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Different types of hydrogen bonds: correlation analysis of interaction energy components[†]

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ABSTRACT: *Ab initio* calculations at the MP2/6–311++G(d,p) level of approximation were performed for the following complexes: $(C_2H_2)_2$, $FH\cdots OCH_2$, $NF_3H^+\cdots HBeH$, $H_3N\cdots HF$, $NH_4{}^+\cdots HBeH$, $NH_4{}^+\cdots HBeF$, $(H_2O)_2$, $FH\cdots C_2H_2$, $(FHF)^-$, $FH\cdots OH_2$, $FH\cdots HLi$, $HCCH\cdots OH_2$ and $HOH\cdots NH_3$. The decomposition of the interaction energy for these H-bonded dimers was performed, showing that electrostatic and delocalization energy terms are the most important attractive components and together with the repulsive exchange energy term they are the main energy components. Correlation analysis was also applied together with factor analysis, supporting the energetic results of calculations. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: hydrogen bonds; interaction energy decomposition; correlation analysis; factor analysis

INTRODUCTION

Correlation analysis is often applied to solve scientific problems, and it is very important in organic chemistry[1] and physicochemical studies.[2,3] Review articles and monographs on the importance of such analyses in chemistry appeared many years ago,[1,4] and there are also later examples of such studies, e.g. studies on substituent effects deserve particular attention.[5–7]

Another example of the application of correlation analysis is connected with studies on intermolecular interactions, particularly hydrogen bonds.[8] Relationships between geometric parameters of H-bond interactions controlling the arrangement of molecules in crystals have been detected.[9] Such correlations were most often observed for O—H···O bonds,[10] a typical example being the relationship between H···O distance and O—H bond length.[11–13] It was pointed out that such dependences correspond to the bond valence (BV) model, which is based on the idea of atomic and bond valences.[14,15] The relationships between geometric parameters[11,12,15] also allow isotopic effects to be observed. Also, the acceptor groups are sensitive to hydrogen bonding interactions; the correlation between C═O bond length and H···O distance for a sample of C═O···H—O—C contacts taken from high-precision neutron diffraction results supports this statement.[13] However, it is worth mentioning that these correlations are noted rather for closely related complexes.[8] For the results taken from x-ray and neutron diffraction measurements, concerning the solid state, the intermolecular interactions may strongly influence the parameters considered. Hence highly related systems are rather those examined using theoretical *ab initio* or density functional theory (DFT) results, where environmental effects are usually neglected. If for such theoretically considered complexes the sample is homogeneous (concerns the related species), often correlations between different parameters could be observed. Theoretical calculations on H-bonded systems have provided numerous examples of such correlations not only between geometric parameters but also concerning energetic and topological characteristics.[8] Correlations between X—H or H···Y for the X—H···Y H-bridge on one hand and H-bond energy on the other were often detected. The same concerns topological parameters derived from the Bader theory,[16] such as characteristics of X—H and H···Y critical points, which may be treated as measures of H-bond strength.

The early Pauling definition states that for the X—H···Y H-bond, both X and Y atoms should be electronegative, the H···Y distance should be shorter than the corresponding sum of van der Waals radii and this interaction is mostly electrostatic in nature.[17] Pauling also stated that for very short and very strong H-bonds the covalent contribution could be considered within this interaction, for example for $(FHF)^-$.[17] During the last three to four decades, the definition of H-bond interaction was extended.

