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# The electrostatic potential at atomic sites as a reactivity index in the hydrogen bond formation

B. Galabov\*, P. Bobadova-Parvanova, S. Ilieva, V. Dimitrova

*Department of Chemistry, University of Sofia, St Kliment Ohridsky, 1 Janes Bourchier Ave., 1164 Sofia, Bulgaria*

Received 7 August 2002; accepted 15 November 2002

## Abstract

The paper reviews results from computational studies by molecular orbital and density functional theories on several series of hydrogen bonded complexes. These studies aim at quantifying the reactivity of molecules for the complexation process. Excellent linear relationships are found between the electrostatic potential values at the sites of the electron donor and electron accepting atoms and the energy of hydrogen bond formation ( $\Delta E$ ). The series studied are: (a) complexes of R-CHO and R-CN molecules with hydrogen fluoride; (b) complexes of mono-substituted acetylene derivatives with ammonia; (c) (HCN)<sub>n</sub> hydrogen bonded cluster for  $n = 2-7$ . All 22 studied complexes of carbonyl and nitrile compounds with hydrogen fluoride fall in the same dependence between the energy of hydrogen bond formation and the electrostatic potential at the atomic site of the carbonyl oxygen and nitrile nitrogen atoms, with linear regression correlation coefficient  $r = 0.979$ . In the case of complexes of mono-substituted acetylene and diacetylene derivatives with NH<sub>3</sub>, the correlation coefficient for the dependence between the electrostatic potential at the acidic hydrogen atom and  $\Delta E$  equals 0.996. For the series of hydrogen bonded (HCN)<sub>n</sub> clusters, the correlation coefficient for the relationship between the electrostatic potential at the end nitrogen atom and  $\Delta E$  is  $r = 0.9996$ . Similarly, the analogous relationship with the electrostatic potential at the end hydrogen atom has a regression coefficient equal to 0.9994. The dependencies found are theoretically substantiated by applying the Morokuma energy decomposition scheme. The results show that the molecular electrostatic potential at atomic sites can be successfully used to predict the ability of molecules to form hydrogen bonds.

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**Keywords:** Hydrogen bonding; Molecular electrostatic potential; Carbonyl derivatives; Nitrile derivatives; Acetylene derivatives; Hydrogen bond descriptor

## 1. Introduction

In the present study we summarize computational results on the reactivity of several series of organic compounds with respect to hydrogen bond formation.

The principal aim is to quantify the ability of isolated molecules to form hydrogen bonds with model proton donor and proton acceptors. It is well known that electrostatic forces have essential role in hydrogen bonding [1–14]. Thus, theoretically estimated or experimental molecular quantities linked to the electric charge distribution in molecules are of interest in the search for appropriate reactivity descriptors for the hydrogen bonding process. Atomic charges at

\* Corresponding author. Tel.: +359-2-6256-421; fax: +359-2-9625-438.

E-mail address: galabov@chem.uni-sofia.bg (B. Galabov).

the proton donor and acceptor atoms and minima and maxima of the molecular electrostatic potential are natural choices in this respect. The position of the minima of the molecular electrostatic potential associated with the electron donating centers in isolated molecules have been successfully used to predict the sites and directionality of hydrogen bonds in a number of systems [15–17]. In most of these studies properties of the molecular surface electrostatic potential have been used.

In the present paper we review results obtained in this laboratory on the applicability of molecular electrostatic potential values at the sites of the binding atoms as reactivity descriptors for the process of hydrogen bonding. The systems studied are: (a) complexes of aliphatic carbonyl derivatives with hydrogen fluoride; (b) complexes of aliphatic nitrile derivatives with hydrogen fluoride; (c) complexes of monosubstituted acetylenes with ammonia; (d) hydrogen bonded (HCN)<sub>n</sub> clusters.

## 2. Computational details

Ab initio MO and density functional theory computations were carried out to evaluate properties of isolated molecules and hydrogen bonded complexes at the following levels of theory; (a) MP2/6-31 + G(d,p) ab initio computations for the aliphatic carbonyl and nitrile derivatives and their complexes; (b) B3LYP/6-31G(d,p) computations for the complexes of acetylene derivatives with ammonia; (c) HF/6-31 + G(d) ab initio computations for the (HCN)<sub>n</sub> clusters,  $n = 2-7$ . In determining the energy of hydrogen bond formation, the zero-point vibrational energy was taken into account. A scaling factors of 0.9135 for HF, 0.9676 for MP2 and 0.9804 for B3LYP calculations were used [18]. The obtained interaction energies were also corrected for the basis set superposition error (BSSE) including the fragment relaxation energy terms [19]. All calculations were carried out with the GAUSSIAN92 and 98 program packages [20].

Electric charge properties of the isolated molecules from the series studied were theoretically determined in order to describe the reactivity of the molecules studied with respect to the process of hydrogen bonding. Atomic charges according to the schemes of

the Mulliken [21], Breneman and Wiberg (CHELPG) [22], Merz-Kollman-Singh (MK) [23] and Bader (AIM) [24] were evaluated using the GAUSSIAN98 program package [20]. The molecular electrostatic potential at the sites of the binding atoms were also evaluated. The electrostatic potential at a particular nucleus (Y) is defined by Eq. (1) at  $r = R_Y$  (radius vector of the nuclei) as the term at  $R_Y = R_A$  is dropped out [15,19]:

$$V_Y \equiv V(R_Y) = \sum_{A \neq Y} \frac{Z_A}{|R_Y - R_A|} - \int \frac{\rho(r')}{|R_Y - r'|} dr' \quad (1)$$

In this equation  $Z_A$  is the charge on nucleus A with radius-vector  $R_A$ ,  $\rho(r)$  is the electronic density function of the respective molecule as obtained from ab initio calculations and  $r'$  is a dummy integration variable. Eq. (1) is written in atomic units and contains a summation over all atomic nuclei, treated as positive point charges as well as integration over the continuous distribution of the electronic charge. The molecular electrostatic potential at each atom of the isolated molecules from the series studied is obtained as a standard option of the GAUSSIAN98 program [20]. It should be underlined that the electrostatic potentials at nuclei (EPN) of the monomer molecules were determined in the present study. These quantities can, therefore, be considered as intrinsic properties of the monomers and not of the hydrogen bonded complexes.

