How Short Can the H···H Intermolecular Contact Be? New Findings that Reveal the Covalent Nature of Extremely Strong Interactions

Sławomir J. Grabowski,*[†,‡] W. Andrzej Sokalski,[§] and Jerzy Leszczynski[‡]

Department of Crystallography and Crystal Chemistry, University of Łódź, 90-236 Łódź, ul. Pomorska 149/153, Poland, Computational Center for Molecular Structure and Interactions, Department of Chemistry, Jackson State University, Jackson, Mississippi 39217, and Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland

Received: December 8, 2004; In Final Form: March 21, 2005

Ab initio calculations at the MP2/6-311++G(d,p) and MP2/aug-cc-pVDZ//MP2/aug-cc-pVTZ levels have been performed for the following complexes: $H_2OH^+\cdots HBeH$, $H_2OH^+\cdots HBeBeH$, $H_2OH^+\cdots HBeF$, $HClOH^+\cdots HBeH$, $Cl_2OH^+\cdots HBeH$, and $Cl_2OH^+\cdots HBeF$. For all dimers considered, extremely short H···H intermolecular contacts (1.0−1.3 Å) were obtained. These are the shortest intermolecular distances which have ever been reported, with binding energies within the range of 13.7−24.3 kcal/mol (MP2/aug-cc-pVDZ//MP2/aug-cc-pVTZ level). The interaction energies of the complexes analyzed were also extrapolated to the complete basis set (CBS) limit. To explain the nature of such strong interactions, the Bader theory was applied, and the characteristics of the bond critical points (BCPs) were analyzed. It was pointed out that for the major part of the H···H contacts considered here the Laplacian of the electron density at H···H BCP is negative indicating the partly covalent nature of such a connection. The term "covalent character of the hydrogen bond" used sometimes in recent studies is discussed. An analysis of the interaction energy components for dihydrogen bonded systems considered indicates that in contrast to conventional hydrogen bonded systems the attractive electrostatic term is outweighed by the repulsive exchange energy term and that the higher order delocalization energy term is the most important attractive term.

Introduction

A hydrogen bond phenomenon which plays a crucial role in many chemical, physical, and particularly bio-chemical processes is a unique interaction. On the other hand, this phenomenon is not strictly defined.[1−3] Up until the 1980s, the H-bond was usually understood in the following way. An H-bond may be designated as an X−H···Y interaction, where X−H is the proton donating bond and Y is an acceptor center. Its interaction energy ranges between the values of the typical covalent bonds and van der Waals interactions, usually 2−10 kcal/mol.[4,5] The H···Y distance should be smaller than the corresponding sum of van der Waals radii. The X−H proton donating bond is elongated due to the H-bond formation; hence, there is a shift of the stretching frequency of the X−H bond into the red and an increase of its intensity by several times. Y and X are electronegative atoms; Y contains at least one unshared electron pair. Finally, the H-bond interaction is electrostatic in nature.[2,3] Such meaning of the hydrogen bonding was partly related to the Pauling definition that "under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms, instead of only one, so that it may be considered to be acting as a bond between them. This is called the hydrogen bond."[4] Pauling also claimed that the hydrogen bond "is formed only between the most electronegative atoms."[4]

Nowadays, the picture of the interaction of hydrogen bonding is not so clear. Suttor has found C−H···Y H-bonds in some organic crystal structures,[6] and the possibility that a C−H bond with a nonelectronegative carbon atom acts as a proton donor was commonly accepted after the appearance of the study of Taylor and Kennard.[7] X−H···C, X−H···π-electrons, or even C−H···C/π interactions have been also detected and classified as hydrogen bonds.[2,3,8] It was pointed out that C−H···Y H-bonds are weak, but electrostatic forces act far beyond the most often applied van der Waals cutoff; hence, the criterion that the H···Y distance should be less than the sum of van der Waals radii fails.[3] The statement that the X−H proton donating bond is elongated within the hydrogen bridge is also not always fulfilled since systems where the proton donating bonds are shortened were found.[9] Such a decrease of the proton donating bonds is accompanied by a shift to the blue of the stretching mode and most often by a decrease in the intensity of the band. Such interactions were named as blue-shifting hydrogen bonds.[10] The other statement that an H-bond is electrostatic is also controversial since, especially, for strong H-bonds the other attractive terms could be more important than the electrostatic term.[11] It has been also claimed that H-bonds are partly covalent for very strong resonance assisted hydrogen bonds (RAHBs),[12] and the main support for the covalent nature of such interaction is that the Laplacian of the electron density at the H···Y bond critical point is negative.

In the middle of the 1990s a new kind of interaction designated as X−H···H−E was described where X−H is the typical proton donating bond (such as O−H or N−H) and E designates a transition metal or boron.[13] It was pointed out that the H-atom acting as the proton acceptor differs from typical acceptors such as oxygen and nitrogen where the lone electron pairs are responsible for the existence of H-bonding. Such

---

* To whom correspondence should be addressed. E-mail: slagra@uni.lodz.pl.

[†] University of Łódź.

[‡] Jackson State University.

[§] Wrocław University of Technology.

10.1021/jp0444215 CCC: $30.25

H-atoms should be negatively charged, and this occurs for some of the transition metal hydrides existing in metal organic crystal structures. These interactions were named as dihydrogen bonds to acknowledge that it is a special kind of hydrogen bond.[14] One can see that almost none of the features of typical H-bonds are preserved for different kinds of so-called unconventional hydrogen bonds.

Dihydrogen bonds (DHBs) have been investigated extensively since the mid 1990s by experimental[15] as well as theoretical methods.[16] There are a number of reviews concerning DHB systems.[17] Species with DHBs may sometimes be transformed into covalently bound materials thereby opening new opportunities in materials science.[18] The most important for the discussion of the nature of DHBs is that such interactions cover a broader energetic range compared to other conventional H-bonds. C−H···Y and C−H···C interactions are usually weak,[3] except for the few cases considered in theoretical model studies.[19] The first ab initio calculations of systems taken from metal organic crystal structures and also of model systems show that the binding energies for dimers are often greater than 10 kcal/mol.[16] For example, the binding energy for the FH···HLi dimer calculated at the QCISD(T)/6-311++G(d,p) level of theory and corrected for BSSE amounts to 11.9 kcal/mol.[20]

It has been also shown that the properties of some DHBs often do not differ much from the typical H-bonds.[20,21] The calculations carried out up to the MP4(SDQ)/6-311++G(d,p) and QCISD(T)/6-311++(d,p) levels of theory on DHBs with hydrogen fluoride as the proton donor and the simple hydrides of the first and second groups as the acceptors have shown various correlations between geometrical, energetic, and topological parameters. For example, the HF proton donating bond is elongated due to complexation, and such elongation correlates well with the H-bond energy, the H···H distance, and other parameters.[20,21]

The complexation leading to the formation of DHB causes changes similarly as for conventional H-bonds. Among the affected characteristics are vibrational frequencies, shifts of the proton donating X−H bands and the increase of their intensities, changes in the magnetic resonance shielding constants, and changes in the topological parameters derived from the Bader theory (atoms in molecules, AIM, theory).[22] For example, a detailed analysis of the $(BH_3NH_3)_2$ dimer based on the AIM theory was performed by Popelier.[23] The optimization of the geometry of the dimer was carried out at the HF and MP2 levels of theory using the 6-31G(d,p) basis set. There are three B−H···H−N contacts for the optimized $(BH_3NH_3)_2$ dimer; because of its symmetry (C_s symmetry) two of them are equivalent due to the presence of a mirror plane. These H···H contacts are equal to 1.726 and 2.149 Å (MP2/6-31G(d.p) level), less than the corresponding sum of van der Waals radii. The other geometrical criteria of the existence of hydrogen bonding are also fulfilled as well as the topological parameters derived from the Bader theory indicate this type of interaction.[23]

Kar and Scheiner [24] have used the Kitaura and Morokuma energy decomposition scheme[25] to obtain deeper insight into the nature of DHBs between H_3BNH_3, H_2BNH_2, and NH_3 molecules. They pointed out that for DHBs there is significant contribution from polarization, charge transfer, correlation, and higher-order components of total interaction energy, whereas for conventional H-bonds, the electrostatic, first-order term is the most important attractive contribution. The other systems with H···H intermolecular contacts were also analyzed at the MP2/aug-cc-pVTZ/CCSD(T)/aug-cc-pVTZ level of theory with the inclusion of the vibrational contribution[22c] as well as using the perturbational IMPPT decomposition scheme.[26] The following complexes were investigated: LiH···H_2, LiH···CH_4, LiH···C_2H_6, and LiH···C_2H_2.[22c] The authors found that the components of the interaction energy of the LiH···C_2H_2 complex are similar to those of the water dimer; the main binding energy contributions come from the electrostatic energy, followed by the induction and dispersion energies, whereas for the other complexes, the partitioning is different. However, for the remaining complexes, the H···H interactions were not classified as dihydrogen bonds but as van der Waals complexes.

