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Ab Initio Calculations on Conventional and Unconventional Hydrogen Bonds—Study of the Hydrogen Bond Strength

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Different measures of H-bond strength based on X−H proton donating bond properties and on parameters of H···Y distance (Y−proton acceptor within X−H···Y H bridges) are investigated. Correlations between such measures and H-bond energy are studied. The parameters of H-bonds are taken from geometry of simple complexes optimized within HF/6-311++G** and MP2/6-311++G** levels of theory. The Bader theory of atoms in molecules is also applied for an estimation of electronic densities at bond critical points and Laplacians of these densities, these topological parameters are also used to define H-bond strength measures. Apart from the conventional statistical analysis, the factor analysis is applied to study the properties of H bridges. The results show that the set of geometrical, energetic, and topological variables describing the H bridge may be replaced by one new variable, one factor. It is also shown that the geometrical and topological parameters of the proton donating bond better correlate with the H-bond energy and with the new factor than the parameters of H···Y contact.

1. Introduction

Hydrogen bonds are the most important interactions encountered in gas, liquid, and solid phases and play a crucial role in many chemical and biological processes.[1−3] The conventional hydrogen bond is usually defined as X−H···Y interaction where X−H is the typical covalent bond being the proton donating moiety and Y is a proton accepting center. For conventional hydrogen bonds, X and Y are electronegative atoms such as O, N, F, Cl, and others existing within well-studied systems such as, for example, O−H···O, N−H···O, N−H···N, or F−H···O. The existence and strength of H-bond depend on the Lewis acidity of X−H bond and on the Lewis basicity of Y center. The understanding of hydrogen bonding has changed in last 2−3 decades since new types of H bonds have been investigated.[4−7] Such interactions known as nonconventional hydrogen bonds may be generalized in four ways: H bonds with C−H bonds as unconventional donors,[4−6,8−10] those with unconventional acceptors (π electrons within aromatic systems or the other π-electronic moieties or simple C-atoms),[11] hydrogen bonds with unconventional donors and unconventional acceptors such as C−H···C (or C−H···π) systems,[12] and dihydrogen bonds.[13−15] The last case concerns $X{-}H^{+\delta}\cdots{}^{-\delta}H{-}M$ systems (designated as DHBs) for which X−H is usually the typical proton donating bond with an electronegative X atom and M−H is the metal−hydride σ bond behaving as an acceptor. In some cases of DHBs, the B−H is an accepting bond.[13]

Another point coming to light is the nature of strong hydrogen bonds. It is known that very strong O−H···O bonds can occur because of severe intramolecular strain; in connection with protonated oxyanions $-O{-}H\cdots O^{-}-$ or solvated protons $=O\cdots H^{+}\cdots O=$[2] and due to the fact that the neutral donor and acceptor atoms are connected by a system of π-conjugated double bonds.[16] The cases presented above belong to three fundamental types of strong H bonds: negative charge assisted hydrogen bonding [(−)CAHB], positive charge assisted hydrogen bonding [(+)CAHB], and RAHB (resonance assisted hydrogen bonding). The $(F\cdots H\cdots F)^-$ system[17] is an example of (−)CAHB and is considered in this study.

Despite the great variability of systems which are classified as hydrogen bonds, we may specify the criteria of the existence of such interactions. The most important geometrical characteristic of X−H···Y hydrogen bond is that the distance between the proton and the acceptor atom (H···Y) is shorter than the sum of their van der Waals radii.[18] For strong and medium conventional H bonds, H···Y distance is usually much less than the corresponding sum of van der Waals radii but for weaker C−H···Y (Y = O, N, or C) bonds it may be only slightly less than such sum or even equal to it.[5,9,12] However, the mentioned above geometrical characteristic should not be applied rigorously because it is known that a van der Waals cutoff is not the physical limit of the long-range electrostatic hydrogen bond interaction.[16d] The use of energetic criteria is more problematic. The H-bond strength is intermediate between a strength of strong covalent bonds and weaker intermolecular interactions. Typical H-bonded interaction energies vary between 2 and 15 kcal/mol.[19] The H-bond energy is much greater if one of the two subunits is electrically charged, in which case the interaction energy can reach as much as 40 kcal/mol.[19] The term “strong H bonds” may be also reserved to some of the resonance assisted H-bonded systems[16] or to low-barrier hydrogen bonds (LBHBs) for which the stabilization energy is of 10−20 kcal/mol or even more.[20]

The term “weak H bonds” was generally reserved to unconventional H bonds. However it was pointed out that it need not be the rule. For example, MP2/6-311++G(3d,3p) calculations indicate that the C−H···C hydrogen bond with strength of 8.2 kcal/mol (BSSE included) exists in complex of $H_3N^+{-}CH_2^-$ with acetylene.[12c] Similarly, the high level ab initio studies on simple dihydrogen bonded complexes show that the H-bond energy for such systems is often over 10 kcal/mol. For example, the H-bond energy amounts to 12.7 kcal/

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mol for LiH···HF and 13.4 kcal/mol for NaH···HF at the QCISD(T)/6-311++G** level of theory (BSSE included).[15d]

Besides crystal structure determinations, IR and NMR measurements have been the most often employed for testing the existence and the strength of hydrogen bonding. The stretching vibration of the proton donating bond changes upon H-bonding formation. This mode is typically shifted to the red by hundreds of cm^{-1}, and the band is intensified severalfold. This red shift is correlated with the strength of the H bond as well as with the other parameters such as for example the bond length.[1,10b,21] NMR is an another technique which is often used in identification of H bonds. The proton chemical shift anisotropy is sensitive to the existence of the H bond.[22] The shifts in isotropic and anisotropic chemical shielding of bridging hydrogen relative to isolated monomer often correlate with the proton donating bond length and with the strength of the H bond.[23]