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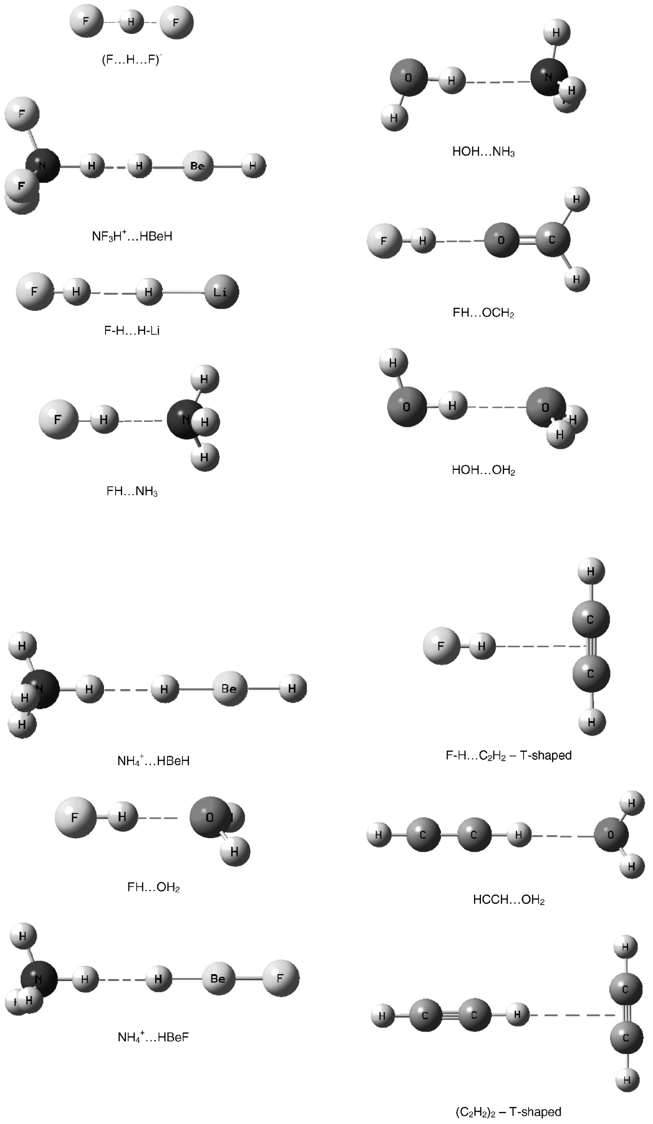
$C—H\cdots Y$ interactions, systems without an electronegative X-atom, were also classified as H-bonds.[18,19] Later it was even found that some of the $X—H\cdots C$, $X—H\cdots\pi$, $C—H\cdots C$ and $C—H\cdots\pi$ systems fulfil the criteria of the existence of hydrogen bonding.[20,21] There is also the kind of hydrogen bonding where an H-atom with an excess of negative charge plays the role of an acceptor, which is designated $X—H\cdots H—Y$ and termed a dihydrogen bond.[22] Very recently, $X—H\cdots\sigma$[23] and $\pi\cdots H^+\cdots\pi$ interactions[24] were considered as possible variants of hydrogen bonds.

There are different criteria for the existence of hydrogen bonding:[10] geometric, energetic, spectroscopic, topological[25,26] and others. None of them is fulfilled for the broad spectrum of interactions mentioned here. Sometimes for some kinds of these interactions a few criteria are not fulfilled but the others are met. Hence there is the question of whether the hydrogen bonding interaction may be defined unequivocally. Another question is also very important, namely whether there are properties of hydrogen bonds which allow the determination of the strength of H-bonding not only for homogeneous samples of complexes. It was pointed out that a topological parameter, the electron density at the $H\cdots Y$ bond critical point (BCP), is less sensitive to the diversity of the complexes considered than geometric parameters such as $H\cdots Y$ distance;[8] in other words, the electron density at the BCP often correlates with H-bond energy even for heterogeneous samples. However, a geometrical parameter, the $H\cdots Y$ distance, is often reported as a rough measure of H-bond strength.[27] The way to avoid 'the effect of diversity' is to introduce a normalized parameter; such a complex parameter based on the topological and geometric properties of the proton-donating bond was introduced and it was observed that it correlates well with the H-bond energy for different samples of complexes, even heterogeneous samples.[28]

Desiraju claimed that 'the hydrogen bond is not a simple interaction but a complex conglomerate of at least four component interaction types: electrostatic (acid/base), polarization (hard/soft), van der Waals (dispersion/repulsion) and covalency (charge transfer).'[29] Hence the aim of this study was to analyze the interaction energy components for representatives of different types of H-bonds: $O—H\cdots O$, $C—H\cdots O$, $C—H\cdots\pi$, dihydrogen bond, etc. In addition, relationships between the interaction energy terms derived from the decomposition scheme, and also between them and the $H\cdots Y$ distance, were analyzed. The proton–acceptor distance was included as it is often treated as a rough measure of H-bond strength. Additionally, factor analysis was applied.

