Covalent Character of Hydrogen Bonds Enhanced by π-Electron Delocalization*

Sławomir Janusz Grabowski

Department of Chemistry, University of Łódź, Pomorska 149/153, 90 236 Łódź, Poland

(*E-mail: slagra@uni.lodz.pl*)

Abstract. Interactions classified as intermolecular resonance assisted hydrogen bonds (RAHBs) are analyzed here. Hence the MP2/6-311++G(d,p) calculations for dimers of formic, acetic and pyrrole-2-carboxylic acid (PCA) were performed. The similar calculations were carried out for formamide and its fluorine derivatives' dimers as well as the tautomeric forms of the latter species. The Quantum theory of Atoms in Molecules (QTAIM) and the decomposition of the interaction energy are applied to analyze hydrogen bonds enhanced by the π-electron delocalization. It is indicated that these interactions possess the covalent character. It is expressed by the negative values of the total electron energy density at the proton-acceptor bond critical point as well as by the meaningful contribution of the delocalization interaction energy.

Keywords: resonance assisted hydrogen bonding, formamide, carboxylic acid, Quantum Theory of Atoms in Molecules, decomposition of the interaction energy, covalency of hydrogen bonding, π-electron delocalization

INTRODUCTION

There are numerous studies concerning the nature of hydrogen bonding since it is an important interaction in biological, chemical and physical processes.[1] The studies on very strong hydrogen bonds are also well known,[2,3] for example the studies on so-called Low Barrier Hydrogen Bonds (LBHBs) which play the crucial role in enzymatic catalysis.[4]

It was pointed out that there are three kinds of strong hydrogen bonds, negatively charged assisted hydrogen bond (−)CAHB, positively charged assisted hydrogen bond (+)CAHB and resonance assisted hydrogen bond RAHB.[5,6] It is worth mentioning that also hydrogen bonds enhanced by the so-called σ-cooperativity often belong to very strong ones.[7] The A−H⋯B is often applied designation for hydrogen bonding where A−H is the proton donating bond while B is an acceptor center. One can mention that there are specific characteristics of strong and very strong hydrogen bonds. First of all, the proton–acceptor distance (H⋯B) for such systems is very short, there is even a term SSHB (Short, Strong Hydrogen Bond).[2] The elongation of the proton donating bond (A−H) is an effect of

the complexation leading to the hydrogen bonding formation.[1] Only the blue-shifting hydrogen bonding where there is the shortening of A−H bond as a result of the complexation is an exception of the mentioned above rule.[8] However for the latter kind of hydrogen bonding it rather may not be classified as the strong interaction.

In the other words the strength of hydrogen bonding is reflected by geometrical parameters, the stronger hydrogen bond thus the greater A−H bond elongation and the shorter H⋯B distance. The other parameters, not only geometrical ones, may be useful to assess the strength of hydrogen bonding.[9] This is the energy of such an interaction. There are different classifications of hydrogen bonding. For example, Desiraju and Steiner[10] claim that there are weak, moderate and strong hydrogen bonds for which the following energy ranges may be attributed: 1−4 kcal mol^{-1}; 4−15 kcal mol^{-1} and 15−40 kcal mol^{-1}, respectively. However these energy ranges were chosen arbitrary, for example, the classification based on the other, topological characteristics seems to be free from arbitrary numbers.[9] Such a classification based on the parameters derived from the Quantum Theory of Atoms in Molecules (QTAIM)[11,12] was

---

* Dedicated to Professor Zvonimir Maksić on the occasion of his 70th birthday.

proposed by Rozas *et al.*[13] who proposed for weak H-bonds that both $\nabla^2\rho_{BCP}$ and $H_{BCP} > 0$; for medium H-bonds it is: $\nabla^2\rho_{BCP} > 0$ and $H_{BCP} < 0$, while for strong ones both $\nabla^2\rho_{BCP}$ and $H_{BCP} < 0$. $\nabla^2\rho_{BCP}$ designates the Laplacian of the electron density at the bond critical point (BCP) corresponding to the H···B distance, H_{BCP} is the total electron energy density at this BCP.