In recent years the Bader theory (atoms in molecules theory, AIM)[24] is often applied to study atom−atom interactions, i.e., typical covalent bonds, ionic bonds, or weak interactions between closed-shell systems as for example hydrogen bonds. A first necessary condition to confirm the presence of a hydrogen bond is a correct topology of the gradient vector field.[25] Bond critical points have to appear between the hydrogen atom and the acceptor atom. Additionally the other topological parameters have to change and have to appear due to the complexation. Koch and Popelier have introduced eight criteria based on the theory of AIM to characterize hydrogen bonds.[15b,25]

We see that a lot of ways to detect the presence of H bonds exist: geometrical and energetic criteria, the use of spectroscopic methods, and the analysis of topological parameters. The aim of this study is to compare simple conventional and unconventional H bonds in terms of their geometry and energy. Because it is known that different measures of H-bond strength may be successfully applied only for systems existing within related complexes the aim of this work is also to test measures which may be applied for samples containing H bridges of different complexes. Such measures may be based on geometrical and/or topological parameters.

2. Methods

All of the computations in the present study were performed using the Gaussian 94[26] and 98[27] sets of programs. The calculations in the framework of the HF and MP2[28] theories have been carried out on the different H-bonded dimers. The choice of the set of various complexes is dictated by the study of measures of the H-bond strength. These measures are to be useful not only for samples of related dimers but also for more various samples. The conventionally H-bonded systems and the complexes with unconventional H bonds, the dimers with weak and with strong H bonds, are taken into account. In other words, the sample investigated here contains not only related systems.

H-bond energy was calculated as the difference between the total energy of the complex and the sum of the total energies of isolated monomers. Basis set superposition error (BSSE) was corrected by the counterpoise method of Boys and Bernardi.[29] The geometries of monomers and complexes were fully optimized. All of the computations employed the 6-311++G** basis set. The inclusion of diffuse components in the basis is a clear requirement to adequately describe hydrogen-bonded systems. Hence, HF/6-311++G** and MP2/6-311++G** levels of theory were applied in this investigation.

Topological properties of the electronic density were characterized using the AIM methodology.[24] By means of the AIMPAC series of programs,[30] the bond critical points have been located. The information on the relative strength of the linkage can be obtained in terms of the electronic density at proton···acceptor (H···Y) bond critical point ($\rho_{H\cdots Y}$) and in terms of the Laplacian ($\nabla^2\rho_{H\cdots Y}$).

3. Results

3.1. Description of the Sample. As mentioned in the Introduction, the main objective in this study is to test the usefulness of new measures of the H-bond strength on a variety of hydrogen-bonded complexes. Hence, the following complexes are taken into account (see Scheme 1): $(F\cdots H\cdots F)^-$, $F-H\cdots Cl^-$, $CH_2O\cdots HF$, $H_2O\cdots HF$, $H_3N\cdots HF$, $LiH\cdots HF$, $C_2H_2...HF$, $(H_2O)_2$, $(HCOOH)_2$, $H_2O\cdots HCCH$, $C_2H_2...HOH$, $(C_2H_2)_2$, $LiH\cdots HCCH$, and $H_3N\cdots HOH$. There are the systems with very strong H-bonds such as $(F\cdots H\cdots F)^-$ and $F-H\cdots Cl^-$; the systems with conventional hydrogen bonds such as $O-H\cdots O$, $O-H\cdots N$, $F-H\cdots O$, and $F-H\cdots N$; and complexes with unconventional H-bonds such as $C-H\cdots O$, $O-H\cdots\pi$ electrons, $C-H^{+\delta}\cdots{}^{-\delta}H$, $Li-H^{-\delta}\cdots{}^{+\delta}H-F$, and the T-shaped $C_2H_2\cdots HF$ complex where π electrons of an acetylene molecule are an acceptor of the proton. Almost all of the complexes presented here were investigated earlier experimentally and/or theoretically. For example, the experimental gas-phase H-bond energies are 39 ± 1[17c] and 21.8 kcal/mol[31] for $(F\cdots H\cdots F)^-$ and $F-H\cdots Cl^-$, respectively; the corresponding energies calculated using ab initio methods are in good agreement with experimental data.[15d] A well-known and investigated extensively linear (trans) dimer of water[19b] is also taken into account in this study. $C_2H_2\cdots HF$ and $(C_2H_2)_2$ are T-shaped dimers with π electrons acting as Lewis bases (proton acceptors). These two complexes were investigated earlier, and it was shown that their binding energies are not negligible.[32,33] $CH_2O\cdots HF$ and $H_2O\cdots HF$ complexes investigated here approximately have C_{2v} symmetry, the same as the symmetry of a free water molecule (Scheme 1). The $H_2O\cdots HCCH$ dimer has the same C_{2v} symmetry (Scheme 1J). The C_{2v} symmetry for the complexes mentioned above is not perfect because the geometries of the complexes, being the result of optimization only, approximately fulfill the symmetry rules (detailed geometries of investigated complexes are given in Supplementary Information). There is also the second $H_2O + C_2H_2$ complex within the chosen sample for which a water molecule donates proton and π electrons of acetylene molecule are a proton acceptor (Scheme 1K).

The centrosymmetric formic acid dimer is also considered here (Scheme 1I). The centrosymmetric dimers of carboxylic acids have been investigated early on in crystal structures[9b] and in the gas phase.[34] For such complexes the double proton transfer is often responsible for the existence of dynamic disorder.[35] For centrosymmetric dimers of carboxylic acids, two $O-H\cdots O$ bonds are geometrically and energetically equivalent.