There are different kinds of DHBs; for example, studies of C−H···H−C interactions in organoammonium tetraphenylborates were performed.[27] The authors applied the Bader theory[28] to the experimental electron density after multipole refinement of the crystal structures.[29] They concluded that the transition from nonshared (closed-shell) X−H···H−Y interactions to covalent (shared-shell) X···H−H···Y interactions is discontinuous. On the other hand, the transition from H···H contacts in DHBs to contacts in van der Waals complexes is continuous without borders. The problem of the nature of C−H···H−C interactions 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 was investigated; an analysis of such interactions with the use of the Bader theory indicated that they may be classified as hydrogen bonds.[30] The detailed topological analysis of H···H intramolecular interactions in biphenyls was performed by Matta et al.[31]

Del Bene et al. [22a,b] have investigated model dihydrogen bonded systems ranging from weak to strong ones. For example, they predicted the binding energy for the $LiNCH^+$···HLi complex (at the MP2/aug′-cc-pVTZ level) to be 27.1 kcal/mol. Our recent studies were performed up to the MP2/6-311++G-(3df,3pd)//MP2/aug-cc-pVQZ level of theory on the following complexes: HCCH···H_2, FCCH···H_2, HCCH···HLi, FCCH···HLi, HCCH···HBeH, FCCH···HBeH, HCCH···HBeF, and FCCH···HBeF.[32] The results of the calculations indicate that some of the complexes may be classified as $X-H^{+\delta}\cdots{}^{-\delta}H-Y$ dihydrogen bonds and some of them as X−H···σ interactions.

The aim of the present study is to analyze complexes characterized by very strong dihydrogen bonds. As was mentioned above, the $LiNCH^+$···HLi complex possesses an H···H intermolecular contact of 1.309 Å and a high binding energy value.[22a] One of our latest studies of DHBs reveals strong dihydrogen bonds within the NH_4^+···HBeH, NF_3H^+···HBeH, and NH_4^+···HBeF dimers.[33] For the NF_3H^+···HBeH dimer optimized at the MP2/aug-cc-pVDZ level of theory, the shortest intermolecular H···H contact of 1.132 Å and the binding energy (corrected for BSSE) of 22.8 kcal/mol were predicted. The binding energy calculated by the MP2 method with aug-cc-pVXZ ($X = 2$ and 3) extrapolated to the complete basis set (CBS) is equal to 21.6 kcal/mol. We have carried out here the calculations on the other very strong dihydrogen bonded systems with the O−H proton donating bond that is more sensitive toward the complexation process than the N−H bond. Additionally, the meaning of the phrase “the covalent nature of the hydrogen bond” is also addressed here.

Computational Details

The calculations have been performed with the Gaussian 98[34] and Gaussian 03[35] sets of codes. The following complexes H_2OH^+···HBeH, H_2OH^+···HBeBeH, H_2OH^+···HBeF, $HClOH^+$···HBeH, Cl_2OH^+···HBeH, and Cl_2OH^+···HBeF with the H···H intermolecular contacts were taken into account. The calculations were performed using the second-order Møller−

Plesset perturbation method (MP2).[36] The 6-311++G(d,p) basis set[37−40] was used: the 6-311++G(d,p) as well as the Dunning type basis sets[41,42] were applied: aug-cc-pVDZ and aug-cc-pVTZ. Full optimizations have been performed at the MP2/6-311++G(d,p) and MP2/aug-cc-pVDZ levels of theory. All results of these optimizations correspond to energy minima since no imaginary frequencies were found. The single point MP2 calculations have been carried out with aug-cc-pVTZ basis set and for the reference geometry as optimized at the MP2/aug-cc-pVDZ level of theory.

Since the basis sets applied are not saturated, the basis set extension effects were evaluated using the extrapolation formula

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

CBS designates the complete basis set[43] and X is the cardinal number of the Dunning basis set. We used here MP2/aug-cc-pVDZ (X=2) and MP2/aug-cc-pVTZ (X=3) results to apply the extrapolation formula. The binding energy for the analyzed complexes has been computed as the difference between the total energy of the complex and the energies of the isolated monomers and further have been corrected for the basis set superposition error (BSSE) using the counterpoise method.[44]

Deeper insight into the nature of the interactions of the molecular complexes analyzed here could be obtained by the analysis of interaction energy components. Hence the variation−perturbation approach[45] was applied. The starting wave functions of the subsystems are obtained in this approach in the dimer-centered basis set (DCBS).[44] In contrast to the Morokuma−Kitaura decomposition[25] applied previously in the analysis of DHB systems,[24] the total interaction energy as well as all of its components are free of basis set superposition error (BSSE) due to the full counterpoise correction.[44,46]

The following interaction energy components can be obtained in this way:

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

where $E_{\mathrm{EL}}^{(1)}$ is the first-order electrostatic term describing the Coulomb interaction of static charge distributions of both molecules, $E_{\mathrm{EX}}^{(1)}$ is the repulsive first-order exchange component resulting from the Pauli exclusion principle, and $E_{\mathrm{DEL}}^{(\mathrm{R})}$ and E_{CORR} correspond to higher order delocalization and correlation terms. The delocalization term contains all classical induction, exchange-induction, etc. from second order up to infinity. A strongly basis set dependent charge-transfer term is included in much less basis set sensitive delocalization contribution.[45a,b] The charge transfer component could be entirely reproduced by a second and higher order induction term in extended basis sets; therefore, it can be regarded as redundant. The second-order induction term could be evaluated by SAPT (symmetry adapted perturbation theory),[47] whereas calculation of higher order terms from perturbation theory expressions could be extremely expensive. The correlation term includes dispersion interactions as well as intramolecular correlated electrostatic, exchange, induction, and dispersion contributions. These contributions define on the same time hierarchy of simplified theory levels starting from MP2, SCF, Heitler−London, down to electrostatic models able to reproduce well structural characteristics of classical hydrogen bonded systems.[48] Corresponding software has been implemented within GAMESS package.[49]

The CHelpG scheme[50] implemented within the Gaussian packages[34,35] was also applied to calculate the atomic charges. The CHelpG procedure produces charges fitted to the electrostatic molecular potential (EMP) using a grid based method. The application of the CHelpG method based on well-defined EMP expectation values yields much better estimates of intermolecular charge transfer than the NBO approach,[51] and any arbitrary population analysis, where the corresponding relative error values were doubled reaching 50%.[52]

The "atoms in molecules" (AIM) theory of Bader [28] was applied to find the critical points[53,54] and to analyze them in terms of electron densities and their Laplacians. The properties of BCPs and hence the interatomic and intermoleculat interactions were also studied in terms of the local energy densities at BCPs: the local energy density at BCP ($H(r_{\mathrm{CP}})$) and its components (the local kinetic energy density $G(r_{\mathrm{CP}})$ and the local potential energy density $V(r_{\mathrm{CP}})$). The AIM calculations were carried out using the AIM2000 program.[55]

Results and Discussion

Geometrical and Energetic Results. For the X−H···Y hydrogen bonds, where X−H is the proton donating bond and Y is the accepting center, the H···Y distance is the most often applied parameter for the verification of the existence of H-bond interactions as well as for the rough estimation of its strength.[1,3,7] Very often, especially for intermolecular contacts in crystals, if the H···Y distance is smaller than the corresponding sum of van der Waals radii, it is assumed that H-bonding exists. This criterion may be applied for moderate or strong H-bonds, since for weaker C−H···Y interactions which very often may be also classified as such interactions, the H···Y distance is close or even greater than the corresponding sum of van der Waals radii. It is explained by the fact that C−H···Y hydrogen bonds are mostly electrostatic in nature and that the electrostatic interaction is long range and acts far beyond the van der Waals cutoff.[3] On the other hand, strong hydrogen bonds are characterized by meaningfully shortened H···Y distances. It was claimed that there are three ways to make hydrogen bonding stronger: by adding to the system an electron, by taking away an electron, or by connecting X and Y atoms by a π-conjugated chain.[12a,b] This leads to three kinds of strong hydrogen bonds, two are charge assisted and are usually designated as CAHB(+) and CAHB(−), and the last one is known as resonance assisted hydrogen bonding (RAHB).[12a,b]

It was claimed by Gilli et al. that "the degree of covalency in the homonuclear O−H···O bond is continuously increasing with the shortening of the bond itself."[12a] Since there is no sharp border between the van der Waals interaction and the weak H-bond on one hand and between the very strong hydrogen bond partly covalent in nature and the covalent bond on the other hand, Desiraju claimed[56] that hydrogen bonding is an interaction without borders. A partly similar situation may be found for dihydrogen bonds. Cameron et al. found that some correlations between parameters for DHBs that are continuous if one considers weak DHBs and van der Waals complexes together.[27] Such dependencies are discontinuous if very strong H-bonds and covalent bonds are considered together, and there is a sharp border between them.[27] Additionally, it is known that the relationships between geometrical, topological, and energetic parameters for DHBs are similar as those for typical H-bonds.[20,21] This is the reason the conclusions obtained for very strong DHBs considered here are more general and may be applied to the broader class of hydrogen bond interactions.

