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Review Commentary

Hydrogen bonding strength—measures based on geometric and topological parameters†

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ABSTRACT: Different methods of estimating H-bond strength are presented. The studies are based on the results of MP2/6–311++G** calculations and the binding energies are corrected for the basis set superposition error (BSSE). The wavefunctions were further applied to localize bond critical points and ring critical points. The characteristics based on the Bader theory are also applied as indicators and measures of hydrogen bonding. This study compares samples of different compounds. The H-bond strength measures such as the proton–acceptor distance (H···Y), the length of the proton donating bond, the electron density at H···Y bond critical point, the H-bond energy and others are analysed. The case of the intramolecular hydrogen bonding is also analysed, and its special characteristics are given. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: hydrogen bonding; measures of H-bond strength; Bader theory; *ab initio* calculations; bond critical points; ring critical points; intermolecular H-bonds; intramolecular H-bonds

INTRODUCTION

Hydrogen bonding is one of the most important interactions encountered in the gas, liquid and solid states. It plays a crucial role in many chemical processes[1] and influences the arrangement of molecules in crystals.[2] It is the interaction which may be treated as a preliminary stage of the proton transfer process.[1] Hydrogen bonding plays an important and dominant role in many life processes.[1] Hydrogen bonding is understood as a very broad phenomenon and hence it is among the terms most frequently used in chemistry, biochemistry and medicine.[3,4]

The knowledge of hydrogen bonding strength is very important in the study of chemical, physical and biochemical processes. The estimation of the H-bond strength is ambiguous since there are a variety of definitions and classifications of this type of interaction.[5–7]

The hydrogen bond is usually symbolized by X—H···Y and results from the interaction between a proton-donating bond X—H and a proton acceptor Y, where X and Y designate electronegative atoms such as O, N and Cl.[8] Hence O—H···O, N—H···N, N—H···O, N—H···Cl and other similar systems are treated as typical, conventional hydrogen bonds. However, the ability of carbon atoms to act as proton donors has been the subject of many studies and C—H···Y hydrogen bonds have been indicated in many systems.[9–11] Additionally, it was pointed out that in a molecular assembly in the case of deficiency of typical H-bond acceptors, π-electrons or carbon atoms may act as such accepting centres[12] and thus X—H···π or X—H···C hydrogen bonds are possible.[13] The above-mentioned interactions, C—H···Y and X—H···C (or π-electrons as acceptor), are usually known as unconventional H-bonds. Such interactions are often weak since binding energies for the corresponding complexes amount to 0.5–4 kcal mol^{-1} (1 kcal = 4.184 kJ).[14,15] Some authors even suggest that C—H···C or C—H···π interactions may stabilize the crystal structures. For example, O—H···O, C—H···O and C—H···π interactions were analysed early for crystal structures of propyne and butyne carbocylcic acids.[16] The role of the C—H···π interactions in the arrangement of molecules of one of the polymorphic forms of acetylene (*Acam* space group) was investigated with the use of the atom–atom potentials.[17]

On the other hand, strong hydrogen bonds are known. Those which are assisted by charge, so-called charge assisted H-bonds: CAHB(+) and CAHB(−); an example of the latter is the [F···H···F]$^-$ system[18,19] and those

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which are assisted by resonance, so-called resonance-assisted hydrogen bonds (RAHBs).[20–22] However, it should be pointed out that for neutral molecules very strong intermolecular hydrogen bonds also exist. For example, phosphonic acid (PA) and its dimethyl derivative (DMPA) have been studied at the MP2(full)/6–31 + G** and B3LYP/6–31 + G** levels of theory.[23] Both PA and DMPA form cyclic dimers, where the two monomers are held together by hydrogen bonds which are stronger than those existing for carboxylic analogues. Dimerization enthalpies for PA and DMPA are the highest reported for neutral homodimers (23.2 kcal mol^{-1} for both complexes). These calculations are in agreement with the experiment since the study of the gas-phase IR spectrum of DMPA showed the existence of the ABC ν(OH) absorption structure compatible with the presence of very strong hydrogen bonds within the dimer.[24]

An approximate classification of the hydrogen bonding interaction according to its strength and a composition of atoms within the X—H···Y system may be given (Table 1). It is worth mentioning that the ranges of energy for several types of H-bonds are different in various monographs and review articles on hydrogen bonding. Hence the values given in Table 1 are a compromise between different classifications and are mainly based on the classification given by Kaplan.[25] For example, Alkorta *et al.*[14] established a new classification of hydrogen bonds with interaction energies up to 5 kcal mol^{-1} considered as weak, with energies between 5 and 10 kcal mol^{-1} defined as medium and those with energy values >10 kcal mol^{-1} defined as strong or very strong.

We see that complexes characterized by weak H-bond strength are similar to van der Waals complexes for which the binding energies are 0.1–1 kcal mol^{-1}. On the other hand, the energy of strong H-bonds is 15–60 kcal mol^{-1} (Table 1), similar to typical covalent bonds for which bond energies are around 100–200 kcal mol^{-1}.

Table 1 shows that the type of hydrogen bonding and the composition of the X—H···Y system is approximately related to the H-bond strength. For example, H-bonds with C—H donors are weaker than H-bonds containing O—H proton donors if, for both cases, the acceptors are the same. However, we should be very careful when applying this crude estimation since there are many specific cases for which more detailed classifications should be applied. Very strong H-bonds in neutral molecules of PA and DMPA are examples of such specific cases. In another example, the theoretical evidence for moderate C—H···C H-bonds was analysed and the binding energy for H_3N^+—$CH_2^-\cdots$HCCH at the MP2/6–311++G(3d,3p) level [basis set superposition error (BSSE) included] was calculated to be 8.16 kcal mol^{-1}.[26] Another example concerns the classes of O—H···O bonds which are usually treated as moderate. The detailed classification shows[27] that such systems may be divided into five classes: strong negative charge assisted, CAHB(−), strong positive charge assisted, CAHB(+), strong resonance assisted, also called π-cooperative H-bonds, RAHB, moderate polarization assisted H-bonds, PAHB, and weak isolated H-bonds which are non-charged, non-resonant and non-cooperative systems. It is worth mentioning that strong resonance assisted (RAHB) O—H···O bonds are often referred to as low-barrier H-bonds (LBHB).[28,29]

Table 1. Types of H-bonds

Type of H-bond	Examples	H-bond energy (kcal mol^{-1})
Strong (RAHB; CAHB)	O—H···O [O—H···O]$^-$ [O—H···O]$^+$ [F—H···F]$^-$	15–60
Moderate	O—H···O N—H···O F—H···O	4–15
Weak	C—H···O, C—H···N, C—H···S O—H···C, N—H···C, O—H··· π, N—H···π C—H···C, C—H··· π	0.5–4

The most widely employed indicators of the presence and strength of hydrogen bonding are those connected with spectroscopic results. The stretching vibration of the X—H proton donating bond changes significantly upon complexation with an acceptor molecule. The stretching mode can be shifted to the red region by hundreds of cm^{-1}, and the band is intensified several fold.[1,5] The red shift may be treated as a measure of the hydrogen bonding strength since it correlates with other typical measures such as H-bond energy and the proton–acceptor (H···Y) distance.[8]

NMR is a very important tool in the analysis of H-bonds. The existence of hydrogen bonding causes electron density shifts which result in perturbation of the proton shielding tensor.[30] The proton chemical shift anisotropy is a sensitive parameter applied to detect the presence of H-bonds.[31] It has been shown that the isotropic and anisotropic shieldings correlate with H···Y distance.[32] Shifts in anisotropic chemical shielding obtained from *ab initio* and DFT calculations have been used for an analysis of weak C—H···O hydrogen bonds within systems where methane or its fluorine derivatives act as proton donor and water or methanol is a proton acceptor.[15,33] NMR parameters were also applied for the analysis of other weak H-bonds such as C—H···O and C—H···C (or π electrons).[34,35]

The aim of this review is to discuss different indicators of the presence and strength of hydrogen bonding. The emphasis is put on the geometric, energetic and topological parameters, the latter being results of the Bader theory.[36] The analysis of other parameters, including those derived from spectroscopic methods, are not taken into account here. Different ways of estimating H-bond strength are presented in next sections. The samples analysed in this study are mainly based on *ab initio* and density-functional theory (DFT)[37] calculations. It is worth mentioning that DFT performs satisfactorily[38] and that generally DFT-optimized geometries are not inferior to geometries predicted by conventional *ab initio* techniques incorporating electron-correlation effects. However, for complexes the DFT predictions of H-bond energies are not as reliable as those of the MP2 method. DFT methods are suitable for studies on intramolecular H-bonds; for example, the B3LYP/6–31G(d) level of theory has been found to give results in good agreement with high-level *ab initio* calculations for such interactions.[39]

This review is restricted to the applications to organic species. Very recently, a review on H-bonds has appeared;[40] however, it is mainly focused on the structure and strength of H-bonds with respect to the various X—H···Y motifs possible in inorganic solids.