The sample considered in this study also contains two dihydrogen bonded systems. The first one, $LiH\cdots HF$, is a very well-known modeled dimer investigated with the use of ab initio and DFT techniques.[14a,15c,d,36] The second dihydrogen bonded complex, $LiH\cdots HCCH$ (Scheme 1M), seems to be the unique one which has not been investigated yet. The system is unconventionally H bonded because of the unconventional donating $C-H$ bond and because of the unconventional acceptor, the hydrogen center of LiH molecule. We see that the sample contains typical conventional H bonds as well as unconventional ones covering a variety of situations. Tables 1 and 2 show the geometrical and topological parameters of the H bridges of the sample investigated here. The following MP2/6-311+G**

SCHEME 1

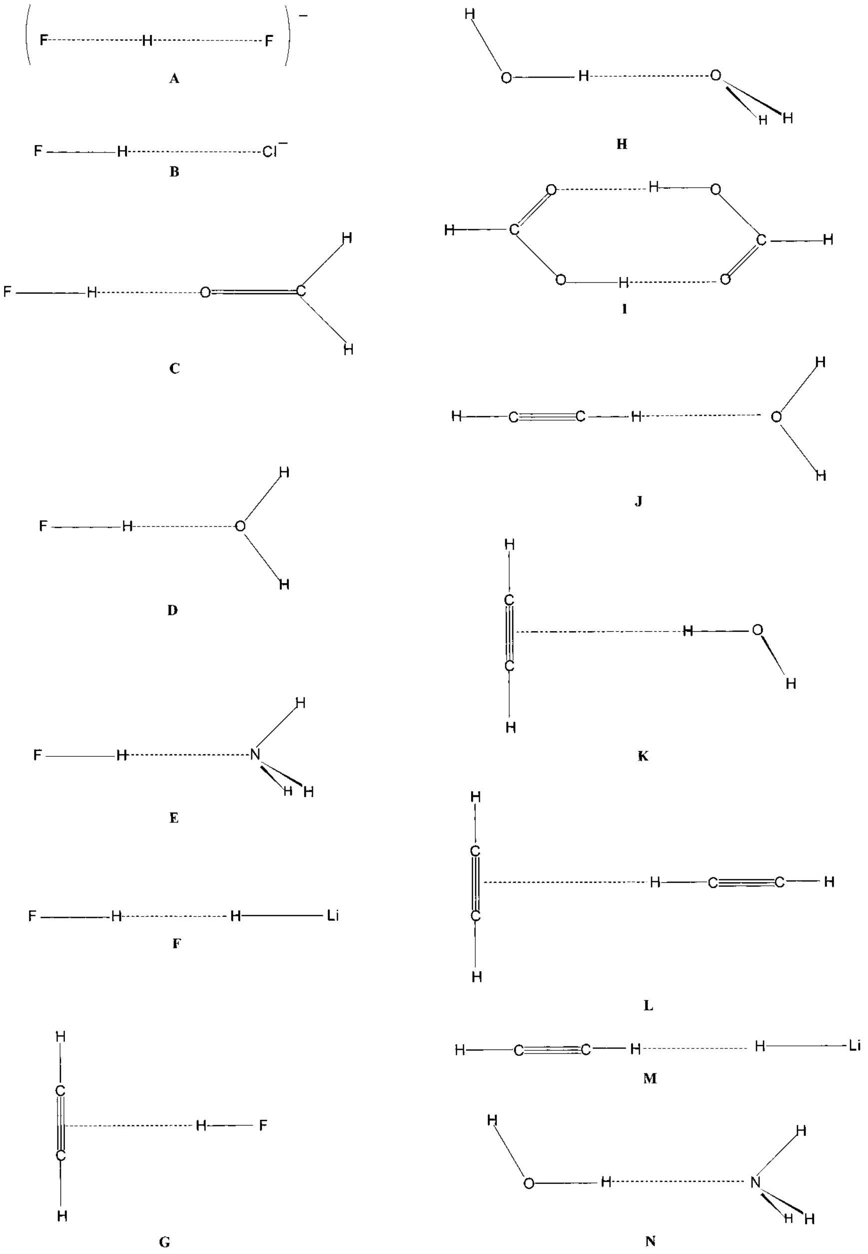


TABLE 1: Geometrical, Energetic, and Topological Parameters of the H-Bonded Systems Investigated Here; Distances in Å, Energies in kcal/mol, and Topological Parameters in au[a]

complex	r_{HX}	$r_{H\cdots Y}$	E_{HB}	BSSE	ρ_{XH}	$\nabla^2\rho_{XH}$	$\rho_{H\cdots Y}$	$\nabla^2\rho_{H\cdots Y}$
$(F\cdots H\cdots F)^-$	1.138	1.138	−39.87	4.51	0.174	−0.349	0.174	−0.349
$(F-H\cdots Cl)^-$	0.968	1.895	−20.94	3.00	0.300	−2.086	0.049	0.073
$FH\cdots OCH_2$	0.923	1.869	−5.43	0.80	0.359	−2.787	0.022	0.107
$FH\cdots OH_2$	0.931	1.730	−7.54	2.19	0.347	−2.652	0.037	0.142
$FH\cdots NH_3$	0.948	1.703	−11.18	0.75	0.325	−2.365	0.050	0.120
$FH\cdots HLi$	0.950	1.399	−12.62	0.72	0.323	−2.327	0.041	0.057
$FH\cdots\pi$	0.923	2.186	−3.15	1.26	0.360	−2.755	0.016	0.053
$(H_2O)_2$	0.966	1.950	−4.45	1.65	0.356	−2.512	0.023	0.091
$(HCOOH)_2$	0.990	1.727	−5.85	1.41	0.326	−2.326	0.040	0.129
$HCCH\cdots OH_2$	1.070	2.198	−2.45	1.38	0.283	−1.033	0.014	0.052
$HOH\cdots\pi$	0.962	2.443	−1.80	1.01	0.361	−2.519	0.010	0.032
$HCCH\cdots\pi$	1.067	2.697	−1.05	0.95	0.284	−1.029	0.007	0.019
$HCCH\cdots HLi$	1.075	2.048	−3.65	0.49	0.280	−1.023	0.011	0.025
$HOH\cdots NH_3$	0.972	1.974	−5.77	1.58	0.348	−2.450	0.028	0.085