First of all, the results of Table 1 show the existence of very short H···H intermolecular contacts for the systems considered here. The H···H distances are in the range 1.0−1.3 Å; this is approximately half of the appropriate sum of the van der Waals radii. It indicates that according to the geometrical criteria those

TABLE 1: Optimized O−H and Be−H Bonds, H···H Distances, and Elongation of O−H and Be−H Bonds (Second Rows, below Corresponding Bond Lengths) Due to Complexation (in Å) for the Dihydrogen-Bonded Complexes, with the O−H···H and H···H−Be Angles also Included (in Degrees)

	MP2/6-311++G(d,p)					MP2/aug-cc-pVDZ				
complex	O−H	H···H	H−Be	∠O−H···H	∠H···H−Be	O−H	H···H	H−Be	∠O−H···H	∠H···H−Be
H_2OH^+···HBeH	1.045	1.229	1.364	179.5	159.1	1.054	1.224	1.371	179.4	163.8
	0.067		0.035			0.071		0.035		
H_2OH^+···HBeBeH	1.089	1.127	1.393	179.1	153.1	1.104	1.118	1.404	179.7	157.2
	0.111		0.057			0.121		0.057		
H_2OH^+···HBeF	1.029	1.280	1.347	177.8	174.8	1.037	1.281	1.356	179.3	160.4
	0.052		0.024			0.054		0.026		
$HClOH^+$···HBeH	1.072	1.157	1.371	179.0	153.9	1.097	1.133	1.381	178.0	152.0
	0.089		0.042			0.108		0.045		
Cl_2OH^+···HBeH	1.129	1.057	1.387	176.7	137.9	1.164	1.049	1.396	176.7	137.9
	0.142		0.058			0.166		0.060		
Cl_2OH^+···HBeF	1.077	1.133	1.355	174.9	178.1	1.116	1.106	1.373	174.9	146.4
	0.090		0.022			0.118		0.043		

are very strong H-bond interactions. The shortest H···H distance of 1.049 Å was found at the MP2/aug-cc-pVDZ level for the Cl_2OH^+···HBeH dimer (the corresponding distance at the MP2/6-311++G(d,p) level amounts to 1.057 Å).

To our knowledge, this is the shortest intermolecular distance which has been reported at such high level of calculations. For example, hydrogen bifluoride is well-known as a system where the strongest H-bond and the shortest hydrogen bond length exist.[2] The bonds' energies reported for the $[FHF]^-$ ion range from 36 to 60 kcal/mol; ab initio calculations performed at different levels of theory reveal H···F distances of 1.134−1.164 Å.[57] Different ab initio and DFT methods with the use of the 6-311++G(2d,p) basis set were also applied to study the hydrogen bifluoride ion, but never has an H···F distance of less than 1.1 Å been obtained.[58] Also for the other very strong resonance assisted H-bonds, the shortest H···O distances are about 1.2 Å.[12a]

Table 1 also shows the other geometrical parameters of the systems considered here. One can observe the meaningful elongation of the O−H proton donating bond due to the complexation, the greatest elongation is for Cl_2OH^+···HBeH complex and amounts to 0.166 Å. Similarly one can observe the elongation of the accepting H−Be bond, it is also the greatest for Cl_2OH^+···HBeH complex and it equals 0.060 Å. Generally, the elongations of BeH bonds are two-three times smaller than those of O−H donating bonds. The H···H distance for the species analyzed here correlates with the elongation of the proton donating O−H bond. Figure 1 shows the correlation between these geometrical parameters (MP2/6-311++G(d,p) results). The linear correlation coefficient for this relationship amounts to 0.965. Table 1 presents the O−H···H and H···H−Be angles. In the first case, the range of angles is of 175−180°, whereas for H···H−Be angle, the range is about 138−164° (MP2/aug-cc-pVDZ level). This is in line with the previous investigations on crystal structures where it was found that for X−H···H−Y (Y designates boron or transition metal) DHBs, the X−H···H angles are usually greater (even close to linearity) than H···H−Y ones.[14]

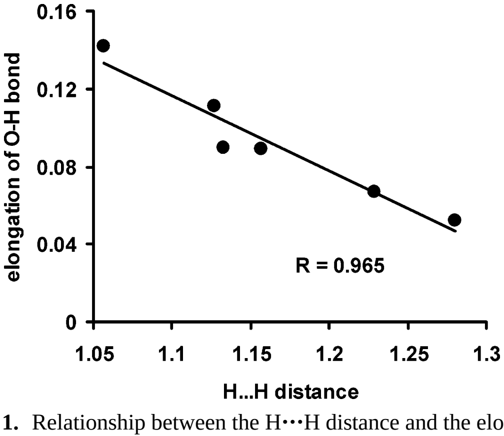

Figure 1. Relationship between the H···H distance and the elongation of the O−H proton donating bond (both values in Å); results obtained at the MP2/6-311++G(d,p) level of theory.

It is worth mentioning that short H···H contacts of the systems investigated here were not observed in crystal structures analyzed by neutron diffraction or X-ray diffraction techniques. For dihydrogen bonded systems in crystals, H···H contacts are usually within the range: 1.7−2.2 Å.[15b,18a,59] For example, the N−H···H_2Re interaction was analyzed in the crystal structure of $[ReH_5(PPh_3)_3]$···indole complex by the neutron diffraction technique and two H···H distances of 1.734(8) and 2.212(9) Å were found.[15a] Another example is the X-ray crystal structure of the triethanolamine···$NaBH_4$ complex, where the shortest dihydrogen bonds are 1.69 and 1.76 Å, which after the normalization of O−H and B−H bonds become 1.62 and 1.67 Å, respectively.[60]

The complexes analyzed here are based on the H_2OH^+···HBeH dimer and its derivatives. The substitution of H-atoms of H_3O^+ (except for the one participating in H-bond interactions) by electronegative atoms increases the strength of the H-bond interaction. In such a case, the H-atom participating in the H-bond is more positive since it loses its electron charge. The opposite situation exists if one substitutes the H-atom of the BeH_2 molecule with an electronegative atom since there is also the loss of electron charge by the H-atom, by an accepting center in such a case. One may also increase the accepting features of the BeH_2 molecule by substituting the H-atom with an electropositive component (for example, Be−H group; see Table 1). One can see from Table 1 that for the appropriate substitution within the H_2OH^+···HBeH dimer there is an increase of H-bond strength and hence a shortening of the H···H distance. In one case, with the H_2OH^+···HBeF dimer, the H···H distance elongates in comparison with the H_2OH^+···HBeH dimer since the F-atom of the former causes a decrease in the accepting properties of BeH_2. It is worth mentioning that the systems analyzed are from the border group which spans between the strong H-bond interactions and the covalent bonds, and this is explained in more detail in this study. Not all of the substitutions were possible during the selection of the systems for investigations. For example, it was not possible to optimize the F_2OH^+···HBeH dimer. In this case the

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

complex	6-311++G(d,p)	aug-cc-pVDZ	aug-cc-pVTZ	CBS[b]	transfer of charge (me)
$H_2OH^+\cdots HBeH$	17.82	18.68	18.52	18.45	205
	17.02	**17.75**	**17.97**		
$H_2OH^+\cdots HBeBeH$	24.18	25.29	24.86	24.66	380
	23.13	**24.12**	**24.27**		
$H_2OH^+\cdots HBeF$	13.31	13.74	14.42	14.71	148
	12.23	12.67	13.72		
$HClOH^+\cdots HBeH$	19.79	21.01	20.95	20.92	368
	18.45	**19.76**	**20.22**		
$Cl_2OH^+\cdots HBeH$	22.76	24.32	24.16	24.09	353
	20.66	**22.71**	**23.22**		
$Cl_2OH^+\cdots HBeF$	17.52	18.29	19.07	19.41	234
	14.99	**16.50**	**17.98**		

[a] Calculations performed within the MP2 theory; BSSE correction is included (for bold results). Charge transfer from the BeH_2 molecule to the proton donating molecule is shown (in me). [b] Basis set limit achieved due to the extrapolation formula applied for aug-cc-pDTZ and aug-cc-pVTZ.

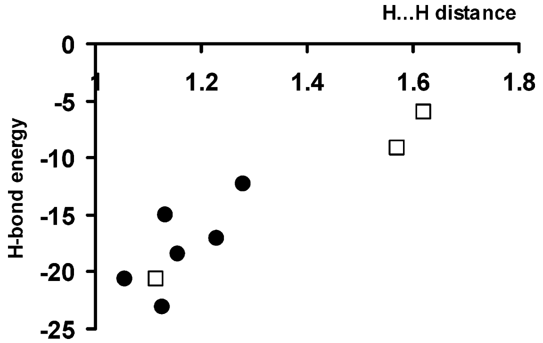

Figure 2. Relationship between the H···H distance (in Å) and H-bond energy (in kcal/mol), MP2/6-311++G(d,p) level of theory. Black circles correspond to the species analyzed here, white squares to the systems investigated previously (ref 33) − $NH_4^+\cdots HBeH$, $NF_3H^+\cdots HBeH$, $NH_4^+\cdots HBeF$.

H-atoms formed the molecular hydrogen, and the system collapsed into the $F_2O\cdots H_2\cdots BeH^+$ complex.

Table 2 presents the energetic parameters of the systems analyzed in this study; the binding energies corrected for BSSE are given. The binding energy, often identified with the H-bond energy, is calculated as a difference between the energy of the dimer and the energies of the monomers constituting the complex. It is worth noticing that the energies mentioned above usually are taken for the optimized structures with the dimers and monomers optimized separately. Hence the H-bond energy defined in such a way contains also the effect of the deformation of monomers due to the process of complexation. One can see (Table 2) that the greatest binding energy of 24.12 kcal/mol calculated at the MP2/aug-cc-pVDZ level of theory is for the $H_2OH^+\cdots HBeBeH$ complex. The H-bond energy for this complex at the MP2/aug-cc-pVDZ/ MP2/aug-cc-pVTZ level is equal to 24.27 kcal/mol. The value obtained by the extrapolation of the energies of the complex and monomers to the complete basis set (CBS) is equal to 24.66 kcal/mol. Hence one can see that the MP2 results obtained with the use of the aug-cc-pVTZ basis set are very close to the CBS limit. Figure 2 shows the relationship between the H···H distance and the H-bond energy. The other three complexes analyzed earlier, $NH_4{}^+\cdots HBeH$, $NF_3H^+\cdots HBeH$, and $NH_4^+\cdots HBeF$, are also included [33] as related systems where strong DHBs exist. One can see that there is no good linear correlation between H-bond energy and H···H distance for these species; however, a rough dependence may be detected.