COMPUTATIONAL DETAILS

The calculations were performed with the Gaussian 98[30] and Gaussian 03[31] sets of codes. The complexes $(C_2H_2)_2$, $FH\cdots OCH_2$, $NF_3H^+\cdots HBeH$, $H_3N\cdots HF$, $NH_4^+\cdots HBeH$, $NH_4^+\cdots HBeF$, $(H_2O)_2$, $FH\cdots C_2H_2$, $(FHF)^-$, $FH\cdots OH_2$, $FH\cdots HLi$, $HCCH\cdots OH_2$ and $HOH\cdots NH_3$ with different types of hydrogen bonds were considered. The calculations were performed using the second-order Møller–Plesset perturbation method (MP2)[32] and the 6–311++G(d,p) basis set[33–36] was used. Full optimizations were performed at the MP2/6–311++G(d,p) level of approximation. Scheme 1 shows ball- and -stick models of the complexes considered. These systems have been analyzed previously,[28,37] but the decomposition of the interaction energy was not analyzed.



Scheme 1

The binding energies of the analyzed complexes were computed as the differences between the total energies of the complexes and the energies of the isolated monomers and further were corrected for the basis set superposition error (BSSE) using the counterpoise method.[38]

A 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[39] was applied. The starting wavefunctions of the subsystems were obtained in this approach in the dimer-centred basis set (DCBS).[38a] For the total interaction energy and all of its components, the BSSE was eliminated entirely.

The following interaction energy components free of BSSE can be obtained consistently in the dimer basis set:

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

where $E_{\mathrm{EL}}^{(1)}$ is the first-order electrostatic term describing the Coulomb interaction of static charge distributions of both molecules calculated from perturbational expression,[39] $E_{\mathrm{EX}}^{(1)}$ is the repulsive first-order exchange component resulting from the Pauli exclusion principle and defined as the difference of the Heitler–London energy and electrostatic term[39] and $E_{\mathrm{DEL}}^{(\mathrm{R})}$and E_{CORR} correspond to higher order delocalization and correlation terms. The delocalization term calculated as the difference of the SCF and Heitler–London energy[39] contains all classical induction, exchange–induction, etc., from the second order up to infinity. The correlation term, defined as the difference of correlated and SCF interaction energy, includes dispersion interactions and also intramolecular correlated electrostatic, exchange, induction and dispersion contributions. These contributions define at the same time gradually simplified theory levels starting from MP2, SCF, Heitler–London down to electrostatic models able to reproduce well structural characteristics of classical hydrogen-bonded systems.[40] Moreover, the tests performed using the complete basis set for benchmark He_2 and $(H_2O)_2$ systems indicate that our first-order electrostatic and exchange terms display a considerably reduced basis set dependence compared with other conventional decomposition results.[41] In addition, owing to the implementation of direct integral processing, the variation–perturbation approach allows the analysis of the physical nature of interactions of much larger molecular systems with 1700 AOs including entire enzyme active sites.[42,43]

RESULTS AND DISCUSSION

Table 1 shows the total interaction energies and their components derived from the delocalization energy scheme of the dimers considered here. The proton–acceptor distances are also included. The complexes presented are connected through different types of hydrogen bonds. There are so-called conventional H-bonds such as O—H···O, O—H···N, F—H···O and F—H···N and the charge-assisted and very strong $(F\cdots H\cdots F)^-$ hydrogen bond. There are also so-called unconventional H-bonds, such as C—H···O where an acetylene molecule is the proton donor and a water molecule is an acceptor. For the latter system, the C—H bond is known as a weak proton donor. However, among C—H bonds that with a carbon atom of sp hybridization is the strongest proton donor since the following order of the strength of such bonds was found: $C(sp) > C(sp^2) > C(sp^3)$.[44] There are also two systems with π-electrons as proton acceptor: a T-shaped acetylene dimer with a C—H···π hydrogen bond and a T-shaped dimer with hydrogen fluoride as the proton-donating molecule, where an F—H···π H-bond exists. The remaining complexes considered here contain dihydrogen bonds, there is, the F—H···H—Li system analyzed earlier in several studies and also systems which may be classified as charge-assisted dihydrogen bonds and with NH_4^+ or NF_3H^+ ion as a donor. One can see that different types of complexes are included here and it is possible to analyze the nature of the considerably diverse subcategories of H-bond complexes.