[a] The results obtained at the MP2/6-311++G** level of theory.

(Table 1) and HF/6-311++G** (Table 2) results are given: the lengths of proton donating bonds, r_{XH}'s, H···Y distances, $r_{H\cdots Y}$'s, electronic densities at bond (XH or H···Y) critical points, ρ_{XH}'s and $\rho_{H\cdots Y}$'s, respectively, and the Laplacians of these densities, $\nabla^2\rho_{XH}$'s and $\nabla^2\rho_{H\cdots Y}$'s. Tables 1 and 2 also contain the BSSE corrections which are greater for MP2 results

TABLE 2: Geometrical, Energetic, and Topological Parameters of the H-Bonded Systems Investigated Here; Distances in Å, Energies in kcal/mol, and Topological Parameters in au[a]

complex	r_{HX}	$r_{H\cdots Y}$	E_{HB}	BSSE	ρ_{XH}	$\nabla^2\rho_{XH}$	$\rho_{H\cdots Y}$	$\nabla^2\rho_{H\cdots Y}$
$(F\cdots H\cdots F)^-$	1.120	1.120	−40.46	1.01	0.176	−0.498	0.176	−0.498
$(F-H\cdots Cl)^-$	0.928	2.063	−19.39	0.29	0.341	−2.979	0.030	0.079
$FH\cdots OCH_2$	0.904	1.898	−6.13	0.35	0.382	−3.431	0.018	0.106
$FH\cdots OH_2$	0.908	1.812	−8.16	0.82	0.375	−3.366	0.027	0.130
$FH\cdots NH_3$	0.918	1.820	−10.18	0.80	0.358	−3.160	0.036	0.177
$FH\cdots HLi$	0.917	1.590	−10.57	0.23	0.361	−3.153	0.025	0.056
$FH\cdots \pi$	0.902	2.407	−2.70	0.25	0.388	−3.403	0.010	0.034
$(H_2O)_2$	0.946	2.056	−4.25	0.56	0.381	−2.878	0.017	0.075
$(HCOOH)_2$	0.959	1.864	−6.09	0.35	0.359	−2.799	0.026	0.110
$HCCH\cdots OH_2$	1.060	2.278	−2.50	0.45	0.298	−1.180	0.011	0.044
$HOH\cdots \pi$	0.942	2.822	−1.35	0.14	0.387	−2.884	0.006	0.016
$HCCH\cdots \pi$	1.057	3.073	−0.69	0.11	0.298	−1.170	0.003	0.009
$HCCH\cdots HLi$	1.062	2.244	−3.11	0.16	0.296	−1.176	0.008	0.018
$HOH\cdots NH_3$	0.949	2.130	−4.99	0.48	0.376	−2.845	0.019	0.067

[a] The results obtained at the HF/6-311++G** level of theory.

than for SCF calculations and are meaningful for $(F\cdots H\cdots F)^-$ and $F-H\cdots Cl^-$ ionic systems. It is generally in line with the observations concerning the BSSE corrections.[3]

3.2. Relationships between the H-Bond Energy and the Other Topological and Geometrical Parameters. Different correlations between the H-bond energy and the other parameters are known showing that various measures of the H-bond strength may be applied.[16d,37] The X···Y or H···Y distance for the X−H···Y bridge may be treated as a measure of the H-bond strength. It may also be the topological parameter as the electronic density at the H···Y bond critical point, $\rho_{H\cdots Y}$, or the Laplacian, $\nabla^2\rho_{H\cdots Y}$.[38] The most often investigated correlations concern O−H···O bonds and related complexes.[37] The correlations between geometrical parameters are also known; for example, for stronger O−H···O bonds, the greater elongation of OH covalent bond and the shorter H···O contacts are observed.[37] For C═O···H−O systems, the elongation of C═O bond due to the hydrogen bonding formation is observed. The C═O bond elongation is greater for shorter H···O contacts as it is visible from accurate neutron diffraction results.[39] The H-bond strength may be described by the parameters of intermolecular contacts, proton accepting centers or proton donating bonds. The relation between the H-bond energy and H···Y distance was often investigated for different complexes and different types of H-bonds. The correlations were often found but rather for samples of related compounds. It seems that in the case of the sample of not related complexes investigated in this study such relation should not be fulfilled. Hence, the geometrical parameter H···Y distance is modified in this study. The difference between the sum of H and Y van der Waals radii and H···Y distance (eq 1) is taken into account, and the relation between such parameter and H-bond energy is presented in Figure 1.

$$\Delta_{H\cdots Y} = R_H^{vdW} + R_Y^{vdW} - r_{H\cdots Y} \qquad (1)$$

R_H^{vdW} and R_Y^{vdW} are the van der Waals radii of H and Y atoms, respectively, and $r_{H\cdots Y}$ is the H···Y distance.