The systems analyzed here belong to the strongest DHBs ever considered. There are no reports on the DHBs systems with such short H···H contacts as those revealed here. Only for the $NF_3H^+\cdots HBeH$ dimer analyzed earlier by us, the H···H distance for the geometry optimized at the MP2/aug-cc-pVDZ level amounts to 1.132 Å, and its H-bond energy corrected for the BSSE is equal to 21.2 kcal/mol. The strongest H-bond for a DHB system was found for the $LiNCH^+\cdots HLi$ complex optimized at the MP2/aug′-cc-pVTZ level (aug′ means that there is a Dunning's correlation-consistent polarized valence triple-split basis set on the H and Li atoms, and this basis is augmented with diffuse functions on the C and N atoms).[22a] However, in such a case, the H···H distance is equal to 1.309 Å.

It is well-known that there is a transfer of electron density from the acceptor to the donor within the X−H···Y H-bonds.[61] Table 2 presents these values for the DHB systems analyzed here. The amount of such transfer corresponds approximately to the descriptors of hydrogen bonding strength: with the H···H distance and H-bond energy, the greater the transfer, then the stronger the H-bond and the shorter the H···H distance. The greatest transfer occurs for the $H_2OH^+\cdots HBeBeH$ dimer and amounts to 380 me. The amounts of transferred charge from acceptors to donors were calculated using the CHelpG method at the MP2/aug-cc-pVDZ// MP2/aug-cc-pVTZ level of theory. It is worth mentioning that these values are much lower for the conventional H-bonds. For example, for the trans-linear conformation of water, this value calculated at the same level of approximation amounts to 32 me, that is certainly an order of magnitude difference. Significant transfer of electron charge has been also noted for the $\pi\cdots H^+\cdots\pi$ systems investigated recently.[11]

Analysis of Topological Parameters. The Bader theory is a very useful tool for the description of interatomic interactions.[28] The characteristics of the bond critical points (BCPs) (the electron density at BCP, $\rho(r_{BCP})$, and its Laplacian, $\nabla^2\rho(r_{BCP})$) reveal the nature of the interactions. When $\nabla^2\rho(r_{BCP}) < 0$ and is large in magnitude, $\rho(r_{BCP})$ is also large which means that there is a concentration of electronic charge in the internuclear region. This is also an indication of a sharing of electronic charge between both nuclei that defines the covalent (polar) bond. When $\nabla^2\rho(r_{BCP}) > 0$ there is a depletion of electronic charge in the internuclear region. This is observed for interactions between closed-shell systems such as ionic interactions, van der Waals interactions or hydrogen bonds. There are also other properties of BCP such as the electronic energy density H_C of the charge distribution which may be expressed as

$$H_C = G_C + V_C \tag{3}$$

where G_C is a local one-electron kinetic energy density and V_C is the local potential energy density. The relation between

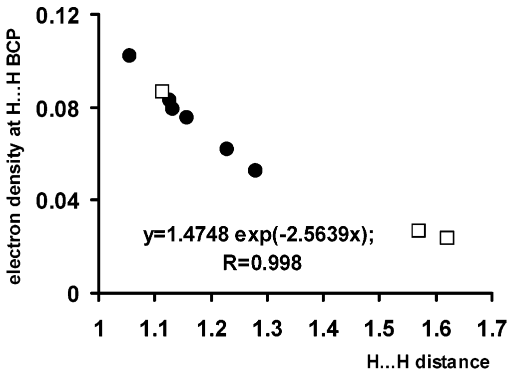

Figure 3. Relationship between the H···H distance (in Å) and the electron density at H···H BCP (in au), MP2/6-311++G(d,p) level of theory. Black circles correspond to the species analyzed here, white squares to the systems investigated previously (ref 33) − NH_4^+···HBeH, NF_3H^+···HBeH, NH_4^+···HBeF.

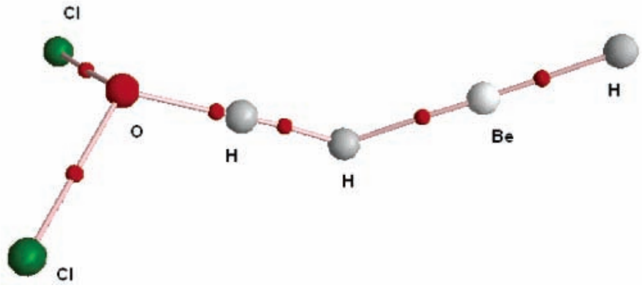

Figure 4. Molecular graph of the H_2OH^+···HBeBeH complex; big circles correspond to attractors, small ones to bond critical points.

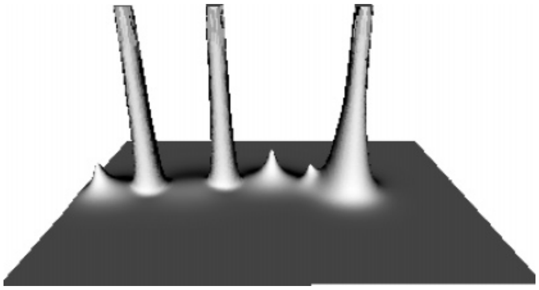

Figure 5. Relief map of the electron density for H_2OH^+···HBeBeH complex in the plane of the HBeBeH accepting molecule. The electron density of HBeBeH is at the left side of the picture and the electron density of the proton donating bond H−O− is placed at the right side.

TABLE 3: Properties of Electron Density (au) in Complexes at the H···H Bond Critical Point[a]

complex	6-311++G(d,p)	aug-cc-pVDZ	aug-cc-pVTZ
	electron density at BCP− ρ		
H_2OH^+···HBeH	0.0617	0.0616	0.0782
H_2OH^+···HBeBeH	0.0830	0.0837	0.0873
H_2OH^+···HBeF	0.0525	0.0525	0.0551
$HClOH^+$···HBeH	0.0757	0.0801	0.0836
Cl_2OH^+···HBeH	0.1019	0.1036	0.1080
Cl_2OH^+···HBeF	0.0789	0.0865	0.0903
	laplacian $\nabla^2\rho$'s		
H_2OH^+···HBeH	0.0239	0.0348	−0.0174
H_2OH^+···HBeBeH	−0.0351	−0.0357	−0.0960
H_2OH^+···HBeF	0.0402	0.0593	0.0051
$HClOH^+$···HBeH	−0.0097	−0.0160	−0.0791
Cl_2OH^+···HBeH	−0.0992	−0.1228	−0.1873
Cl_2OH^+···HBeF	−0.0191	−0.0376	−0.1056

[a] Wave functions obtained at the MP2 level of theory, electron densities (ρ's) and their laplacians ($\nabla^2\rho$'s) at H···H BCPs are given.

Laplacian and the components of the local energy density H_C is given by the equation

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

or in atomic units

$$(1/4)\ \nabla^2\rho(r_{BCP}) = 2G_C + V_C \tag{5}$$

The sign of Laplacian at a specific 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, whereas in the positive regions, there is the domination of the kinetic energy.

It is worth mentioning that electron density at BCP is a good descriptor of the H-bond strength since it well correlates with the H-bond energy. This holds not only for conventional H-bonds [62] but also for DHBs.[20] Figure 3 shows the exponential relationship between the H···H distance and the electron density at H···H BCP; apart from the systems which are the subject of this study, the other strong dihydrogen bonds considered earlier are included.[33] The correlation coefficient for this relationship amounts to 0.998. Topological criteria were also proposed to detect the existence of H-bond interactions.[63,64] Three among them are the most often applied; the first criterion states that the bond path with the bond critical point between the proton and proton acceptor should exist. There are such paths for H···H contacts for the complexes analyzed here. Figure 4 shows the molecular graphs for the Cl_2OH^+···HBeH complex. The attractors (big circles) attributed to the nuclei, BCPs (small circles), and the bond paths connecting atoms are visible. Figure 5 presents the relief map of the electron density for H_2OH^+···HBeBeH complex in the plane passing approximately through the atoms of the accepting molecule HBeBeH and the proton donating bond O−H; the maxima of two other H-atoms of the H_3O^+ donating molecule are not visible since their attractors lie below this plane.

The two other criteria require that the topological parameters at H···Y BCP are within the proper range of 0.002−0.04 au for the electron density and 0.02−0.15 au for its Laplacian. Table 3 shows the electron densities and their Laplacians for H···H contacts of the complexes analyzed here. One can see that all values of the electron density at BCP are outside the range proposed by Koch and Popelier since they are greater than the upper limit and similar to those usually found for weak covalent bonds. The Laplacian values for BCPs of H···.H contacts are positive in two cases, H_2OH^+···HBeH and H_2OH^+···HBeF, as is usual for closed-shell interactions. For the remaining, the Laplacian values are negative as for the covalent bonds. Similar cases were found earlier for the other species,[12d,e,65] for the resonance assisted H-bonds, where for some very strong intramolecular H-bonds the Laplacian values are negative.

