very interesting to compare them with the MP4 and CI calculation results, which is partly the aim of this study. Because BSSE[26] is one of the major factors limiting the accuracy of ab initio intermolecular complex calculations, it will be taken into account at all levels of calculations in the present investigations. The correlations based on the high-level ab initio calculations will be compared with the relations obtained from the bond valence model.

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TABLE 1: Total Energies, Basis Set Superposition Error (BSSE), and Corrected H-bond Energies for DHB Complexes[a,b]

complex and method	energy (complex)	energy (accepting molecule)	BSSE	H-bond energy
LiH···HF				
MP2/6-31G**	−108.2137824	−8.0016086	0.88	−10.12
MP2/6-311++G**	−108.3088362	−8.0086853	0.72	−12.62
MP4/6-311++G**	−108.3171289	−8.0158246	0.72	−12.47
QCISD/6-311++G**	−108.3176392	−8.0166214	0.71	−11.61
QCISD(T)/6-311++G**	−108.3221387	−8.0166214	0.73	−11.94
NaH···HF				
MP2/6-31G**	−262.6062566	−162.3929735	0.88	−10.82
MP2/6-311++G**	−262.7037267	−162.4016083	0.76	−13.81
MP4/6-311++G**	−262.7117124	−162.4089872	0.74	−12.74
QCISD/6-311++G**	−262.7123470	−162.4102792	0.70	−12.28
QCISD(T)/6-311++G**	−262.7169391	−162.4102790	0.72	−12.66
BeH$_2$···HF				
MP2/6-31G**	−116.0146520	−15.8157423	0.43	−2.25
MP2/6-311++G**	−116.1074545	−15.8232476	0.40	−2.94
MP4/6-311++G**	−116.1248464	−15.8385069	0.39	−2.81
QCISD/6-311++G**	−116.1258273	−15.8394276	0.39	−2.75
QCISD(T)/6-311++G**	−116.1304411	−15.8399023	0.40	−2.87
MgH$_2$···HF				
MP2/6-31G**	−300.9637339	−200.7607824	0.61	−4.61
MP2/6-311++G**	−301.0682399	−200.7788679	0.56	−6.02
MP4/6-311++G**	−301.0845812	−200.7934600	0.54	−5.66
QCISD/6-311++G**	−301.0858172	−200.7947621	0.53	−5.53
QCISD(T)/6-311++G**	−301.0904523	−200.7951303	0.55	−5.72
CH$_4$···HF				
MP2/6-31G**	−140.5593507	−40.3646251	0.13	+0.08
MP2/6-311++G**	−140.6587648	−40.3796379	0.24	+0.39
MP4/6-311++G**	−140.6830109	−40.4015052	0.24	−0.35
QCISD/6-311++G**	−140.6836876	−40.4020370	0.24	+0.08
QCISD(T)/6-311++G**	−140.6920252	−40.4063743	0.26	+0.06
SiH$_4$···HF				
MP2/6-31G**	−391.5350453	−291.3389966	0.23	−0.65
MP2/6-311++G**	−391.6532015	−291.3723360	0.39	−0.85
MP4/6-311++G**	−391.6834222	−291.4001922	0.41	−0.74
QCISD/6-311++G**	−391.6847004	−291.4013496	0.41	−0.82
QCISD(T)/6-311++G**	−391.6912295	−291.4038028	0.43	−0.89

[a] Total energies are in hartrees, BSSEs and corrected H-bond energies are in kcal/mol. [b] Total energies (in hartrees) of the proton-donating molecule (HF) are as follows: MP2/6-31G**, −100.194639; MP2/6-311++G**, −100.2788923; MP4(SDQ)/6-311++G**, −100.2812437; QCISD, −100.2813907; and QCISD(T), −100.2853308.

Computational Methods

All ab initio calculations described in this paper were performed with the Gaussian 94[27] series of programs using the standard 6-311++G** basis set. In the present study, a Hartree−Fock calculation was performed, followed by a Møller−Plesset correlation energy correction[28] truncated at fourth-order (MP4).[29] The MP4(SDQ) level of theory,[30] which specifyies use of the space of single, double, and quadruple substitutions, was applied in this study.