The application of eq 1 allows us to compare contacts with different Y centers which exist within the sample investigated here. Full circles and the solid line in Figure 1 correspond to MP2 results of calculations; empty squares and the broken line correspond to HF calculations. Two equations presented below (eqs 2 and 3) show the quadratic polynomial regression lines for the relations between the geometrical parameter $\Delta_{H\cdots Y}$ and the H-bond energy, for MP2 and HF results, respectively:

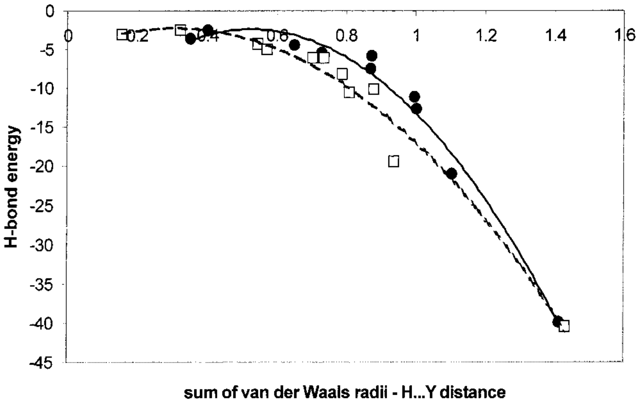


Figure 1. Correlations between the geometrical parameter (the difference between the sum of H and Y van der Waals radii and H···Y distance) and the H-bond energy (in kcal/mol); the geometrical parameter in Å. Full circles correspond to MP2/6-311++G** results and empty squares to HF/6-311++G** ones. The solid line represents the quadratic polynomial regression of MP2 results and the broken line the regression of HF calculations.

$$y = -47.662x^2 + 50.011x - 15.119, \quad R = 0.991 \text{ (MP2 results)} \qquad (2)$$

$$y = -30.735x^2 + 18.904x - 5.1818, \quad R = 0.985 \text{ (HF results)} \qquad (3)$$

For both relations, y corresponds to the H-bond energy (in kcal/mol) and x to the $\Delta_{H\cdots Y}$ geometrical parameter. We see that the correlations are good despite the sample which contains not related complexes. The van der Waals radii used in this study are those introduced by Pauling and often applied in many chemical problems.[40,41]

There is another parameter connected with H···Y contact, the electronic density at H···Y bond critical point. It comes from the Bader theory (AIM theory). This topological parameter well correlates with the H-bond energy, so it well describes the H-bond strength, but again, it may be applied rather for samples of related compounds. However, for the sample investigated here, the correlation is rather good, the linear correlation coefficients for MP2 and HF methods amount to 0.957 and 0.947, respectively. Figure 2 shows these correlations.

It seems that the parameters of the proton donating bond better correlate with the H-bond energy than the parameters of H···Y contacts. On the other hand, the parameters connected with the proton accepting centers have not been investigated extensively. A new measure of the hydrogen bonding strength based on the

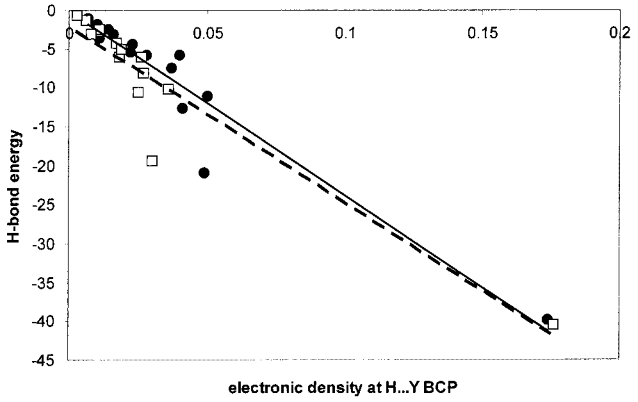


Figure 2. Correlations between the topological parameter, the electronic density at H···Y bond critical point, $\rho_{H\cdots Y}$ (in au), and the H-bond energy (in kcal/mol). Full circles correspond to MP2/6-311++G** results and empty squares to HF/6-311++G** ones. The solid line represents the linear regression of MP2 results, and the broken line represents the regression of HF calculations.

proton donating bond properties have been introduced recently and tested on a small sample of complexes.[42] It is based on the geometrical and topological parameters of the X−H bond:

$$\Delta_{com} = \{[(r_{X-H} - r^0_{X-H})/r^0_{X-H}]^2 + [(\rho^0_{X-H} - \rho_{X-H})/\rho^0_{X-H}]^2 + [(\nabla^2\rho_{X-H} - \nabla^2\rho^0_{X-H})/\nabla^2\rho^0_{X-H}]^2\}^{1/2} \quad (4)$$

where r_{X-H}, ρ_{X-H}, and $\nabla^2\rho_{X-H}$ correspond to the parameters of proton donating bond involved in H-bonding, i.e., the bond length, electronic density at H−X bond critical point, and the Laplacian of that density, respectively, and r^0_{X-H}, ρ^0_{X-H}, and $\nabla^2\rho^0_{X-H}$ correspond to the same parameters of X−H bond not involved in H-bond formation.

