



Ab initio and AIM studies on measures of hydrogen bonding strength— $R-C\equiv N \cdots HF$ and $R-C\equiv N \cdots HCl$ complexes

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Abstract

The $R-C\equiv N \cdots H-X$ ($R = H, F, Li, CH_3, CH_2F, CHF_2, CF_3, NO_2, NH_2, BH_2, OH; X = F, Cl$) complexes are considered here as the simple sample for the consideration of different measures of H-bond strength. MP2/6-311++G** level of theory is applied for an optimisation of geometries of complexes and monomers. Measures of H-bond strength based on geometrical and topological parameters of H–X proton donating bond and on parameters of $H \cdots N$ distance are analysed. Additionally the factor analysis is applied to confirm correlations found between H-bond energy and investigated measures. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Bond critical points; Hydrogen bonding; Atoms in molecules

1. Introduction

Hydrogen bonding plays one of the most important roles in an arrangement of molecules in crystals [1,2]. A large number of papers appeared dealing with the Lewis acidity and basicity of functional groups involved in H-bonds as for example: nitro [3], formyl [4], carboxylic [5], carbonyl [6,7], hydroxyl [8], cyano group [9], etc.

The cyano group is not known as a strong proton acceptor but is often described as a factor playing an important role in crystal engineering [9]. For example, two polymorphic forms of crystals of HCN are known where HCN molecules form chains linked by $C-H \cdots N$ interactions with $N \cdots C$ distances of about 3.18 Å [10]. It was pointed out that for cyano groups two hydrogen bonding modes are possible; the first

one with a nitrogen atom as a proton accepting centre and the second one with π -electrons of $C\equiv N$ group as an acceptor [9]. The first case is realised in the crystal structures of HCN. There is no computational support for the $X-H \cdots \pi$ bonding. IMPT calculations made for thiocyanate–methanol system [11] show that the complex linked through $O-H \cdots N$ bond is more stable than H-bonded system linked through π -electrons. However, some of the crystal structure reports indicate an existence of intermediate modes close to the $X-H \cdots \pi$ link. For the crystal structure of 2-methyl-3-(2-methylphenyl)-but-1-ene-1,1-dicarbonitrile [12] the intramolecular H-bond between proton donating methyl $-CH_3$ group and $-C\equiv N$ acceptor was found and π -electrons or C-negative charged atom were suggested as more probable accepting centres than the nitrogen atom.

In the present work the calculations on the linear $-C\equiv N \cdots H-X$ ($X = F, Cl$) complexes as convenient model systems were performed. Such systems were

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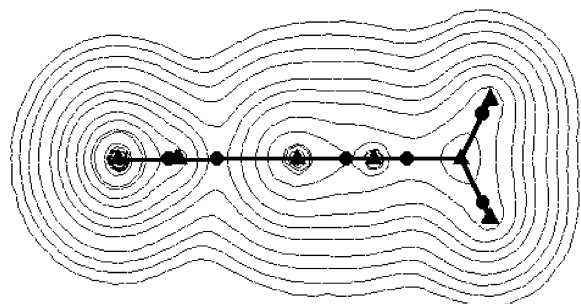


Fig. 1. The contour map representing $\text{NH}_2\text{CN}\cdots\text{HF}$ complex, circles correspond to BCPs while triangles to attractors; bond paths (solid lines connecting attractors and BCPs) are also given.

chosen because of their simplicity: simple diatomic HF and HCl donors of proton and simple often linear proton accepting molecules. N-atom was chosen as a proton accepting centre since it was pointed out earlier that such situation is much more probable for $\text{C}\equiv\text{N}$ group than π -electrons as an acceptor.

The aim of this paper is also to analyse different measures of H-bond strength for the simple sample of complexes considered here. Among different indicators of H-bond strength are those derived from the