GEOMETRIC PARAMETERS

The proton donating bond and the proton–acceptor distance

The geometry of the X—H···Y hydrogen bond may be defined by three scalar quantities,[5] X—H covalent bond length, H···Y hydrogen bond length and X···Y distance; these parameters define the X—H···Y hydrogen bond angle. It is well known that the formation of hydrogen bonding is connected with the elongation of the proton-donating bond. The shorter the H···Y contact, the greater is the X—H elongation, the closer the X—H···Y angle is to linearity and the stronger is the hydrogen bonding. These dependences were often examined with the use of experimental and theoretical results. For example, the relationship between the O—H bond length and the O···O distance for O—H···O systems taken from x-ray diffraction results for organic compounds has been investigated for various species.[41,42] It was found that this relationship is better for homogeneous samples of compounds.[43] For example, for accurate neutron diffraction data ($R \leq 8\%$, e.s.d.s ≤ 0.005 Å) of C═O···H—O systems there is an H—O vs H···O relationship. The experimental results are in agreement with this relationship obtained from the bond valence model.[43]

The H···Y distance is often applied as a criterion of the presence of hydrogen bonds; it should be shorter than the corresponding sum of H-atom and Y-atom van der Waals radii, $\Sigma r = r_H^{vdW} + r_Y^{vdW}$.[9] However, there are problems with the application of this criterion since the hydrogen bonding is mainly of an electrostatic nature and hence this interaction acts far beyond the van der Waals radii cut-off.[6,21]

It has been pointed out that the difference between Σr and the H···Y distance ($r_{H\cdots Y}$) may be treated as a measure of the strength of hydrogen bonding even for heterogeneous samples of complexes since it correlates with the H-bond energy:[44]

$$\Delta r = \Sigma r - r_{H\cdots Y} \qquad (1)$$

The H-bond strength depends on the type of proton donor and also on the type of accepting centre. Table 2 shows the geometric and energetic parameters of H-bonds characterized by the same type of proton donor, F—H···Y hydrogen bonds. All systems in Table 2 belong to strong or moderate H-bonds and are linear or approximately linear. The greatest H-bond energies are those of the $(F\cdots H\cdots F)^-$ and $(F\cdots H\cdots Cl)^-$ systems: the charge assisted hydrogen bonds, CAHB(−). The π-electron system of the C_2H_2 molecule is the weakest proton acceptor for this sample. The results in Table 2 were obtained for optimized complexes calculated at the MP2/6–311++G** level of theory.[44] For the estimation of H-bond energies, the BSSE correction of Boys and Bernardi was taken into account.[45] This error has been extensively studied for intermolecular H-bonded systems.[46,47] It is due to the fact that each monomer in the complex uses to some extent the basis functions of the other monomer, causing a lowering of the energy of the system. The data presented in Table 2 are based on results obtained earlier.[44,48] They concern dimers optimized with the use of the Gaussian 94[49] and Gaussian 98 sets[50] of codes.

Table 2. Hydrogen-bonded systems with hydrogen fluoride as a proton donor and different proton acceptors[a]

Proton acceptor	HF bond length	H···Y contact	H-bond energy
F^-	1.138	1.138	−39.87
Cl^-	0.968	1.895	−20.94
OCH_2	0.923	1.869	−5.43
OH_2	0.931	1.73	−7.54
NH_3	0.948	1.703	−11.18
LiH	0.950	1.399	−12.62
C_2H_2	0.923	2.186	−3.15
LiCN	0.941	1.732	−12.3
CH_3CN	0.931	1.835	−7.9
CH_2FCN	0.928	1.878	−6.47
HCN	0.927	1.887	−6.51
FCN	0.926	1.901	−5.86
CHF_2CN	0.926	1.915	−5.42
CF_3CN	0.924	1.946	−4.68
NO_2CN	0.923	1.974	−4.03
NH_2CN	0.931	1.823	−8.27
BH_2CN	0.928	1.875	−6.61
HOCN	0.929	1.847	−7.42

[a] The geometric data are given: H···Y contacts and HF bond lengths (in Å) and also the H-bond energies corrected for BSSE (in kcal mol^{-1}). All results were obtained at the MP2/6–311++G** level of theory. Results taken from Refs. 44 and 48.

Figure 1 shows the relationship between the above-mentioned Δr parameter [Eqn. (1)] and H-bond energy for the sample in Table 2. The correlation coefficient for a polynomial regression of second order amounts to 0.971.

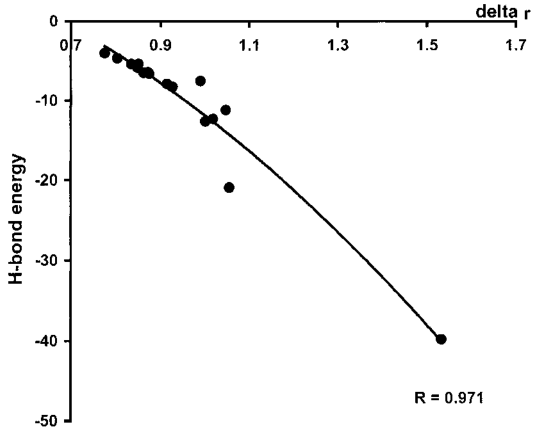


Figure 1. Dependence of the difference between the sum of H-atom and Y-atom van der Waals radii in the X—H···Y system and H···Y distance (in Å) on H-bond energy (in kcal mol^{-1}); the data used for this relationship are given in Table 2

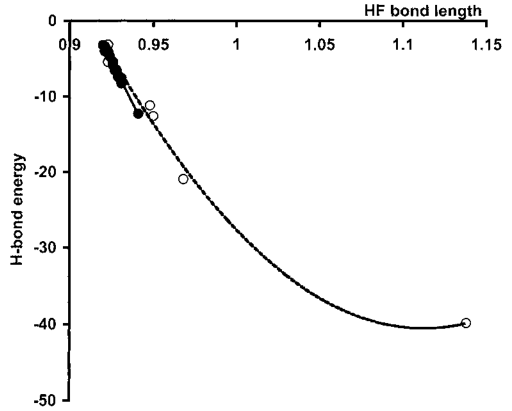


Figure 2. Relationship between the HF bond length (in Å) and H-bond energy (in kcal mol^{-1}). Results from Table 2. The broken line is the polynomial regression applied for all results and the solid line corresponds to the linear regression for N≡C—R acceptors

The better H-bond strength measure for this sample is the H—F bond length. Figure 2 shows the correlation between H—F bond length and the H-bond energy; the linear correlation coefficient is 0.962 for all entries; the correlation coefficient for the polynomial regression of second order is better, 0.994. Table 2 shows that the sample contains a sub-sample of F—H···N≡C—R complexes. If we take into account only that sub-sample and thus for the relationship between HF bond length and E_{HB}, the linear correlation coefficient equals to 0.995. We see that the linear correlation is better if only strongly related systems are considered.

The geometry of the proton donor may be applied as a measure of the H-bond strength even for heterogeneous samples since the normalization of the X—H bond length elongation is possible[51] according to the relation

$$\delta_{\mathrm{XH}} = \frac{(r_{\mathrm{X-H}} - r^{0}_{\mathrm{X-H}})}{r^{0}_{\mathrm{X-H}}} \qquad (2)$$

where $r_{\mathrm{X-H}}$ is the length of the X—H bond within the X—H···Y system and $r_{\mathrm{X-H}}{}^{0}$ is the length of the free bond not involved within H-bonding. In other words, δ_{XH} is the elongation of the X—H bond due to H-bridge formation in relation to the free X—H bond length.

It should be pointed out that there are correlations between geometric and energetic parameters for homogeneous samples of dimers connected by strong or moderate H-bonds. Hence the relationships presented in the literature usually concern O—H···O systems most often existing in liquids and solids and belonging to moderate hydrogen bonds. The sample in Table 2 contains systems for which there is the same proton-donating molecule and hence we may order the strength of acceptors from the results in Table 2. The order of the strength of acceptors is $F^{-} > Cl^{-} > H^{-}$ (LiH) $> CN^{-}$ (LiCN) $> NH_3 > H_2O > HCN > CH_2O > C_2H_2$.

The dependences analysed in this section are not so evident for weak H-bonds such as those of C—H···O type. There is no dependence between C—H bond length and H···O distance for C(sp^2)—H···O systems[52] taken from the Cambridge Structural Database (CSD);[53] only neutron diffraction results of high accuracy were included ($R \leq 5\%$; e.s.d.s ≤ 0.005 Å). In other words, elongation of the C—H bond due to H-bond formation is not observed since all neutron diffraction-measured C—H bond lengths are close to 1.08 Å. The lack of correlation for C(sp^2)—H···O systems may be caused by the heterogeneous character of the sample. A correlation between C—H bond length and H···O distance was found[54] for a homogeneous sample—neutron diffraction results concerning amino acids and taken from the CSD. However, a C—H length vs H···O distance relationship is not linear or easily detectable; the Spearman test has been applied to justify such a relationship.[54]

The acidity of donors decreases in the following order: C(sp)—H > C(sp^2)—H > C(sp^3)—H,[55] since the electronegativity of the carbon atom also decreases for such an order of bonds.[56] C(sp)—H···O hydrogen bonds were analysed[34] and compared with other C—H···O systems with sp^2 and sp^3 hybridizations of carbon atoms and the results of calculations of H-bond energies are in agreement with the acidity of donors. Table 3 presents C(sp)—H···O systems for which a water molecule is the

Table 3. Geometric and energetic parameters of complexes with a water molecule as a proton acceptor and different R—C—H proton donors[a]

	HCCH	FCCH	ClCCH	HCN
H-bond energy	−2.48	−2.61	−2.64	−4.67
X···Y distance	3.268	3.250	3.247	3.142
ΔR	4.8	6.0	6.0	7.3

[a] H-bond energies corrected for BSSE (in kcal mol^{-1}), X···Y distances in Å; ΔR is the elongation of the proton-donating bond (in mÅ); results obtained at the MP2/6–311++G** level of theory. Results taken from Ref. 34.

proton acceptor. Hence we may analyse the strength of proton donors, since the acceptor is fixed. We see that the HCN molecule is the strongest donor and HCCH is the weakest. The strength of the C(sp)—H···O bond corresponds to the lengthening of the C—H donor (Table 3).