The parameter describing H-bond strength may be based only on geometrical data:

$$\Delta_{geo} = (r_{X-H} - r^0_{X-H})/r^0_{X-H} \quad (5)$$

or only on topological parameters:

$$\Delta_{el} = (\rho^0_{X-H} - \rho_{X-H})/\rho^0_{X-H} \quad (6)$$

or on Laplacian values:

$$\Delta_{lap} = |\ (\nabla\rho^{20}_{X-H} - \nabla^2\rho_{X-H})/\nabla^2\rho^0_{X-H}| \quad (7)$$

We know from the earlier studies that $r_{X-H} - r^0_{X-H}$ or $\rho^0_{X-H} - \rho_{X-H}$ often correlate with the H-bond energy.[15d] However, in such a case, the correlation is possible if the proton donating molecule is the same within the investigated sample. The relations 4−7 may be applied for the samples with different proton donating molecules. For example, eq 5 represents the elongation of the proton donating bond due to the H-bond formation in relation to the free donating molecule not involved in H bond. It has been shown that correlations between the H-bond energy and the geometrical parameter described by eq 5 exist even for samples consisting of not related complexes.[42] Such a finding may be very useful in the analysis of H-bonded complexes, especially in the case when the topological parameters are not approachable and eq 4 cannot be applied.

The results presented in Tables 1 and 2 were used to study the correlation between the Δ_{com} parameter and the H-bond energy for MP2 and HF results. Figure 3 presents the corresponding dependencies. Equations 8 and 9 show the regression lines for these correlations:

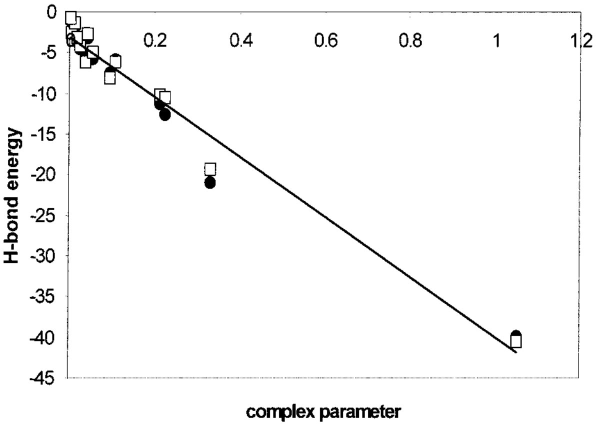


Figure 3. Correlations between the complex parameter defined by eq 4, Δ_{com}, and the H-bond energy (in kcal/mol). Full circles correspond to MP2/6-311++G** results and empty squares to HF/6-311++G** ones. The solid line represents the linear regression of MP2 results, and the broken line represents the linear regression of HF calculations (broken line is not visible because it lies almost at the same place as the solid one).

$$y = -36.75x - 3.1582; \quad R = 0.981 \text{ (MP2 results)} \quad (8)$$

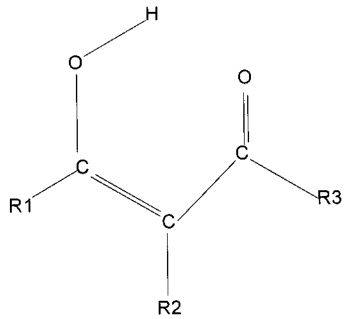
$$y = -37.036x - 2.7429; \quad R = 0.986 \text{ (HF results)} \quad (9)$$

In the present study, the following correlations were presented: E_{HB} vs the modified geometrical parameter based on the H···Y distance, $\Delta_{H\cdots Y}$, E_{HB} vs $\rho_{H\cdots Y}$, and E_{HB} vs Δ_{com} (eq 4). If we take into account only those complexes where the HF molecule is the donor of the proton, thus, we obtain the following correlations. For E_{HB} vs $\Delta_{H\cdots Y}$, the correlation coefficient (the quadratic polynomial regression) amounts to 0.993 and 0.986 for MP2 and HF results, respectively. For E_{HB} vs $\rho_{H\cdots Y}$, dependence the linear correlation coefficient is equal to 0.954 and 0.946 for MP2 and HF results, respectively, and for the relationship between the H-bond energy and the Δ_{com} parameter, the linear correlation coefficient for both MP2 and HF results amounts to 0.982. We see that the correlations for the sample with the same proton donating hydrogen fluoride molecule are not much better than the correlations for the sample with different proton donating bonds. Such results may be connected with different acceptor centers within the sample. It means that the sample still contains not related complexes despite the same proton donor.

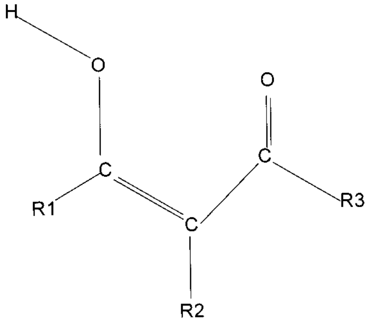
The situation is better if we take into account the sample consisting of H-bonds with the same proton donator and the same type of proton acceptor. It seems that such a sample was investigated earlier.[15d] The dihydrogen bonded systems were taken into account with HF donating molecule and the following acceptors: LiH, NaH, MgH_2, BeH_2, SiH_4, and CH_4. For the above-mentioned acceptor molecules, the proton acceptor centers are negative charged H atoms. For the relations between the H-bond energy and Δ_{com}, $\rho_{H\cdots H}$, or $r_{H\cdots H}$ (H···H distance), the linear correlation coefficient amounts to 0.993, 0.994, and 0.985, respectively, if we consider the results of the MP2/6-311++G** calculations reported earlier.[15d]

3.3. Case of Intramolecular H Bonds. The complex parameter designated as Δ_{com} (eq 4) and based on the geometrical and topological parameters of the proton donating bond may be very useful in the analysis of intramolecular H bonds. For intramolecular H bonds, there is no direct way to calculate

SCHEME 2



SCHEME 3



H-bond energy as a difference between the energy of the complex and of the isolated molecules. Sometimes the H-bond energy for intramolecular systems is defined as a difference between the bridging system (refered to later as "closed system"; Scheme 2) energy and the energy of the corresponding system obtained after the rotation of the X−H proton donating bond 180° around the X−Y bond (refered to later as "open system"; see Scheme 3), Y is an atom connected through bond with X atom of the proton donating bond.[43,44] However, such approach does not correctly reflect the H-bond energy because the other effects during the transition from closed to open configuration should be taken into account.[43] We may say that the difference mentioned above only roughly corresponds to H-bond energy; it will be later designated as $E_{\mathrm{HB}}^{\mathrm{intra}}$ energy.