The negative value of $\nabla^2\rho_{BCP}$ Laplacian indicates the concentration of the electron density in the interatomic region and occurs for sharing interactions like covalent bonds while the positive value of this Laplacian indicates the depletion of the electron density for the interaction of the closed-shell systems such as ionic bond or van der Waals interaction.[11] The positive value of Laplacian is also typical for hydrogen bonds. However it should be pointed out that the covalency of the interaction is connected with very strong hydrogen bonds where the Laplacian of the electron density at the H···B BCP is negative.[9,14] Sometimes, it is claimed that hydrogen bond is partially covalent in nature if $\nabla^2\rho_{BCP}$ is positive but H_{BCP} is negative.[15] The existence of different hydrogen bonds characterized in such a way is a consequence of the virial theorem.[11]

$$(1/4)\cdot\nabla^2\rho_C = 2G_C + V_C \qquad (1)$$

where G_C is the kinetic electron energy density at BCP, V_C is the potential electron energy density at BCP, the former is positive while the latter value is negative. Thus one can see that if the modulus of V_C outweighs two times the G_C value thus the Laplacian is negative and the interactions are covalent in nature. If the modulus of V_C only one time outweighs G_C thus the interaction is partially covalent since H_C is negative according to the other known relation.

$$H_C = V_C + G_C \qquad (2)$$

The QTAIM analyses of different kinds of hydrogen bonds were the subject of numerous studies and the problem of the covalent character of strong hydrogen bonds was often undertaken.[2,3,5,9,16,17]

Desiraju has pointed out that weak and moderate hydrogen bonds possess the character of an electrostatic interaction while the short and strong hydrogen bonds are characterized by covalency revealed by the important contribution of the charge transfer energy of interaction.[18] The analysis of the nature of any kind of interaction, particularly hydrogen bonding, may be based on the decomposition scheme. There are different schemes of the partitioning of the energy of interaction. According to the well known scheme of Morokuma and Kitaura[19] the energy of interaction may be partitioned into the following terms: electrostatic energy of interaction (ES),

polarization contribution (PL), charge transfer energy (CT), exchange (EX) and MIX term being the energy difference between SCF interaction energy and the above-mentioned four components. Only the EX term is always positive (repulsive) while the other interaction energy terms are usually negative (attractive). Such a partitioning concerns the SCF energy of interaction and if the other beyond Hartree-Fock level method is applied which takes into account the correlation of electrons thus the correlation energy (CORR) is included. It is worth mentioning that the most meaningful attractive term of the correlation energy is the dispersive energy (DISP).[20]

The intermolecular hydrogen bonds which are often classified as RAHB systems are the subject of this study. The RAHB model was introduced for the intramolecular hydrogen bonds and such systems were investigated extensively.[5,6] However for intramolecular interactions the decomposition scheme of the energy of interaction may not be applied.[21] Since the energy partitioning and the QTAIM theory are used in this study thus the intermolecular interactions were chosen for investigations. The main goal is to analyze different relationships between QTAIM parameters and the terms of the energy of interaction. It was mentioned here that RAHB systems are those classified as strong or very strong hydrogen bonds possessing characteristics of covalent interactions. Thus the analysis of these characteristics is also the subject of this study.

COMPUTATIONAL DETAILS

The calculations were performed with the Gaussian 03 sets of codes.[22] The hydrogen bonds are considered in dimers of formic (HCOOH), acetic (CH$_3$COOH) as well as pyrrole-2-carboxylic acid (PCA). In the case of PCA three configurations of dimers are taken into account, for two of them (A and B) O−H···O hydrogen bonds exist for the other one (C) there are N−H···O interactions. The dimer A consists of *s-trans* conformers of molecules, for the remaining, B and C dimers, *s-cis* conformer molecules are linked (Fig. 1). Additionally dimers of formamide (HCONH$_2$) and its fluorine derivatives are taken into account. The fluorine atoms are attached to nitrogen, to carbon atom or to both of them. For the latter group of complexes (formamides) the molecules are linked through N−H···O hydrogen bonds. All dimers analyzed were optimized at MP2/6-311++G(d,p) level of approximation and the systems are in minima since no imaginary frequencies were found. It is worth mentioning that the analyzed dimers are centrosymmetric since there is the inversion center within the eight- or ten-member pseudo-ring created by two hydrogen bonds as well as typical covalent bonds (see

Figure 1). The tautomeric forms of the mentioned formamide dimers are also considered here. These are the centrosymmetric complexes linked through O−H···N hydrogen bonds. All these systems were partially analyzed earlier.[23,24] However there was no for them the analysis based on the comparison of QTAIM parameters and the energetic characteristics derived from the decomposition of the interaction energy. Such an analysis is performed here to show various relationships for the sample of species where strong hydrogen bonds possessing covalent character exist.

The variation-perturbation approach[25,26] was applied in order to characterize the interactions analyzed here. The starting wave functions of the subsystems are obtained in this approach in the dimer-centred basis set (DCBS)[27] thus the total interaction energy as well as all of its components are free of basis set superposition error (BSSE) due to the full counterpoise correction.