Rozas et al. have introduced a new classification of hydrogen bonds according to their strength.[66] Weak hydrogen bonds show both $\nabla^2\rho(r_{BCP})$ and H_C values positive; in such a case the H-bond energy is less than 12 kcal/mol. For medium H-bonds $\nabla^2\rho(r_{BCP})>0$ and $H_C<0$, and the range of H-bond energy is 12−24 kcal/mol. For strong hydrogen bonds the Laplacian value as well as the electron density at BCP are negative, and the H-bond energies are higher than 24 kcal/mol. Table 4 presents the energetic properties of H···H BCPs; the H_C, V_C, and G_C values are given. All H_C values are negative indicating that all hydrogen bonds considered here are at least of medium strength. Four of the complexes are characterized by the negative Laplacian values for the H···H BCPs showing that they may be classified as

TABLE 4: Local Properties (a.u.) of Intermolecular H···H BCP; the Local Kinetic G_C and potential V_C Energy Densities and H_C, the Total Energy Density

	6-311++G(d,p)			aug-cc-pVDZ			aug-cc-pVTZ		
complex	G_C	V_C	H_C	G_C	V_C	H_C	G_C	V_C	H_C
$H_2OH^+\cdots HBeH$	0.0298	−0.0536	−0.0238	0.0288	−0.0490	−0.0202	0.0270	−0.0583	−0.0313
$H_2OH^+\cdots HBeBeH$	0.0341	−0.0770	−0.0429	0.0328	−0.0745	−0.0417	0.0302	−0.0844	−0.0542
$H_2OH^+\cdots HBeF$	0.0268	−0.0436	−0.0168	0.0260	−0.0393	−0.0133	0.0246	−0.0479	−0.0233
$HClOH^+\cdots HBeH$	0.0331	−0.0687	−0.0356	0.0326	−0.0691	−0.0365	0.0301	−0.0799	−0.0498
$Cl_2OH^+\cdots HBeH$	0.0363	−0.0973	−0.0610	0.0333	−0.0973	−0.0640	0.0306	−0.1079	−0.0773
$Cl_2OH^+\cdots HBeF$	0.0337	−0.0723	−0.0386	0.0332	−0.0758	−0.0426	0.0306	−0.0877	−0.0571

strong H-bonds. It is also in line with the studies of RAHB systems which conclude that the H···H interactions are partly covalent in nature. The energetic properties of H···H BCPs given in Table 4 well correlate with the other descriptors of H-bond strength. For example, there is the linear correlation between the H_C and H···H distance, and the linear correlation coefficient amounts to 0.995.

The topological parameters presented in Table 3 may be compared with those obtained by Gatti et al. for different types of hydrogen bonds.[67] The following complexes were considered at the B3LYP/6-31G(d,p) level of approximation by the authors: $H_5O_2^+$, formic acid−formate anion, malonaldehyde equilibrium form, malonaldehyde transition state, cyclic water trimer, water dimer at equilibrium geometry, and acetylene−water complex. These systems represent such H-bond types as CAHB(+), CAHB(−), RAHB, PAHB (polarization assisted hydrogen bonding), intramolecular hydrogen bonding, etc. One can observe that for very strong H-bonds CAHB(+) of $H_5O_2^+$, CAHB(−) of formic acid−formate anion, and for the transition state of maloaldehyde there are the high values of proton···acceptor electron densities amounting to 0.167, 0.167, and 0.177 au respectively; for all of them, Laplacians are negative and equal to −0.415, −0.392, and −0.425 au, respectively. This shows the covalent nature of H-bond interactions within complexes analyzed. These values are not well comparable with those presented in Table 3 due to different levels of calculations. However, the broad spectrum of different types of H-bonds with the use of AIM analysis was investigated at the MP2/6-311++G(d,p) level of approximation[68] what allows for such comparison. For the following complexes—$(FHF)^-$, water dimer, FH···HLi DHB system, and T-shaped dimer of acetylene the electron densities at H···.Y (Y designates acceptor, π-electrons in the case of acetylene dimer)—BCP are equal to 0.174, 0.023, 0.041, and 0.007 respectively, whereas Laplacians amount to −0.349, +0.091, +0.057, and +0.019 indicated that in the first case of CAHB(−) system there is the covalent contribution to the H-bond interaction.

Deeper Insight into the Covalent Character of Hydrogen Bonds; Partitioning of the Interaction Energy. The covalent nature of some of hydrogen bonds was pointed out early on by Pauling[4] who claimed that "the bond was for some time thought to result from the formation of two covalent bonds by the hydrogen atom, the hydrogen fluoride ion $[HF_2]^-$ being assigned the structure $[:\ddot{\underset{\cdot\cdot}{F}}:H:\ddot{\underset{\cdot\cdot}{F}}:]^-$." Pauling also considered the structure of ice and concluded that, if the H···O distance in ice amounts to 1.68 Å, then it corresponds to the bond number value of 0.05, and it is possible to have a rough estimation of "the amount of covalent bonding" for H-bond of 5%. The idea of the bond number was introduced to discuss the interatomic distances in metals and to describe the fractional bonds.[4,69]

$$D(n) = D(1) - 0.60 \log n \tag{6}$$

Here $D(n)$ is the bond length for the bond number n and $D(1)$ is the bond length for a single bond of the same type for which the bond number is equal to unity. The idea was applied later in many physical and chemical problems.[70]

The Pauling idea nicely corresponds to the statement that for the shorter proton···acceptor H···Y distance there is an increase in the covalent nature of the H-bond. Hence one can see that the proposal that very short and strong H-bonds are partially covalent in nature is not a new one. This topic has been considered early on by others[71] finally leading to the conclusion that very strong homonuclear O−H···O H-bonds are three-center-four electron covalent bonds.[12a] Generally, it seems that charge, resonance, or cooperative assistance leads to a decrease in the H···Y distance within H-bonds and to an increase in the covalent character of such interactions.[56,72] The strong influence of the cooperative effects on the H-bond strength was presented recently using the experimental microwave and ab initio techniques for $H_3N\cdots HF$ and $H_3N\cdots HF\cdots HF$ complexes.[73] The authors found that the addition of the second HF molecule causes a 0.21(6) Å contraction of the N···H hydrogen bond relative to that in the $H_3N\cdots HF$ complex.

There is also other experimental evidence concerning the partly covalent nature of the strong hydrogen bonds. A low temperature study of intramolecular hydrogen bonding in benzoylacetone was carried out with X-ray (8.4 K) and neutron diffraction data (20 K).[74] The charge density obtained from X-ray and neutron data has been analyzed by using multipolar functions and topological methods, which provided evidence of π-electron delocalization in the keto−enol group. It is shown that the hydrogen position is stabilized by both electrostatic and covalent bonding contributions at each side of the hydrogen atom. The covalent nature of hydrogen bonds has also been the subject of NMR[75] and Compton scattering[76] as well as theoretical investigations[77] discussions and controversies.

To get a more detailed understanding of the nature of DHBs analyzed here, which in view of the topological analysis described in the previous section, are covalent in nature, the decomposition of the interaction energy was performed according to eq 2. The results for these complexes are given in Tables 5 and 6, at the MP2/6-311++G(d,p) and MP2/aug-cc-pVTZ levels of theory, respectively. It is very interesting to note that according to the results given in the tables, for all of the complexes, the first-order Heitler-London energy is positive. This is because the first-order exchange energy component, $\Delta E_{EX}^{(1)}$, outweighs the first-order electrostatic energy component, $\Delta E_{EL}^{(1)}$, and this situation is not common for typical hydrogen bonds. It is well-known that for moderate and weak H-bonds the electrostatic term is the most important attractive term and outweighs the exchange energy.[61] For very strong dihydrogen bonds analyzed in this study, large values of 33.8 and 27.7 kcal/mol for the exchange energy are revealed for the $Cl_2OH^+\cdots HBeH$ and $H_2OH^+\cdots HBeBeH$ dimers. For all of the complexes the higher order energy delocalization term, $\Delta E_{DEL}^{(R)}$, is the most important attractive term and is responsible for the

TABLE 5: Interaction Energy Terms (in kcal/mol) for Complexes Analyzed in This Study, at the MP2/6-311++G(d,p) Level

energy component[a]	$H_2OH^+\cdots HBeH$	$H_2OH^+\cdots HBeBeH$	$H_2OH^+\cdots HBeF$	$HClOH^+\cdots HBeH$	$Cl_2OH^+\cdots HBeH$	$Cl_2OH^+\cdots HBeF$
$\Delta E^{(1)}$	7.78	10.46	9.76	12.14	20.55	18.09
$E_{EL}^{(1)}$	−12.16	−17.27	−6.10	−12.57	−13.25	−6.01
$E_{EX}^{(1)}$	19.94	27.72	15.86	24.70	33.81	24.10
$E_{DEL}^{(R)}$	−23.95	−35.64	−19.69	−29.87	−43.12	−30.00
ΔE_{SCF}	−16.17	−25.18	−9.93	−17.74	−22.57	−11.91
E_{CORR}	−3.37	−4.01	−4.03	−4.72	−6.42	−7.08
ΔE_{MP2}	−19.54	−29.19	−13.96	−22.45	−28.99	−18.99

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

TABLE 6: Interaction Energy Terms (in kcal/mol) for Complexes Analyzed in This Study, at the MP2/aug-cc-pVTZ Level

energy component[a]	$H_2OH^+\cdots HBeH$	$H_2OH^+\cdots HBeBeH$	$H_2OH^+\cdots HBeF$	$HClOH^+\cdots HBeH$	$Cl_2OH^+\cdots HBeH$	$Cl_2OH^+\cdots HBeF$
$\Delta E^{(1)}$	7.85	10.71	9.73	13.63	20.63	20.43
$E_{EL}^{(1)}$	−12.00	−16.90	−6.49	−12.49	−12.79	−6.96
$E_{EX}^{(1)}$	19.85	27.61	16.22	26.12	33.42	27.39
$E_{DEL}^{(R)}$	−24.44	−37.01	−20.17	−32.71	−45.74	−34.69
ΔE_{SCF}	−16.59	−26.30	−10.44	−19.08	−25.11	−14.27
E_{CORR}	−4.24	−5.03	−4.64	−6.32	−8.25	−8.91
ΔE_{MP2}	−20.84	−31.33	−15.08	−25.40	−33.36	−23.18