## 3. Results and discussion

### 3.1. Complexes of aliphatic carbonyl and nitrile derivatives with hydrogen fluoride

In the original studies [25,26] on aliphatic carbonyl and nitrile compounds of the type R-CHO and R-CN, respectively, where R = -H, -OH, -SH, -OCH<sub>3</sub>, -NH<sub>2</sub>, -NO<sub>2</sub>, -CN, -F, -Cl, -CH<sub>3</sub> and -CF<sub>3</sub> we used HF/6-31 + G(d,p) ab initio computations in estimating the binding energies and properties of isolated molecules and their complexes with hydrogen fluoride. Here we report MP2/6-31 + G(d,p) results for the same systems. The higher level computations are aimed at obtaining more reliable estimates for the respective properties. The calculated fully corrected

Table 1

MP2/6-31 + G(d,p) ab initio calculated corrected energy of hydrogen bond formation ( $\Delta E^{\text{COR}}$ ) and molecular electrostatic potential at the carbonyl oxygen ( $V_O$ ) and at the nitrile nitrogen ( $V_N$ ) in the isolated molecules

Carbonyl derivatives			Nitrile derivatives		
Molecule	$\Delta E^{\text{COR}}$ (kcal/mol)	$V_O$ (a.u.)	Molecule	$\Delta E^{\text{COR}}$ (kcal/mol)	$V_N$ (a.u.)
HCHO	−4.823	−22.2841	HCN	−4.713	−18.3057
HOCHO	−4.987	−22.2919	HOCN	−5.642	−18.3220
HSCHO	−4.971	−22.2829	HSCN	−5.490	−18.3116
CH <sub>3</sub> OCHO	−5.767	−22.3025	CH <sub>3</sub> OCN	−6.261	−18.3334
NH <sub>2</sub> CHO	−7.331	−22.3315	NH <sub>2</sub> CN	−6.922	−18.3449
NO <sub>2</sub> CHO	−1.740	−22.2049	NO <sub>2</sub> CN	−2.526	−18.2350
CNCHO	−3.048	−22.2357	NCCN	−2.883	−18.2505
FCHO	−2.904	−22.2544	FCN	−4.037	−18.2896
ClCHO	−3.165	−22.2523	ClCN	−4.742	−18.2975
CH <sub>3</sub> CHO	−6.048	−22.3027	CH <sub>3</sub> CN	−6.262	−18.3345
CF <sub>3</sub> CHO	−3.056	−22.2401	CF <sub>3</sub> CN	−3.099	−18.2629

binding energies for the two series of complexes are presented in Table 1. The optimized structures of the hydrogen-bonded complexes for acetaldehyde and acetonitrile are shown in Fig. 1. In this study the attention is focused on complexes formed at the carbonyl and nitrile groups binding sites. It should be mentioned that the magnitudes of the BSSE corrections at the MP2/6-31 + G(d,p) level of theory are 3 to 8 times higher than the respective values at the HF/6-31 + G(d,p) level [25]. This is a further evidence that the inclusion of electron correlation results in increasing the BSSE correction [27,28]. Attempt to rationalize the reactivity of the two series of molecules in terms of theoretically calculated Mulliken, CHELPG and MK atomic charges did not produce positive results. Details on the dependences between the binding energies and the atomic charges will be reported in the subsequent section for complexes of acetylenic compounds with ammonia.

The molecular electrostatic potential at the sites of the proton accepting atoms offers an excellent opportunity to discuss the reactivity of isolated molecules from the series studied. As mentioned, minima in the molecular surface electrostatic potential [17] as well as values of the electrostatic potential at selected points in the vicinities of the binding atoms [15] have been used to explain the ability of molecules to form hydrogen bonds. Here we select a simply defined and easily accessible quantity to express the electrostatic driving force for the complexation

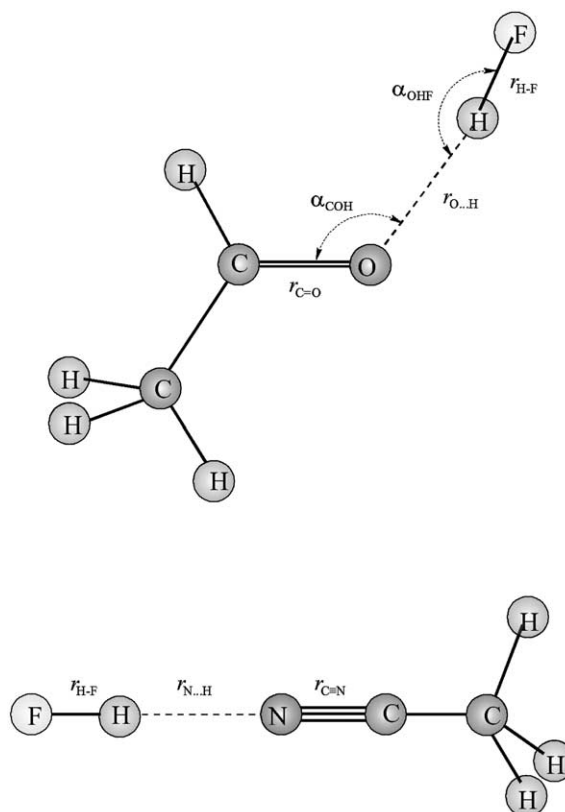


Fig. 1. Hydrogen bonded complexes of acetaldehyde and acetonitrile with HF.

process: the atomic potentials at the binding atoms. These quantities are obtained as a standard option of the GAUSSIAN program. The computed values for the electrostatic potentials at the sites of the carbonyl oxygen ( $V_O$ ) and nitrile nitrogen ( $V_N$ ) atoms are given in Table 1. The statistical analysis reveals that the binding energies for the two series of complexes are linearly related with the respective atomic potentials  $V_O$  and  $V_N$ . The respective linear regression correlation coefficients are  $r = 0.981$  for the carbonyl compounds, and  $r = 0.988$  for the aliphatic nitrile compounds. Interestingly, the dependence between changes in the binding energy  $\Delta E'$  ( $\Delta E' = \Delta E^{R-CN} - \Delta E^{H-CN}$  and  $\Delta E' = \Delta E^{R-CHO} - \Delta E^{H-CHO}$ ) and the similarly defined  $\Delta V$  ( $\Delta V = \Delta V^{R-CN} - \Delta V^{H-CN}$  and  $\Delta V = \Delta V^{R-CHO} - \Delta V^{H-CHO}$ ) values fall into the same linear regression equation for the two series of compounds ( $r = 0.979$ ). The plot is shown in Fig. 2 for all 22 compounds from the carbonyl and nitrile series. The linear regression result is:

$$\Delta E' = 0.02 \Delta V + 0.01$$

(2)

$n = 22, r = 0.979, SD = 0.01$

The results clearly show that the molecular electrostatic potentials at the sites of the proton accepting atoms can be used as reactivity descriptor of the respective molecular sites.