Use of the bond valence model

The concept of bond number was introduced by Pauling[57] and was later used successfully in many chemical problems.[58,59] It is particularly useful for the systems which fall between the typical covalent bonds and non-bonded contacts. A coherent model similar to the Pauling idea of the bond number was introduced by Brown and Shannon[60] and named the bond valence (BV) model. The designations and definitions of the BV model are used in this paper since this model was introduced to describe interactions and it seems to be convenient for describing hydrogen bonding interactions. According to the BV model,[61] the strength of the bond and of the inter- or intra- molecular contacts is related to the bond valence. In Pauling's original definition it was stated that the bond number is the number of electron pairs involved in the bond; the bond valence has a similar meaning to the meaning of the bond number. The bond valence definition may be expressed by the following exponential function, although the other relations may be also applied:

$$s_{ij} = \exp[(r_0 - r_{ij})/B] \tag{3}$$

where r_0 and B are constants and r_{ij} is the length of the given bond or contact. The constant r_0 is often related to the length of a bond of unit valence. For example, for an O—H bond not involved in any intermolecular interaction (such as the OH bond of the water molecule in the gas phase), the bond valence amounts to unity and $r_{ij} = r_0$. The O—H bond length within the O—H···O system is usually elongated and hence the s_{ij} value is lower than unity. The difference between unity and the s_{ij} value of the OH bond (s_{OH}) corresponds to the bond valence of the H···O contact ($s_{\mathrm{H\cdots O}}$). Hence we may write the expression

$$\exp[(r_0 - r_{\mathrm{OH}})/B] + \exp[(r_0 - r_{\mathrm{H\cdots O}})/B] = 1 \tag{4}$$

The constant B is usually calculated from Eqn. (3) for a system for which the bond valence and the bond length are known. Such calculation is possible from the geometry of symmetrical and strong O···H···O H-bonds where the proton is in the middle of the O···O distance and the bond valence of H···O is equal to 0.5.

It is worth mentioning that for some studies both constants r_0 and B are related to the experimental results: both are fitted to experimental data.[60,61] Equation (4) is a special case of the more general expression called as the valence sum rule (VSR):

$$V_i = \sum_j s_{ij} \tag{5}$$

This means that the atomic valence V_i of the ith atom is equal to the sum of the bond valences of all its connections, bonds and contacts. According to the BV model, atomic valences V_i are equal to the oxidation states of atoms. For the O—H···O system, the VSR may be applied to the construction of the relation between the length of the O—H bond and the H···O (or O···O) distance.[62] Furthermore, it was found that Eqn (4) based on the VSR is in excellent agreement with experimental results.[21,43,63] A similar situation was observed for the other H-bonded systems such as N—H···O, O—H···N, O—H···S and S—H···O, for which accurate neutron diffraction results taken from the Cambridge Structural Database are in agreement with the relations obtained from the BV model.[64] For some cases, a correlation between X—H bond length and H···Y distance may be detected in spite of a slight elongation of the proton-donating bond due to H-bond formation. It has been pointed out earlier[21] that the N—H bond can be only slightly stretched by hydrogen bond formation (from 1.01 to 1.06 Å), in spite of the strong electronegativities of the donor and acceptor atoms involved in the N—H···O system. Such a situation occurs not only for N—H···O H-bonds but also for the other systems considered by Steiner.[64]

The above-presented relationships also exist for modelled unconventional dihydrogen bonds calculated with the use of different *ab initio* and DFT levels of theory.[65,66] Dihydrogen bonds have been investigated recently both experimentally[67–69] and theoretically.[70–72] The concept of the dihydrogen bond has been introduced a few years ago[67] to express the interaction occurring between a conventional hydrogen bond donor such as an N—H or O—H bond as the weak acid component and an element–hydride bond as the weak base component, where the element in question can be a transition metal or boron; they are usually designated X—H$^{\delta+}$···$^{\delta-}$H—M (Me = metal or boron atom).

The relationship between the H$^{\delta+}$···$^{\delta-}$H distance and H—F bond length for simple H—F···H—M (M = C, Si, Li, Na, Be, Mg) dimers was based[65,66] on MP2/6–311++G**, MP4(SDQ)/6–311++G** and QCISD(T)/6–311++G** levels of theory, showing that the application of the BV model is also possible for such systems, since the relationship obtained from the VSR is in agreement with the calculated results. The VSR for the H$^{\delta+}$ atom within the F—H$^{\delta+}$···$^{\delta-}$H system may be written in the following way:

$$\begin{aligned} V_{\mathrm{H}} = {} & \exp[(r_0^{\mathrm{H-F}} - r_{\mathrm{H-F}})/B_{\mathrm{HF}}] \\ & + \exp[(r_0^{\mathrm{H\cdots H}} - r_{\mathrm{H\cdots H}})/B_{\mathrm{H\cdots H}}] \end{aligned} \tag{6}$$

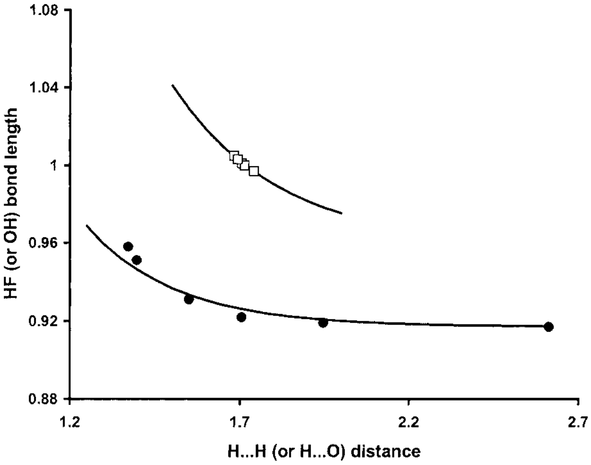


Figure 3. Relationship between the H···Y distance and the proton-donating bond length (in Å) for two samples, the first one calculated at the MP2/6–311++G** level of theory for dihydrogen bonds (●) and the second calculated at the B3LYP/6–31G** level (□) for O—H···O systems. The continuous lines correspond to the relations obtained from the valence sum rule

where $r_{\mathrm{H—F}}$ and $r_{\mathrm{H\cdots H}}$ are the H—F bond length and the H···H distance within the F—H···H system and $r_0^{\mathrm{H-F}}$, B_{HF}, $r_0^{\mathrm{H\cdots H}}$ and $B_{\mathrm{H\cdots H}}$ are constants. Figure 3 shows the relationships between intermolecular contacts and the proton-donating bond lengths for two samples of complexes, those connected through typical, conventional O—H···O hydrogen bonds and those connected through unconventional dihydrogen bonds. The relationships are based on the calculations performed for complexes of acetic acid derivatives with water (B3LYP/6–31G** level of theory)[63] and for the above-mentioned modeled systems with dihydrogen bonds (MP2/6–311++G** calculations).[65] For both samples, the correlations are compared with the relations obtained from the VSR. The VSR is represented by Eqn. (6) for dihydrogen bonds and for O—H···O H-bonds it may be expressed by Eqn. (4).

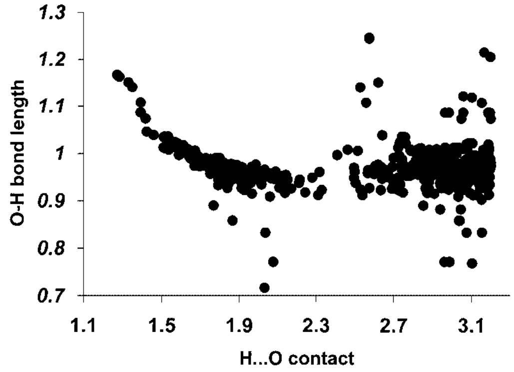


Figure 4. OH vs H····O dependence for a heterogeneous sample taken from neutron diffraction results. Bond lengths and distances in Å

Figure 3 shows that the results of calculations are in agreement with the BV model. The H···Y contacts and H—X proton-donating bond lengths correlate, and are good descriptors of H-bond strength. These dependences are fulfilled for both calculations and experimental data. However, for experimental results, for example those of neutron diffraction measurements, the relationships are not so evident. This is due to the many possible effects existing for crystal structures. Figure 4 shows the relationship between H···O distance and O—H bond length for O—H···O systems taken from CSD.[53] Only accurate neutron diffraction structures were included (with $R \leq 7\%$ and e.s.d.s ≤ 0.005 Å, error free and not disordered). The only restriction that was given was for H···O distances to be <3.2 Å. We see that for these experimental results, in spite of the high accuracy, a correlation is not detectable. One reason disturbing the correlation is the shortening of O—H proton-donating bonds for some O—H···O systems,[73] especially for water molecules as proton donors.[74] This effect is visible in Fig. 4. The second reason is connected with the longer H···O distances for which H-bonds are weaker or do not exist. For such cases, the influence of intermolecular forces in crystals causes a greater perturbation of the geometry of O—H···O systems and hence the correlation between OH and H···O is disturbed. Additionally, for longer H···O distances the existence of bifurcated H-bonds is more probable.

To avoid factors disturbing the correlation analysed above, the sample of O—H···O systems is considered again (Fig. 5). The accuracy of neutron diffraction results is the same. However, the sample is homogeneous, only C=O···H—O—C systems are taken into account. There are two limits: H···O contacts <2.6 Å are considered (the sum of Pauling's van der Waals radii of hydrogen and oxygen atoms) and O—H bonds which are >0.957 Å (the length of the OH bond for the water molecule in the gas phase). Figure 5 shows that for this sample the correlation is good; the solid line represents the polynomial regression of second order with a correlation coefficient of 0.983.

