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A new measure of hydrogen bonding strength – ab initio and atoms in molecules studies

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Abstract

MP2/6-311++G** calculations were performed on $HF\cdots H_2O$, $HF\cdots NH_3$, $HF\cdots LiH$, $(H_2O)_2$, $(HCOOH)_2$, $C_2H_2\cdots H_2O$, $H_2O\cdots NH_3$, $(C_2H_2)_2$ complexes to characterise different hydrogen bonds; typical as $O–H\cdots O$ and $O–H\cdots N$, weak like $C–H\cdots O$ and $C–H\cdots\pi$, dihydrogen bonds, etc. For such heterogeneous samples a new measure of hydrogen bond strength was introduced. The Bader theory was also applied to characterise hydrogen bonds.

1. Introduction

Hydrogen bonding is one of the most important interactions playing a crucial role in many chemical and biochemical processes [1,2]. Hence many studies are connected with the description of H-bond geometry and energy. The use of ab initio and DFT calculations seems to be the most appropriate approach to calculate H-bond energy as the difference between the energy of the dimer and the energies of corresponding monomers [3]. However in many cases such estimation of the H-bond energy is not possible. For example for intramolecular H-bonds the other approaches have to be used [4–6]. The most known semiempirical models of hydrogen bonding allow to calculate the H-bond energy from the positions of three atoms directly forming hydrogen bridge – $X–H\cdots Y$ [7]; where X–H is the proton-donating bond and Y is the acceptor centre. Such approach seems to be so crude an approximation and may be useful only in comparative studies and only for homogenous samples.

A lot of works show correlations between H-bond energy and the other parameters like for example $X\cdots Y$ distance, X–H bond length, $H\cdots Y$ distance, electronic density at $H\cdots Y$ bond critical point, etc. [7–10]. We see that the geometrical parameters of the hydrogen bridge may be useful to estimate the strength of H-bond. In recent years the topological parameters derived from the Bader theory (atoms in molecules theory – AIM) [11] are often used to describe hydrogen bonds. However, both classes of parameters – geometrical and topological – may be useful only for narrow ranges of H-bond energies and for homogenous samples.

The aim of the present study is to introduce a new measure allowing to estimate the H-bond strength for heterogenous systems. This measure is to be useful for typical intermolecular H-bonds

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and in such cases where the direct estimation of the H-bond energy is not possible.

2. Computational details

Calculations were carried out with the GAUSSIAN 98 program [12] at MP2/6-311++G** level of theory. For all complexes and monomers the geometry was fully optimised. H-bond energies were computed as the difference in energy between the complex, on the one hand, and the sum of isolated monomers, on the other hand. Basis set superposition error (BSSE) was corrected by the counterpoise method of Boys and Bernardi [13]. All calculations were performed at MP2/6-311++G** level of theory. The hydrogen bonding properties predicted on the basis of the Bader theory [11] were obtained from AIMPAC programs [14].

3. Results and discussion

Different types of hydrogen bonds are investigated here since the aim of the present study is to construct a new measure of H-bond strength. Such measure is to be applied for samples of heterogenous systems.

Table 1 shows the values of geometrical and topological H-bond parameters obtained at MP2/6-311 + +G** level of theory. The following complexes are taken into account: F–H···OH_2, F–H···NH_3, F–H···H–Li, HOH···OH_2, $(HCOOH)_2$, C_2H_2···OH_2, HOH···C_2H_2, HOH···NH_3. We see that different types of H-bonds are considered: F–H···O, F–H···N, O–H···O, C–H···O, O–H···N, O–H···π-electrons (of C_2H_2 molecule) and F–$H^{+\delta}$ ···$^{-\delta}$ H. There are conventional H-bonds with HF as proton-donating molecule and O or N as Lewis basicity centres. O–H···O bond exists in two complexes; water linear (trans) dimer and centrosymmetric configuration of formic acid dimer. Centrosymmetric dimers of simple carboxylic acids with two equivalent O–H···O bonds were often studied [15,16]. O–H···N bond in HOH···NH_3 complex is another case of the conventional H-bond included within the sample. Two configurations of $H_2O + C_2H_2$ complex are investigated here: the first one with C(sp)–H proton-donating bond and O-atom as an acceptor (C_2H_2···OH_2) – such complex has C_{2v} symmetry as H_2O molecule, the second complex with O–H proton-donating bond and π-electrons of C_2H_2 as an acceptor (HOH···C_2H_2). There are also two other cases of unconventional H-bonds within the sample: C–H···π bond of T-shaped acetylene dimer and F–H···H dihydrogen bond. Dihydrogen bonds are the systems which have been investigated both experimentally [17,18] and theoretically [19–23, 5,10] in recent years.