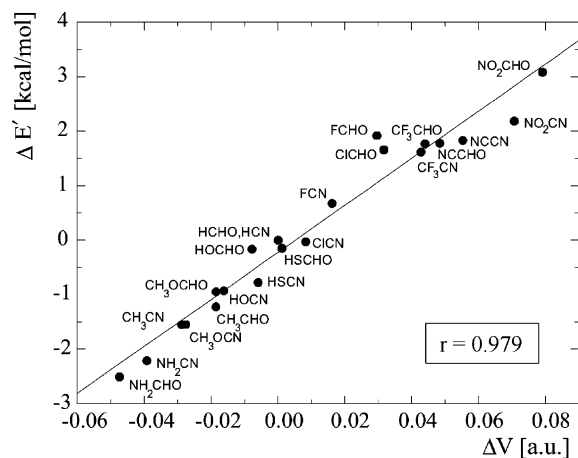


Fig. 2. Dependence between shifts of calculated at MP2/6-31 + G(d,p) level energy of hydrogen bond formation and molecular electrostatic potential with respect to the values: for the simplest member of the respective series ( $R = H$ ).

### 3.2. Complexes of monosubstituted acetylene derivatives with ammonia

In this section we briefly review the results from a computational study [29] on the applicability of several types of molecular structure descriptors associated with the electric charge distribution to rationalize the reactivity of a series of monosubstituted acetylene derivatives towards the process of hydrogen bond formation with ammonia as a model proton acceptor. In a recent computational study Hartmann and Radom [30] reported state-of-the-art computational results for the acetylene-ammonia dimer. The authors apply a number of theoretical methods (HF, B3LYP, MP2, QCISD and CCSD(T)) and basis sets from 6-31G(d) to 6-311 + G(3df,2p). The results described in this section illustrate the effect of changes in structure of the proton donor molecules on the energy profile of the interaction in the case of monosubstituted acetylene derivatives with general formula  $R-C\equiv C-H$ , where  $R = H, F, Cl, CH_3, CH_2F, CHF_2, CF_3, CH_2Cl, CHCl_2, CCl_3, CN, H-C\equiv C, F-C\equiv C, Cl-C\equiv C$ . Ammonia is used as a model proton acceptor in the respective hydrogen bonded complexes. The selected series of molecules and their complexes offer also an opportunity to analyze the reactivity of C–H acidic systems. Density functional theory at B3LYP/6-31G(d,p) level was applied in calculating the optimized geometries and vibrational frequencies for the isolated acetylenic derivatives and their hydrogen-bonded complexes with ammonia. The estimated energies of hydrogen-bond formation were corrected for zero-point vibrational energy, basis-set superposition error and fragment relaxation energy contributions. The calculated fully corrected energy of hydrogen bond formation ( $\Delta E^{COR}$ ) for the complexes of monosubstituted acetylenes and diacetylenes with ammonia are given in Table 2. The optimized structures of the hydrogen-bonded complexes for some molecules of the series are shown in Fig. 3.

Electric charge properties of the isolated acetylene derivatives were theoretically determined in order to describe the reactivity of the molecules studied with respect to the process of hydrogen bonding with ammonia. Mulliken, CHELPG, MK, and AIM atomic charges were evaluated using

Table 2

B3LYP/6-31G(d,p) ab initio calculated non-corrected energy of hydrogen-bond formation ( $\Delta E$ ), zero-point vibrational energy correction ( $\Delta E^{\text{ZPE}}$ ), BSSE correction ( $\Delta E^{\text{BSSE}}$ ), relaxation correction ( $\Delta E^{\text{REL}}$ ) and totally corrected energy ( $\Delta E^{\text{COR}}$ ) for the substituted acetylene derivatives. All values are in kcal/mol

Acetylenic monomer	$\Delta E$	$\Delta E^{\text{ZPE}}$	$\Delta E^{\text{BSSE}}$	$\Delta E^{\text{REL}}$	$\Delta E^{\text{COR}}$
H-C≡C-H	-5.287	1.402	0.896	0.111	-2.878
F-C≡C-H	-5.529	1.397	0.891	0.163	-3.078
Cl-C≡C-H	-5.882	1.352	0.873	0.141	-3.516
H <sub>3</sub> C-C≡C-H	-4.354	1.243	0.838	0.111	-2.162
FH <sub>2</sub> C-C≡C-H	-5.549	1.310	0.829	0.147	-3.263
F <sub>2</sub> HC-C≡C-H	-6.501	1.359	0.803	0.209	-4.130
F <sub>3</sub> C-C≡C-H	-7.240	1.417	0.825	0.233	-4.765
ClH <sub>2</sub> C-C≡C-H	-5.754	1.331	0.802	0.169	-3.452
Cl <sub>2</sub> HC-C≡C-H	-6.797	1.377	0.757	0.235	-4.428
Cl <sub>3</sub> C-C≡C-H	-7.425	1.397	0.712	0.270	-5.046
NC-C≡C-H	-8.190	1.516	0.769	0.243	-5.662
H-C≡C-C≡C-H	-6.049	1.393	0.820	0.157	-3.679
F-C≡C-C≡C-H	-5.862	1.337	0.820	0.153	-3.552
Cl-C≡C-C≡C-H	-6.127	1.393	0.820	0.155	-3.759

the GAUSSIAN98 program package [20]. Finally the electrostatic potential at the site of the C-H hydrogen were also theoretically estimated. The computed values are given in Table 3. All of these quantities were plotted against the calculated binding energies. The partial atomic charges at the binding site of the substituted acetylene derivatives are expected to describe the reactivity of the molecules towards formation of hydrogen bonded complexes with ammonia. The results obtained can be summarized as follows: (1) The Mulliken charges do not correlate well with the variation of binding energy (linear regression correlation coefficient  $r = 0.750$ ); (2) The electrostatic potential related atomic charges CHELPG and MK do not provide a quantitative description of the ability of the acetylenic compounds to form a hydrogen bond with ammonia. The respective linear regression coefficients are  $r = 0.087$  for CHELPG charges and  $r = 0.142$  for MK charges; (3) A satisfactory description of the hydrogen bonding ability of the acetylenic derivatives is provided by the AIM atomic charges of Bader [24]. The following equation linking binding energy and

AIM atomic charges is obtained:

$$\Delta E^{\text{COR}} = -68.17Q_{\text{H}}^{\text{AIM}} + 5.78 \quad (3)$$

$$n = 14, \quad r = 0.963, \quad \text{SD} = 0.26$$

The dependence is illustrated in Fig. 4.