Bader theory (atoms in molecules theory, AIM) [13]. Hence the H-bond interaction is often investigated in terms of topological parameters. The AIM theory was applied for the study of conventional H-bonds [14,15] as well as for unconventional ones, like for example $\text{C}-\text{H}\cdots\text{O}$ bonds [16]. Eight criteria based on the theory of ‘atoms in molecules’ were proposed to characterize hydrogen bonds [16,17]. For example, these criteria were applied to analyse dihydrogen bond interaction for a dimer structure of BH_3NH_3 [18]. AIM parameters were also used to describe the new type of hydrogen bonding—blue-shifting H-bond [19]. It has also been pointed out that the topological descriptors, those obtained from AIM as well as those derived from ELF function may be useful to distinguish weak, medium and strong interactions of hydrogen bonded complexes [20]. The electron localization function (ELF) is a local scalar function proposed by Becke and Edgecombe [21] and related to the Fermi hole curvature. The detailed study of dihydrogen bonds in terms of AIM theory and the ELF function [22] allowed to check the hypothesis that the dihydrogen bond corresponds to the predissociative

Table 1

The geometrical, energetic and topological parameters of the H-bonded systems investigated here; distances in Å, energies in kcal/mol and topological parameters in a.u. The results obtained at MP2/6-311++G** level of theory. The binding energies corrected for BSSE

Complex	HX bond length	ρ_{XH}	$\nabla^2\rho_{\text{XH}}$	H...N distance	$\rho_{\text{X}\cdots\text{N}}$	$\nabla^2\rho_{\text{H}\cdots\text{N}}$	H-bond energy
LiCN + HF	0.9412	0.3326	-2.5070	1.7316	0.0419	0.1220	-12.30
CH_3CN + HF	0.9305	0.3478	-2.6750	1.8345	0.0311	0.1098	-7.90
CH_2FCN + HF	0.9277	0.3521	-2.7160	1.8781	0.0276	0.1029	-6.47
HCN + HF	0.9274	0.3527	-2.7200	1.8872	0.0270	0.1013	-6.51
FCN + HF	0.9260	0.3547	-2.7380	1.9012	0.0253	0.0986	-5.86
CHF_2 + HF	0.9257	0.3552	-2.7430	1.9153	0.0249	0.0966	-5.42
CF_3CN + HF	0.9243	0.3573	-2.7610	1.9455	0.0230	-0.0915	-4.68
NO_2CN + HF	0.9231	0.3594	-2.7750	1.9740	0.0211	0.0863	-4.03
NH_2CN + HF	0.9314	0.3466	-2.6620	1.8229	0.0317	0.1117	-8.27
BH_2CN + HF	0.9281	0.3516	-2.709	1.8754	0.0280	0.1031	-6.61
HOCN + HF	0.9293	0.3497	-2.693	1.8473	0.0295	0.1078	-7.42
LiCN + HCl	1.3010	0.2449	-0.7159	1.8673	0.0330	0.0946	-8.40
CH_3CN + HCl	1.2854	0.2421	-0.7117	2.0346	0.0217	0.0741	-5.02
CH_2FCN + HCl	1.2822	0.2440	-0.7145	2.0932	0.0189	0.0661	-4.02
HCN + HCl	1.2821	0.2442	-0.7152	2.1055	0.0184	0.0643	-4.04
FCN + HCl	1.2808	0.2449	-0.7159	2.1178	0.0174	0.0623	-3.64
CHF_2CN + HCl	1.2802	0.2452	-0.7158	2.1356	0.0171	0.0605	-3.31
CF_3CN + HCl	1.2790	0.2459	-0.7159	2.1700	0.0158	0.0560	-2.89
NO_2CN + HCl	1.2783	0.2463	-0.7148	2.1977	0.0147	0.0523	-2.41
NH_2CN + HCl	1.2862	0.2416	-0.7112	2.0154	0.0224	0.0768	-5.31
BH_2CN + HCl	1.2827	0.2437	-0.7140	2.0859	0.0193	0.0671	-4.11
HOCN + HCl	1.2842	0.2429	-0.7133	2.0493	0.0206	0.0720	-4.71

Table 2

Geometrical (HX bond lengths in Å) and topological parameters (in a.u.): electron density at HX bond critical point— ρ_{HX} and its Laplacian— $\nabla^2\rho_{\text{HX}}$. Results obtained at MP2/6-311++G** level of theory

Donator	HX bond length	ρ_{HX}	$\nabla^2\rho_{\text{HX}}$
HF	0.9164	0.3707	-2.839
HCl	1.2731	0.2488	-0.711

protonation whereas the conventional hydrogen bond $\text{A}-\text{H}\cdots\text{B}$ can be considered as the initial step of a proton transfer reaction.

The above-mentioned examples show that the Bader theory is one of the most important tools in the analysis of H-bonding. Hence AIM theory is also applied here to study this interaction in connection with geometrical parameters and statistical analysis.