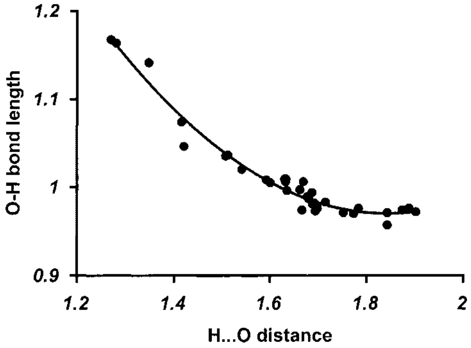


Figure 5. OH vs H····O dependence for a homogeneous sample taken from neutron diffraction results. Bond lengths and distances in Å

Proton acceptors

In the previous section, it was shown that systematic changes in proton-donating bonds are detectable owing to the formation of hydrogen bonding. The situation is more complicated for the proton acceptors and has been not investigated extensively. For example the relationship between the C=O bond length and the H···O distance in C=O···H—O—C systems was investigated[43] and a correlation was detected; for shorter H···O distances there are longer C=O bonds. This correlation was observed for neutron diffraction results of high accuracy taken from the CSD. In other words, the elongation of an accepting carbonyl bond within an H-bonded system may be treated as a measure of the H-bond strength. This correlation is supported[43] by the BV model, since the neutron diffraction experimental data are in good agreement with the valence sum rule applied to the oxygen atom of the carbonyl group.

$$S_{\mathrm{H}\cdots\mathrm{O}} + S_{\mathrm{C}=\mathrm{O}} = V_{\mathrm{O}} = 2 \qquad (7)$$

Equation (7) may be understood in the following way; the sum of bond valences of the H···O contact and of the C=O bond is equal to the atomic valence of oxygen atom, i.e. 2 (the oxidation number of oxygen).

Studies concerning the influence of intermolecular interactions on the geometry of the methoxy group have been carried out recently.[75] Methoxybenzene and its complexes with HF, H_2O, C_2H_2, C_2H_4, CH_4, CH_3F and NH_2CH_3 were investigated with the use of DFT calculations (B3LYP/6–311 + G* level of theory and BSSE included). The results show that the oxygen atom of the methoxy group is the proton acceptor for different types of H-bonds: F—H···O, O—H···O, C—H···O, N—H···O. The calculations on methoxybenzene complexes are in line with the BV model. It has been pointed out that the bond valence of the H···O contact correlates with the H-bond energy. Additionally, these H-bond strength measures are related to the changes in geometry of the methoxy group. For stronger H-bonds the H···O contact is shorter and the corresponding H···O bond valence increases; additionally, the sum of C—O bond valences of the methoxy group decreases. This is in line with the relation obtained from the valence sum rule for the oxygen atom of the methoxy group:

$$V_{\mathrm{O}} = S_{\mathrm{C(arom)-O}} + S_{\mathrm{C(methyl)-O}} + S_{\mathrm{H}\cdots\mathrm{O}} = 2 \qquad (8)$$

Figure 6 shows the molecular graph of the complex of methoxybenzene with hydrogen fluoride to illustrate the situation described above. This graph was obtained using the Bader theory[36] as a powerful method to investigate intermolecular interactions, including H-bonds. The descriptors of hydrogen bonds based on this theory are presented in the following sections.

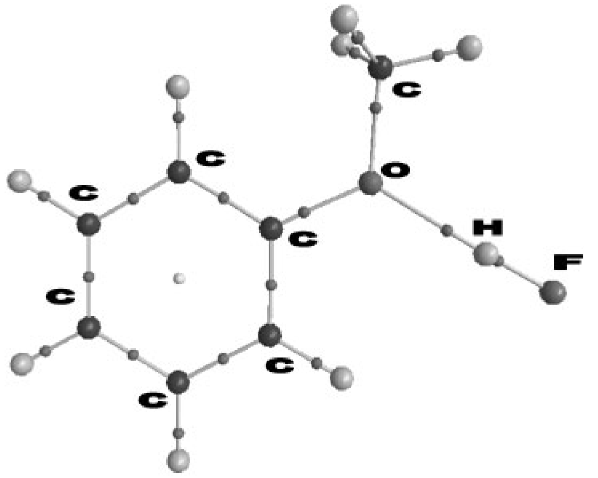


Figure 6. Molecular graph of the complex of methoxybenzene with hydrogen fluoride. The large circles represent attractors attributed to atomic nuclei and the small circles show the bond critical points and the ring critical point (inside the benzene ring). Solid lines represent the bond paths

The above-mentioned dependences between different parameters are very useful for studing reaction pathways. It has been pointed out that for molecules or molecular fragments taken from crystal structures, the shape of the correlation curves between geometric parameters of molecules may be reminiscent of structural changes occurring along the pathways of the respective chemical reactions.[76,77] The points of the correlation curve correspond to different stages of the investigated structure during the reaction. Different types of reactions have been studied using this method, such as nucleophilic substitution or addition and elimination reactions.[78] Proton transfer reactions have been also investigated for C=O···H—O—C systems,[79] and the proton transfer from the neutral to zwitterionic forms of amino acids supported by a water molecule-mediated mechanism has been analysed.[80] The BV model was also applied to N—H···N ⇔ N···H—N[81] and N—H···O ⇔ N···H—O [82] proton transfer reactions. The relationships between the hydrogen bond length (N···O or N···O distance) and the proton transfer coordinate (the distance between the position of proton and the middle of N···N or N···O) were studied. It was found that these curves obtained from the BV model are in excellent agreement with the neutron diffraction data, similarly as for O—H···O systems.[79,80]

It may be generalized that in proton transfer reactions, the geometry of the donating molecule changes in the direction of the deprotonated species and the geometry of the acceptor changes in the direction of the protonated species.[11] This has been observed for the changes of the geometries of phenol—amine adducts during the proton transfer process.[83,84] Relationships between the geometric parameters of O—H···N and N—H···O systems have been found, and the analysis showed that the shortest H-bonds exist for the position of the hydrogen atom being close to the centre of O···N; such quasi-symmetric H-bonds are sensitive to pressure, temperature and deuteration.[83]

The geometric parameters analysed here are useful as descriptors of hydrogen bonds. Hence the so-called 'geometrical criteria' of the existence of hydrogen bonding are often applied[85] in studies, and they may be summarized as follows:[9]

- the distance between the proton and the acceptor atom is shorter than the sum of their van der Waals radii;
- the donor–proton–acceptor angle in a hydrogen bond must be at least 90 °;
- there is the elongation of the proton-donating bond due to hydrogen bond formation.

However, these criteria are often the subject of controversy. Some authors claim that the difference between the sum of van der Waals radii mentioned within the first criterion and the corresponding H···Y distance should be >0.3 Å. Others point out that the H-bond interaction is electrostatic in nature and hence the limit for the H···Y distance should be even greater than the corresponding sum of van der Waals radii.[21] There are problems with the second criterion since it is not possible to determine the angle limit arbitrarily. The third criterion seems to be unequivocal. However, for weak C—H···Y hydrogen bonds there is only a slight elongation of the proton-donating bond, or the effect is not detectable. For all the criteria mentioned here, there are problems with their application to x-ray crystal structure results. It is well known that x-ray crystalloography is unsuitable for determining H-atom positions, and neutron diffraction methods have to be used. However, the number of the neutron diffraction measurements within the CSD is less than 0.5% of the whole; the remainder are x-ray measurements. Hence investigations are usually based on inaccurate geometries of the hydrogen bonds. There are various ways to avoid such inaccuracy.[86] There are many simple semi-empirical models of the hydrogen bond for which the knowledge of the accurate geometry of the X—H···Y system is needed. One of the most often applied was introduced early on by Lippincott and Schroeder[87] and applied later in many chemical and physical problems.[21,88] Hence the use of neutron diffraction results or the improvement of x-ray data is important.

Topological parameters

The distribution of the electron density (ρ) is additional information often used to describe hydrogen bonding. The 'atoms in molecules' (AIM) theory of Bader,[36] mainly based on an analysis of the electron distribution, is an additional tool allowing the detection and characterization of hydrogen bonding. The analysis of critical points in the electron density obtained from AIM theory seems to be the most important for studies on interatomic interactions. These interactions may be connected with typical covalent bonds and with the intermolecular non-bonded contacts such as hydrogen bonds. For the critical points (CPs) the gradient of $\rho(r)$ vanishes:

$$\nabla\rho(r_c) = 0 \qquad (9)$$

CPs are classified according to the number of negative eigenvalues of the Hessian of ρ (matrix of partial second derivatives with respect to $\{x, y, z\}$):

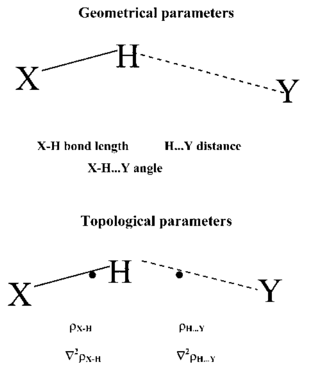
$$h_{pq} = \frac{\partial^2}{\partial p \partial q}\rho(r_c) \qquad p, q = x, y, z \qquad (10)$$

Stable critical points fall into one of four categories: maxima in $\rho(r)$ correspond to attractors (which are almost always attributed to nuclei), minima are connected with cage points and saddle points; and the last-mentioned ones correspond to bond or ring critical points.

Koch and Popelier introduced new criteria based on AIM theory to detect and characterize hydrogen bonds.[89] They were later described in detail by Popelier in a monograph on the AIM theory.[90] The criteria may be briefly summarized as follows:

- there is a BCP for the H···Y (proton···acceptor) contact which topologically proves the existence of a hydrogen bonding interaction;
- the value of electron density at the BCP of H···Y ($\rho_{H\cdots Y}$) lies within the range 0.002–0.040 au;
- the corresponding Laplacian ($\nabla^2\rho_{H\cdots Y}$) is 0.024–0.139 au;
- there is a 'mutual penetration' of the hydrogen and acceptor atoms;
- we observe a loss of charge of the hydrogen atom;
- there is an energetic destabilization of the hydrogen atom;
- a decrease of the dipolar polarization of the hydrogen atom;
- a decrease in the volume of the hydrogen atom.