It was of interest, in view of the results for aliphatic carbonyl and nitrile derivatives, to study the applicability of the atomic electrostatic potential as descriptor of the hydrogen bonding ability of proton donor molecules such as the studied series of acetylene derivatives. The atomic potential values obtained are given in Table 3. An excellent linear link, as shown in Fig. 5, is found between the electrostatic potential at the acetylenic hydrogen and the binding energy. The relationship is as follows:

$$\Delta E^{\text{COR}} = -59.46V_{\text{H}} - 65.02 \quad (4)$$

$$n = 14, \quad r = 0.997, \quad \text{SD} = 0.08$$

It should be underlined that in recent years the molecular surface electrostatic potential (MSEP) has been mostly employed in describing hydrogen bonding [17,31,32]. In strict scientific terms the use of the MSEP appears more plausible. However, the analysis involves considerable additional computations. The present results underline the applicability of the electrostatic potential at nuclei as a reactivity index describing in quantitative terms the ability of proton donor molecules to form hydrogen bonds. As is well known several different factors, besides electrostatic forces, contribute to hydrogen bonding. According to Morokuma et al. [33–35] the following terms contribute to the binding energy: electrostatic interaction, polarization interaction, exchange repulsion, and charge transfer of electron delocalization interaction. It was, therefore, of considerable interest to explain why such perfect linear relationship between binding energy and electrostatic potential at nuclei was found. The treatment of this problem is presented in Section 3.4.

### 3.3. (HCN)<sub>n</sub> hydrogen-bonded clusters

We have seen that the electrostatic potential at the nuclei participating in hydrogen bonding both as proton acceptors and proton donors can adequately describe the reactivity of the respective molecules towards the complexation process. In this section we

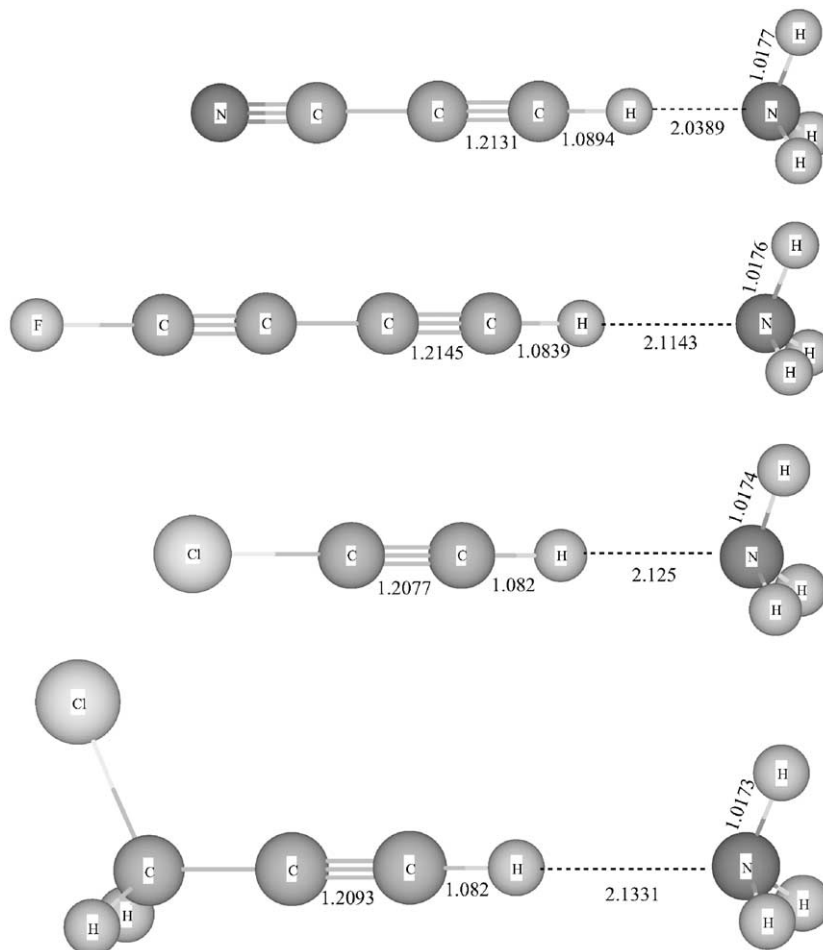


Fig. 3. Optimized structures of hydrogen-bonded complexes for some acetylene derivatives with ammonia from B3LYP/6-31(d,p) computations.

present briefly the principal results from the computational study on the applicability of the electrostatic potential in analyzing the co-operative effects in longer hydrogen bonded associates of the type  $(\text{HCN})_n$ ,  $n = 2-7$  [36]. It is known that HCN molecules form linear hydrogen-bonded clusters in all phases [18,37]. Ab initio MO results of King and Weinhold [38] have revealed that the co-operative effects in  $(\text{HCN})_n$  are essentially non-linear and can be rationalized in terms of  $\pi_{\text{N}} \rightarrow \sigma_{\text{CH}}^*$  'charge transfer' nature of hydrogen bonding. More recently Sokolov [14] demonstrated that the non-linear effects can be explained with a simple model including Coulomb interaction of the effective atomic charges,

inductive action of these charges on the neighboring chemical bonds and the exchange repulsion of the atoms. As was shown in the previous parts, the molecular electrostatic potential at atomic sites can quantitatively predict the variations of the energy of hydrogen bond formation for several series of molecules. It was of interest, therefore, to see whether such easily obtainable, accurately defined, and simple molecular quantity can adequately explain the non-linear co-operative effects of  $(\text{HCN})_n$  clusters and serve as a reactivity index in describing the formation of hydrogen bonded clusters. The properties of hydrogen-bonded  $(\text{HCN})_n$  associates for  $n = 2-7$  were calculated at HF/6-31 + G(d) level of theory.