Quadratic CI calculations were also performed including single and double substitutions (QCISD level) and with a triples contribution to the energy added [QCISD(T) level of theory]. This means that full geometry optimization was performed in all calculations for the complexes and molecules studied in this paper at the MP4(SDQ)/6-311++G** and QCISD/6-311++G** levels of theory. For the QCISD-optimized geometries of complexes, the calculations were performed with triples added to the energies, i.e., at the QCISD(T) level.[31] The results are compared with MP2 calculations (6-31G** and 6-311++G** basis sets) reported earlier.[18]

The basis set superposition error (BSSE) was computed for all levels of calculations using the counterpoise method of Boys and Bernardi,[32] employing the MASSAGE keyword in the Gaussian programs.[27]

Results and Discussion

In the present work, a series of simple dihydrogen-bonded complexes is considered. The HF molecule was chosen as a strong proton donor; CH$_4$, SiH$_4$, MgH$_2$, BeH$_2$, NaH, and LiH were chosen as proton-accepting molecules because, in all cases, there is a negative electronic charge on the hydrogen atoms[18] (except for the methane molecule, for which the charge is negligible).

1. Binding Energies. Table 1 presents the total energies and H-bond energies for the above complexes (MP2, MP4, and QCISD results). The estimation of the basis set superposition error (BSSE) for all of the structures presented here was performed by the full counterpoise method at both the MP4 and QCISD levels. These results are also presented in Table 1. The BSSE goes from 0.26 kcal/mol for the CH$_4$···HF dimer to 0.73 kcal/mol for the LiH···HF complex at the QCISD(T) level of theory and with the geometries of the dimers optimized at the QCISD level. The BSSE at the MP2 level (6-31G** basis set) ranges from 0.13 to 0.88 kcal/mol. Table 1 shows that the BSSE is higher for ionic accepting molecules and lower for covalent accepting bonds, such as the C−H bond of the CH$_4$···HF system. However, if we take into account the BSSE as a percentage contribution of the H-bond energy, then it is also significant for the CH$_4$···HF and SiH$_4$···HF complexes.

Table 1 shows that the results are practically independent of the level of theory. Only the MP2/6-31G** results differ slightly from the results of the remaining calculations. This means that diffuse functions strongly influence the optimized geometries of dihydrogen-bonded complexes. For example, for the $BeH_2\cdots HF$ complex, the H-bond energy at the MP2/6-31G** level amounts to −2.3 kcal/mol, while for the other levels of theory, it is −2.8 to −2.9 kcal/mol. The BSSE correction for this complex is the same for all levels of calculation and equals 0.4 kcal/mol. A similar situation can be observed for the other complexes. The differences between the results for different levels of theory are greater for ionic complexes, athough the calculations on the unstable $CH_4\cdots HF$ complex give positive and negative values for the H-bond energy; the difference between MP2 and MP4 results (the same 6-311++G** basis set) is about 0.8 kcal/mol.

Table 1 shows that, for some of the dihydrogen-bonded complexes, the bonding energies can surprisingly reach more than10 kcal/mol. The most stable dihydrogen-bonded systems are those of ionic accepting molecules. The H-bond energy amounts to −12.7 kcal/mol for $LiH\cdots HF$ and −13.4 kcal/mol for $NaH\cdots HF$ at the QCISD(T)/6-311++G** level (Table 1). It is evident that the $CH_4\cdots HF$ complex is not stable for all levels of calculations [except of MP4(SDQ)] if the BSSE correction is taken into account. The H-bond energy for the $SiH_4\cdots HF$ system (Si−H as a covalent accepting bond) is about −1 kcal/mol for all levels of theory, approximately in the range of the H-bond energies for the $C-H\cdots O$ and $C-H\cdots C$ bonds.[8,33,34]

In this paper, the calculations were performed on simple, modeled DHB complexes with geometries and bonding energies that are not known experimentally. The dihydrogen bonds were detected and investigated experimentally for the complexes with B−H and M−H (M designates transition metal) σ accepting bonds. For example, X-ray and neutron diffraction studies on the $ReH_5(PPh_3)-indole-C_6H_6$ complex[9] showed the presence of an $N-H\cdots H_2Re$ hydrogen bond. It is a three-center H-bond with $H\cdots H$ distances of 1.734(8) and 2.212(9) Å. The ν(NH) band in the IR spectrum moves from 3437 cm^{-1} in free indole to 3242 cm^{-1} in the $ReH_5(PPh_3)_3$−indole complex, a shift corresponding[35] to a H-bond strength of 4.3 kcal/mol. For the $ReH_5(PPh_3)_2$−imidazole complex, the shift of the ν(NH) band in the IR for the $N-H\cdots H-Re$ bond corresponds to a H-bond strength of 5.3 kcal/mol.[10]