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

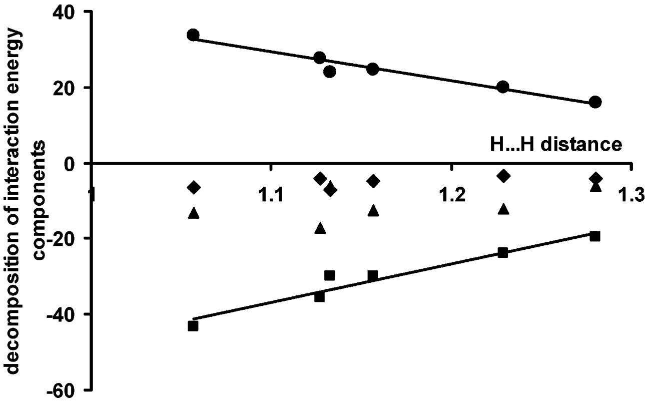

Figure 6. Relationships between the H···H distance (in Å) and the decomposition energy components (in kcal/mol); circles with the regression line correspond to the exchange energy term, squares with the regression line to the delocalization, triangles to the electrostatic energy term, and rotated squares to the correlation energy term.

stabilization of the dimers. The correlation energy term ΔE_{CORR} is about 3−4 times smaller in absolute value in comparison with the delocalization term. Hence, one can see that the exchange energy term as a repulsive term, and the delocalization energy term as an attractive term is dominant within the total H-bond energy. This is different for the typical hydrogen bonds, usually known as electrostatic in nature.

Hence we state that the domination of the energy terms mentioned above ($\Delta E_{DEL}^{(R)}$, $\Delta E_{EX}^{(1)}$) is the main feature of the hydrogen bonds which are known to be very strong and covalent in nature. The covalency of the hydrogen bond is connected not only with the negative value of the Laplacian of H···Y (Y designates the accepting center) as was pointed out before but also with the driving force of the delocalization and the exchange energy terms. This statement is supported by Figure 6, which presents the relationships between the energy decomposition components analyzed here and the H···H intermolecular distance. These dependencies are given for the DHBs complexes that represent energy minima and for calculations carried out at the MP2/6-311++G(d,p) level of theory, since the MP2/aug-cc-pVTZ energy decomposition calculations were performed for the structures optimized at the MP2/aug-cc-pVDZ level. One can see the linear correlations between the H···H distance and the energy terms of the greatest absolute values, $\Delta E_{DEL}^{(R)}$ and $\Delta E_{EX}^{(1)}$. The linear correlation coefficients amount to 0.969 and 0.976, respectively, for these dependencies. There are no correlations for the remaining attractive energy terms, ΔE_{CORR} and $\Delta E_{EL}^{(1)}$. One can see that these findings are in line with the statement of Pauling concerning the covalent character of H-bonds.[4] For shorter H···H distances the corresponding value of the bond number increases following the appropriate increase of the absolute values of the delocalization and exchange energy terms.

It is worth mentioning that according to the results of Table 6 there is the strongest dihydrogen bond for the $Cl_2OH^+\cdots HBeH$ system since the binding energy is equal to 33.36 kcal/mol. However, the results of Table 2 indicate that the strongest H···H interaction occurs for the $H_2OH^+\cdots HBeBeH$ dimer. The results of Table 5 show again the strongest interaction for the $H_2OH^+\cdots HBeBeH$ complex. The differences between the results of Tables 5 and 6 are connected with the different levels of calculations, whereas differences between Tables 2 and 6 need additional explanation. The results of Table 2 were obtained according to the formula of the calculation of the binding energy described earlier. For the $Cl_2OH^+\cdots HBeH$ dimer, the H-bond energy is equal to 24.27 kcal/mol (MP2/aug-cc-pVDZ/ MP2/ aug-cc-pVTZ level), and the deformation energy connected with the complexation is included here. In the supermolecular approach applied for the results of Tables 5 and 6, the interaction energy of the two systems A and B is calculated as the difference between the energy of the dimer, E_{AB}, and the energies of the monomers, E_A and E_B, each calculated for a given nuclear configuration.[78] It means that the geometries of the monomers in the geometry of the complex are taken into account and are not relaxed as in isolation. In such an approach, the deformation due to the complexation is not taken into account. Hence, one can see the source of differences in energies for $Cl_2OH^+\cdots HBeH$ where there is meaningful deformation due to complexation

TABLE 7: Interaction Energy Terms (in kcal/mol) for Various H-Bonded Complexes, at the MP2/6-311++G(d,p) Level

energy component[a]	HOH··· OH_2	FH··· OCH_2	HCCH··· OH_2	HCCH···π	Na^+Cl^-
$\Delta E^{(1)}$	−1.974	−3.850	−1.399	0.080	−117.000
$E_{EL}^{(1)}$	−8.750	−8.869	−4.785	−2.126	−142.285
$E_{EX}^{(1)}$	6.776	5.018	3.386	2.206	25.285
$E_{DEL}^{(R)}$	−2.190	−2.647	−1.059	−0.544	−10.342
ΔE_{SCF}	−4.164	−6.497	−2.458	−0.465	−127.342
E_{CORR}	−0.293	1.060	−0.010	−0.591	0.181
ΔE_{MP2}	−4.457	−5.438	−2.468	−1.056	−127.161

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

since, for example, there is an elongation of the O−H proton donating bond of 0.166 Å.

To compare the nature of the interactions for the species analyzed here with the other types of hydrogen bonds, the decomposition of interaction energy was performed for a few representative H-bonded complexes: $(H_2O)_2$, trans-linear dimer of water, and FH···OCH_2, HCCH···OH_2, HCCH···π and the Na^+ Cl^- ionic pair. Table 7 shows the results obtained at the MP2/6-311++G(d,p) level of theory. One can see that for the two first cases there are hydrogen bonds of medium strength. The first-order Heitler−London energy term is negative since the electrostatic energy, the most important attractive contribution, outweighs the exchange energy. The attractive delocalization energy term is much less important than the electrostatic term but is not meaningless. The delocalization term constitutes 25% and 30% of the electrostatic term for these dimers, respectively. For the C−H···O hydrogen bond within the acetylene-water dimer, the electrostatic interaction energy is still the most important attractive term. It is in line with the statement of Desiraju and Steiner[3] that "the van der Waals cutoff criterion in the H···Y distance for the assignment of hydrogen bond character is inappropriate for weak hydrogen bonds." The long range electrostatic interaction acts far beyond such a cutoff, especially for weak C−H···Y bonds. Table 7 shows that the electrostatic energy term is the most important attractive term for the HCCH···OH_2 dimer. In the T-shaped acetylene complex, where there is a C−H···π hydrogen bond, the exchange energy term is slightly greater than the electrostatic term; the delocalization constitutes 26% of the electrostatic term. Finally, one can see that for the Na^+ Cl^- interaction the electrostatic energy term is really the most important; the exchange is not comparable with it in magnitude, and the delocalization term constitutes only 7% of the electrostatic interaction energy.

These findings characterize the phenomena in the systems that are contrary to the nature of the interactions analyzed here. Table 5 shows the MP2/6-311++G(d,p) level results for these DHB systems. For example, for the Cl_2OH^+···HBeH complex, the delocalization energy term is over three times larger than the electrostatic term. The latter is also approximately two to three times smaller than the exchange energy term. This means that the percentage contribution of the delocalization energy term as well as of the exchange energy roughly reveal the meaning of covalency within H-bond interactions.

Summary

Very strong dihydrogen bonds for which the binding energy is in the range of 13.7−24.3 kcal/mol were analyzed here. The predicted H···H intermolecular distances are in the range of 1.0−1.3 Å (the shortest yet reported) one-half of the corresponding sum of van der Waals radii. This may suggest that H···H interactions are partly covalent. This is confirmed by the Bader theory results since, for the four cases investigated, the Laplacian of the electron density at H···H BCP is negative showing the concentration of the electron density within the internuclear region. For all complexes considered, the energy density at H···H BCP is negative which is typical for stronger or at least moderate H-bonds.

Another feature of the dihydrogen bonds analyzed here is the large transfer of the electron charge from the acceptor to the proton donating bond due to the process of complexation. The transfer predicted for the H_2OH^+···HBeBeH complex amounts to 380 me, much larger than for typical H-bonds. The main goal of this study was to explain the meaning of the partly covalent hydrogen bonding. The energy decomposition allows a more detailed insight into the nature of very strong dihydrogen bonds investigated here to be obtained. It is shown that the delocalization energy (an attractive energy term) and the exchange energy components are the most important terms and correlate with H···H distance being the driving force within these complexes.

Since it was pointed out earlier that dihydrogen bonds are similar in nature to the other conventional H-bonds,[20,21] then the conclusions concerning DHBs may be successfully applied to a broader class of H-bond interactions. It was found earlier that for stronger DHBs the most important attractive energy term is the electrostatic term as was also assumed for other conventional H-bonds of medium strength.[22c,32] We have performed here the decomposition of the interaction energy for very strong DHBs and have compared the results with the decomposition of the other interaction energies: typical H-bonds, weak C−H···O and C−H···π hydrogen bonds, and ionic Na^+ Cl^- interaction. The conclusions are as follows: for the interaction of ions the electrostatic energy term is the most important, and the delocalization one is negligible, similarly as for typical H-bonds of medium strength. However, in the latter case the electrostatic energy is not so important as for the former. For weaker H-bonds the electrostatic energy term is still the most important attractive component; however, it is comparable in magnitude with the exchange energy term. Thus the other attractive contributions such as delocalization and correlation are very important in order to stabilize the system. In the case of very strong H-bonds (covalent in nature) there is the dominant role of the delocalization energy term since it is about two to three times greater than the electrostatic term; the latter is fully outweighed by the exchange energy term.