Table 3

B3LYP/6-31G(d,p) ab initio calculated values of atomic charges (in electrons) at the acetylenic hydrogen atom in isolated molecules  $Q_H$ , derived via different procedures (Mulliken, CHELPG, MK and AIM) and molecular electrostatic potential  $V_H$  (in atomic units)

Acetylenic monomer	$Q_H^{\text{Mulliken}^a}$	$Q_H^{\text{CHELPG}^b}$	$Q_H^{\text{MK}^c}$	$Q_H^{\text{AIM}^d}$	$V_H^e$
H-C≡C-H	0.1487	0.2372	0.2664	0.1257	−1.0444
F-C≡C-H	0.1534	0.2939	0.3202	0.1403	−1.0392
Cl-C≡C-H	0.1604	0.2623	0.2678	0.1387	−1.0349
H <sub>3</sub> C-C≡C-H	0.1477	0.2706	0.3154	0.1139	−1.0595
FH <sub>2</sub> C-C≡C-H	0.1647	0.2638	0.3037	0.1306	−1.0396
F <sub>2</sub> HC-C≡C-H	0.1776	0.2611	0.2959	0.1429	−1.0247
F <sub>3</sub> C-C≡C-H	0.1887	0.2602	0.2941	0.1524	−1.0134
ClH <sub>2</sub> C-C≡C-H	0.1676	0.2739	0.3131	0.1335	−1.0364
Cl <sub>2</sub> HC-C≡C-H	0.1809	0.2816	0.3136	0.1468	−1.0211
Cl <sub>3</sub> C-C≡C-H	0.1904	0.2926	0.3087	0.1565	−1.0103
NC-C≡C-H	0.2095	0.2576	0.2789	0.1666	−0.9985
H-C≡C-C≡C-H	0.2004	0.2622	0.2892	0.1417	−1.0325
F-C≡C-C≡C-H	0.1956	0.2788	0.2994	0.1385	−1.0351
Cl-C≡C-C≡C-H	0.2029	0.2646	0.2789	0.1424	−1.0309

<sup>a</sup> Ref. [21].

<sup>b</sup> Ref. [22].

<sup>c</sup> Ref. [23].

<sup>d</sup> Ref. [24].

<sup>e</sup>  $V_H$ —electrostatic potential at the site of the hydrogen atom in the acetylenic C–H bond in isolated molecules.

The choice of this basis set allows full comparison with the results of King and Weinhold [38]. Harmonic vibrational frequencies (at the same level of theory) confirmed that the located structures correspond to minima having no imaginary frequencies. The non-corrected energy of hydrogen bond formation calculated as a difference between the respective SCF energies ( $\Delta E_n^{\text{SCF}}$ ), the zero-point vibrational energy correction ( $\Delta E_n^{\text{ZPE}}$ ), the counterpoise correction ( $\Delta E_n^{\text{BSSE}}$ ), the relaxation correction ( $\Delta E_n^{\text{REL}}$ ), and totally corrected energy of hydrogen bond formation ( $\Delta E^{(n)}$ ) of the hydrogen-bonded (HCN)<sub>n</sub> clusters studied are presented in Table 4. It is worth mentioning that the values of  $\Delta E_n^{\text{BSSE}}$  and  $\Delta E_n^{\text{REL}}$  are of the same order of magnitude. This is a further evidence that the omission of the fragment relaxation energy terms in estimating the BSSE corrections can introduce significant errors [26,39]. As is discussed by King and Weinhold [38] the dependence of  $\Delta E^{(n)}$  versus  $n$  is non-linear. The values of the interaction energy tend asymptotically to approximately 5 kcal/mol. This is a manifestation of the non-linear co-operative effects in (HCN)<sub>n</sub> clusters. As will be shown further in the text the non-linear dependence between  $\Delta E^{(n)}$  and  $n$  can be

predicted in terms of molecular electrostatic potential at the sites of the binding atoms. The HF/6-31 + G(d) ab initio calculated molecular electrostatic potentials at the end nitrogen  $V_N^{(n)}$  and hydrogen  $V_H^{(n)}$  atom for the hydrogen-bonded (HCN)<sub>n</sub> clusters studied are presented in Table 5. These quantities are also defined in Fig. 6. As mentioned above,

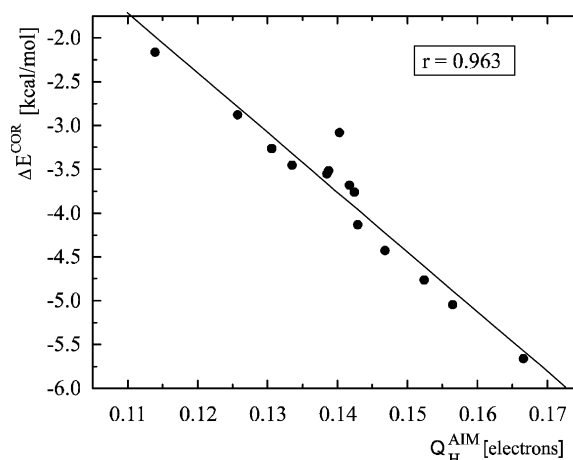


Fig. 4. Dependence between energy of hydrogen-bond formation ( $\Delta E^{\text{COR}}$ ) and the partial hydrogen atomic charge in the isolated acetylene derivatives, derived via AIM scheme.



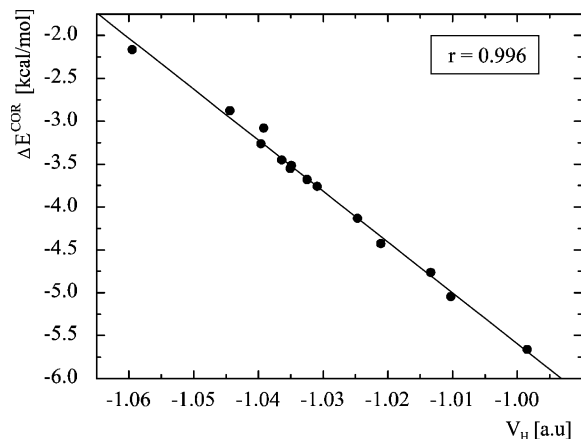


Fig. 5. Dependence between energy of hydrogen-bond formation ( $\Delta E^{\text{COR}}$ ) and the molecular electrostatic potential at the acetylenic hydrogen atoms in isolated molecules ( $V_{\text{H}}$ ).