Accurate calculations on complexes containing transition metal atoms can present a computational problem. Different dihydrogen-bonded systems were studied using the HF/3-21G and DFT/B3LYP, BLYP, and B3PW91 methods.[15] For the $Mo(CO)_2(NO)(PH_3)_2H\cdots HF$ complex, the DFT results for the H-bond energy [15a] are in the 11−13 kcal/mol range; the experimental estimation is 7 kcal/mol.[36] Such disagreement between experiment and theory may be the result of the poor quality of the basis sets used for calculations.[15a] For the systems investigated here, higher-level methods were used.

TABLE 2: MP2/6-311++G Results for Different H-bonded Complexes[a]**

complex	E_{HB}	$X-H\cdots Y$	$H\cdots Y$ distance	ref
$(F\cdots H\cdots F)^-$	−39.87	$F\cdots H\cdots F$	1.138	*b*
$(Cl\cdots H-F)^-$	−20.94	$F-H\cdots Cl$	1.894	*b*
$(H_2O)_2$	−4.45	$O-H\cdots O$	1.949	*b*
$(C_2H_2)_2{}^c$	−1.72	$C-H\cdots\pi$	2.697	*b*
$CH_4\cdots CH_2-NH_3$	−0.65	$C-H\cdots C$	2.849	3
$C_2H_2\cdots CH_2-NH_3$	−7.27	$C-H\cdots C$	2.191	3
$LiH\cdots HF$	−12.62	$F-H\cdots H$	1.371	*b*

[a] H-bond energies (E_{HB}) are in kcal/mol, distances are in Å. [b] This work. [c] T-shaped configuration.

TABLE 3: HF/3-21G Results for Different H-bonded Complexes[a]

complex	E_{HB}	$X-H\cdots Y$	$H\cdots Y$ distance	ref
$(F\cdots H\cdots F)^-$	−78.61	$F\cdots H\cdots F$	1.145	*b*
$(Cl\cdots H-F)^-$	−23.54	$F-H\cdots Cl$	2.107	*b*
$(H_2O)_2$	−10.97	$O-H\cdots O$	1.825	*b*
$NH_4{}^+\cdots C_2H_4$	−10.91	$N-H\cdots\pi$	2.328	41
$CH_3OH\cdots HCCCH_3$	−1.79	$O-H\cdots C$	2.66	1b
$(C_2H_2)_2{}^c$	−1.58	$C-H\cdots\pi$	2.864	*b*
$LiH\cdots HF$	−10.93	$F-H\cdots H$	1.611	*b*
$Mo(CO)_2NO(PH_3)_2H\cdots HF^d$	−14.7	$F-H\cdots H$	1.517	15a
$Mo(CO)_2NO(PH_3)_2H\cdots HF^d$	−17.6	$F-H\cdots H$	1.529	15a

[a] H-bond energies (E_{HB}) are in kcal/mol, distances are in Å. [b] This work. [c] T-shaped configuration. [d] Two conformations of the complex.

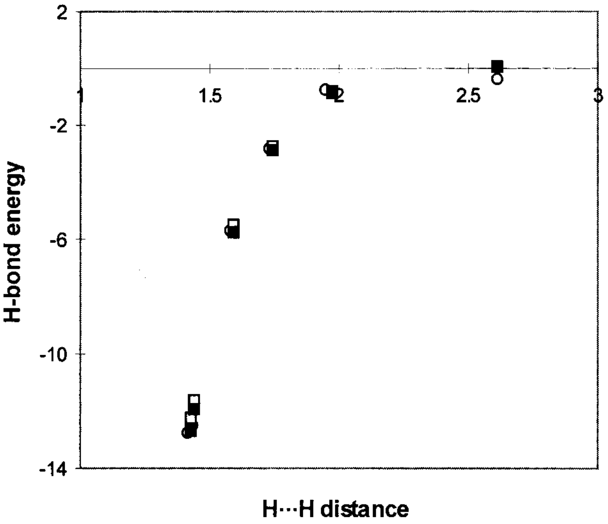

Figure 1. 1. Relationship between the H-bond energy (in kcal/mol) and $H\cdots H$ distance (in Å) for dihydrogen-bonded complexes at the MP4/6-311++G** (○), QCISD/6-311++G** (□), and QCISD(T)/6-311++G** (■) levels of theory.