Simple monofluoro and monochloro derivatives of malonaldehyde were investigated (Scheme 2) to estimate their H-bond energies.[44] For seven such systems optimized within MP2/6-311++G** level of theory, the following quadratic polynomial correlations were found: for $E_{\mathrm{HB}}^{\mathrm{intra}}$ vs $\rho_{\mathrm{H}\cdots\mathrm{O}}$, the correlation coefficient $R = 0.963$, and for $E_{\mathrm{HB}}^{\mathrm{intra}}$ vs $r_{\mathrm{H}\cdots\mathrm{O}}$ ($r_{\mathrm{H}\cdots\mathrm{O}}$, the H···O distance), $R = 0.972$. The same results of intramolecular H-bonded systems are analyzed here to study the correlation between $E_{\mathrm{HB}}^{\mathrm{intra}}$ energy and the complex parameter Δ_{com} defined by eq 4. For the quadratic polynomial regression, the correlation coefficient amounts to 0.942. Figure 4 shows this relationship. We see that for the intramolecular H bonds the correlations between the energy and the other parameters are not so good as those for intermolecular ones, but they are still meaningful. In general, correlations are quadratic in the case of intramolecular H bonds and they turn out to be linear for the intermolecular H bonds. The worse and quadratic correlations for intramolecular H-bonds may be the result of the rough estimation of H-bond energy ($E_{\mathrm{HB}}^{\mathrm{intra}}$) and the strain effects which are meaningful for such systems. For the intramolecular H-bonds considered in this section, $r_{\mathrm{O-H}}^{0}$, $\rho_{\mathrm{O-H}}^{0}$, and $\nabla^2\rho_{\mathrm{O-H}}^{0}$ used in eq 4 correspond to parameters of "open configuration" and $r_{\mathrm{O-H}}$, $\rho_{\mathrm{O-H}}$, and $\nabla^2\rho_{\mathrm{O-H}}$ are those of the "closed" one.

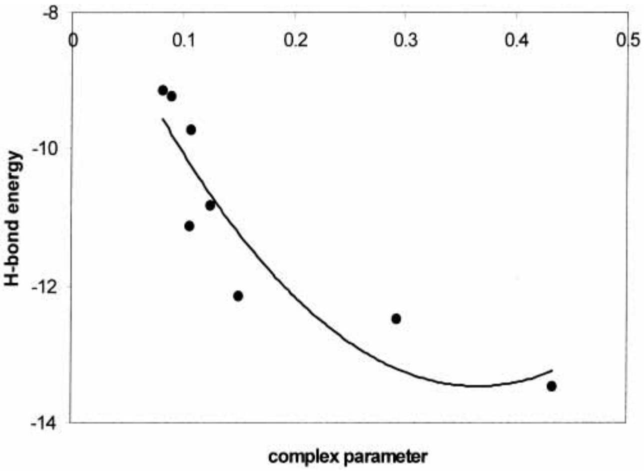


Figure 4. Correlation between the complex parameter defined by eq 4, Δ_{com}, and $E_{\mathrm{HB}}^{\mathrm{intra}}$ energy (in kcal/mol). Full circles correspond to MP2/6-311++G** results, the solid line represents the quadratic polynomial regression of these results.

3.4. Use of Factor Analysis. The findings of the previous section may be supported by factor analysis.[45] The main applications of factor analytic techniques are to reduce the number of variables and to detect structure in the relationships between variables, that is, to classify variables. Factor analysis is often applied in many problems of chemistry, biology, and physics. For example, one of the first applications of this statistical technique in chemistry was connected with the thermodynamic data describing solvent effects.[46]

Factor analysis is applied in this study for the geometrical, energetic and topological data describing H bridges. The following variables are taken into account: E_{HB}, the H-bond energy ($E_{\mathrm{HB}}^{\mathrm{intra}}$ in the case of intramolecular H-bonded systems); three variables corresponding to the proton donating bond (defined by eqs 5−7) and corresponding to its length, electronic density at bond critical point, and the Laplacian of its density; and three variables corresponding to H···Y contact, i.e., the modified geometrical parameter ($\Delta_{\mathrm{H}\cdots\mathrm{Y}}$), electronic density at H···Y bond critical point, and its Laplacian.

The samples considered in previous sections are also taken into account in this section to apply factor analysis to support the relations and findings of this study. The following samples may be specified: the sample consisting of items of different types of H bonds, the sample with different H bonds but restricted to the same proton donating hydrogen fluoride molecule, that of dihydrogen bonds, and the last one. the sample of intramolecular H-bonded systems (MP2/6-311++G** results for all cases).

Some of results of the factor analysis are presented in Table 3. Factor loadings and eigenvalues are given. For all cases of samples, only one factor was retained. It means that the loadings presented in Table 3 refer to the first eigenvalue which explains the largest part of the variance. For all samples, the second eigenvalue refers to the part of variance which is at least 10 times smaller than the part of the first eigenvalue. The part of variance which refers to the third eigenvalue is about 20−80 times smaller than the part referred to the first eigenvalue. For example, for sample 1, the first eigenvalue refers to 91.33% of the total variance (see Table 3), the rest of the variance refers to the remaining eigenvalues; for the second eigenvalue, it is 5.96% of the total variance. Only the first eigenvalues are given in Table 3.