the absolute values of the energy of formation of the last hydrogen bond increase non-linearly with increased cluster size and tend asymptotically to a given value. It can be seen from Table 5 that the absolute values of the molecular electrostatic potential at the end nitrogen atom ( $|V_{\text{N}}^{(n)}|$ ) also increase non-linearly with  $n$ . On the contrary, the absolute values of molecular electrostatic potential at the end hydrogen atom ( $|V_{\text{H}}^{(n)}|$ ) decrease non-linearly with increased  $n$ . It can also be noted that the higher is  $|V_{\text{N}}^{(n)}|$ , the smaller is  $|V_{\text{H}}^{(n)}|$  and there is a perfect linear correlation between these two quantities ( $r = 0.99997$ ). Fig. 7 represents the dependence between

Table 4

HF/6-31 + G(d) ab initio calculated non-corrected energy of hydrogen bond formation ( $\Delta E_n^{\text{S}}$ ), zero-point vibrational energy correction ( $\Delta E_n^{\text{ZPE}}$ ), counterpoise correction ( $\Delta E_n^{\text{CP}}$ ), relaxation correction ( $\Delta E_n^{\text{REL}}$ ), and totally corrected energy of hydrogen bond formation ( $\Delta E^{(n)}$ ) for the hydrogen bonded (HCN) $_n$  clusters studied. All values are in kcal/mol

$n$	$\Delta E_n^{\text{S}}$	$\Delta E_n^{\text{ZPE}}$	$\Delta E_n^{\text{CP}}$	$\Delta E_n^{\text{REL}}$	$\Delta E^{(n)}$
2	-4.342	0.759	0.147	0.089	-3.347
3	-5.407	0.794	0.130	0.118	-4.365
4	-5.769	0.809	0.126	0.128	-4.706
5	-5.922	0.814	0.124	0.131	-4.853
6	-5.996	0.818	0.146	0.112	-4.920
7	-6.039	0.821	0.149	0.122	-4.947

Table 5

HF/6-31 + G(d) ab initio calculated molecular electrostatic potentials at the end nitrogen ( $V_{\text{N}}^{(n)}$ ) and hydrogen ( $V_{\text{H}}^{(n)}$ ) atom for the hydrogen bonded (HCN) $_n$  clusters studied. All values are in a.u.

$n$	$V_{\text{N}}^{(n)}$	$V_{\text{H}}^{(n)}$
1	-18.3230	-0.9559
2	-18.3464	-0.9331
3	-18.3543	-0.9252
4	-18.3579	-0.9215
5	-18.3599	-0.9196
6	-18.3611	-0.9183
7	-18.3619	-0.9175

$\Delta E^{(n)}$  and  $V_{\text{N}}^{(n-1)}$ . The linear regression result is:

$$\Delta E^{(n)} = 42.53V_{\text{N}}^{(n-1)} + 775.94 \quad (5)$$

$$n = 6, \quad r = 0.9996, \quad \text{SD} = 0.02$$

The relation found clearly shown that the molecular electrostatic potential can adequately describe the cooperative effects in hydrogen bonding. When  $n$  is small, with increasing the cluster size molecular electrostatic potential at the end nitrogen atom becomes more negative. Consequently, the participation of the atom in the formation of a new hydrogen bond becomes more favorable. For higher  $n$  there is a gradual saturation,  $V_{\text{N}}^{(n)}$  becomes approximately constant value and consequently the energies of all new formed hydrogen bonds become approximately equal. It was interesting to also study the dependence between  $\Delta E^{(n)}$  and the molecular electrostatic potential at the other atom participating in hydrogen bond formation: the end hydrogen atom of each cluster. In the light of the fact mentioned above that there is perfect relation between  $V_{\text{N}}^{(n)}$  and  $V_{\text{H}}^{(n)}$ , a linear dependence can be expected. Indeed, as can be seen from Fig. 8, there is an excellent correlation between  $\Delta E^{(n)}$  and  $V_{\text{H}}^{(n-1)}$ . The obtained linear regression coefficient is

$$\Delta E^{(n)} = 43.12V_{\text{H}}^{(n-1)} - 44.58 \quad (6)$$

$$n = 6, \quad r = 0.9994, \quad \text{SD} = 0.02$$

As expected, the trends of changes of the molecular electrostatic potentials of nitrogen and hydrogen atom are opposite reflecting the different role of the two atoms in the process of hydrogen bonding. The

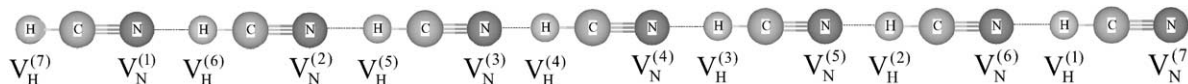


Fig. 6. Structure of hydrogen-bonded  $(\text{HCN})_n$  clusters studied and definition of geometrical parameters and molecular electrostatic potentials ( $V_N^{(n-1)}$ ,  $V_H^{(n-1)}$ ).

more negative the molecular electrostatic potential of the electron donating atom is, the higher is its ability to form hydrogen bonds. On the contrary, the less negative the molecular electrostatic potential of the electron accepting atom is, the higher is its ability to form a hydrogen bond.

### 3.4. Theoretical considerations

In the previous sections it was demonstrated that the molecular electrostatic potential at the atoms participating in hydrogen bonding can be successfully employed as a reactivity descriptor reflecting the ability of isolated molecules to form hydrogen bonds. These dependences are in accordance with literature data showing that minima and maxima in the molecular surface electrostatic potential can be used to rationalize the hydrogen bonding processes for series of related molecules. As already mentioned in Section 3.2, there are other energy terms contributing to the hydrogen bonding apart from the term associated with the electrostatic attraction. According to the energy decomposition analysis (EDA) of Morokuma et al. [33–35] the binding energy of the interacting system can be decomposed into the following components:

$$\Delta E = \text{ES} + \text{PL} + \text{EX} + \text{CT} + \text{MIX} \quad (7)$$

ES is the electrostatic interaction term reflecting the interaction between the undistorted electron distribution of the two monomers. PL, the polarization interaction term, accounts for the effect of the polarization of the electron distribution in the two monomers. EX is the exchange repulsion term, accounting for the short-range repulsion due to the overlap of charge densities of the two interacting molecules. CT is the charge transfer of electron delocalization interaction term. Finally, MIX is a coupling term, accounting for higher order interactions. These energy decomposition terms were evaluated by the EDA procedure implemented in the GAMESS \*program package [40].