2. Computational details

All calculations on complexes and corresponding monomers were carried out at MP2/6-311++G** level of theory using the GAUSSIAN 98 program [23]. Basis set superposition error (BSSE) was corrected by the counterpoise procedure of Boys and Bernardi [24]. The binding energies were computed as the difference in energy between the complex on one hand, and the sum of isolated monomers, on the other hand.

The topological analysis based on the properties of bond critical points (BCPs) is also included here. Such analysis of BCPs derives from the Bader theory—AIM [13]. The electron densities and their Laplacians

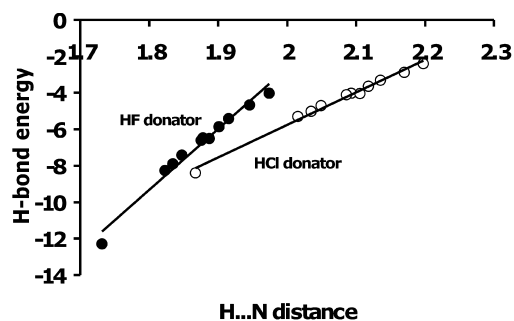


Fig. 2. The relationship between the $\text{H}\cdots\text{N}$ distance (in Å) and H-bond energy (in kcal/mol); open circles correspond to the complexes with HCl donator and full circles to the complexes with HF donator.

at BCPs are discussed. All topological calculations were performed using AIM set of programs [25]. Fig. 1 presents the contour map of one of the complexes investigated here— $\text{NH}_2\text{CN}\cdots\text{HF}$ dimer. The triangles represent attractors and the circles show BCPs.

3. Results and discussion

The simple H-bonded complexes are considered in this study—the linear systems with nitrogen of cyano group as a proton accepting centre and HF or HCl as proton donating molecules: $\text{R}-\text{C}\equiv\text{N}\cdots\text{H}-\text{X}$ ($\text{X} = \text{F}, \text{Cl}$; $\text{R} = \text{H}, \text{F}, \text{Li}, \text{CH}_3, \text{CH}_2\text{F}, \text{CHF}_2, \text{CF}_3, \text{NO}_2, \text{NH}_2, \text{BH}_2, \text{OH}$). Table 1 presents the geometrical and topological parameters of $\text{H}-\text{X}$ bonds and $\text{H}\cdots\text{N}$ contacts—their lengths, electron densities at BCPs and Laplacians of these densities; the binding energies (corrected for BSSE) are also included. Table 1 shows that H-bonds of $\text{LiCN}\cdots\text{HX}$ complexes belong to the strongest ones – 12.3 and – 8.4 kcal/mol for HF and HCl proton donating molecules, respectively. It seems to be justified since if the metal atom donates electrons into the cyano group, better acceptor potentials than for organic cyano groups may be expected. The remaining hydrogen bonds (Table 1) may be treated as systems of a mediate strength (about 3–7 kcal/mol) similarly as mediate H-bond for the water dimer [26]. Table 1 also shows that the binding energies for the complexes with HF donating molecule are of about 2–3 kcal/mol greater than the corresponding energies of complexes with HCl. This result is in line with the well known fact that HF molecule is the stronger proton donator than HCl molecule [26]. Table 2 shows the geometrical and topological parameters of HF and HCl monomers for which optimisations were done to calculate binding energies of complexes.

The results collected in Table 1 confirm dependencies known for the other samples of H-bonded systems. The correlations between different geometrical, energetic and topological parameters exist particularly for homogeneous samples. For shorter $\text{H}\cdots\text{Y}$ distances binding energies are greater. Such correlation was found for $\text{O}-\text{H}\cdots\text{O}$, $\text{N}-\text{H}\cdots\text{O}$ and the other types of hydrogen bonds [27]. In this study, the linear correlation coefficient for the dependence between $\text{H}\cdots\text{N}$ distance and the binding energy is