All variables used as indicators of the H-bond strength tell us the same because they are linearly dependent. The eigenvalue

TABLE 3: Factor Loadings for One Factor Extracted and Seven Variables[a]

variable	1[b]	2[c]	3[d]	4[e]
E_{HB}	−0.98	−0.96	−0.97	−0.95
Δ_{geo}	0.99	0.97	0.95	0.98
Δ_{el}	1.00	0.98	0.96	0.99
Δ_{lap}	1.00	0.98	0.94	0.98
$\Delta_{H\cdots Y}$	0.82	0.92	0.87	1.00
$\rho_{H\cdots Y}$	0.99	0.96	0.98	0.99
$\nabla^2\rho_{H\cdots Y}$	−0.88	−0.95	0.74	0.80
eigenvalue	6.39	6.44	5.89	6.43
% total variance	91.33	92.05	84.21	91.79
eigenvalue[f]	3.95	3.96	3.99	3.81
% total variance[f]	98.76	99.06	99.67	95.22

[a] Four different samples investigated in this paper are taken into account (the samples are designated by Arabic numbers); eigenvalues are also given. [b] The sample of various types of H-bonds, MP2/6-311++G** level of theory; the sample is presented in Table 1. [c] The sample of various types of H-bonds restricted to HF as a proton donating molecule, MP2 method; see the seven first entries of Table 1. [d] The sample of dihydrogen-bonded systems. [e] The sample of intramolecular H bonds. [f] The eigenvalue and percentage of the total variance of factor restricted to four first variables connected with the H-bond energy and proton donating bond properties

for the first sample amounts to 6.39 which means that one factor accounts for 91.33% of the variance. If we consider the sample with a HF proton donating molecule, thus, the eigenvalue slightly increases and is equal to 6.44 (92.05% of the total variance). For the sample of dihydrogen bonds, the eigenvalue is equal to 5.89 (84.21% of the total variance), and for the sample of intramolecular H bonds, the eigenvalue amounts to 6.43 (91.79% of the variance). A little surprising results concern the sample of dihydrogen bonds, the lowest value of the eigenvalue.

Table 3 shows that the greatest loadings are for variables describing the proton donating bond, for E_{HB} (or E_{HB}^{intra}) and for the electronic density at $H\cdots Y$ bond critical point ($\rho_{H\cdots Y}$). The loadings inform us about the correlations between the old variables and the factors (the new variables). As it was mentioned above, in all cases, only one factor was extracted. The loadings are lower for the variable connected with the modified geometrical parameter of $H\cdots Y$ contact ($\Delta_{H\cdots Y}$) and with the Laplacian, $\nabla^2\rho_{H\cdots Y}$. The sample consisting of the intramolecular H bonds slightly differs in this matter, with only one old variable, $\nabla^2\rho_{H\cdots Y}$, badly correlating with the new factor.

We see that the parameters describing the proton donating bond in principle better correlate with the new factor than the parameters describing $H\cdots Y$ contacts (Table 3). It may be connected with the fact that the Δ_{com} parameter (eq 4) based on H−X proton donating bond properties well correlates with the H-bond energy. For the sample with the same hydrogen fluoride proton donating molecule, the eigenvalue of new factor increases in comparison with the eigenvalue for the sample with different donating bonds. It may suggest that the composition of the sample influences on the eigenvalue; for the samples consisting of the related complexes, the eigenvalues are greater than for the samples consisting of the various systems. However, for the most various sample considered here, the eigenvalue is still high: 6.39. The lowest eigenvalue was obtained for the sample of dihydrogen bonds which seems to consist of the most related systems, because of the same type of proton donor (HF molecule) and the same type of proton acceptor (hydrogen atom). Such a result is probably connected with the fact that the sample does not really consist of related systems despite the same type of $H^{-\delta}\cdots{}^{+\delta}H$ contacts. There are different types of proton accepting bonds: ionic like NaH or LiH and covalent like Si−H or C−H.

4. Conclusions

Different types of indicators of H-bond strength have been investigated in this study. They may be based on the parameters describing $H\cdots Y$ contacts or on the parameters of the proton donating bond. It has been confirmed that the Δ_{com} parameter (eq 4) well describes the H-bond strength. If the values of the topological parameters are not known, then the measure based only on the length of the donating bond may be used (eq 5).

Factor analysis shows that all variables used for describing the H bond are strictly correlated and can then be equally used to describe the properties of H bonds. Factor analysis also shows that the parameters of the proton donating bond better correlate with the factor than the parameters of $H\cdots Y$ contact. It explains why the Δ_{com} H-bond strength measure well correlates with H-bond energy. It means that we do not have to know the environment of the reference molecule to estimate the influence of such environment. In other words, the proton donating bond “feels” its environment and reflects the strength of H-bonding interaction. It is in accordance with the fact that for the vibrational spectrum the frequency associated with the H−X stretch is typically red-shifted and that such shifts often inform us of the H-bond strength. [1,10b] If we consider only four variables in the factor analysis, E_{HB} and three parameters of the H−X bond, then for all samples only one factor is extracted (as for seven variables) and the eigenvalues increase (Table 3). For all cases of samples, the factors account for more than 95% of the total variance. It means that E_{HB} and the parameters of the H−X bond may be replaced by one new variable independently of the kind of the sample.

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Supporting Information Available: Atomic coordinates are given for complexes considered in the paper. Distance matrices and interatomic angles are present. Geometries for systems are opimized at the MP2/6-311++G** level of theory. This information is available free of charge via the Internet at http://pubs.acs.org.

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