The partitioning of the interaction energy leads to the following components:

$$\Delta E = E_{EL}^{(1)} + E_{EX}^{(1)} + E_{DEL}^{(R)} + E_{CORR}^{(2)} \qquad (3)$$

where $E_{EL}^{(1)}$ is the first order electrostatic term describing the Coulombic interaction of static charge distributions of both molecules; $E_{EX}^{(1)}$ is the Pauli repulsive first order exchange component; and $E_{DEL}^{(R)}$ and $E_{CORR}^{(2)}$ correspond to higher order delocalization and correlation terms, respectively. It is worth mentioning that the delocalization term approximately corresponds to the sum of POL and CT terms of the Kitaura and Morokuma decomposition.

The Quantum Theory of "Atoms in Molecules" (QTAIM)[11] was applied in this study to find critical points (CPs) and further to analyze them in terms of electron densities, Laplacians and the other characteristics such as for example the local kinetic energy density G_C, the local potential energy density V_C and the total electron energy density H_C. The AIM calculations were performed using the AIM2000 program.[28]

RESULTS AND DISCUSSION

Figure 1 shows selected species analyzed here, three configurations of PCA dimers are presented, the formic acid dimer and the fluorine derivative of formamide dimer. In the latter case the tautomeric form of this dimer obtained after the double proton transfer is also shown.

Table 1 presents the proton–acceptor $R_{H···B}$ distance and the interaction energy terms (Eq. (3)) being the result of the binding energy partitioning. The Heit-

A

B

C

Formic acid dimer

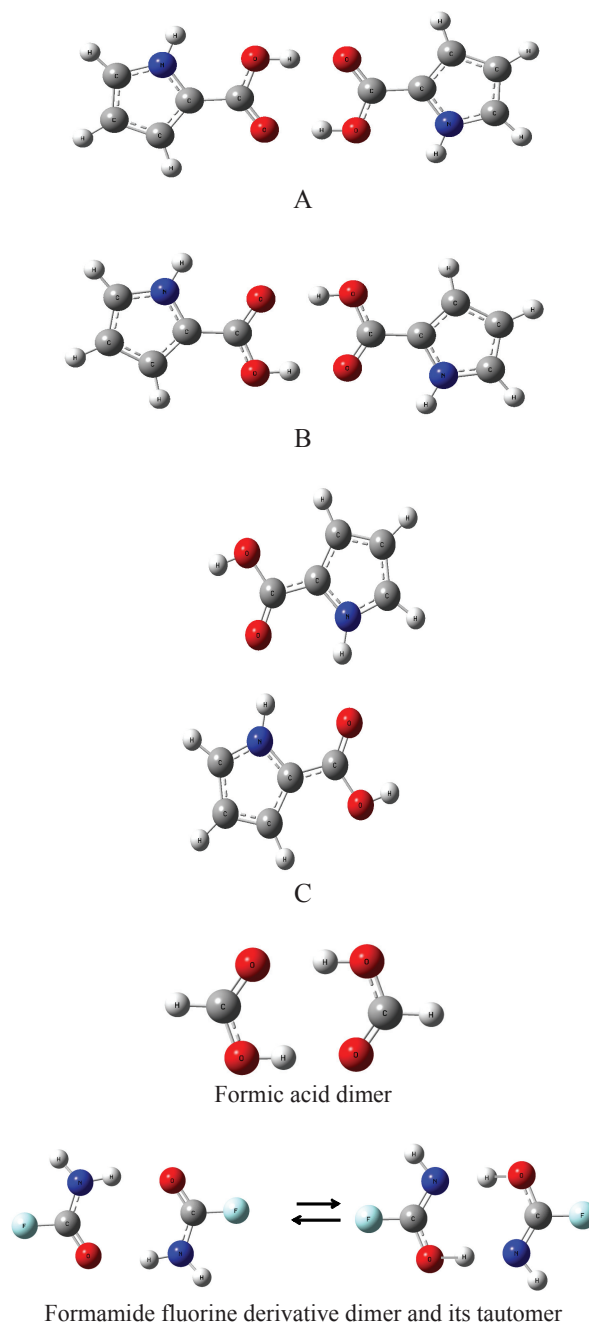Formamide fluorine derivative dimer and its tautomer

Figure 1. The selected systems analyzed here, three configurations of pyrrole-2-carboxylic acid (PCA) dimer, formic acid, the formamide derivative dimer and the tautomeric form of the latter species are presented.