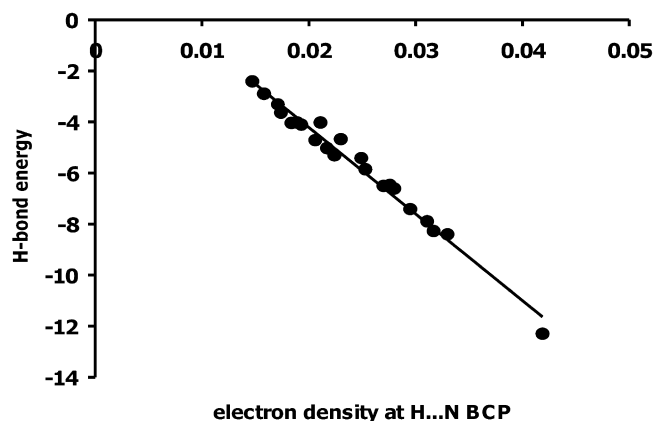


Fig. 3. The dependence between the electronic density at H...N bond critical point ($\rho_{H...N}$ in a.u.) and the H-bond energy (in kcal/mol).

equal to 0.988 for the sample of complexes with HF molecule and 0.995 for complexes with HCl molecule (Fig. 2). The corresponding regression lines are given below:

$$y = 33.436x - 69.518; \text{ for HF donating molecule;}$$

$$y = 17.844 - 41.454; \text{ for HCl donating molecule}$$

(1)

where y corresponds to H-bond energy and x corresponds to H...N distance.

Similarly, the electron density at H...Y BCP is often considered as a measure of H-bond strength [28, 29]. A good linear correlation between the interaction energy per hydrogen bond and the electronic charge density, $\rho_{H...Y}$, at the corresponding BCP was found for water trimers [30,31], methanol trimers [32] and hydrogen peroxide dimers [33]. Such correlation is often fulfilled for non-conventional hydrogen bonds like for example dihydrogen bonds [34,35]. Fig. 3 shows the dependence between the electron density at H...N BCP and H-bond energy. Eq. (2) presents the corresponding regression line:

$$y = -338.93x + 2.5654; \quad R = 0.991 \quad (2)$$

where y corresponds to H-bond energy and x to electron density at H...N BCP.

The H-bond formation also causes the elongation of the proton donating bond. The dependence between the X–H (X = F, Cl) bond length and H-bond energy is given by Eq. (3).

$$y = -453.26x + 414.04;$$

$$R = 0.996; \text{ for HF donator}$$

$$y = -253.87x + 321.58;$$

$$R = 0.985; \text{ for HCl donator}$$

(3)

where y corresponds to H-bond energy given in kcal/mol and x corresponds to HF or HCl bond length.

There are also two subsets of the sample studied here: one subset for complexes with HF and the second one for complexes with HCl as a proton donating molecule. Similar subsets are presented in Fig. 1. Eq. (3) shows the regression lines for both subsets and the dependence between the proton donating bond length and H-bond energy.

It has been demonstrated recently that the geometrical parameter describing the elongation of the proton donating bond may be normalized [36] according to the relation given below:

$$\Delta_{\text{geo}} = (r_{X-H} - r_{X-H}^0) / r_{X-H}^0 \quad (4)$$

where r_{X-H} is the length of X–H bond within X–H...Y system and r_{X-H}^0 is the length of the free bond not involved in H-bonding. In other words Δ_{geo} is the elongation of X–H bond due to H-bridge formation in relation to the free X–H bond length. Such approach leads to the elimination of subsets in this study. This relation has been proposed as a new measure of H-bond strength which may be applied for different samples [36,37], not only for homogeneous samples, but also for heterogeneous ones. Fig. 4 confirms this

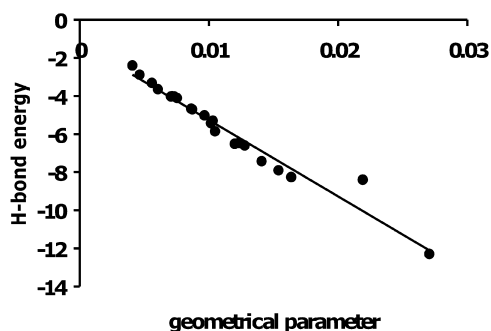


Fig. 4. The relationship between the geometrical parameter (Δ_{geo}) and H-bond energy (in kcal/mol).

idea since the whole sample containing complexes with HF and HCl donating molecules is well described by Eq. (4). The geometrical parameter Δ_{geo} correlates with H-bond energy; the correlation coefficient R amount to 0.980 and the linear regression is given by equation presented below:

$$y = -401.36x - 1.2414, \quad (5)$$

where y stands for H-bond energy and x represents the geometrical parameter, Δ_{geo} .