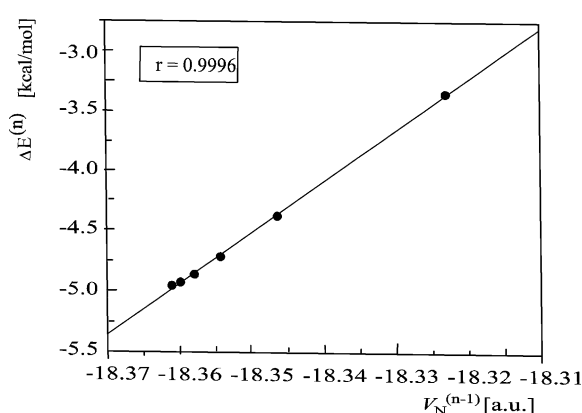


Fig. 7. Dependence between the energy of hydrogen bond formation ( $\Delta E^{(n)}$ ) and the molecular electrostatic potential at the end nitrogen atom ( $V_N^{(n-1)}$ ) for the hydrogen-bonded  $(\text{HCN})_n$  clusters studied,  $n = 2-7$ .

The calculated total binding energies and the different decomposition terms for complexes of 15 monosubstituted acetylenes with ammonia are presented in Table 6. As can be seen the highest contribution to the energy comes from the electrostatic interaction and the exchange repulsion terms.

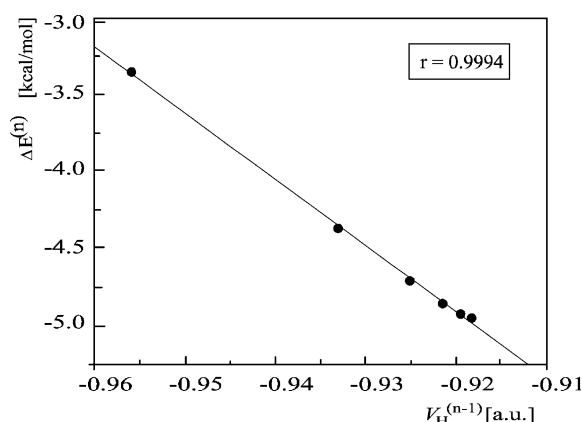


Fig. 8. Dependence between the energy of hydrogen bond formation ( $\Delta E^{(n)}$ ) and the molecular electrostatic potential at the end hydrogen atom ( $V_H^{(n-1)}$ ) for the hydrogen-bonded  $(\text{HCN})_n$  clusters studied,  $n = 2-7$ .

Table 6

Morokuma energy decomposition terms for hydrogen bonded complexes of monosubstituted acetylene derivatives and ammonia (in kcal/mol) (from B3LYP/6-31G(d,p) calculations.): electrostatic interaction term (ES), exchange repulsion term (EX), polarization interaction term (PL), charge transfer interaction term (CT), coupling term for higher order interactions (MIX) and a energy of hydrogen-bond formation (E total)

Acetylenic monomer	ES	EX	PL	CT	MIX	E total	$V_H$ (a.u.) <sup>a</sup>
H-C≡C-H	-7.11	6.13	-0.78	-1.60	0.05	-3.32	-1.0444
F-C≡C-H	-7.77	6.61	-0.87	-1.72	0.10	-3.65	-1.0392
Cl-C≡C-H	-8.09	6.84	-0.95	-1.79	0.07	-3.92	-1.0349
H <sub>3</sub> C-C≡C-H	-6.12	5.59	-0.70	-1.46	0.09	-2.60	-1.0595
FH <sub>2</sub> C-C≡C-H	-7.53	6.39	-0.87	-1.68	0.12	-3.57	-1.0396
F <sub>2</sub> HC-C≡C-H	-8.90	7.33	-1.05	-1.92	0.16	-4.37	-1.0247
F <sub>3</sub> C-C≡C-H	-10.00	8.03	-1.22	-2.11	0.22	-5.08	-1.0134
ClH <sub>2</sub> C-C≡C-H	-7.76	6.61	-0.91	-1.72	0.12	-3.67	-1.0364
Cl <sub>2</sub> HC-C≡C-H	-9.15	7.70	-1.13	-1.98	0.16	-4.40	-1.0211
Cl <sub>3</sub> C-C≡C-H	-9.99	8.35	-1.27	-2.15	0.18	-4.87	-1.0103
NC-C≡C-H	-11.15	8.93	-1.46	-2.36	0.27	-5.77	-0.9985
H-C≡C-C≡C-H	-8.24	6.93	-1.01	-1.83	0.16	-3.98	-1.0325
F-C≡C-C≡C-H	-8.09	6.67	-0.99	-1.78	0.15	-4.03	-1.0351
Cl-C≡C-C≡C-H	-8.43	6.98	-1.05	-1.85	0.16	-4.19	-1.0309

<sup>a</sup> Electrostatic potential at the acetylenic hydrogen atom.

Nevertheless, the principal question that needs to be answered is why the electrostatic potential at the binding atoms in the monomers predicts so well the variations in binding energy upon changes in substitutions in the series of molecules studied. It should be underlined that the EDA procedure provided clear and convincing evidence to the origin of the dependence between the binding energy and atomic electrostatic potentials.

To elucidate the various contributions to the energy of hydrogen bond formation, additional

calculations were carried out on the series of complexes of 14 monosubstituted acetylene derivatives with ammonia.

We plotted the electrostatic potential at the site of the acidic acetylenic hydrogen atoms against the different decomposition terms as well as the total energy. It should be noted that not corrected energies are analyzed. The dependences obtained are shown in Figs. 9–13. It is clearly seen that very good linear relations are found between the variations of  $V_H$  and the values for the ES,

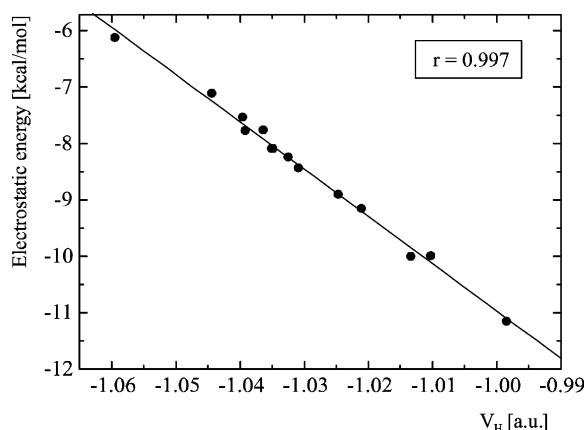


Fig. 9. Dependence between electrostatic interaction term (ES) and the molecular electrostatic potential at the acetylenic hydrogen atoms in isolated molecules ( $V_H$ ).

