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FEATURE ARTICLE

Dimers of Formic Acid, Acetic Acid, Formamide and Pyrrole-2-carboxylic Acid: an Ab Initio Study

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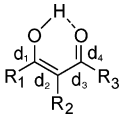
The intermolecular hydrogen bonds in dimers of formic acid, acetic acid, and formamide were investigated. Additionally, three configurations of the pyrrole-2-carboxylic acid (PCA) dimer were studied to analyze how the pyrrole π-electron system influences the carboxylic groups connected by double O−H···O hydrogen bonds. The ab initio calculations for the systems investigated were performed at MP2/6-311++G(d,p), MP2/aug-cc-pVDZ, and MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ levels of theory. The "atoms in molecules" theory of Bader was used and the analysis of the critical points was performed to study the nature of hydrogen bonds. The decomposition of the total interaction energy applied here reveals that the delocalization energy term is a particularly important attractive contribution in these systems, more important in the case of systems forming homonuclear O−H···O double hydrogen bonds than in the case of those connected through heteronuclear N−H···O bonds. Because the systems analyzed may be formally classified as the resonance-assisted hydrogen bonds (RAHBs), it seems that the dominant contribution from the delocalization interaction energy term is a distinguished feature of such interactions.

Introduction

There are two known kinds of hydrogen bond cooperativity.[1] The first kind concerns systems with multiple π-bonds and is usually designated as the resonance-assisted hydrogen bonding (RAHB); the second one contains continuous chains or cycles of hydrogen bonded functional groups possessing both donor and acceptor properties. The latter occurs usually between hydroxyl groups; for example, it was found in the crystal structures of carbohydrates.[2] However, other studies on the cooperativity through chains of functional groups participating in H-bonds, for instance, through the H−F molecules,[3] have also been carried out.

The main goal of this study is to explain the nature of the first kind of cooperativity that has been observed in the RAHB systems. This type of hydrogen bond is strongly affected by the π-electron delocalization, and the system is commonly considered as a combination of the possible resonance forms. The π-electron delocalization within the H-bonded systems was discussed early on.[4] However, the coherent model of RAHBs was reported by Gilli and co-workers.[5] The authors investigated the case of the intramolecular homonuclear O−H···O hydrogen bonding where the two oxygen atoms were interconnected through a system of conjugated π−bonds.[5,6] Such a situation occurs, for instance, in malonaldehyde and its derivatives.



Several conclusions can be drawn regarding the distinctive features of the intramolecular resonance-assisted hydrogen bonds.[5] The π-electron delocalization causes the equalization of the C−O and C=O bonds (the decrease of $q_1 = d_1 - d_4$ value), as well as the C−C and C=C bonds (the decrease of the $q_2 = d_3 - d_2$ value). Moreover, the significant decrease of the O···O and H···O distances is observed (in the case of the O···O distance for some of the species up to 2.4 Å or even less) and the associated elongation of the O−H proton donating bond (in the extreme cases the H-atom was shifted toward the midpoint of the O···O distance). As a convenient measure of the observed correlation between the symmetry coordinates q_1 and q_2 and the π-electron delocalization the parameter $Q = q_1 + q_2$ was introduced.[5] Numerous systems that could be regarded as the heteronuclear RAHBs were also investigated. Among them, the N−H···O interaction seems to be the most important, because its function is crucial in such phenomena as protein folding and DNA pairing. Its role in the crystal engineering is also noteworthy.[7] Studies of the N−H···O RAHBs existing in the crystal structures were performed for β-enaminones,[8] β-ketoarylhydrazones,[9] ketohydrazone−azoenol,[6c] chromone derivatives,[10] and many others.

The main features of the resonance-assisted hydrogen bonds were characterized by Gilli et al. within the electrostatic-covalent H-bond model (ECHBM).[6b,11] The authors argue that the weak

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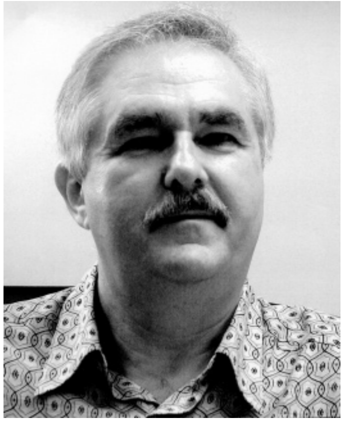

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hydrogen bonds are electrostatic in nature and their covalent character enhances with an increase of their strength (very strong H-bonds are the three-center-four-electron covalent bonds). The strongest H-bonds are homonuclear and symmetrical because the VB resonance forms are isoenergetic and their effective mixing is possible. The last statement is in line with the principle of the minimum difference between X and Y proton affinities ΔPA within the X$-$H$\cdots$Y H-bond or of minimum ΔpK_a, where ΔpK_a is the difference between the two interacting groups as measured in a proper polar solvent.[12]