Table 1 presents geometrical, energetic and topological parameters of the above-mentioned H-bonds: X–H proton-donating bond lengths, H···Y distances, H-bond energies (BSSE included), electronic densities at X–H bond critical points – ρ_{XH}, and electronic densities at H···Y bond critical points – $\rho_{H\cdots Y}$, Laplacians of these densities – $\nabla^2\rho_{XH}$ and $\nabla^2\rho_{H\cdots Y}$, respectively. One can see that LiH···HF dihydrogen bonded system

Table 1
Geometrical (in Å) and topological (in a.u.) parameters of hydrogen bonds; H-bond energies – E_{HB} (BSSE included) in kcal/mol

Complex[a]	r_{XH}	$r_{H\cdots Y}$	E_{HB}	ρ_{XH}	$\nabla^2\rho_{XH}$	$\rho_{H\cdots Y}$	$\nabla^2\rho_{H\cdots Y}$
HF···H_2O	0.931	1.730	−7.54	0.347	−2.652	0.037	0.142
HF···NH_3	0.948	1.703	−11.18	0.325	−2.365	0.050	0.120
HF···LiH	0.950	1.399	−12.62	0.323	−2.327	0.041	0.057
$(H_2O)_2$	0.966	1.950	−4.45	0.356	−2.512	0.023	0.091
$(HCOOH)_2$	0.990	1.727	−5.85	0.326	−2.326	0.040	0.129
C_2H_2···OH_2	1.070	2.198	−2.45	0.283	−1.033	0.014	0.052
HOH···C_2H_2	0.962	2.443	−1.80	0.361	−2.519	0.010	0.032
$(C_2H_2)_2$	1.067	2.697	−1.05	0.284	−1.029	0.007	0.019
HOH···NH_3	0.972	1.974	−5.77	0.348	−2.450	0.028	0.085

[a] As first molecule the proton donor is given.

is the most stable in spite of unconventional hydrogen bonding, its H-bond energy (E_{HB}) is equal to −12.6 kcal/mol. For the other unconventional H-bond – C–H$\cdots\pi$ system of $(C_2H_2)_2$ complex, the H-bond is the weakest, E_{HB} amounts to −1.1 kcal/mol. Similarly we observe the weak H-bond for O–H$\cdots\pi$ system ($HOH\cdots C_2H_2$ dimer), E_{HB} of this complex is equal to −1.8 kcal/mol.

Different correlations between H-bond energy and the other parameters are known [5,7–10]. The most known is that one between H-bond energy and proton–proton acceptor (H$\cdots$Y) distance. However, such relationship is fulfilled only for homogenous samples, i.e., for the same type of hydrogen bonding like for example O–H$\cdots$O and for related compounds. The sample investigated here is not homogenous and the simple distance–energy relationship cannot be fulfilled. However, the choice of the heterogeneous sample is connected with the trial to construct a new universal parameter describing H-bond strength. The way to obtain a reasonable X$\cdots$Y distance – H-bond energy correlation is to modify the geometrical parameter for application to different H-bonds. Such modification may be based on the most important geometrical criterion of the existence of hydrogen bonding [24] that the distance between the proton and the acceptor atoms is shorter than the sum of their van der Waals radii. The difference between such sum and the H$\cdots$Y distance is considered here and its correlation with H-bond energy is presented (Fig. 1). The following values of van der Waals radii were taken into account: H – 1.2 Å, O – 1.4 Å, N – 1.5 Å as the most often used values [25]. Two systems with π-electrons as acceptors of protons are excluded from this relationship (HOH$\cdots\pi$ and $C_2H_2\cdots\pi$) because it is difficult for them to estimate the corresponding van der Waals radii. For the remaining seven H-bonds (Fig. 1) the linear correlation coefficient R amounts to 0.924, the regression for the polynomial of degree two gives the R-value of 0.972. We see that the linear correlation is not satisfactory and that the universal parameter should be based on the other hydrogen bonding characteristics.

In recent years the topological parameters derived from the Bader theory [11] are often applied

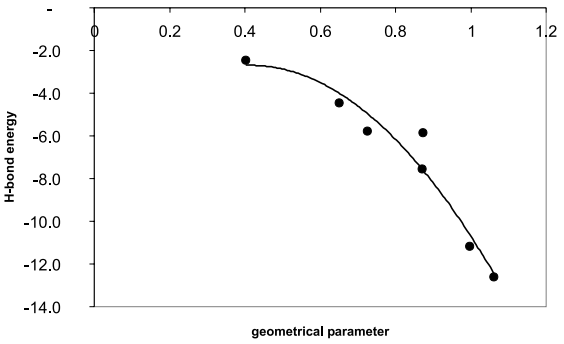

Fig. 1. The relationship between H-bond energy (in kcal/mol) and the modified distance parameter (the sum of the appropriate van der Waals radii minus the H$\cdots$Y distance – in Å) for the sample of heterogeneous complexes.