Table 1. Interaction energy terms (kcal mol^{-1}) for various H-bonded complexes optimized at the MP2/6–311++G(d,p) level, and proton–acceptor (H···Y) distances (Å)

Dimer	$E_{\mathrm{H\text{-}L}}^{(1)\,\mathrm{a}}$	$E_{\mathrm{EL}}^{(1)}$	$E_{\mathrm{EX}}^{(1)}$	$E_{\mathrm{DEL}}^{(\mathrm{R})}$	$E^{\mathrm{SCF\,b}}$	E_{CORR}	ΔE	$R_{\mathrm{H\cdots Y}}$
$(F\cdots H\cdots F)^-$	−4.22	−78.15	73.93	−63.92	−68.14	7.08	−61.05	1.138
$NF_3H^+\cdots HBeH$	15.58	−13.37	28.95	−38.69	−23.12	−3.63	−26.74	1.114
F—H···H—Li	−0.88	−19.27	18.39	−10.75	−11.64	−1.74	−13.37	1.399
$FH\cdots NH_3$	−1.34	−22.47	21.13	−10.09	−11.43	−0.40	−11.83	1.703
$NH_4^+\cdots HBeH$	0.36	−8.62	8.98	−8.15	−7.79	−1.77	−9.57	1.571
$FH\cdots OH_2$	−2.82	−14.23	11.41	−5.08	−7.90	0.21	−7.69	1.730
$NH_4^+\cdots HBeF$	2.95	−4.26	7.20	−6.92	−3.97	−2.32	−6.28	1.620
$HOH\cdots NH_3$	−1.16	−12.09	10.92	−3.80	−4.96	−0.91	−5.87	1.974
$FH\cdots OCH_2$	−3.85	−8.87	5.02	−2.65	−6.50	1.06	−5.44	1.869
$HOH\cdots OH_2$	−1.97	−8.75	6.78	−2.19	−4.16	−0.29	−4.46	1.950
$F—H\cdots C_2H_2$ (T-shaped)	0.10	−6.27	6.37	−2.82	−2.73	−0.46	−3.19	2.186
$HCCH\cdots OH_2$	−1.40	−4.79	3.39	−1.06	−2.46	−0.01	−2.47	2.443
$(C_2H_2)_2$ (T-shaped)	0.08	−2.13	2.21	−0.54	−0.47	−0.59	−1.06	2.697

[a] First-order Heitler–London energy term: $E_{\mathrm{H\text{-}L}}^{(1)} = E_{\mathrm{EL}}^{(1)} + E_{\mathrm{EX}}^{(1)}$.
[b] SCF interaction energy: $E^{\mathrm{SCF}} = E_{\mathrm{EL}}^{(1)} + E_{\mathrm{EX}}^{(1)} + E_{\mathrm{DEL}}^{(\mathrm{R})}$.

The total interaction energies shown in Table 1 were calculated according to the supermolecular approach. In that approach, 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.[45] Hence the deformation of monomers due to the complexation is not taken into account. Figure 1 presents the dependence between the proton–acceptor distance (H···Y) and the binding energy. Squares correspond to dihydrogen bonds, triangles designate the $(FHF)^-$ system and circles are attributed to the remaining systems, i.e. weaker hydrogen bonds and those of the medium strength. Closed symbols correspond to the supermolecular approach mentioned above and open symbols to the approach described in the section on computational details, where the binding energy is calculated as the difference between the energy of the complex and the energies of monomers optimized separately. In other words, in the latter case the deformation energy due to the complexation is taken into account. One can observe (Fig. 1) that meaningful differences between the two both approaches mentioned are apparent for stronger H-bonds, particularly for $(FHF)^-$ where the 'cost' of deformation amounts to about 20 kcal mol^{-1} (1 kcal = 4.184 kJ). For the medium strength and weak H-bonds, the differences are meaningless (one cannot see open circles in Fig. 1 as they are covered by the closed circles). For stronger dihydrogen bonds the differences are visible (Fig 1). However, in spite of the diversity of complexes considered within the sample, if one excludes the $(FHF)^-$ ion, the correlation coefficient for the dependence between H···Y distance and the binding energy and for the polynomial regression of the second rank amounts to 0.96 (for both approaches of the calculation of binding energies). Hence one may state that the H···Y distance is really a rough measure of H-bonding strength.