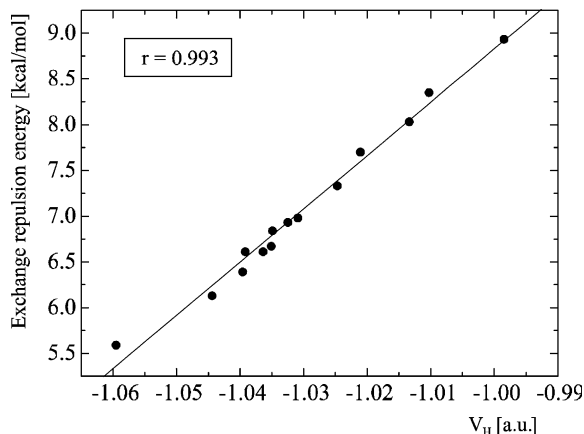


Fig. 10. Dependence between exchange repulsion term (EX) and the molecular electrostatic potential at the acetylenic hydrogen atoms in isolated molecules ( $V_H$ ).

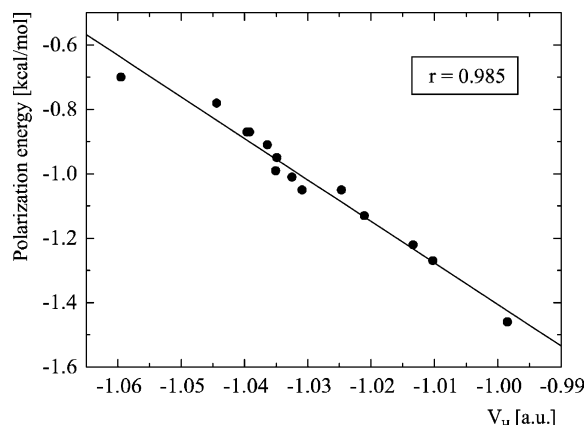


Fig. 11. Dependence between polarization interaction term (PL) and the molecular electrostatic potential at the acetylenic hydrogen atoms in isolated molecules ( $V_H$ ).

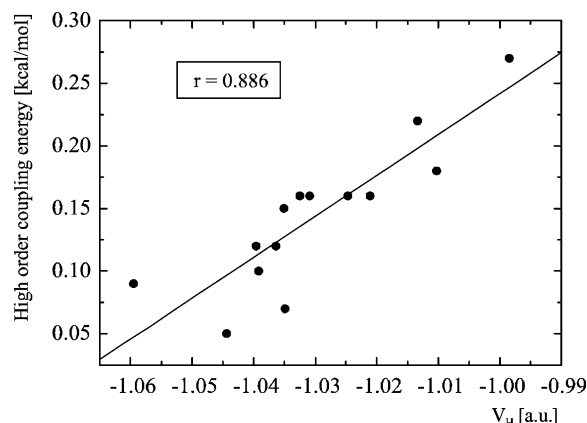


Fig. 13. Dependence between high order coupling term (MIX) and the molecular electrostatic potential at the acetylenic hydrogen atoms in isolated molecules ( $V_H$ ).

PL, EX and CT (Eq. (7)) decomposition terms. It is seen that these energy terms change in phase with each other with high correlation coefficients. Thus, the electrostatic potential at the acetylenic hydrogen atom basically correlates linearly not only with the electrostatic energy term (ES) but also with the three other energy terms. Much poorer link is found between  $V_H$  and the changes in the higher order coupling term (MIX). However, as can be seen from Table 6, the MIX term makes small contributions to the total binding energy in the range of 1.5–4.7%. In general, the changes in

the MIX energy term in the studied series of molecules cannot influence the overall dependence between  $V_H$  and total binding energy. Thus, the application of the EDA procedure of Morokuma et al. [33–35] provided clear theoretical explanation for the linear relationships between electrostatic potential at the binding atom and the energy of hydrogen bond formation. These results substantiate the usefulness of the molecular electrostatic potential at atomic sites as reactivity descriptor for the process of hydrogen bonding.

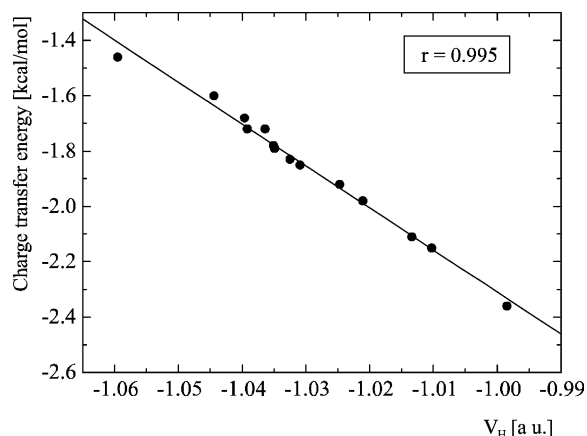


Fig. 12. Dependence between charge transfer interaction term (CT) and the molecular electrostatic potential at the acetylenic hydrogen atoms in isolated molecules ( $V_H$ ).

#### 4. Conclusions

Computational studies on hydrogen bonded complexes of four different series of organic molecules show that the molecular electrostatic potential at the nuclei participating in hydrogen bonding can be employed as an accurate reactivity descriptor for the process of hydrogen bonding. Excellent linear relationships between electrostatic potential at the reacting atoms and binding energy were found.

The results are theoretically substantiated by applying the Morokuma energy decomposition analysis in the case of complexes of monosubstituted acetylenes with ammonia. Very good linear relationships are found between the electrostatic potential at the acetylenic hydrogen atom and four energy decomposition terms: the electrostatic

interaction term, the polarization interaction term, the exchange repulsion term, and the charge transfer of electron delocalization interaction term. Poorer relationship is only found with the higher order interaction term. This term accounts for only 1.5–4.7% of the binding energy. Thus, the molecular electrostatic potential at the sites of the proton donor or proton accepting atoms reflects in quantitative term the overall ability of the molecules studied to form hydrogen bonds.

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