The above-mentioned topological criteria are very useful since the geometric criteria are not sufficient to decide if hydrogen bonding exists. The topological criteria were applied to detect C—H···O hydrogen bonds,[89] to characterize dihydrogen bonds [91] or to analyse an agostic bond.[92] The criteria connected with the critical point of the H···Y contact seem to be the most often used. For example, it was pointed out for clusters of water with methanol that there is a reasonably good linear correlation between the charge density at H···Y BCP and the strength of hydrogen bonding.[93,94] It was detected later in many papers that the electron density at H···Y BCP and its Laplacian well correlate with the hydrogen bond energy.[44] Similarly, the relationships between H-bond energy and topological parameters of the

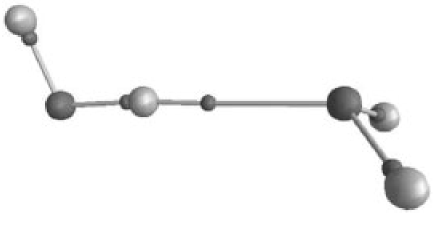


Scheme 1

proton-donating bond are often detected for different samples of compounds.[44] Hence the following parameters may be applied as additional topological measures of the hydrogen bonding strength: electron densities at the BCP of proton donating bond and at the BCP of proton–acceptor contact, and the Laplacians of these electron densities. Scheme 1 shows geometric parameters which are usually used to characterize H-bonds and the topological parameters as new measures of the H-bond strength.

Scheme 2 shows the molecular graph obtained from the MP2/6–311++G** wavefunction for water dimer; the critical points are detected (small circles), those corresponding to typical covalent bonds and that corresponding to the H···O intermolecular contact. We see the increase in the hydrogen atom radius towards the oxygen-accepting centre for the hydrogen atom participating in the hydrogen bonding. This increase is connected with the location of the H···O bond critical point since CP lies on the boundary between the oxygen and hydrogen atoms.

We may roughly find the following tendencies for the hydrogen bonding interaction: the increase in the H-bond strength is connected with the elongation of the proton-donating bond, a shorter proton–acceptor (H···Y) contact, and the tendency of the X—H···Y system to be linear. These changes are also connected with changes in topological parameters: the decrease of the electron density at the proton-donating BCP and the increase in the electron density at the H···Y BCP. An increase in H-bond strength also causes changes in $\nabla^2\rho(r_c)$, the Laplacian of the electron density at X—H BCP increases (it has a negative sign for a covalent bond and its modulus decreases); the Laplacian of the electron density at the H···Y BCP is positive and it increases.



Scheme 2

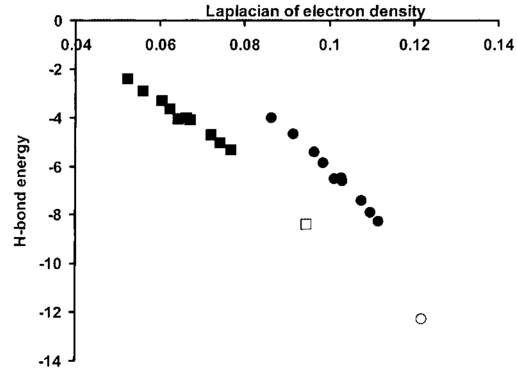


Figure 7. Relationship between the Laplacian of the electron density at H···Y BCP (in au) and the H-bond energy (in kcal mol^{-1}); the circles correspond to the systems with the hydrogen fluoride donor and the squares correspond to the systems with the hydrogen chloride as the proton donor. The open square and the open circle designate the LiCN···HCl and LiCN···HF systems, respectively. Results obtained at the MP2/6–311++G** level of theory

Figures 7 and 8 reflect these dependences for the sample with the hydrogen fluoride donating molecule and for the sample with the hydrogen chloride molecule; R—C≡N molecules are proton acceptors.[48] Figure 7 shows the dependence between the Laplacian of the electron density at the H···Y BCP and hydrogen bond energy; Fig. 8 presents the correlation between the electron density at HX donator (HF or HCl) BCP and H-bond energy. In both figures, there are linear correlations for sub-samples: the first one with HF as donor and the second with HCl. There are slight incompatibilities with the linear correlations for systems with LiCN ionic acceptors, since such a type of acceptor breaks the homogeneity of the sub-samples.

The topological parameters mentioned in this section are connected with the electron density in different regions of the complex: in the proton-donating bond or the proton···acceptor contact. The Bader theory also delivers information on energetic parameters. Hence the so-called energy density, $H(r)$, has been proposed as an index to describe the H-bond strength.[23,95] $H(r)$ seems to

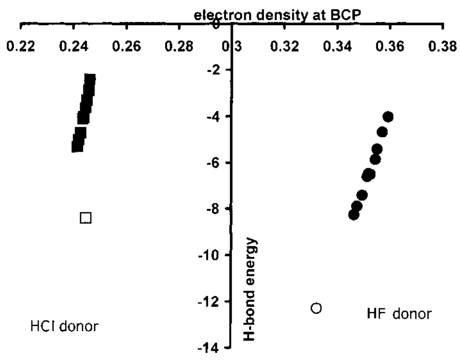


Figure 8. Relationship between the electron density at X—H BCP (in au) and the H-bond energy (in kcal mol^{-1}); designations of the systems as in Fig. 7. Results obtained at the MP2/6–311++G** level of theory

be a more reliable parameter than the Laplacian. The Laplacian identifies regions of space where the electron charge is locally depleted ($\nabla^2\rho > 0$) or concentrated ($\nabla^2\rho < 0$). The former case is connected with interactions between closed-shell systems such as ionic bonds, van der Waals systems or hydrogen bonds. The latter is associated with covalent bonds where there is the concentration of the electron density within the inter-nuclear region. However, there are exceptions such as those concerning the connections between electronegative atoms. Hence $H(r)$ at the bond critical point of the proton$\cdots$acceptor contact has been proposed as a useful index to characterize hydrogen bonding.[96] Rozas *et al.*[96] suggested that both the Laplacian and the energy density at H$\cdots$Y BCPs should be used as criteria to characterize hydrogen bonding. They found that weak H-bonds show both $\nabla^2\rho_{\mathrm{BCP}}$ and $H_{\mathrm{BCP}} > 0$; medium H-bonds show $\nabla^2\rho_{\mathrm{BCP}} > 0$ and $H_{\mathrm{BCP}} < 0$, while strong ones show both $\nabla^2\rho_{\mathrm{BCP}}$ and $H_{\mathrm{BCP}} < 0$. This is in line with the statement of Gilli *et al.*[21] that for the strong resonance-assisted hydrogen bonds the H$\cdots$O contact of the O—H$\cdots$O bond has partly covalent nature; hence for such a case we may observe that $\nabla^2\rho_{\mathrm{BCP}}$ and $H_{\mathrm{BCP}} < 0$.

Theoretical studies based on *ab initio* or DFT calculations deliver both electronic and energetic properties at critical points. Experimental studies of electron density do not provide a description of energetic properties of critical points. However, Abramov has proposed[97] the evaluation of $G(r)$, the local kinetic energy density, in terms of electron density $\rho(r)$, its gradient $\nabla\rho(r)$ and its Laplacian $\nabla^2\rho(r)$ functions. At the critical point, where $\nabla\rho(r_{\mathrm{CP}}) = 0$, the Abramov relation takes the form

$$G(r_{\mathrm{CP}}) = (3/10)\,(3\pi^2)^{2/3}\,\rho^{5/3}(r_{\mathrm{CP}}) + (1/6)\nabla^2\rho(r_{\mathrm{CP}}) \tag{11}$$

All values in this relation are expressed in atomic units. The local potential energy density $V(r_{\mathrm{CP}})$ can be obtained from the virial equation

$$2G(r_{\mathrm{CP}}) + V(r_{\mathrm{CP}}) = (1/4)\nabla^2\rho(r_{\mathrm{CP}}) \tag{12}$$

It was found for samples taken from the crystal structures that $V(r_{\mathrm{BCP}})$ correlates with the H-bond energy, E_{HB} [$E_{\mathrm{HB}} \approx 1/2V(r_{\mathrm{BCP}})$].[98] $V(r_{\mathrm{BCP}})$ designates the local electron potential energy density at the H$\cdots$Y bond critical point. Hence the AIM theory is also useful for the estimation of H-bond energy from the electron density obtained experimentally, for example from high-resolution x-ray diffraction measurements. It is worth mentioning that the first topological analyses based on such measurements were reported about 5 years ago[22,99] and nowadays this type of the study is more often applied.

In the theoretical case, where the wavefunction is accessible, both $G(r_{\mathrm{BCP}})$ and $V(r_{\mathrm{BCP}})$ values may be obtained directly. Additionally, $V(r_{\mathrm{BCP}})$ may be estimated from the Abramov relations [Eqns (11) and (12)] and it may be treated as an approximation of the true $V(r_{\mathrm{BCP}})$ value. There is an excellent correlation between $V(r_{\mathrm{BCP}})$ values obtained from both approaches for samples of H-bonded systems.[100,101] The linear correlation coefficient between $V(r_{\mathrm{BCP}})$, values obtained from the Abramov relation applied to the electron density, and $V(r_{\mathrm{BCP}})$, values obtained directly from the theoretical wavefunctions, amounts to 1.000 or to 0.999.[100,101] We see that due to the finding of Espinosa *et al.*[100] that $E_{\mathrm{HB}} \approx 1/2Vr_{\mathrm{BCP}}$, it is possible to estimate the H-bond energy directly from the energetic parameters of AIM. If the experimental electron density is accessible, it is also possible to calculate those energetic parameters due to the Abramov relations and hence further to calculate the hydrogen bonding energy.