If we take into account H-bond energies known from experiment, then DHB complexes can be clasified as medium-strength H-bonds. This observation is partly supported by the results in Tables 2 and 3, in which H-bond energies for different systems are presented. The calculations were performed at the same levels of theory, specifically, MP2/6-311++G** (BSSE included) for Table 2 and HF/3-21G for Table 3. The results in Table 2 for the $(F\cdots H\cdots F)^-$, $(Cl\cdots H-F)^-$, and $(H_2O)_2$ systems are in good agreement with experimental results. The experimental gas-phase H-bond energies are 39 ± 1 and 21.8 kcal/mol for $(F\cdots H\cdots F)^-$ [37] and $(Cl\cdots H-F)^-$,[38] respectively. The MP2/6-311++G** calculations on $(H_2O)_2$ represent a linear (trans) geometrical conformation of the dimer and are in line with the experimental value of 5 kcal/mol and with the other high-level calculations.[34,39] These results suggest the accuracy of energies for the other systems presented in Table 2 and the accuracy of the results of the DHB systems investigated here (Table 1). In Table 2, the $C_2H_2\cdots CH_2-NH_3$ system presents an unexpectably strong $C-H\cdots C$ bond (7.27 kcal/mol).[3] This complex was studied theoretically, but other unconventional $C-H^{\delta+}\cdots X$ systems were investigated experimentally, giving H-bond energies in the range of 8−10 kcal/mol or even higher.[40] However, generally, as is evident from Tables 2 and 3, $C-H\cdots\pi$ and $C-H\cdots C$ bonds are weaker than the H-bond for the $LiH\cdots HF$ complex and even weaker than medium H-bonds such as $O-H\cdots O$ for the water dimer. Table 3 shows the results for the other unconventional ionic $NH^+\cdots\pi$ hydrogen bond,[41] which may be overestimated because of the theoretical level used (HF/3-21G). The energies of 10.97 and 78.61 kcal/mol for the H_2O dimer and the $(F\cdots H\cdots F)^-$ system, respectively, show such an overestimation. However, the results for LiH···HF and $(C_2H_2)_2$ are in agreement with the MP2/6-311++G** calculations (Table 2). Table 3 also shows results for the $Mo(CO)_2NO(PH_3)_2\cdots HF$ complex investigated by Scheiner.[15a]

Figure 1 presents the relationship between the H-bond energy and the $H^{-\delta}\cdots{}^{+\delta}H$ distance for the dimers investigated in this work. Such a dependence was found previously[18] for dihydrogen-bonded systems calculated at the MP2/6-31G** and MP2/6-311++G** levels of theory. The equations presented below show the polynomial regressions for such dependences for different levels of theory.

$$
\begin{aligned}
y &= -22.261x^2 + 99.591x - 110.29;\ \text{MP2/6-31G**};\ R = 0.991\\
y &= -19.197x^2 + 87.161x - 96.48;\ \text{MP2/6-311++G**};\ R = 0.985\\
y &= -20.882x^2 + 93.977x - 103.48;\ \text{MP4/6-311++G**};\ R = 0.987\\
y &= -18.858x^2 + 85.927x - 95.854;\ \text{QCISD/6-311++G**};\ R = 0.986\\
y &= -19.311x^2 + 88.028x - 98.277;\ \text{QCISD(T)/6-311++G**};\ R = 0.986 \quad (1)
\end{aligned}
$$

where y and x correspond to H-bond energy and H···H distance, respectively.

Figure 1 presents results for the MP4 and QCISD levels of theory. The results for the MP2/6-311++G** level differ only slightly from those presented in Figure 1 (see also Table 1).

The relationship between the H-bond energy and the distance of the proton from the proton-accepting atom is well-known for the medium and strong H-bonds such as O−H···O systems.[42] It was pointed out that there is no direct evidence for such a relation.[43] However, it is also known that, for short O···O distances (2.35−2.5 Å), the so-called low-barrier hydrogen bonds (LBHBs) exist,[44] for which the potential barrier height for the reaction of proton transfer is low (1 kcal/mol or less). Sometimes for such systems, the proton is centered, and the H-bond energies are significant (about 20−30 kcal/mol).[45] For longer O···O distances, the H-bonds are not as strong.