Fig. 4 shows the greatest difference between the calculated MP2 H-bond energy and that energy obtained from modelled regression line for $\text{LiCN} \cdots \text{HCl}$ complex. If we exclude the corresponding point from the regression line, which may be statistically justified, then the correlation coefficient is equal to 0.996.

Table 3

Dipole moment of complex relative to monomers and charge transferred from proton acceptor to donor molecule (MP2/6-311++G** level)

Proton acceptor	HF donator		HCl donator	
	$\Delta\mu$ (D)	CT (me)	$\Delta\mu$ (D)	CT (me)
CH_3CN	1.126	40	1.086	17
HCN	0.890	26	0.823	9
FCN	0.907	18	0.806	6
CH_2FCN	0.752	32	0.687	14
CHF_2CN	0.595	26	0.485	11
CF_3CN	0.952	19	0.781	7
LiCN	1.423	39	1.683	37
NO_2CN	0.914	16	0.722	11
NH_2CN	1.139	31	1.112	19
BH_2CN	1.102	39	0.989	19
HOCN	0.845	24	0.852	11

The similar results as those presented in Fig. 4 may be obtained applying the other relations instead of Eq. (4). The more complex H-bond strength measure based on the geometrical and topological proton donating bond parameters was proposed [36,37]:

$$\begin{aligned} \Delta_{\text{com}} = & \left\{ \left[(r_{\text{X-H}} - r_{\text{X-H}}^0) / r_{\text{X-H}}^0 \right]^2 \right. \\ & + \left[(\rho_{\text{X-H}}^0 - \rho_{\text{X-H}}) / \rho_{\text{X-H}}^0 \right]^2 \\ & \left. + \left[(\nabla^2 \rho_{\text{X-H}} - \nabla^2 \rho_{\text{X-H}}^0) / \nabla^2 \rho_{\text{X-H}}^0 \right]^2 \right\}^{1/2} \quad (6) \end{aligned}$$

where $r_{\text{X-H}}$, $\rho_{\text{X-H}}$ and $\nabla^2 \rho_{\text{X-H}}$ correspond to the parameters of proton donating bond involved in H-bonding: the bond length, electronic density at H–X BCP, the Laplacian of that density, respectively, and $r_{\text{X-H}}^0$, $\rho_{\text{X-H}}^0$ and $\nabla^2 \rho_{\text{X-H}}^0$ correspond to the same parameters of X–H bond not involved in H-bond formation.

The parameter describing H-bond strength may be based only on geometrical data as it was defined by Eq. (4) or only on topological parameters:

$$\Delta_{\text{el}} = (\rho_{\text{X-H}}^0 - \rho_{\text{X-H}}) / \rho_{\text{X-H}}^0. \quad (7)$$

$$\Delta_{\text{lap}} = \left| (\nabla^2 \rho_{\text{X-H}}^0 - \nabla^2 \rho_{\text{X-H}}) / \nabla^2 \rho_{\text{X-H}}^0 \right|. \quad (8)$$

Normalized parameters given by Eqs. (4), (6)–(8)—i.e. Δ_{geo} , Δ_{com} , Δ_{el} and Δ_{lap} , respectively, may be treated as measures of H-bond strength and for the sample investigated here all correlate with H-bond energy. It was shown for Δ_{geo} parameter in Fig. 4.

The study of shifts in electron density that accompany the formation of H-bond may be very useful in an analysis of molecular interactions. Upon forming the complexes, a certain amount of electron density is transferred from the proton acceptor to the donor molecule [26]. The charges transferred from proton acceptors to donor molecules for complexes investigated here are given in Table 3. We see that the electron shift only roughly corresponds to the H-bonding strength—the greatest transfer is for $\text{CH}_3\text{CN} + \text{HF}$, $\text{LiCN} + \text{HF}$, $\text{LiCN} + \text{HCl}$ and $\text{BH}_2\text{CN} \cdots \text{HF}$ complexes; 40, 39, 37 and 39 me, respectively. The effect of the electron shift causes the dipole moment of the complex to differ from a simple vector sum of the moments of the two monomers. These differences ($\Delta\mu$ s) along the

Table 4
Shift in frequency of H–F (H–Cl) stretch caused by complexation with R–CN; results were computed at MP2/6-311++G** level; ratio of intensity in the complex/isolated subunit is also given