in analysis of H-bonds [6,9,10,23,26]. The most known is the correlation between the electronic density at H$\cdots$Y bond critical point – $\rho_{H\cdots Y}$ and H-bond energy. Such relationship is fulfilled for typical O–H$\cdots$O bonds [27] and for unconventional bonds like dihydrogen bonds [5,10,28] but rather for homogenous samples. Indeed for the heterogeneous sample presented here the correlation is not satisfactory – the linear correlation coefficient for the relation between $\rho_{H\cdots Y}$ and H-bond energy amounts to 0.692.

Two correlations presented above show that for the heterogeneous sample investigated here the parameters of H$\cdots$Y contact do not correspond to H-bond strength. The main concept of this study is to introduce the measure of H-bond strength based on the parameters of the proton-donating bond. The analysis based on such parameters seems to be reasonable since the X–H bond is less sensitive to the other effects than H$\cdots$Y contact. In other words the proton-donating bond is sensitive to the stronger directional hydrogen bonding and much less to weaker intermolecular interactions, we may say that this bond 'feels' the Y-centre and is changed due to the strength of H-bonding. One of the most known characteristics of H–X bond within X–H$\cdots$Y systems is its elongation in comparison with the free X–H bond. Correlations between H-bond energy and the length of X–H bond were found for different types of hydrogen bonds, even for dihydrogen bonds [10] but for the same type of X–H

within investigated systems. For the sample presented here the following parameter is proposed:

$$\delta_{XH} = \frac{(r_{X-H} - r^0_{X-H})}{r^0_{X-H}}, \quad (1)$$

where r_{X-H} is the length of X–H bond within X–H$\cdots$Y system and r^0_{X-H} is the length of the free bond not involved within H-bonding. In other words δ_{XH} is the elongation of X–H bond due to H-bridge formation in relation to the free X–H bond length. The linear correlation coefficient for the relationship between this parameter and H-bond energy amounts to 0.969.

The topological parameters of the Bader theory are very useful to describe the characteristic of hydrogen bonding but mainly the relationship between $\rho_{H\cdots Y}$ and E_{HB} is taken into account. It was found that the electronic density at the F–H proton-donating bond – ρ_{FH} within dihydrogen bonded systems strongly correlates with H-bond energy [10]. The similar correlation was found for the sample investigated here. However, due to the heterogeneity of the sample the following parameter is introduced:

$$\delta(\rho_{XH}) = \frac{(\rho^0_{X-H} - \rho_{X-H})}{\rho^0_{X-H}}, \quad (2)$$

where the parameters are defined in a similar way as for Eq. (1): ρ_{X-H} is the electronic density at X–H bond critical point and ρ^0_{X-H} concerns the free bond not involved within H-bond. The linear correlation for the relation between the $\delta(\rho_{XH})$ parameter and the H-bond energy amounts to 0.971. We see that $\delta(\rho_{XH})$ for T-shaped acetylene dimer is equal to 0; ρ_{FH} does not decrease due to such H-bonding formation. It means that the topological parameter – the electronic density at the proton-donating bond critical point is even less sensitive to weak interactions than the length of the donating bond.

We may also introduce the complex parameter including the Laplacian of electronic density at X–H bond critical point – $\nabla^2\rho_{X-H}$

$$\Delta_{com} = \left\{ [(r_{X-H} - r^0_{X-H})/r^0_{X-H}]^2 + [(\rho^0_{X-H} - \rho_{X-H})/\rho^0_{X-H}]^2 + [(\nabla^2\rho_{X-H} - \nabla^2\rho^0_{X-H})/\nabla^2\rho^0_{X-H}]^2 \right\}^{1/2}. \quad (3)$$

It is slightly similar to the measure introduced by Popelier [29] for the description of the similarity of benzoic acid derivatives. Fig. 2 presents the relationship between the complex parameter Δ_{com} and H-bond energy

$$E_{HB} = -46.62\Delta_{com} - 2.13; \quad R = 0.971. \quad (4)$$

Tables 1 and 2 show that $\nabla^2\rho_{X-H}$ increases due to the H-bonding formation and it is connected with the elongation of the bond and the decrease of ρ_{X-H} value. However, for very weak H-bonds (for both cases of water–acetylene dimer and for acetylene dimer) the decrease of ρ_{X-H} is meaningless and we do not observe the increase of the corresponding Laplacian. In such cases the change of the Laplacian was approximated to be zero. It confirms the statement that the topological parameters connected with the donating bonds within H-bonded complexes may not be sensitive to very weak interactions.