ler-London energy $E_{H-L}^{(1)}$ is included which is the sum of first order energy terms: $E_{EL}^{(1)}$ and $E_{EX}^{(1)}$. There is also E_{CORR} energy which is the difference between the MP2 and Hartree-Fock binding energies. $\Delta E_{n_B \to \sigma^*_{AH}}$ NBO (Natural Bond Orbitals method)[29] energy is also given in Table 1. The latter is connected with the transfer of electronic charge from the n_B lone electron pair orbital to the antibond orbital σ_{AH}^*. This $n_B \to$

Table 1. The decomposition of interaction energy for dimers of formamide and its tautomeric form as well as their fluoro derivatives. The results on dimers of carboxylic acids are included. The energy components correspond to Eq. (3) and their description in the text and they are given in kcal mol^{-1}, the MP2/6-311++G(d,p) level of approximation was applied. H···B distances are included ($R_{H···O(N)}$ /Å) as well as the binding energies (ΔE /kcal mol^{-1}) and the NBO $\Delta E_{n_B \to \sigma^*_{AH}}$ energies /kcal mol^{-1}.

Complex[a][b]	$R_{H···O(N)}$ Å	$E_{EL}^{(1)}$ kcal mol^{-1}	$E_{EX}^{(1)}$ kcal mol^{-1}	$E_{H-L}^{(1)[c]}$ kcal mol^{-1}	$E_{DEL}^{(R)}$ kcal mol^{-1}	E_{CORR} kcal mol^{-1}	ΔE kcal mol^{-1}	$\Delta E_{n_B \to \sigma^*_{AH}}$ kcal mol^{-1}
N−H···O	1.903	−23.3	19.7	−3.6	−8.5	0.0	−12.1	12.9
N(F)−H···O	1.870	−22.6	20.1	−2.5	−9.0	0.1	−11.3	13.9
N−H···O(C−F)	1.938	−20.0	15.1	−5.0	−6.5	0.1	−11.3	10.3
N(F)−H···O(C−F)	1.946	−17.3	13.8	−3.5	−6.1	0.3	−9.4	9.2
O−H···N	1.673	−45.4	54.2	8.8	−26.6	−2.7	−20.5	40.6
O−H···N(F)	1.772	−32.0	35.6	3.6	−17.4	−1.9	−15.7	25.4
O−H···N(C−F)	1.556	−57.1	71.0	14.0	−40.1	−3.6	−29.8	63.2
O−H···N(F)(C−F)	1.683	−37.7	44.1	6.5	−23.8	−2.9	−20.3	36.7
HCOOH···HCOOH	1.726	−30.1	30.0	−0.1	−14.3	0.9	−13.6	23.2
CH$_3$COOH···CH$_3$COOH	1.705	−32.2	32.3	0.1	−15.2	0.5	−14.5	25.6
C$_4$H$_4$NCOOH···C$_4$H$_4$NCOOH (A)	1.657	−36.7	37.6	0.9	−18.6	0.6	−17.1	30.5
C$_4$H$_4$NCOOH···C$_4$H$_4$NCOOH (B)	1.670	−34.8	36.1	1.3	−17.3	0.3	−15.7	29.0
C$_4$H$_4$NCOOH···C$_4$H$_4$NCOOH (C)	1.879	−19.9	16.1	−3.8	−6.9	−1.4	−12.1	11.0

[a] N(F) – there is fluoro-substituent at nitrogen atom.
[b] (C−F) – fluoro-substituent connected with carbon atom.
[c] First order Heitler-London energy term; $E_{H-L}^{(1)} = E_{EL}^{(1)} + E_{EX}^{(1)}$.

σ_{AH}^* interaction may be estimated by second order perturbation theory contribution (Eq. (4)).[30]

$$\Delta E_{n_B \to \sigma^*_{AH}} = -2 \frac{\left\langle n_B \left| \hat{F} \right| \sigma^*_{AH} \right\rangle^2}{\varepsilon_{\sigma^*_{AH}} - \varepsilon_{n_B}} \qquad (4)$$

$\left\langle n_B \left| \hat{F} \right| \sigma^*_{AH} \right\rangle$ is the Fock matrix element while $\varepsilon_{\sigma^*_{AH}} - \varepsilon_{n_B}$ is the orbital energy difference (the difference of diagonal Fock matrix elements).