Proton acceptor	HF donator		HCl donator	
	$\Delta\nu$	I/I_0	$\Delta\nu$	I/I_0
CH ₃ CN	–317	8.14	–165	19.28
HCN	–245	6.11	–116	12.97
FCN	–214	5.84	–98	11.65
CH ₂ FCN	–253	7.02	–119	14.70
CHF ₂ CN	–208	6.18	–91	11.91
CF ₃ CN	–176	5.59	–73	10.11
LiCN	–554	11.22	–395	39.73
NO ₂ CN	–149	5.43	–62	9.39
NH ₂ CN	–333	8.37	–177	20.68
BH ₂ CN	–262	7.35	–127	15.60
HOCN	–287	7.01	–146	16.75

direction of the X–H···N axis are also given in Table 3. The greatest $\Delta\mu$ values were obtained for LiCN + HF and LiCN + HCl complexes.

Table 4 shows the shifts in frequency ($\Delta\nu$) of the proton donating bonds for the complexes investigated here. These shifts correlate with the H-bond energies and are the greatest for the strongest hydrogen bonds. For LiCN···HF, LiCN···HCl and NH₂CN···HF they are the greatest; the lowest value of the shift is for NO₂CN···HCl dimer for which the H-bond energy is the lowest—2.4 kcal/mol. The correlation coefficient between H-bond energy and $\Delta\nu$ for the whole sample amounts to 0.991. Similarly the intensity ratio I/I_0 and H-bond energy are well correlated but if both subsamples (with HF donator and with HCl donator) are analysed separately.

Table 5
Factor loadings for the sample investigated here and for seven energetic, topological and geometrical variables

Variable	Factor loadings
Δ_{geo}	0.924
Δ_{el}	0.939
Δ_{lap}	0.917
$r_{\text{H}\cdots\text{N}}$	–0.967
$\rho r_{\text{H}\cdots\text{N}}$	0.986
$\nabla^2 \rho r_{\text{H}\cdots\text{N}}$	0.957
E_{HB}	–0.974
Eigenvalue	6.3441
Percentage of total variance	90.63

The results of this study on R–CN···HX complexes may be supported by factor analysis [38–40]. Factor analysis is often applied in chemical and physical studies; one of the first applications of this statistical technique in chemistry was connected with the thermodynamic data describing solvent effects [41].

Factor analysis is applied in this study for the geometrical, energetic and topological data describing H-bridges. The following variables are taken into account: E_{HB} —the H-bond energy, three variables corresponding to the proton donating bond (defined by Eqs. (4), (7) and (8)) and corresponding to its length, electron density at BCP and the Laplacian of its density; and three variables corresponding to H···N contact; H···N distance, electron density at H···Y BCP and its Laplacian.

For the sample considered in this study (22 complexes and seven variables described above) only one factor was retained. The eigenvalue for the sample amounts to 6.34 which means that one factor accounts for 90.63% of the total variance. It is worth mentioning that for the second factor the eigenvalue amounts to 0.41 which corresponds only to 5.83% of the total variance. Hence the second factor was not taken into account since the factor should correspond at least to the eigenvalue of unity [40]—14.29% of the total variance in the case of the sample considered here.

Table 5 presents factor loadings for seven variables taken into account in factor analysis. The loadings inform about the correlations between old variables and factors (new variables). We see that the new variable (one factor retained) well correlates with all old variables. It means that all parameters considered as H-bond strength—old variables presented in Table 5 are equivalent. All may be replaced by one factor.

4. Conclusions

The values of binding energies (Table 1) show that for R–C≡N···HX complexes investigated here we may say about H-bonds of the mediate strength. The greatest binding energies are observed for the complexes with LiCN as a proton accepting molecule. We observe two subsamples for the sample of complexes: the first one with HF molecule as a proton

donating species and the second one with HCl molecule. Such situation is connected with the parameters of the proton donating bond as those used to describe the H-bond strength. However, if we apply the normalized parameters, Δ -parameters or the electronic density at H \cdots N BCP ($\rho_{\text{H}\cdots\text{N}}$) they may be treated as measures of H-bond strength for the whole sample. In other words they may be applied for heterogeneous samples. Factor analysis shows that all variables used for describing the H-bond are strictly correlated and can then be equally used to describe the properties of H-bonds.

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