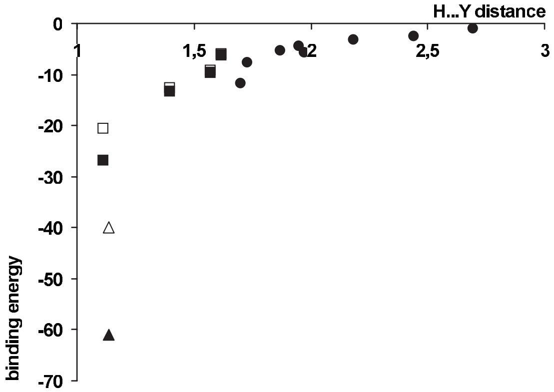


Figure 1. Relationship between the proton–acceptor distance (Å) and the binding energy for different complexes considered (kcal mol^{-1}). Squares correspond to dihydrogen bonds, triangles to the $(FHF)^-$ system and circles to the other complexes. Open symbols correspond to the binding energies calculated in such a way that the deformation energy is taken into account and closed symbols correspond to the supermolecular approach

Let us look at the details in Table 1. For medium strength and weak hydrogen bonds, the most important attractive energy term is the electrostatic term, and additionally for these systems the electrostatic energy term outweighs the exchange energy, except for T-shaped dimers, where the repulsive term outweighs the electrostatic component and hence the first-order Heitler–London energy term is positive. For the FH···HLi dimer the decomposition of the interaction energy is similar to the typical, conventional H-bonds with the most important attractive electrostatic term. An analogous nature of the interaction energy was observed for the other dihydrogen bonds, e.g. the HCCH···HLi complex.[23,46] For the charge-assisted dihydrogen bonds considered here the delocalization energy term becomes more important than the electrostatic term. In the case of NH_4^+···HBeH both terms are comparable, whereas for NH_4^+···HBeF and NF_3H^+···HBeH the delocalization term outweighs the electrostatic term. In the latter case the electrostatic energy component is −13.4 kcal mol^{-1} and the delocalization component is −38.7 kcal mol^{-1}. For all three complexes connected through the charge-assisted dihydrogen bond the first-order Heitler–London energy is positive (i.e. repulsive). This is because of short H···H intermolecular contacts and hence the increase in the exchange energy. This topic was investigated by us very recently for H_2OH^+···HBeH and related complexes connected through dihydrogen bonds[47] and it was pointed out that for the species considered there are the strong correlations between H···H intermolecular distance and such energy terms as exchange and delocalization.

Considering the entire group of diverse complexes analyzed here, one may conclude that there are two 'diffuse borders' of H-bond interactions. The first border is close to weak H-bonds, between them and van der Waals complexes, and the second border is between strong H-bonds and covalent bonds. In both cases of 'borderline' hydrogen bonds, the exchange energy term outweighs the electrostatic term; however, for very strong H-bonds the delocalization is very important and causes a magnification of the binding energies. The correlation energy is not as important as the other energy terms analyzed here (Table 1). Figure 2 confirms the conclusions found here, and shows the dependence between H···Y distance and the energy components. There is an increase in the exchange energy as the H···Y distance decreases, followed by greater importance of the electrostatic and delocalization attractive energy terms. It seems surprising that those terms of interaction energy are interrelated in spite of the great diversity of the complexes considered. One can observe that the correlation energy term does not depend on the proton–acceptor distance. Figure 3 shows the relationships between attractive interaction energy term (electrostatic or delocalization) and the exchange energy. The charge-assisted

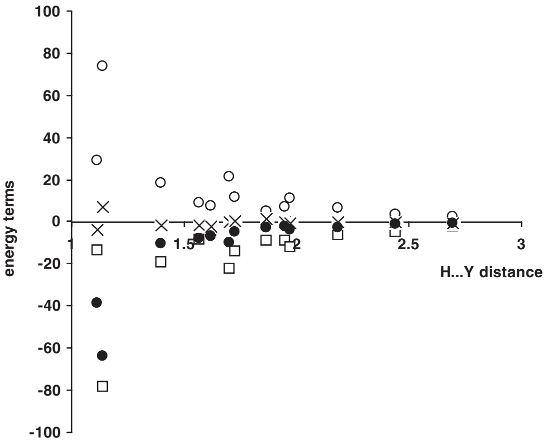


Figure 2. Relationships between the proton–acceptor distance (Å) and the different components (kcal mol^{-1}) of the interaction energy. Open circles correspond to exchange energy, closed circles to the delocalization energy term, crosses to the correlation energy and open squares to the electrostatic energy term