ΔE binding energies correspond to two hydrogen bonding interactions. Since these are the centrosymmetric dimers thus both hydrogen bonds are equivalent and the binding energy should be divided by 2 to have the hydrogen bonding energy. One can see (Table 1) that O−H···N are the strongest hydrogen bonds among those analyzed here. This is in line with the Leffler-Hammond postulate[31,32] since hydrogen bonds are stronger for systems closer to the transition state. Similar analyses were performed for the intramolecular N−H···O resonance-assisted hydrogen bonds,[33] and the results being in agreement with the Leffler-Hammond postulate were found. Table 1 also shows that the O−H···O hydrogen bonds of formic acid, acetic acid and PCA are stronger than N−H···O hydrogen bonds and weaker than

O−H···N ones. These considerations on the strength of hydrogen bonds are supported by the H···B distances, the shortest H···B contacts are observed for O−H···N hydrogen bonds while the longest ones for N−H···O systems.

It was found that for stronger hydrogen bonds the delocalization interaction energy becomes more important than the electrostatic energy or at least the $E_{DEL}^{(R)}$/$E_{EL}^{(1)}$ ratio increases with the hydrogen bond strength increase.[34] The delocalization energy is often treated as such a term which reflects the importance of covalent character of interaction. Thus the results of Table 1 clearly show that the covalency is more important for stronger and shorter hydrogen bonds.

Numerous correlations between binding energy, energy terms and H···B distance may be found here. However different H···B contacts are considered, (O)H···O, (N)H···O and (O)H···N. Hence it seems that not H···B distance but the other parameters may be better fitted to the strength of interaction. For example, it was found that the electron density at BCP and the other QTAIM parameters may be successfully applied as descriptors of hydrogen bond strength for the homogeneous and even heterogeneous samples of systems.[9] Table 2 presents topological parameters for the sample of intermolecular interactions analyzed here. One can

Table 2. Topological parameters of the complexes analyzed here; the electron density at BCP (ρ_C), its Laplacian ($\nabla^2\rho_C$), the potential electron energy density (V_C), the kinetic electron energy density (G_C) and the total electron energy density at BCP (H_C). The results obtained at MP2/6-311++G(d,p) level of approximation correspond to H···B BCPs

Complex[a] [b]	$\dfrac{\rho_C}{\text{a.u.}}$	$\dfrac{\nabla^2\rho_C}{\text{a.u.}}$	$\dfrac{G_C}{\text{a.u.}}$	$\dfrac{V_C}{\text{a.u.}}$	$\dfrac{H_C}{\text{a.u.}}$
N−H···O	0.0273	0.0961	0.0227	−0.0214	0.0013
N(F)−H···O	0.0289	0.1031	0.0246	−0.0235	0.0011
N−H···O(C−F)	0.0239	0.0919	0.0207	−0.0184	0.0023
N(F)−H···O(C−F)	0.0231	0.0911	0.0203	−0.0179	0.0024
O−H···N	0.0559	0.1052	0.0404	−0.0545	−0.0141
O−H···N(F)	0.043	0.1066	0.0324	−0.0386	−0.0062
O−H···N(C−F)	0.0742	0.0962	0.0515	−0.0789	−0.0274
O−H···N(F)(C−F)	0.0531	0.1108	0.0398	−0.0519	−0.0121
HCOOH···HCOOH	0.0401	0.1293	0.0348	−0.0374	−0.0026
CH$_3$COOH···CH$_3$COOH	0.0424	0.1336	0.0369	−0.0404	−0.0035
C$_4$H$_4$NCOOH···C$_4$H$_4$NCOOH (A)	0.0478	0.1422	0.0418	−0.048	−0.0062
C$_4$H$_4$NCOOH···C$_4$H$_4$NCOOH (B)	0.0463	0.1409	0.0406	−0.046	−0.0054
C$_4$H$_4$NCOOH···C$_4$H$_4$NCOOH (C)	0.0259	0.1065	0.0241	−0.0216	0.0025

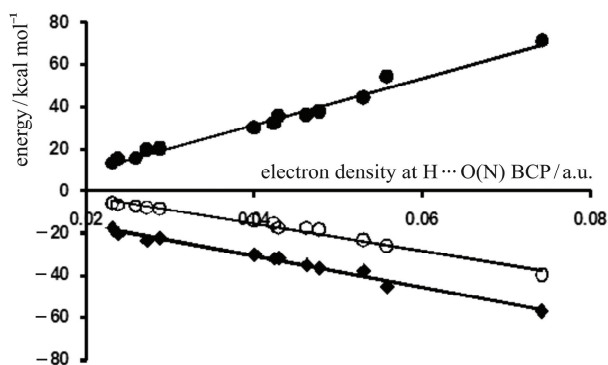[a] N(F) – there is fluoro-substituent at nitrogen atom.
[b] (C−F) – fluoro-substituent connected with carbon atom.

see that the greatest electron densities at H···B BCP are for (O)H···N interactions, next for (O)H···O and (N)H···O hydrogen bonds. This is in agreement with the results of Table 1 since the greater electron density at BCP correspond to the stronger interaction. Table 2 also shows that for (O)H···N and (O)H···O interactions the total electron energy density at the corresponding BCP (H_C) is negative. This indicates that such interactions are partially covalent in nature.