Complex measure of the H-bond strength

A new measure of the hydrogen bonding strength based on the proton-donating bond properties has been introduced and tested on a small sample of complexes.[44,51] This measure is based on both geometric and topological parameters of the X—H bond and may be named as a 'complex parameter:'

$$\begin{aligned}\Delta_{\mathrm{com}} = \{&[(r_{\mathrm{X-H}} - r^0_{\mathrm{X-H}})/r^0_{\mathrm{X-H}}]^2\\ &+ [(\rho^0_{\mathrm{X-H}} - \rho_{\mathrm{X-H}})/\rho^0_{\mathrm{X-H}}]^2\\ &+ [\left(\nabla^2\rho_{\mathrm{X-H}} - \nabla^2\rho^0_{\mathrm{X-H}}\right)/\nabla^2\rho^0_{\mathrm{X-H}}]^2\}^{1/2}\end{aligned} \tag{13}$$

where $r_{\mathrm{X—H}}$, $\rho_{\mathrm{X—H}}$ and $\nabla^2\rho_{\mathrm{X—H}}$ correspond to the parameters of the proton-donating bond involved in H-bonding: the bond length, electronic density at the H—X bond critical point and the Laplacian of that density, respectively; $r^0_{\mathrm{X-H}}$, $\rho^0_{\mathrm{X-H}}$ and $\nabla^2\rho_{\mathrm{X-H^0}}$ correspond to the same parameters of the X—H bond not involved in H-bond formation. The parameter Δ_{com} was introduced to avoid problems connected with the heterogeneity of the analysed sample. We see that squared terms in Eqn. (13) may be divided into three parts: the first one may be called a geometric term, the second is based on electron densities and the last is based on Laplacians. Each of these terms is normalized. For example, for the geometric term the normalization is related to the free proton-donating bond length not involved in H-bond interaction.

The parameter describing H-bond strength may be based only on geometric data as mentioned earlier [Eqn. (2)]. The measures of H-bond strength may also be based on the term connected with electron densities or on the term connected with Laplacians. It has been shown that for heterogeneous samples of hydrogen bonds there are correlations between H-bond energy and the complex parameter.[44,51] There are also good correlations only if

Table 4. The complex parameter Δ_{com} as a measure of H-bond strength and H-bond energies (E_{HB}) corrected for BSSE (in kcal mol^{-1})[a]

Acceptor–donor complex	Δ_{com}[b]	E_{HB}[b]	Δ_{com}[c]	E_{HB}[c]
$(F\cdots H\cdots F)^-$	1.085	−40.5	1.054	−39.9
$(F\cdots H—Cl)^-$	0.417	−19.4	0.332	−20.9
$CH_2O\cdots HF$	0.190	−6.1	0.038	−5.4
$H_2O\cdots HF$	0.233	−8.2	0.094	−7.5
$H_3N\cdots HF$	0.325	−10.2	0.211	−11.2
$HLi\cdots HF$	0.334	−10.6	0.225	−12.6
$\pi(C_2H_2)\cdots HF$[d]	0.197	−2.7	0.043	−3.2
$H_2O\cdots HOH$	0.021	−4.3	0.026	−4.5
$HCOOH\cdots HCOOH$	0.067	−6.1	0.106	−5.9
$H_2O\cdots HCCH$	0.004	−2.5	0.006	−2.5
$\pi(C_2H_2)\cdots H_2O$	0.005	−1.4	0.011	−1.8
$\pi(C_2H_2)\cdots HCCH$[d]	0.001	−0.7	0.002	−1.1
$HLi\cdots HCCH$	0.009	−3.1	0.017	−3.7
$H_3N\cdots H_2O$	0.037	−5.0	0.056	−5.8

[a] HF and MP2 results are given. Results of H-bond energies taken from Ref. 44; Δ_{com} descriptors calculated from geometric parameters of Ref. 44.

[b] HF/6–311++G** level of calculations.

[c] MP2/6–311++G** level of calculations.

[d] T-shaped configuration.

the normalized geometric part is considered as a measure of the H-bond strength.[44,48,51]

Table 4 presents the Δ_{com} measure calculated for different hydrogen bonds of the heterogeneous sample of complexes considered earlier.[44] The results based on MP2/6–311++G** and HF/6–311++G** calculations are included and compared with H-bond energies corrected for BSSE. We see that Δ_{com} correlates well with H-bond energy since the linear correlation coefficients for the dependence between the complex parameter and H-bond energy for a heterogeneous sample of complexes are 0.986 and 0.981 for HF and MP2 levels of theory, respectively.

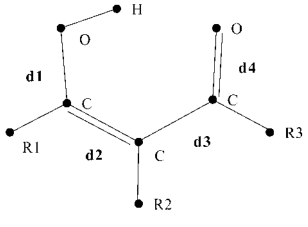
It is worth mentioning that Δ_{com} in some cases may not be a good measure of H-bond strength, since in recent years complexes with unusual H-bonds were detected.[102] For these interactions, the contraction of the X—H donating bond and hence a decrease of the stretching vibration frequency compared with the non-interacting species is observed (blue shift). Such interactions were first called 'anti-hydrogen bonds' but currently the term 'improper' or 'blue-shifting' hydrogen bond is preferred. Few examples of investigations are known concerning blue-shifting hydrogen bonds, studied both experimentally and theoretically. The large blue shift of 47 cm^{-1} predicted theoretically was reported for the $F_3CH\cdots OHCH_3$ complex.[15] Blue shifts of >100 cm^{-1} were detected from infrared spectra for $X^-\cdots H_3CY$ ionic complexes ($X = Cl$, I; $Y = Br$, I); the theoretical calculations are in excellent agreement with these experimental data.[102] Blue shifts were also theoretically predicted for intramolecular H-bonds existing in aromatic *N*-sulfinylamines with *ortho* C—H bonds as proton donors.[103] For such interactions, the use of the complex parameter is not justified.

THE CASE OF INTRAMOLECULAR HYDROGEN BONDING

The intermolecular H-bond energy (E_{HB}) is calculated as a difference in energy between the complex on the one hand and the sum of isolated monomers on the other.[104] It is worth mentioning that if this energy is a result of *ab initio* or DFT calculations, the energies are connected with the optimized geometry of the complex and with the optimized geometries of the monomers. In the case of intramolecular hydrogen bonds (IMHBs), such an approach cannot be applied and so far there is no way to calculate directly the H-bond energy for such systems. However, several approximate estimations have been proposed. For example, for malonaldehyde and its derivatives (Scheme 3) it may be roughly estimated as a difference between the bridging intramolecular system and the corresponding one obtained after the rotation of the O—H bond 180° around the C—O bond. For the other systems a similar procedure is usually applied to compare the so-called 'closed conformation' where the intramolecular H-bond exists with the 'open' one obtained after the rotation described above; both compared conformations are obtained after geometry optimisations.

Intramolecular hydrogen bond energies may be also calculated by means of the corresponding isodesmic equations.[105,106] However, in both cases other effects may influence the calculated H-bond energies. Hence such energies often only approximately correspond to H-bond energies.[107,108] The analysis of the calculation of intramolecular H-bond energy has been presented previously.[109,110] Recently, a method for the estimation of intramolecular H-bond energy based on utilizing barriers of the donor and/or of the acceptor groups was proposed and tested successfully.[110]

Additional possibilities for estimating the H-bond energy for intramolecular interactions may be considered for resonance-assisted hydrogen bonds (RAHBs).[20] The above-mentioned malonaldehyde is an example of RAHB. For malonaldehyde, π-electron delocalization of the O=C—C=C—O—H keto–enol group is observed. Similar delocalization may be detected for the other resonance-assisted H-bonds of $O—H\cdots O$ type[21,27] and of $N—H\cdots O$ or $O—H\cdots N$ type.[111,112] For RAHBs the real structure may be treated as a mixture of two tautomers; the wavefunction of such a structure is a linear combination, $\Psi = a_1\Psi_1 + a_2\Psi_2$, of its VB resonance forms.



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The consequences of π-electron delocalization within intramolecular RAHBs of malonaldehyde and within similar systems are as follows:

(i) the shortening of O$\cdots$O distances;
(ii) the strengthening of H-bonds;
(iii) the shift of the proton towards the centre of O$\cdots$O contact;
(iv) the equalization of C—C, C═C bonds and of C—O, C═O bonds.

A parameter for describing electron delocalization in RAHBs has been proposed:[20]

$$Q = (d_1 - d_4) + (d_3 - d_2) \tag{14}$$

where d_1, d_2, d_3 and d_4 are bond lengths (see Scheme 3). Correlations of Q with the other parameters of the hydrogen bond have been found, such that the lower the value of Q the stronger is the H-bond and the greater is the π-electron delocalization.[21,107] However, the meaning of the Q parameter is very limited; Q correlates well with E_{HB} for malonaldehyde derivatives[107] but there is no such correlation for derivatives of *o*-hydroxybenzaldehyde.[108]

The topological parameters described in the previous sections, the electron density of the proton$\cdots$acceptor contact within H-bonding, the electron density of the proton-donating bond and the Laplacians of those densities, better reflect the energy of intramolecular H-bonds. Recently, new parameters connected with ring critical points have been proposed as measures which may describe the H-bond strength for intramolecular interactions.[108,113] The ring critical point (RCP) is a point of the minimum electron density within the ring surface and a maximum on the ring line.[90] For example, in the case of benzene the RCP lies in the centre of the ring owing to symmetry constraints. In the absence of symmetry, an RCP can be found anywhere inside the ring. Figure 9 shows the molecular graph for the fluoro derivative of *o*-hydroxybenzaldehyde; there are bond paths, bond critical points and two RCPs—one for the benzene ring and a second for the ring created due to intramolecular H-bond formation.