The distance−energy relationship for dihydrogen-bonded systems is presented in Figure 1. However, such a dependence can be shown at the same level of theory and for the homogeneous series of complexes with HF as the donating molecule and simple, small accepting molecules.

2. Geometries of Complexes. Figure 2 shows the optimized geometries for dihydrogen-bonded dimers. The geometries were optimized at four levels of theory, namely, MP2/6-31G**, MP2/6-311++G**, MP4/6-311++G**, and QCISD/6-311++G**. The results show that, for donating (HF, hydrogen fluoride) and accepting molecules, there are practically no differences in their geometries obtained from optimizations at the MP2, MP4, or QCISD levels of theory if we consider the same basis set (6-311++G**). Only the MP2/6-31G** results differ significantly from the others (Figure 2). This shows that the inclusion of the diffuse functions is very important for the systems considered in this work. Figure 2 also shows that H···H intermolecular contacts are much more dependent on the level of theory than typical covalent or ionic bonds. The optimized distances are practically the same for the MP4/6-311++G** and QCISD/6-311++G** levels. There is the following tendency for changes in the geometrical parameters: for smaller H···H distances, the elongation of H−F donating bond is greater. Such a relation is not observed for accepting bonds. For ionic molecules such as LiH and NaH, there is even a shortening of the accepting bonds (Na−H and Li−H) because of the H-bond formation. The greatest elongation of the H−F bond is observed for the strongest H-bonds, i.e., for the NaH···HF and LiH···HF complexes, for which the lengths of the H−F bond are 0.958 and 0.951 Å, respectively, at the MP2/6-311++G** level of theory. This observation corresponds to the results of calculations on the strongest H-bonds, such as those in the $(Cl\cdots H-F)^-$ and $(F\cdots H\cdots F)^-$ systems presented in Tables 2 and 3. The H−F bond length calculated at the MP2/6-311++G** level amounts to 0.968 and 1.138 Å for $(Cl\cdots H-F)^-$ and $(F\cdots H\cdots F)^-$, respectively.

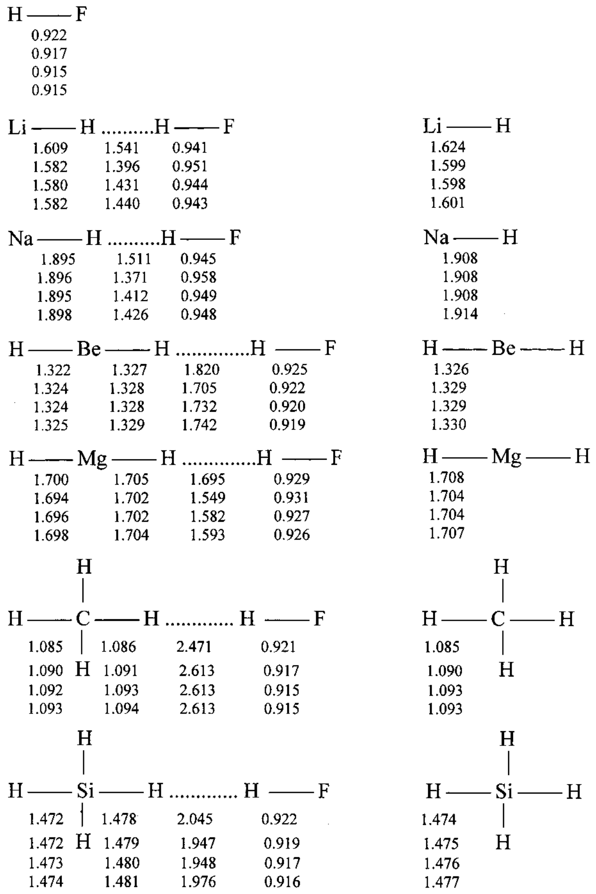

Figure 2. Optimized geometries of DHB complexes (distances in Å). The results are given in the following order: MP2/6-31G**, MP2/6-311++G**, MP4(SDQ)/6-311++G**, and QCISD/6-311++G** levels of theory.