Finally, we see that the Δ_{com} parameter correlates well with the H-bond strength. The results are

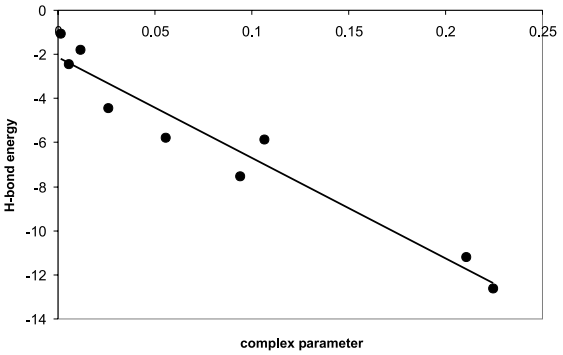

Fig. 2. The correlation between the complex parameter (Δ_{com}) introduced in this report and H-bond energy (in kcal/mol) for the sample of heterogeneous complexes.

Table 2
Geometrical (in Å) and topological (in a.u.) parameters of bonds of isolated molecules which are proton donors within the complexes presented in Table 1

Molecule	Bond	r_{XH}	ρ_{XH}	$\nabla^2\rho_{XH}$
HF	HF	0.916	0.371	−2.839
H_2O	OH	0.959	0.365	−2.518
HCOOH	OH	0.969	0.354	−2.495
C_2H_2	CH	1.065	0.284	−1.024

promising but obtained for a rather small data set. For example different relationships between topological and geometrical parameters for 57 molecules yielding 731 bond critical points were investigated [30]. The existence of local linear relationship was observed if bonds vary little in their chemical surroundings. Such correlations break down for larger subsets of bond critical points encompassing a wider variety of bonds. It seems that new measures of H-bond strength proposed here may be applied to different and heterogeneous samples but it needs additional and detailed studies on greater samples. More adequate investigations are in progress.

The Δ_{com} measure is also applied here to homogenous samples. The small set of dihydrogen bonded systems investigated earlier [10] is chosen because of the same kind of proton-donating molecule (HF) and the same kind of proton acceptor centre ($^{-\delta}$ H). Besides the high correlation coefficients for different parameters were observed for that sample in spite of the unconventional nature of H-bonds [10]. Fig. 3 shows the relation between Δ_{com} and H-bond energy for DHBs summarised in Table 3

$$E_{HB} = -52.00\Delta_{com} - 0.34; \quad R = 0.993. \tag{5}$$

The results presented in this Letter show that correlation between Δ_{com} measure and H-bond energy is better for homogenous samples than for heterogeneous ones. It is in line with the findings for the other parameters – the relationship is worse if the variety of the sample is greater. However, in the case of the Δ_{com} parameter the correlation coefficient for heterogeneous sample only slightly decreases in comparison with the homogenous sample and it is still high.

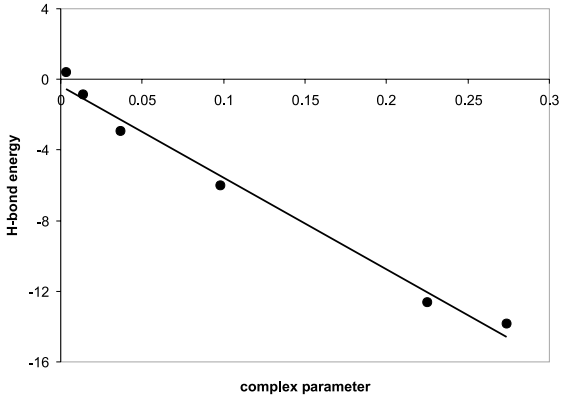

Fig. 3. The correlation between the complex parameter (Δ_{com}) and H-bond energy (in kcal/mol) for the sample of homogenous dihydrogen bonded complexes.

Table 3
Geometrical (in Å) and topological (in a.u.) parameters of proton-donating molecule (HF) of dihydrogen bonded systems; H-bond energies (E_{HB}, BSSE included) are also given (in kcal/mol); the results taken from [10][a]

Complex	R_{FH}	E_{HB}	ρ_{XH}	$\nabla^2\rho_{XH}$
$LiH\cdots HF$	0.951	−12.62	0.323	−2.323
$NaH\cdots HF$	0.958	−13.81	0.314	−2.205
$BeH_2\cdots HF$	0.922	−2.94	0.361	−2.763
$MgH_2\cdots HF$	0.931	−6.02	0.348	−2.624
$CH_4\cdots HF$	0.917	+0.39	0.370	−2.830
$SiH_4\cdots HF$	0.919	−0.85	0.367	−2.810

[a] The corresponding results for the isolated HF molecule are given in Table 2.

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