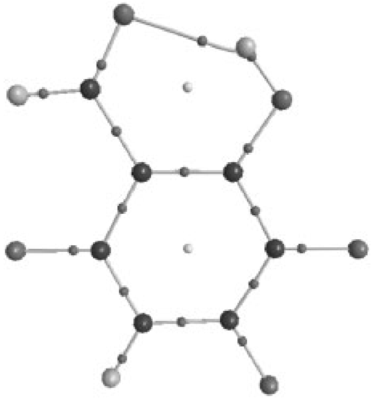
Figure 9. Molecular graph for the fluoro derivative of *o*-hydroxybenzaldehyde

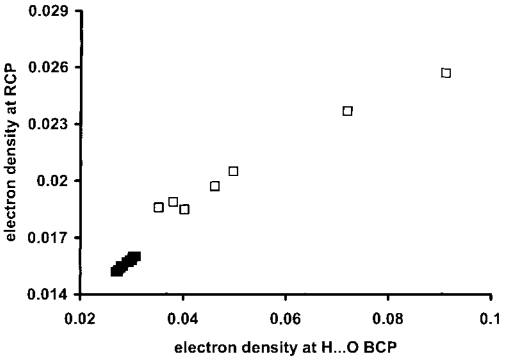

Figure 10. Correlation between the electron density at H$\cdots$O BCP and the electron density at the ring critical point (both values in au) for intramolecular H-bonds of malonaldehyde derivatives (■) and derivatives of *o*-hydroxybenzaldehyde (□)

It was found that the electron density at the RCP created due to the hydrogen bond formation and the Laplacian of its density correlate well with the H-bond energy.[108] Figure 10 shows the dependence between the electron density at the proton$\cdots$acceptor contact and the electron density at the ring critical point of intramolecular systems. Two samples are considered: the derivatives of malonaldehyde (closed squares) and the fluoro derivatives of *o*-hydroxybenzaldehyde (open squares).

CONCLUSION

This study of hydrogen bonding strength is based on the geometric parameters which may be known from experiment, from the CSD, or which may be derived from *ab initio* or DFT calculations. Since the geometric criteria of the existence of hydrogen bonding are controversial, the 'atoms in molecules' (AIM) theory was applied here to analyse this type of interaction. To avoid vagueness, this study was restricted only to geometric and topological parameters derived from the Bader theory and many powerful tools have been omitted, such as spectroscopic and NMR techniques, new computational methods, etc.

The measures analysed here are usually connected with the proton-donating bond and with the proton... acceptor contact; however, the parameters attributed to acceptors may also be useful. It was also shown in this study that these parameters correlate, especially for homogeneous samples of compounds. In other words, the change in one parameter, for example the elongation of the proton-donating bond, is connected with the other changes, the shortening of the H$\cdots$Y contact and the changes of topological parameters. This means that such changes describe practically the same effect—the increase in H-bond strength. It may be supported by the use of factor analysis,[114] which is often applied in physical and chemical problems.[115] For example, one of the first applications of factor analysis in chemistry was connected with the thermodynamic data describing solvent effects.[116] For hydrogen bonding, factor analysis was applied for heterogeneous samples of H-bonded complexes.[44] The following variables were considered: those connected with the proton-donating bond—the bond length, the electron density at BCP and its Laplacian, all normalized in the way described in this study—those connected with the H···Y contact (one geometric and two topological parameters) and the H-bond energy. For these variables only one factor was retained; this means that the loadings obtained refer to one eigenvalue which explains the largest part of the variance (91.3%). Similar results based on factor analysis were obtained for other samples of H-bonded complexes.[44,48]

The other ways to detect and describe the hydrogen bond introduced recently are analysed here, including the relations introduced by the groups of Abramov and Espinosa, which allow estimation of the H-bond energy from the electron density and the properties of the ring critical point.

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REFERENCES

1. Jeffrey GA, Saenger W. *Hydrogen Bonding in Biological Structures*. Springer: Berlin, 1991.
2. Desiraju GR. *Crystal Engineering—The Design of Organic Solids*. Elsevier: Amsterdam, 1989.
3. Krygowski TM, Cyrański MK, Czarnocki Z, Häfelinger G, Katritzky AR. *Tetrahedron* 2000; **56**: 1783–1796.
4. Krygowski TM, Cyrański MK. *Chem. Rev.* 2001; **101**: 1385–1419.
5. Jeffrey GA. *An Introduction to Hydrogen Bonding*. Oxford University Press: New York, 1997.
6. Desiraju GR, Steiner T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*. Oxford University Press: New York, 1999.
7. Scheiner S. *Hydrogen Bonding: A Theoretical Perspective*. Oxford University Press: New York, 1997.
8. Pimentel GC, McClellan AL. *The Hydrogen Bond*. Freeman: San Francisco, 1960.
9. Taylor R, Kennard O. *J. Am. Chem. Soc.* 1982; **104**: 5063–5070.
10. Desiraju GR. *Angew. Chem., Int. Ed. Engl.* 1995; **34**: 2311–2327.
11. Steiner T. *Angew. Chem., Int. Ed. Engl.* 2002; **41**: 48–76.
12. Etter MC. *Acc. Chem. Res.* 1990; **23**: 120–126.
13. Viswamitra MA, Radhakrishnan R, Bandekar J, Desiraju GR. *J. Am. Chem. Soc.* 1993; **115**: 4868–4869.
14. Alkorta I, Rozas I, Elguero J. *Chem. Soc. Rev.* 1998; **27**: 163–170, and references cited therein.
15. Gu J, Kar T, Scheiner S. *J. Am. Chem. Soc.* 1999; **121**: 9411–9422.
16. Leiserowitz L. *Acta Crystallogr., Sect. B* 1976; **32**: 775–802.
17. Grabowski SJ. *Pol. J. Chem.* 1995; **69**: 223–228.
18. Larson JW, McMahon TB. *J. Am. Chem. Soc.* 1983; **103**: 2944–2950.
19. Latajka Z, Bouteller Y, Scheiner S. *Chem. Phys. Lett.* 1995; **234**: 159–164.
20. Gilli G, Bellucci F, Ferretti V, Bertolasi V. *J. Am. Chem. Soc.* 1989; **111**: 1023–1028.
21. Gilli P, Bertolasi V, Ferretti V, Gilli G. *J. Am. Chem. Soc.* 1994; **116**: 909–915.
22. Madsen GKH, Iversen BB, Larsen FK, Kapon M, Reisner GM, Herbstein FH. *J. Am. Chem. Soc.* 1998; **120**: 10040–10045.
23. González L, Mó O, Yáñez M, Elguero J. *J. Chem. Phys.* 1998; **109**: 2685–2693.
24. Tokhadze KG, Denisov GS, Wierzejewska M, Drozd M. *J. Mol. Struct.* 1997; **404**: 55–62.
25. Kaplan IG. *Theory of Molecular Interactions*. Studies in Physical and Theoretical Chemistry, vol. 42. Elsevier: Amsterdam, 1986.
26. Platts JA, Howard ST, Woźniak K. *Chem. Commun.* 1996; 63–64.
27. Gilli G, Gilli P. *J. Mol. Struct.* 2000; **552**: 1–15.
28. Hibbert F, Emsley J. *Adv. Phys. Org. Chem.* 1990; **26**: 255.
29. Garcia-Viloca M, Gelabert R, González-Lafont A, Moreno M, Lluch JM. *J. Phys. Chem. A* 1997; **101**: 8727–8733.
30. Berglund B, Vaughan RW. *J. Chem. Phys.* 1980; **73**: 2037–2043.
31. Gerald R, Bernhard T, Haeberlen U, Rendell J, Opella S. *J. Am. Chem. Soc.* 1993; **115**: 777–782.
32. Kaliaperumal L, Sears REJ, Ni QW, Furst JE. *J. Chem. Phys.* 1989; **91**: 7387–7391.
33. Scheiner S, Gu Y, Kar T. *J. Mol. Struct. (Theochem)* 2000; **500**: 441–452.
34. Scheiner S, Grabowski SJ, Kar T. *J. Phys. Chem. A* 2001; **105**: 10607–10612.
35. Scheiner S, Grabowski SJ. *J. Mol. Struct.* 2002; **615**: 209–218.
36. Bader RFW. *Atoms in Molecules: A Quantum Theory.* Oxford University Press: New York, 1990.
37. Parr RG, Yang W. *Density-Functional Theory of Atoms and Molecules*. Oxford University Press: New York, 1989.
38. Alcamí M, Mó O, Yáñez M. *Mass Spectrom. Rev.* 2001; **20**: 195–245.
39. González L, Mó O, Yáñez. *J. Org. Chem.* 1999; **64**: 2314–2321.
40. Lutz HD. *J. Mol. Struct.* 2003; **646**: 227–236.
41. Ichikawa M. *Acta Crystallogr., Sect. B* 1978; **34**: 2074–2080.
42. Ichikawa M. *J. Mol. Struct.* 2000; **552**: 63–70.
43. Grabowski SJ. *Tetrahedron* 1998; **54**: 10153–10160.
44. Grabowski SJ. *J. Phys. Chem. A* 2001; **105**: 10739–10746.
45. Boys SF, Bernardi F. *Mol. Phys.* 1970; **19**: 553.
46. van Duijneveldt FB, van Duijneveldt-van de Rijdt JGCM, van Lenthe JH. *Chem. Rev.* 1994; **94**: 1873–1885.
47. Simon S, Bertran J, Sodupe M. *J. Phys. Chem. A* 2001; **105**: 4359–4364.
48. Grabowski SJ. *J. Mol. Struct.* 2002; **615**: 239–245.
49. Frisch MJ, Trucks GW, Schlegel HB, Gill PMW, Johnson GB, Robb MA, Cheeseman JR, Keith TA, Petersson GA, Montgomery JA, Raghavachari K, Al.-Laham MA, Zakrzewski VG, Ortiz JV, Foresman JB, Cioslowski J, Stefanov BB, Nanayakkara A, Challacombe M, Peng CY, Ayala PY, Chen W, Wong MW, Andres JL, Replogle ES, Gomperts R, Martin LR, Fox DJ, Binkley JS, Defrees DJ, Steward JJ, Head-Gordon M, Gonzalez G, Pople JA. *Gaussian 94*. Gaussian: Pittsburgh, PA, 1995.
50. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin LR, Fox DJ, Keith T, Al.-Laham MA, Peng CY, Nanayakkara A, Gonzalez G, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA. *Gaussian 98, Revision A.6*. Gaussian: Pittsburgh, PA, 1998.
51. Grabowski SJ. *Chem. Phys. Lett.* 2001; **338**: 361–366.
52. Grabowski SJ. In *Neutrons and Numerical Methods—N_2M*, Grenoble, France December 1998; AIP (American Institute of Physics) College Park, MD; Conference Proceedings 479,