Figure 2 presents the well linear correlations between the electron density at the proton-acceptor BCP and the energy terms: exchange, electrostatic and delocalization. One can see that for the analyzed systems the electrostatic attractive interaction is approximately cancelled by the repulsive exchange energy. This means that the delocalization is responsible for the stabilization of the dimers considered. Since the sum of exchange and electrostatic energies is the Heitler-London first order perturbation theory energy term ($E_{\text{H-L}}^{(1)}$) thus its relationship with the delocalization energy term is very interesting (Figure 3). One can see that the increase of the Heitler-London energy is connected with decrease of the delocalization energy (increase of the modulus of that energy term). This is in agreement with the results of Table 1, for (O)H···N interactions, $E_{\text{H-L}}^{(1)}$ is positive, for (O)H···O ones it is close to zero while for (N)H···O interactions it is negative indicating the greater and dominant importance of the attractive electrostatic ener-

gy for the weaker interactions.

Figure 4 shows the relationship between the delocalization/electrostatic energies ratio and $-V_C/G_C$. Both these indicators were applied as descriptors of the covalent character of hydrogen bonding.[16,34] The ratio of energies indicates that for weaker hydrogen bonds the electrostatic energy is the most important attractive term while for shorter and covalent interactions the delocali-

Figure 2. The relationships between the electron density at H···B BCP (in a.u.) and the interaction energy components (in kcal mol^{-1}); full circles correspond to the exchange energy, open circles to the delocalization energy while the squares to the electrostatic energy, R^2 for the linear correlations between the electron density and the exchange, delocalization and electrostatic energies amounts to 0.982, 0.976 and 0.982, respectively.
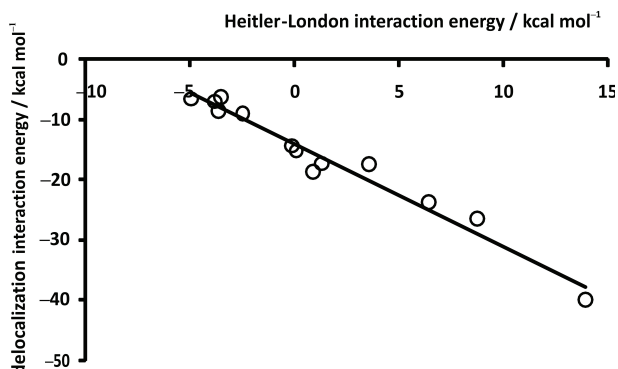
Figure 3. The linear relationship between the Heitler-London interaction energy term and the delocalization energy (R^2 = 0.967, both in kcal mol^{-1}).
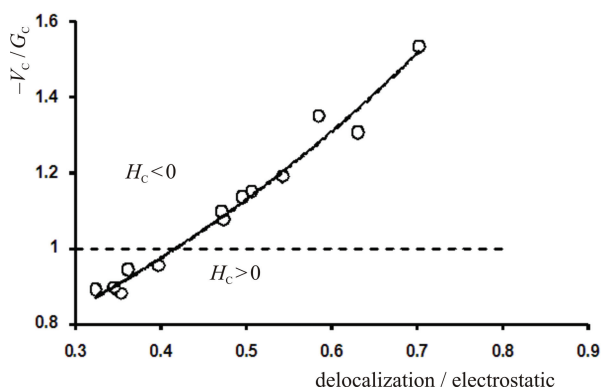