The elongation of the H−F bond for shorter H···H distances in DHB systems is also in line with the findings concerning O−H···O systems. It is well-known that the elongation of the O−H covalent bond is greater for shorter H···O or O···O intermolecular distances.[23b,42] For C═O···H−O systems, the neutron diffraction data of high accuracy from Cambridge Structural Database[46] reveal the same relationship between the C═O bond length and the H···O intermolecular distance,[23b] showing the influence of H-bonding on the proton-accepting group. However, the influence of H-bond formation on the proton-accepting groups or bonds is not usually so evident, which is in line with the findings of this work concerning DHB complexes.

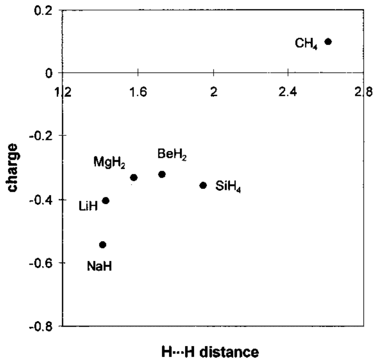

Figure 3. Relationship between net atomic charge (in electronic units) on the hydrogen-accepting atom in the DHB system and the H···H distance (in Å). The results are for the MP4(SDQ)/6-311++G** level of theory. The proton-accepting molecules are indicated.

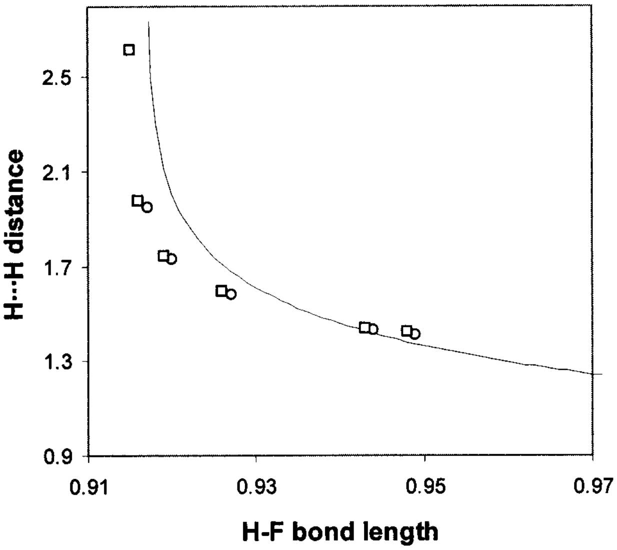

Figure 4. H−F bond length vs H···H distance for dihydrogen-bonded systems optimized at the MP4 (○) and QCISD (□) levels of theory, for the 6-311++G** basis set (distances in Å). The solid line corresponds to the curve obtained from the valence sum rule.

H-bond formation for dihydrogen-bonded systems causes an increase in the positive charge on the hydrogen atom of the HF donating molecule and an increase in the negative charge on one of the hydrogen atoms of the accepting molecule. However, there is no strong linear or polynomial relationship between the H-bond energy or H···H distance and the net atomic charge on the hydrogen atoms (Figure 3).

Figure 4 presents the relationship between the H···H distance and the H−F bond length. Such a relationship was studied previously [18] at the MP2 level of theory for the 6-31G** and 6-311++G** basis sets. This relation is also studied here, but additionally, the results at the MP4 and QCISD levels of theory are included (Figure 4). The results are in line with the bond valence (BV) model.[20] There are two main assumptions of the BV model.

First, each bond can be described by its valence, s

$$s_{ij} = \exp[(r_{ij} - r_0)/B] \tag{2}$$

where r_{ij} is the length of the bond between atoms i and j, s_{ij} is its valence, and r_0 and B are constants. Equation 2 is the relation most often used for the description of the bond valence,[18,20−23] but other types of functions have also been proposed for its definition.[20,47]

The second assumption of the bond valence model states that the ith atom can be described by the atomic valence (V_i), which is equal to the sum of the bond valences.

$$V_i = \sum_j s_{ij} \tag{3}$$

This means that an atom in a liquid or in the solid state can be connected with the other atoms by typical covalent bonds (internal bonds) or/and by intermolecular contacts (external bonds). Internal and external bonds of an atom are described by s_{ij} values. The atomic valence can be understood as the oxidation state of an atom. Equation 3 is known as the valence sum rule,[20] and applied to the hydrogen atom in the X−H···Y bond, it can be written in the following form.