Johnson MR, Kearley GJ, Büttner HG (eds). American Institute of Physics, 1999.
53. Allen FH, Davies JE, Galloy JE, Johnson JJ, Kennard O, Macrave CF, Mitchel EM, Smith JM, Watson DG. *J. Chem. Inf. Comput. Sci.* 1991; **31**: 187.
54. Steiner T. *Chem. Soc., Perkin Trans. 2* 1996; 1315–1319.
55. Allerhand A, Schleyer R. *J. Am. Chem. Soc.* 1963; **85**: 1715.
56. McWeeny R. *Coulson's Valence*. Oxford University Press: London, 1979.
57. Pauling L. *J. Am. Chem. Soc.* 1947; **69**: 542.
58. Cieplak AS. In *Structure Correlation*, Bürgi H-B, Dunitz JD (eds). VCH: Weinheim, 1994, and references cited therein.
59. Bürgi HB, Shklover V. In *Structure Correlation*, Bürgi H-B, Dunitz JD (eds). VCH: Weinheim, 1994, and references cited therein.
60. Brown ID, Shannon RD. *Acta Crystallogr., Sect. A* 1972; **29**: 266–282.
61. Brown ID. *Acta Crystallogr., Sect. B* 1992; **48**: 553–572, and references cited therein.
62. Grabowski SJ. *Croat. Chem. Acta* 1988; **61**: 815–819.
63. Grabowski SJ. *J. Mol. Struct.* 2000; **552**: 153–157.
64. Steiner T. *J. Phys. Chem.* 1998; **102**: 7041–7052.
65. Grabowski SJ. *Chem. Phys. Lett.* 1999; **312**: 542–547.
66. Grabowski SJ. *J. Phys. Chem. A* 2000; **104**: 5551–5557.
67. Richardson TB, deGala S, Crabtree RH, Siegbahn PEM. *J. Am. Chem. Soc.* 1995; **117**: 12875.
68. Crabtree RH, Siegbahn PEM, Eisenstein O, Rheingold AL, Koetzle TF. *Acc. Chem. Res.* 1996; **29**: 348–354.
69. Epstein LM, Shubina ES. *Coord. Chem. Rev.* 2002; **231**: 165–181, and references cited therein.
70. Liu Q, Hoffman R. *J. Am. Chem. Soc.* 1995; **117**: 10108.
71. Alkorta I, Elguero J, Foces-Foces C. *Chem. Commun.* 1996; 1633–1634.
72. Orlowa G, Scheiner S, Kar T. *J. Phys. Chem. A* 1999; **103**: 514–520.
73. Grabowski SJ, Pogorzelska M. *J. Mol. Struct.* 2001; **559**: 201–207.
74. Krygowski TM, Grabowski SJ, Konarski J. *Tetrahedron* 1998; **54**: 11311–11316.
75. Palusiak M, Grabowski SJ. *J. Mol. Struct.* 2002; **642**: 97–104.
76. Dunitz JD. *X-Ray Analysis and the Structure of Organic Molecules*. Cornell University Press: Ithaca, NY, 1979; 341–363.
77. Bürgi HB, Dunitz JD. *J. Am. Chem. Soc.* 1987; **109**: 2924–2926.
78. Bürgi HB. *Angew. Chem., Int. Ed. Engl.* 1975; **14**: 460–473.
79. Grabowski SJ, Krygowski TM. *Chem. Phys. Lett.* 1999; **305**: 247–250.
80. Grabowski SJ, Krygowski TM, Stępień B. *J. Phys. Org. Chem.* 2000; **13**: 740–744.
81. Benedict H, Limbach H-H, Wehlan M, Fehlhammer W-P, Golubev NS, Janoschek R. *J. Am. Chem. Soc.* 1998; **120**: 2939–2950.
82. Smirnov SN, Benedict H, Golubev NS, Denisov GS, Kreevoy MM, Schowen RL, Limbach H-H. *Can. J. Chem.* 1999; **77**: 943–949.
83. Majerz I, Malarski Z, Sobczyk L. *Chem. Phys. Lett.* 1997; **274**: 361–364.
84. Sobczyk L. *Ber. Bunsenges. Phys. Chem.* 1998; **102**: 377–383.
85. Hamilton WC, Ibers JA. *Hydrogen Bonding in Solids*. Benjamin: New York, 1968.
86. Grabowski SJ, Krygowski TM. *Tetrahedron* 1998; **54**: 5683–5694.
87. Lippincott ER, Schroeder R. *J. Chem. Phys.* 1955; **23**: 1099–1106.
88. Dziembowska T, Szczodrowska B, Krygowski TM, Grabowski SJ. *J. Phys. Org. Chem.* 1994; **7**: 142–146.
89. Koch U, Popelier PLA. *J. Phys. Chem. A* 1995; **99**: 9747–9754.
90. Popelier P. *Atoms in Molecules. An Introduction*. Prentice-Hall: Englewood Cliffs, NJ, 2000.
91. Popelier PLA. *J. Phys. Chem. A* 1998; **102**: 1873–1878.
92. Popelier PLA, Logothetis G. *J. Organomet. Chem.* 1998; **555**: 101–111.
93. Mó O, Yánez M, Elguero J. *J. Chem. Phys.* 1992; **97**: 6628–6638.
94. Mó O, Yánez M, Elguero J. *J. Mol. Struct. (Theochem)* 1994; **314**: 73–81.
95. Koch W, Frenking G, Gauss J, Cremer D, Collins JR. *J. Am. Chem. Soc.* 1987; **109**: 5917–5934.
96. Rozas I, Alkorta I, Elguero J. *J. Am. Chem. Soc.* 2000; **122**: 11154–11161.
97. Abramov YA. *Acta Crystallogr., Sect. A* 1997; **53**: 264–272.
98. Espinosa E, Molins E, Lecomte C. *Chem. Phys. Lett.* 1998; **285**: 170–173.
99. Mallinson PR, Woźniak K, Smith GT and McCormack KL. *J. Am. Chem. Soc.* 1997; **119**: 11502–11509.
100. Espinosa E, Alkorta I, Rozas I, Elguero J, Molins E. *Chem. Phys. Lett.* 2001; **336**: 457–461.
101. Wojtulewski S, Grabowski SJ. *J. Mol. Struct (Theochem)* 2003; **621**: 285–291.
102. Hobza P, Havlas Z. *Chem. Rev.* 2000; **100**: 4253–4264, and references cited therein.
103. Muchall HM. *J. Phys. Chem. A* 2001; **105**: 632–636.
104. Gordon MS, Jensen JH. *Acc. Chem. Res.* 1996; **29**: 536–543.
105. Hehre WJ, Radom L, Schleyer PvR, Pople JA. *Ab Initio Molecular Orbital Theory*. Wiley: New York, 1986.
106. Rozas I, Alkorta I, Elguero J. *J. Phys. Chem. A* 2001; **105**: 10462–10467.
107. Grabowski SJ. *J. Mol. Struct.* 2001; **563**: 137–143.
108. Grabowski SJ. *Monatsh. Chem.* 2002; **133**: 1373–1380.
109. Craw JS, Bacskay J. *J. Chem. Soc. Faraday Trans.* 1992; **88**: 2315–2321.
110. Buemi G, Zuccarello F. *J. Mol. Struct. (Theochem)* 2002; **581**: 71–85.
111. Bertolasi V, Gilli P, Ferretti V, Gilli G. *Acta Crystallogr., Sect. B* 1994; **50**: 617–625.
112. Rybarczyk-Pirek AJ, Grabowski SJ, Małecka M, Nawrot-Modranka J. *J. Phys. Chem. A* 2002; **106**: 11956–11962.
113. Grabowski SJ. In *Horizons in H-bond Research, Proceeding of the Conference, Torino, September 2001*.
114. Überla K. *Faktorenanalyse*. Springer: Berlin, 1977.
115. Malinowski ER, Howery DG. *Factor Analysis in Chemistry.* Wiley–Interscience: New York, 1980.
116. Fawcett WR, Krygowski TM. *Can. J. Chem.* 1976; **54**: 3283–3292.