Figure 4. The correlation between $E_{DEL}^{(R)}/E_{EL}^{(1)}$ ratio and $-V_C/G_C$ (R^2 = 0.978 for the exponential relationship $y = 0.541e^{1.468x}$).
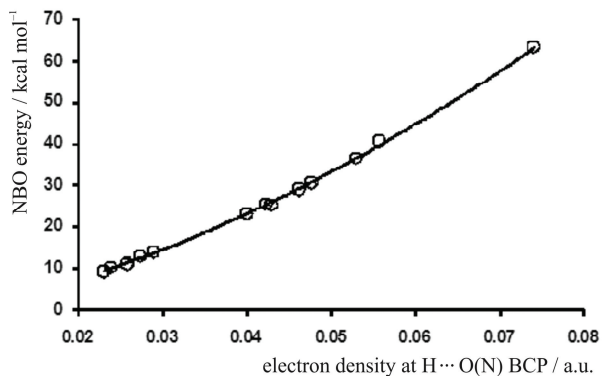

Figure 5. The relationship between the electron density at H$\cdots$B BCP (in a.u.) and the expressed by Eq. (4) NBO energy (in kcal mol^{-1}), R^2 = 0.998 for the power dependence $y = 4340x^{1.626}$.

zation is more important attractive term. The ratio of topological parameters ($-V_C/G_C$) is greater than 2 if Laplacian at the corresponding BCP is negative thus for covalent interaction. If that ratio is in the range <1,2> thus the interaction is partially covalent ($H_C < 0$), when $-V_C/G_C < 1$ thus $H_C > 0$ what corresponds to weakest
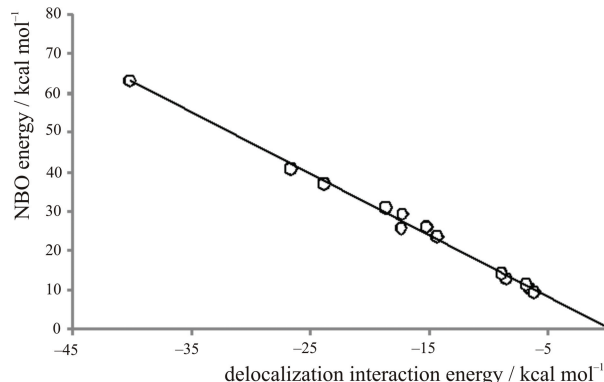
Figure 6. The linear relationship between the delocalization interaction energy term and the expressed by Eq. (4) NBO energy (R^2 = 0.994, both in kcal mol^{-1}).

closed-shell interactions. The well exponential correlation between $E_{DEL}^{(R)}/E_{EL}^{(1)}$ ratio and the topological ratio $-V_C/G_C$ (Figure 4) justifies that both ratios may be applied as indicators of the covalent character of interactions.

Figure 5 presents the power relationship between the electron density at H$\cdots$B BCP and the NBO energy expressed by Eq. (4). This means that such an energy connected with the electron transfer from the acceptor to donor is attributed to hydrogen bonding interaction. This energy is also related to the similar energies being the results of the other decomposition schemes, charge transfer energy within the Kitaura-Morokuma partitioning or the delocalization energy of the partitioning applied in this study. Figure 6 presents well linear correlation between the $E_{DEL}^{(R)}$ (Eq. (3)) and NBO energies (Eq. (4)). This shows that both energies are related and in spite of the fact that their physical meaning in slightly different thus they both are good descriptors of hydrogen bonding strength and particularly of the covalent character of that interaction.

CONCLUSION

The intermolecular N−H$\cdots$O, O−H$\cdots$O and O−H$\cdots$N hydrogen bonds of formamides and carboxylic acids were analyzed here. All these interactions are enhanced by the π-electron delocalization and are expected to possess characteristics of covalent interactions. Such expectations are supported by geometrical, energetic and QTAIM results. Almost for all systems presented here the electrostatic interaction energy is outweighed by the exchange repulsive energy and hence the systems are stable due to the delocalization interaction energy. The latter term is often attributed to covalency. There are well correlations between the delocalization interaction energy and the other parameters describing the

strength of hydrogen bonding. This means that the delocalization is the driving force for hydrogen bonding interaction.