$$s_{\mathrm{H-X}} + s_{\mathrm{H\cdots Y}} = 1 \tag{4}$$

where $s_{\mathrm{H-X}}$ and $s_{\mathrm{H\cdots Y}}$ are the bond valences of the H−X covalent bond and H···Y intermolecular contact, respectively. For the dihydrogen-bonded systems considered here, eq 4 can be written as

$$s_{\mathrm{H\cdots H}} + s_{\mathrm{H-F}} = 1 \tag{5}$$

The constant values r$_0$ and B for the H−F and H−H (or H···H) bonds, which are needed to calculate the s values in eq 5, were proposed by Dunitz.[21,48]

The solid line in Figure 4 is the curve obtained from eq 5, representing the relationship between the H···H distance and the H−F bond length. This curve, obtained from the valence sum rule, is in good agreement with ab initio results.

The bond valence definition is similar to the idea of bond number introduced by Pauling[49] to describe the crystal structures of metals, and the physical meaning of both definitions (bond number and bond valence) is practically the same. The bond valence model and bond number idea have been used widely in many chemical problems.[18,20−23,47] For example, it was shown that the relationships between the geometrical parameters of systems known from neutron diffraction measurements of high accuracy are in agreement with the valence sum rule. Additionally, the BV model may be useful for the study of reaction paths in organic chemistry, for the determination of acidities and basicities of bonds and groups of atoms, and for approaches to other problems of structural chemistry. The results presented in Figure 4 show that the BV model is useful in the analysis of DHB complexes.

3. Bader's Theory Applied to DHB Bonds. In recent years, much attention has been directed toward application of the "atoms in molecules" (AIM) methodology[24] in understanding the properties of molecules and the relations between their geometrical and energetical parameters. Linear relationships were found between the density at the bond critical point ρ_C and the other properties of molecules, such as the length of the covalent bond[50] or the length of the hydrogen bond.[51,52] It was also pointed out that the properties at critical points are useful for the description of the weakest hydrogen bonds, such as C−H···O.[51] Topological AIM analysis was also based on the experimental electron density.[51,53] X-ray and neutron diffraction results were taken into account for the estimation of topological properties and for the new classification of H-bonds.[53]

The AIM methodology was also applied to the study of dihydrogen-bonded systems.[17] A rough correlation was found between the H-bond energy and the ρ_C value for H···H contact ($R^2 = 0.89$ for $n = 8$ points representing dihydrogen-bonded systems). Bader's theory of atoms in molecules was also applied

TABLE 4: Electron Densities ρ_C (e/a_0^3) and Laplacians $\nabla^2\rho_C$ (e/a_0^5) of Covalent or Ionic Bonds for Isolated Monomers and Dihydrogen-Bonded Complexes at Bond Critical Points Calculated at the MP2/6-311++G Level within the AIM Theory[a]**

Isolated Monomers

monomer	ρ_C	$\nabla^2\rho_C$
LiH	0.039	0.167
NaH	0.031	0.131
BeH_2	0.096	0.186
MgH_2	0.052	0.235
CH_4	0.272	−0.912
SiH_4	0.119	0.287
HF	0.370	−0.284

Dihydrogen-Bonded Complexes

	X−H bond		H···H bond		H−F bond	
DHB complex	ρ_C	$\nabla^2\rho_C$	ρ_C	$\nabla^2\rho_C$	ρ_C	$\nabla^2\rho_C$
LiH···HF	0.039	0.175	0.042	0.057	0.323	−2.323
NaH···HF	0.031	0.138	0.046	0.048	0.314	−2.205
BeH_2···HF	0.093	0.197	0.016	0.049	0.361	−2.763
MgH_2···HF	0.051	0.235	0.026	0.060	0.348	−2.624
CH_4···HF	0.270	−0.884	0.002	0.005	0.370	−2.830
SiH_4···HF	0.115	0.285	0.009	0.028	0.367	−2.810

[a] X−H···H−F systems, where X = Li, Na, Be, Mg, C, and Si.

to DHB systems investigated in this paper because it is a very useful tool in analyzing hydrogen bonds, with a large electronic density at the hydrogen bond critical point and a positive value of $\nabla^2\rho_C$ indicating a strong hydrogen bond.[17] Table 4 presents these values (ρ_C and $\nabla^2\rho_C$) for the complexes and isolated monomers analyzed here. It contains the values concerning H···H contacts, donating covalent bonds (H−F in this study), and ionic or covalent accepting bonds (such as Na−H, Si−H, etc.). The molecular properties predicted on the basis of the theory of atoms in molecules were obtained from Gaussian 94[27] calculations in which the AIM method was extended and implemented by Cioslowski.[54,55]