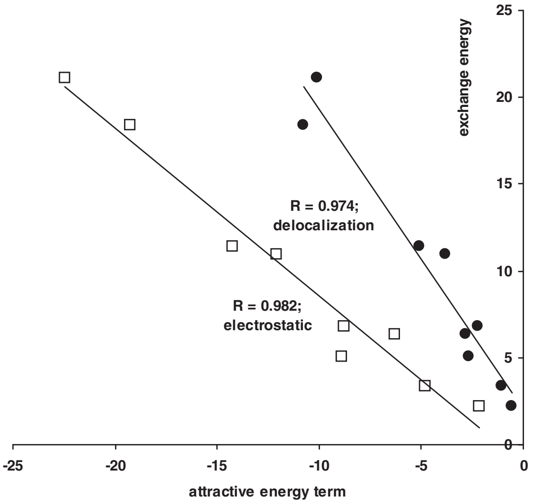


Figure 3. Correlations of attractive energy term (kcal mol^{-1}) vs the exchange energy (kcal mol^{-1})

hydrogen bonds are excluded from the relationships shown in Fig. 3. The linear correlation coefficients for these dependences are 0.98 and 0.97.

The observed relationships between the interaction energy components may be supported by factor analysis.[48] The main applications of factor analytic techniques are to classify variables: find the relationships between them, reduce their number, etc. These statistical approaches have often been applied in physical and chemical studies. One of the first applications of factor analysis was connected with thermodynamic data describing solvent effects.[49] Factor analysis was applied in this study to describe terms of the interaction energy. Hence the variables taken into account here were components of the interaction energy derived from the decomposition scheme: electrostatic, exchange, delocalization, correlation, and additionally the total interaction energy, the Hartree–Fock energy (this means the total energy except of the correlation energy), the Heitler–London first-order energy term (this means the sum of exchange and electrostatic energy terms) and $H \cdots Y$ distance. In other words, there were eight variables. For this set of variables two factors were retained. The first eigenvalue is 5.82 and the second is 1.75; this means that the first factor accounts for 72.8% of variance and the second factor 21.8%. The modulus of first factor loading is in the case of five variables >0.97; for three variables, the Heitler–London energy, the correlation energy and $H \cdots Y$ distance, it is much lower: 0.03, −0.72 and 0.69, respectively. This means that except for the last three variables, the remainder are strongly correlated. If one chooses only four variables corresponding to interaction energy terms, namely electrostatic, exchange, delocalization and correlation, the first factor retains 86% of variables and the factor loadings for it are 0.99, −0.98, 0.92 and −0.81; the order is in agreement with the order of the four variables mentioned above. This means that the correlation energy term is hardly correlated with the other terms whereas the remainder are strongly correlated; this is in agreement with the curves presented in Figs 2 and 3.

CONCLUSION

The results of this study show that for various types of hydrogen bonds examined meaningful correlations may be found between exchange, electrostatic and delocalization interaction energy components. These terms are also related to the proton–acceptor distance. It was shown that for the conventional hydrogen bonds with electronegative acceptor and donor atoms, the electrostatic energy term is the most important attractive component, which is in agreement with the Pauling definition of H-bonds.

For weak and strong H-bonds, the nature of the interaction energy is different: for the latter type of H-bond the delocalization energy term is greater than the electrostatic energy, and additionally the exchange repulsive energy outweighs the attractive electrostatic energy. These findings are confirmed by the factor analysis results.

As both stabilizing contributions, i.e. electrostatic and delocalization, increase in a monotonic way with decreasing intermolecular distance, the equilibrium distance between monomers is controlled solely by the repulsive exchange term. Therefore, the exchange term seems to determine the unique properties of hydrogen bonds. The low electron density at the hydrogen bound to an electronegative atom results in minimal exchange repulsion, allowing a closer approach of hydrogen-bonded molecules and better stabilization by electrostatic and delocalization terms.

Acknowledgments

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