REFERENCES

1. G. A. Jeffrey and W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer-Verlag, Berlin, 1991.
2. S. J. Grabowski, *Ann. Rep. Prog. Chem.*, *Sect. C.* **102** (2006) 131−165.
3. G. K. H. Madsen, G. J. McIntyre, B. Schiøtt, and F. K. Larsen, *Chem. Eur. J.* **13** (2007) 5539−5547.
4. C. L. Perrin and J. B. Nielson, *Annu. Rev. Phys. Chem.* **48** (1997) 511−544.
5. P. Gilli, V. Bertolasi, V. Ferretti, and G. Gilli, *J. Am. Chem. Soc.* **116** (1994) 909−915.
6. G. Gilli and P. Gilli, *J. Mol. Struct.* **552** (2000) 1−15.
7. G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, New York, 1997.
8. P. Hobza and Z. Havlas, *Chem. Rev.* **100** (2000) 4253−4264 (and references cited therein).
9. S. J. Grabowski, *J. Phys. Org. Chem.* **17** (2004) 18−31.
10. G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press Inc., New York, 1999.
11. R. F. W. Bader, *Atoms in Molecules*, *A Quantum Theory*, Oxford University Press, Oxford, 1990.
12. C. Matta and R. J. Boyd (Eds.), *Quantum Theory of Atoms in Molecules: Recent Progress in Theory and Application*, Wiley-VCH, 2007.
13. I. Rozas, I. Alkorta, and J. Elguero, *J. Am. Chem. Soc.* **122** (2000) 11154−11161.
14. L. Sobczyk, S. J. Grabowski, and T. M. Krygowski, *Chem. Rev.* **105** (2005) 3513−3560.
15. S. Jenkins and I. Morrison, *Chem. Phys. Lett.* **317** (2000) 97−102.
16. E. Espinosa, I. Alkorta, J. Elguero, and E. Molins, *J. Chem. Phys.* **117** (2002) 5529−5542.
17. D. B. DuPré and C. Yappert, *J. Phys. Chem. A* **106** (2002) 567−574.
18. G. R. Desiraju, *Acc. Chem. Res.* **35** (2002) 565−573.
19. K. Morokuma and K. Kitaura, in: H. Ratajczak and W. J. Orville-Thomas (Eds.), *Molecular Interactions*, Vol.1, John Wiley and Sons Ltd., New York, 1980, pp. 21−66.
20. G. Chałasiński and M. M.Szczęśniak, *Chem. Rev.* **94** (1994) 1723−1765.
21. J. N. Woodford, *J. Phys. Chem. A* **111** (2007) 8519−8530.
22. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian 03*, Revision B.03, Gaussian, Inc., Pittsburgh PA, 2003.
23. R. W. Gora, S. J. Grabowski, and J. Leszczynski, *J. Phys. Chem. A* **109** (2005) 6397−6405.
24. S. J. Grabowski, W. A. Sokalski, and J. Leszczynski, *J. Phys. Chem. A* **110** (2006) 4772−4779.
25. W. A. Sokalski, S. Roszak, and K. Pecul, *Chem. Phys. Lett.* **153** (1988) 153−159.
26. W. A. Sokalski and S. Roszak, *J. Mol. Struct. (Theochem)*, **234** (1991) 387−400.
27. S. F. Boys and F. Bernardi, *Mol. Phys.* **19** (1970) 553−566.
28. AIM2000 designed by Friedrich Biegler- König, University of Applied Sciences, Bielefeld, Germany.
29. F. Weinhold and C. Landis, *Valency and Bonding, A Natural Bond Orbital Donor - Acceptor Perspective*, Cambridge University Press, 2005.
30. A. E. Reed, L. A. Curtiss, and F. Weinhold, *Chem. Rev.* **88** (1988) 899−926.
31. J. E. Leffler, *Science* **117** (1953) 340−341.
32. G. S. Hammond, *J. Am. Chem. Soc.* **77** (1955) 334−348.
33. S. J. Grabowski, *J. Mol. Struct (Theochem)* **811** (2007) 61−67.
34. S. J. Grabowski, W. A. Sokalski, E. Dyguda, and J. Leszczynski, *J. Phys. Chem. B* **110** (2006) 6444−6446.

SAŽETAK

Kovalentni karakter vodikovih veza pojačan π-elektronskom delokalizacijom

Sławomir Janusz Grabowski

Department of Chemistry, University of Łódź, Pomorska 149/153, 90 236 Łódź, Poland

Analizirane su interakcije klasificirane kao intermolekularne vodikove veze potpomognute rezonancijom (RAHBs). Napravljeni su MP2/6-311++G(d,p) računi za dimere mravlje, octene i pirol-2-karboksilne kiseline (PCA). Slični računi su provedeni za dimere formamida i njegovih fluoro derivata, kao i za tautomerne forme ovih posljednjih. Kvantna teorija atoma i molekula (QTAIM) i dekompozicija interakcijske energije primijenjeni su na analizu vodikove veze koja je pojačana π-elektronskom delokalizacijom. Pokazan je kovalentni karakter ovih interakcija. On je izražen kao negativne vrijednosti energije totalne elektronske gustoće na kritičnoj točki kemijske veze proton-akceptorski atom kao i sa značajnim doprinosom delokalizacijske energije interakcije.