A linear relationship between the H-bond energy (energies are given in Table 1) and ρ_C for H···H contacts was found for the DHB systems studied in this work.

$$y = -336.22x + 1.9344;\ R = 0.994 \qquad (6)$$

where *y* corresponds to the H-bond energy and *x* to the electronic density at critical point of H···H contact. Figure 5 shows this dependence (eq 6), which may be useful for a rough estimation of the H-bond energy if the electronic density at critical point of H···H is known.

Table 4 shows that, for all H···H contacts, we have positive values of $\nabla^2\rho_C$. This means that all complexes are connected through dihydrogen bonds and that the topological properties may be the useful parameters for a description of the H-bonding strength.

Other relationships based on the results given in Tables 1 and 4 can also be shown. A polynomial function represents the correlation between ρ_C for H···H contact and the H···H distance, which is similar to the nonlinear H-bond energy vs H···H distance relationship (see Figure 1).

$$y = 988.24x^2 - 72.295x + 2.6559;\ R = 0.979 \qquad (7)$$

where *y* represents the H···H distance and *x* corresponds to the electron density ρ_C.

It is well-known that covalent donating bonds are elongated for strong or even medium hydrogen bonds. This elongation corresponds to the strength of H-bonding.[42] Similar findings can be shown here for the H−F donating molecule. Equation 8 represents the relationship between the H−F bond length and its electron density at the bond critical point, showing that an elongation of H−F corresponds to a lower ρ_C value; such elongation also corresponds to a stronger H-bond (eq 9).

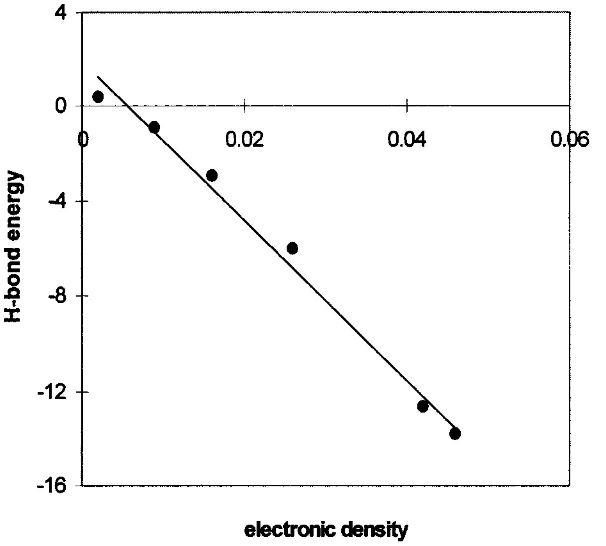

Figure 5. Relationship between the electronic density at the critical point of H···H contact (in electronic units) and the H-bond energy (in kcal/mol) for DHBs optimized at the MP2/6-311++G** level of theory.

$$y = -1.3506x + 1.6073;\ R = 0.998 \qquad (8)$$

where *y* and *x* correspond to ρ_C of the H−F bond and the HF bond length, respectively.

$$y = 253.82x - 94.084;\ R = 0.997 \qquad (9)$$

where *y* and *x* correspond to the H-bond energy and ρ_C of the H−F bond, respectively.

Summary

The results of calculations made at high levels of theory for simple dihydrogen-bonded complexes showed that DHBs may be stable because of their strong H-bonds. The relationships investigated for such complexes are similar to those known for strong H-bonding systems such as O−H···O bonds.

The bond valence model was also applied here to investigate the relations within DHBs. The correlations found between the $H^{-\delta}\cdots{}^{+\delta}H$ distance and the H−F bond length for the investigated dihydrogen-bonded systems optimized at the MP4(SDQ)/6-311++G** and QCISD/6-311++G** levels are in good agreement with the same relations obtained from the bond valence model (Figure 4). Similar agreement can also be obtained at the MP2 level of theory. The relation represented by the solid line at Figure 4 was obtained from eq 5, the valence sum rule.

Application of the theory of Bader, the atoms in molecules approach, shows that the electron density of the H···H contact critical point may be a very useful parameter in describing the strength of H-bonding (Figure 5).

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