Acknowledgment. Support has been provided by grant No. 505/675 2004 (University of Łódź), the State Committee for Scientific Research (KBN No. 3T09A 138 26), NSF CREST No. HRD-0125484, NSF EPSCo 02-01-0067-08/MSU, and ONR Grant N00014-98-1-0592. Use of computational resources of the Wrocław Supercomputing Center (WCSS) is also acknowledged.

Supporting Information Available: Table of coordinates of the optimized systems investigated. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: Berlin, 1991.

(2) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997.

(3) Desiraju, G. R.; Steiner, T. *The weak hydrogen bond in structural chemistry and biology*; Oxford University Press: New York, 1999.

(4) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960.

(5) The binding energy is usually computed as the difference between the total energy of the complex (E_{AB}) and the energies of the isolated monomers (E_A and E_B); for stable dimers in minima such values are negative; for the convenience of discussion the absolute positive values of binding energies are presented ($-E_{AB}$) in the text and in Table 2, whereas E_{AB} values and the terms of the decomposition of the interaction energies are given in Tables 5−7.

(6) Suttor, D. J. *J. Chem. Soc.* **1963**, 1105.

(7) Taylor, R.; Kennard, O. *J. Am. Chem. Soc*. **1982**, *104*, 5063.

(8) (a) Grabowski, S. J. *J. Chem. Res*. **1996**, 534. (b) Grabowski, S. J.; Wilamowski, J.; Osman, D.; Sepiol, J. J.; Rodier, N. *Aust. J. Chem*. **1996**, *49*, 951.

(9) (a) Pinchas, S. *Anal. Chem.* **1955**, *27*, 2. (b) Schneider, W. G.; Bernstein, H. J. *Trans. Faraday Soc*. **1956**, *52*, 13. (c) Trudeau, G.; Dumas, J. M.; Dupuis, P.; Guerin, M.; Sandorfy, C. *Top. Curr. Chem.* **1980**, *93*, 91.

(10) Hobza, P.; Havlas, Z.; *Chem. Rev.* **2000**, *100*, 4253 and references therein.

(11) Grabowski, S. J.; Sokalski, W. A.; Leszczynski, J. *J. Phys. Chem. A* **2004**, *108*, 1806.

(12) (a) Gilli, P.; Bertolasi, V.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc*. **1994**, *116*, 909. (b) Gilli, G.; Gilli, P. *J. Mol. Struct.* **2000**, *552*, 1. (c) Gilli, P.; Bertolasi, V.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc.* **2000**, *122*, 10405. (d) Gilli, P.; Bertolasi, V.; Pretto, L.; Lyčka, A.; Gilli, G. *J. Am. Chem. Soc*. **2002**, *124*, 13554. (e) Gilli, P.; Bertloasi, V.; Pretto, L.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc*. **2004**, *126*, 3845.

(13) (a) Park, S.; Ramachandran, R.; Lough, A. J.; Morris, R. H. *J. Chem. Soc. Chem. Commun*. **1994**, 2201. (b) Lough, A. J.; Park, S.; Ramachandran, R.; Morris, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 8356. (c) Lee, J. C., Jr.; Rheingold, A. L.; Müller, B.; Pregosin, P. S.; Crabtree, R. H. *J. Chem. Soc. Chem. Commun*. **1994**, 1021. (d) Lee, J. C., Jr.; Peris, E.; Rheingold, A. L.; Crabtree, R. H. *J. Am. Chem. Soc*. **1994**, *116*, 11014. (e) Peris, E.; Lee, J. C., Jr.; Crabtree, R. H. *J. Chem. Soc. Chem. Commun*. **1994**, 2573. (f) Peris, E.; Lee, J. C., Jr.; Rambo, J.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc*. **1995**, *117*, 3485. (g) Peris, E.; Wessel, J.; Patel, B. P.; Crabtree, R. H. *J. Chem. Soc. Chem. Commun.* **1995**, 2175.

(14) Richardson, T. B.; de Gala, S.; Crabtree, R. H.; Siegbahn, P. E. M. *J. Am. Chem. Soc*. **1995**, *117*, 12875.

(15) (a) Wessel, J.; Lee, J. C., Jr.; Peris, E.; Yap, G. P. A.; Fortin, J. B.; Ricci, J. S.; Sini, G.; Albinati, A.; Koetzle, T. F.; Eisenstein, O.; Rheingold, A. L.; Crabtree, R. H. *Angew. Chem., Int. Ed. Engl*. **1995**, *34*, 2507. (b) Crabtree R. H.; Siegbahn, P. E.M.; Eisenstein, O.; Rheingold, A. L.; Koetzle, T. F. *Acc. Chem. Res*. **1996**, *29*, 348. (c) Richardson, T. B.; Koetzle, T. F.; Crabtree, R. H. *Inorg. Chim. Acta* **1996**, *250*, 69. (d) Cramer, C. J.; Gladfelter, W. L. *Inorg. Chem*. **1997**, *36*, 5358. (e) Calhorda, M. J.; Costa, P. J. *Cryst. Eng. Commun*. **2002**, *4*, 368.

(16) (a) Liu, Q.; Hoffman, R. *J. Am. Chem. Soc*. **1995**, *117*, 10108. (b) Alkorta, I.; Elguero, J.; Foces-Foces, C. *Chem. Commun*. **1996**, 1633. (c) Remko, M. *Mol. Phys*. **1998**, *94*, 839. (d) Orlova, G.; Scheiner, S. *J. Phys. Chem*. **1998**, *102*, 260. (e) Orlova, G.; Scheiner, S. *J. Phys. Chem*. **1998**, *102*, 4813. (f) Braga, D.; DeLeonardis, P.; Grepioni, F.; Tedesco, E.; Calhorda, M. J. *Inorg. Chem*. **1998**, *37*, 3337. (g) Kulkarni, S. A. *J. Phys. Chem. A* **1998**, *102*, 7704. (h) Kulkarni, S. A. *J. Phys. Chem. A* **1999**, *103*, 9330. (i) Kulkarni, S. A.; Srivastava, A. K. *J. Phys. Chem. A* **1999**, *103*, 2836. (j) Calhorda, M. J.; Lopes, P. E. M. *J. Organomet. Chem*. **2000**, *609*, 53.

(17) (a) Alkorta, I.; Rozas, I.; Elguero, J. *Chem. Soc. Rev*. **1998**, 27, 163. (b) Custelcean, R.; Jackson, J. E. *Chem. Rev*. **2001, *101***, 1963. (c) Epstein, L. M.; Shubina, E. S. *Coord. Chem. Rev*. **2002**, *231*, 165.

(18) (a) Custelcean, R.; Jackson, J. E. *J. Am. Chem. Soc*. **1998**, *120*, 12935. (b) Custelcean, R.; Jackson, J. E. *Thermochim. Acta* **2002**, *388*, 143.

(19) Platts, J. A.; Howard, S. T.; Woźniak, K. *Chem. Commun*. **1996**, 63.

(20) Grabowski, S. J. *J. Phys. Chem. A* **2000**, *104*, 5551.

(21) Grabowski, S. *J. Chem. Phys. Lett*. **1999**, *312*, 542.

(22) (a) Alkorta, I.; Elguero, J.; Mó, O.; Yánez, M.; Del Bene, J. E. *J. Phys. Chem. A* **2002**, *106*, 9325. (b) Del Bene, J. E.; Perera, S. A.; Bartlett, R. J.; Alkorta, I.; Elguero, J.; Mó, O.; Yánez, M. *J. Phys. Chem. A* **2002**, *106*, 9331. (c) Cybulski, H.; Pecul, M.; Sadlej, J. *J. Chem. Phys*. **2003**, *119*, 5094.

(23) Popelier, P. L. A. *J. Phys. Chem.* A **1998**, *102*, 1873.

(24) Kar, T.; Scheiner, S. *J. Chem. Phys*. **2003**, *119*, 1473.

(25) Kitaura, K.; Morokuma, K. *Int. J. Quantum Chem*. **1976**, *10*, 325.

(26) (a) Chałasiński, G.; Szczęśniak, M. M. *Mol. Phys*. **1988**, *63*, 205. (b) Cybulski, S. M.; Chałasiński, G.; Moszyński, R. *J. Chem. Phys.* **1990**, *92*, 4357. (c) Chałasiński, G.; Szczęśniak, M. M. *Chem. Rev.* **1994**, *94*, 1723.

(27) Robertson, K. N.; Knop, O.; Cameron, T. S. *Can. J. Chem*. **2003**, *81*, 727.

(28) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Oxford University Press: New York, 1990.

(29) Coppens, P. *X-ray Charge Densities and Chemical Bonding, IUCr*; Oxford University Press: New York, 1997.

(30) Grabowski, S. J.; Pfitzner, A.; Zabel, M.; Dubis, A. T.; Palusiak, M. *J. Phys. Chem. B* **2004**, *108*, 1831.

(31) Matta, C. F.; Hernández-Trujillo, J.; Tang, T.-H.; R. F. W. Bader, *Chem. Eur. J.* **2003**, *9*, 1940.

(32) Grabowski, S. J.; Sokalski, W. A.; Leszczynski, J. *J. Phys. Chem. A* **2004**, *108*, 5823.

(33) Grabowski, S. J.; Robinson, T. L.; Leszczynski, J. *Chem. Phys. Lett.* **2004**, *386*, 44.

(34) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

(35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.03; Gaussian, Inc.: Wallingford CT, 2004.

(36) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(37) McLean, A. D.; Chandler, G. S. *J. Chem. Phys*. **1980**, *72*, 5639.

(38) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys*. **1984**, *80*, 3265.

(39) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(40) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. V. R. *J. Comput. Chem*. **1983**, *4*, 294.

(41) Woon, D. E.; Dunning, Jr., T. H. *J. Chem. Phys.* **1993**, *98*, 1358.

(42) Kendall, R. E.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys*. **1992**, *96*, 6796.

(43) (a) Wilson, A.; Dunning, T. H., Jr. *J. Chem. Phys*. **1997**, *106*, 8718. (b) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys*. **1997**, *106*, 9639. (c) Halkier, A.; Koch, H.; Christiansen, O.; Jorgensen, P.; Helgaker, T. *J. Chem. Phys*. **1997**, *107*, 849.

(44) Boys, S. F.; Bernardi, F. *Mol. Phys*. **1970**, *19*, 553.

(45) (a) Sokalski, W. A.; Roszak, S.; Pecul, K. *Chem. Phys. Lett*. **1988**, *153*, 153. (b) Sokalski, W. A.; Roszak, S. *J. Mol. Struct. (THEOCHEM)* **1991**, *234*, 387. (c) Gora, R. W.; Bartkowiak, W.; Roszak, S.; Leszczynski J. *J. Chem. Phys.* **2002**, *117*, 1031. (d) Gora, R. W.; Bartkowiak, W.; Roszak, S.; Leszczynski J. *J. Chem. Phys*. **2004**, *120*, 2802.

(46) van Lenthe, J. H.; van Duijneveldt-van de Rijdt, J. C. G. M.; van Duijneveldt, F. B. *Adv. Chem. Phys*. **1987**, *69*, 521.

(47) Jeziorski, B.; Szalewicz, K.; Chałasinski, G. *Int. J. Quantum Chem.* **1978**, *14*, 271.

(48) Buckingham, D. A.; Fowler, P. W. *J. Chem. Phys*. **1983**, *79*, 6426.

(49) Gora, R.; Roszak, S.; Sokalski, W. A.; Leszczynski, J. Jackson State University, 1999, JSU preprint.

(50) Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem*. **1990**, *11*, 361.

(51) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys*. **1985**, *83*, 735.

(52) Szefczyk, B.; Sokalski, W. A.; Leszczynski, J. *J. Chem. Phys*. **2002**, *117*, 6952.

(53) Bader, R. F. W.; MacDougall, P. J.; Lau, C. D. H. *J. Am. Chem. Soc*. **1984**, *106*, 1594.

(54) Bader, R. F. W. *Chem. Rev*. **1991**, *91*, 893.

(55) *AIM2000* designed by Friedrich Biegler- König; University of Applied Sciences: Bielefeld, Germany, 2000.

(56) Desiraju, G. R. *Acc. Chem. Res*. **2002**, *35*, 565.

(57) Frish, M. J.; Del Bene, J. E.; Binkley, J. S.; Schaefer, H. F. *J. Chem. Phys*. **1986**, *84*, 2279.

(58) Latajka, Z.; Bouteller, Y.; Scheiner, S. *Chem. Phys. Lett*. **1995**, *234*, 159.

(59) Custelcean, R.; Vlassa, M.; Jackson, J. E. *Chem. Eur. J.* **2002**, *8*, 302.

(60) Custelcean, R.; Jackson, J. E. *Angew. Chem. Int. Ed.* **1999**, *38*, 1661.

(61) (a) Vanquickenborne, L. G. Quantum Chemistry of the Hydrogen Bond. In *Intermolecular Forces. An Introduction to Modern Methods and Results*; Huyskens, P. L., Luck, W. A. P., Zeegers-Huyskens, T., Eds.; Springer-Verlag: Berlin, 1991. (b) Scheiner, S. *Hydrogen Bonding: A Theoretical Perspective*; Oxford University Press: New York, 1997. (c) Gu, Y.; Kar, S.; Scheiner, S. *J. Am. Chem. Soc.* **1999**, *121*, 9411.

(62) (a) Mó, O.; Yánez, M.; Elguero, J. *J. Chem. Phys.* **1992**, *97*, 6628. (b) Mó, O.; Yánez, M.; Elguero, J. *J. Mol. Struct.* (*THEOCHEM)* **1994**, *314*, 73. (c) Espinosa, E.; Molins, E.; Lecomte, C. *Chem. Phys. Lett.* **1998**, *285*, 170.

(63) Koch, U.; Popelier, P. L. A. *J. Phys. Chem. A* **1995**, *99*, 9747.

(64) Popelier, P. *Atoms in Molecules. An Introduction*, Prentice Hall: New York, 2000.

(65) Rybarczyk-Pirek, A. J.; Grabowski, S. J.; Małecka, M.; Nawrot-Modranka, J. *J. Phys. Chem. A* **2002**, *106*, 11956.

(66) Rozas, I.; Alkorta, I.; Elguero, J. *J. Am. Chem. Soc.* **2000**, *122*, 11154.

(67) Gatti, C.; Cargnoni, F.; Bertini, L. *J. Comput. Chem.* **2003**, *24*, 422.

(68) Grabowski, S. J. *J. Chem. Phys. A* **2001**, *105*, 10739.

(69) Pauling, L. *J. Am. Chem. Soc.* **1947**, *69*, 542.

(70) (a) Bürgi, H.-B. *Angew. Chem., Int. Ed.* **1975**, *14*, 460. (b) Dunitz, J. D. *X-ray Analysis and the Structure of Organic Molecules*; Cornell University Press: Ithaca, NY, 1979. (c) Brown, I. D. *Chem. Soc. Rev.* **1978**, *7*, 359. (d) Brown, I. D. *Acta Cryst.* **1992**, *B48*, 553. (e) Brown, I. D. Altermat, D. *Acta Cryst.* **1985,** *B41*, 244. (f) Grabowski, S. J.; Krygowski, T. M. Molecular Geometry as a Source of Chemical Information − Application of the Bond Valence-Bond Number Models. In *Advances in Quantitative Structure Property Relationships*; Charton, B., Charton, M., Eds.; Elsevier Science: Amsterdam, 2002; Vol. 3, pp 27−66.

(71) (a) Coulson, C. A.; Danielsson, U. *Ark. Fys.* **1954**, *8*, 239. (b) Coulson, C. A.; Danielsson, U. *Ark. Fys.* **1954**, *8*, 245. (c) Pimentel. G. C. *J. Chem. Phys.* **1951**, *19*, 446. (d) Reid, C. *J. Chem. Phys.* **1959**, *30*, 182. (e) Kollman, P. A.; Allen, L. C. *J. Am. Chem. Soc.* **1970**, *92*, 6101. (f) Stevens, E. D.; Lehmann, M. S.; Coppens, P. *J. Am. Chem. Soc.* **1977**, *99*, 2829. (g) Desmeules, P. J.; Allen, L. C. *J. Chem. Phys.* **1980**, *72*, 4731.

(72) (a) Steiner, T.; Majerz, I.; Wilson, C. C. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 2651. (b) Vishweshwar, P.; Nangia, A.; Lynch, V. M. *Chem. Commun.* **2001**, 179. (c) Wilson, C. C. *Acta Cryst.* **2001**, *B57*, 435.

(73) Hunt, S. W.; Higgins, K. J.; Craddock, M. B.; Brauer, C. S.; Leopold, K. R. *J. Am. Chem. Soc.* **2003**, *125*, 13850.

(74) Madsen, G. K. H.; Iversen, B. B.; Larsen, F. K.; Kapon, M.; Reisner, G. M.; Herbstein, F. H. *J. Am. Chem. Soc.* **1998**, *120*, 10040.

(75) Benedict, H.; Shenderovich, I. G.; Malkina, O. L.; Malkin, V. G.; Denisov, G. S.; Golubev, N. S.; Limbach, H. H. *J. Am. Chem. Soc.* **2000**, *122*, 1979.

(76) (a) Isaacs, E. D.; Shukla, A.; Platzman, P. M.; Hamann, D. R.; Barbiellini, B.; Tulk, C. A. *J. Phys. Chem. Solids* **2000**, *61*, 403. (b) Isaacs, E. D.; Shukla, A.; Platzman, P. M.; Hamann, D. R.; Barbiellini, B.; Tulk, C. A. *Phys. Rev. Lett.* **1999**, *82*, 600.

(77) (a) Ghanty, T. K.; Staroverov, V. N.; Koren, P. R.; Davidson, E. R. *J. Am. Chem. Soc.* **2000**, *122*, 1210. (b) Martin, T. W.; Derewenda, Z. S. *Nat. Struct. Biol.* **1999**, *6*, 403. (c) Dannenberg, J. J.; Haskamp, L.; Masunov, A. *J. Phys. Chem. A* **1999**, *103*, 7083. (d) Guerra, C. F.; Bickelhaupt, F. M.; Snijders, J. G.; Baerends, E. J. *Chem. Eur. J.* **1999**, *5*, 3581.

(78) Bukowski, R.; Jeziorski, B.; Szalewicz, K. *J. Chem. Phys.* **1996**, *104*, 3306.