The systems that could be classified as the intermolecular resonance-assisted hydrogen bonds are also quite common, for instance the case of centrosymmetric dimers of carboxylic acids can be regarded as one of the most frequently occurring type of the intermolecular RAHB.[11] As a matter of fact the first remarks regarding the RAHB concept are those referring to the nature of the O$-$H$\cdots$O$=$C chains in carboxylic acids and carboxylate hydrates.[4] The resonance, resulting from the existence of the two resonance forms is a commonly accepted and intuitive explanation of the strength of the double hydrogen bonding in the cyclic dimers of carboxylic acids.[13] In the case of such intermolecular RAHB systems, the similar equalization of the respective single and double carboxylic group bonds occurs as in the discussed above case of the malonaldehyde and its derivatives.[13] However, it is worth mentioning that in the carboxylic acid dimers, especially in the crystal phase, the situation is much more complex, because there are also the effects of static and dynamic disorders that also lead to the equalization of carbon$-$oxygen bonds of the carboxylic group.[13b]

The aim of this study is to achieve a better understanding of the nature of the intermolecular interactions in the systems commonly referred to as the resonance-assisted hydrogen bonds. Such systems are much more convenient for analysis than the case of intramolecular H-bonds. For intermolecular RAHBs it is possible to calculate accurately the binding energies as well as their physically defined components, exploiting the hybrid variational$-$perturbational interaction energy decomposition scheme.[14−16] The latter is a very useful technique helping in the precise characterization of the investigated interactions and rationalization of the obtained results. It should be stressed that in this paper we refer to the resonance-assisted hydrogen bonds not in the context of a unique phenomenon or a new type of the hydrogen bond but merely as a group of compounds with similar properties and topology. In fact, the influence of the so-called resonance assistance in the DNA base pairing was

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recently analyzed by Guerra et al.[17] Moreover, our state of the art complete active space self-consistent field calculations, employing large active spaces and extensive atomic natural orbitals basis sets, performed for some of the systems studied in this work do not indicate any multiconfigurational character of the wave functions whatsoever, because the weight of the leading configuration was always grater than 0.9.[18]

Computational Details

In this work, we have considered the dimers of formic acid $(HCOOH)_2$, acetic acid $(CH_3COOH)_2$, formamide $(HCONH_2)_2$, and three dimers of pyrrole-2-carboxylic acid (PCA). The molecular graphs of the investigated systems are presented in Figure 1. The calculations were performed applying the second-order Møller−Plesset perturbation theory (MP2).[19] The standard 6-311++G(d,p) basis set[20−23] and the two correlation consistent basis sets of Dunning et al.[24,25] (aug-cc-pVDZ and aug-cc-pVTZ) were employed throughout this study. Full optimizations of the geometrical parameters have been performed at the MP2/6-311++G(d,p) and MP2/aug-cc-pVDZ levels of theory. In the case of the $(HCOOH)_2$, $(CH_3COOH)_2$, and $(HCONH_2)_2$ dimers, the single point MP2 calculations have been carried out in the aug-cc-pVTZ basis set for the reference geometry as optimized at the MP2/aug-cc-pVDZ level of theory.

The binding energies of the analyzed dimers have been computed as a difference between the total energy of the complex and the energies of the isolated monomers and were further corrected for the basis set superposition error (BSSE) by applying the counterpoise procedure.[26] One can see that in such a case the binding energy includes the structural deformation energy as an effect of complexation. The binding energy is often referred to as the H-bond energy if the strongest and the only important intermolecular connection is hydrogen bonding. All systems analyzed here are linked through double hydrogen bonds. In the crystal phase, carboxylic acids often form centrosymmetric dimers.[13b,c] Thus, the optimizations were performed here with the imposed symmetry constraints. It was assumed here that two molecules are linked through two equivalent hydrogen bonds (Figure 1), and the dimers are centrosymmetric. Hence each of the dimers constitutes pairs of geometrically equivalent monomers. This means that there is an inversion center between the two linked species. In two of the studied dimers, the intermolecular connections are through the N−H···O bonds (the C dimer of PCA and the formamide dimer, Figure 1), whereas in the remaining dimers, double O−H···O bonds between the carboxylic groups are formed. All symmetry-adapted structural parameters were optimized. There is a subtle difference between the PCA dimers considered in this study that should be commented upon. Dimer A consists of s-trans conformers of the PCA molecules, and the remaining complexes (B and C) consist of s-cis conformers (Figure 1). Because no imaginary frequencies were found, all of the reported results correspond to the minimum energy structures of the studied complexes.

To gain a more detailed insight into the nature of the studied interactions, the interaction energies were decomposed according to the hybrid variational−perturbational scheme.[14−16] In this approach, the wave functions of the subsystems are obtained in the dimer-centered basis set (DCBS). The total interaction energy and all of its components are therefore basis set superposition error (BSSE) free due to the full counterpoise correction.[26]

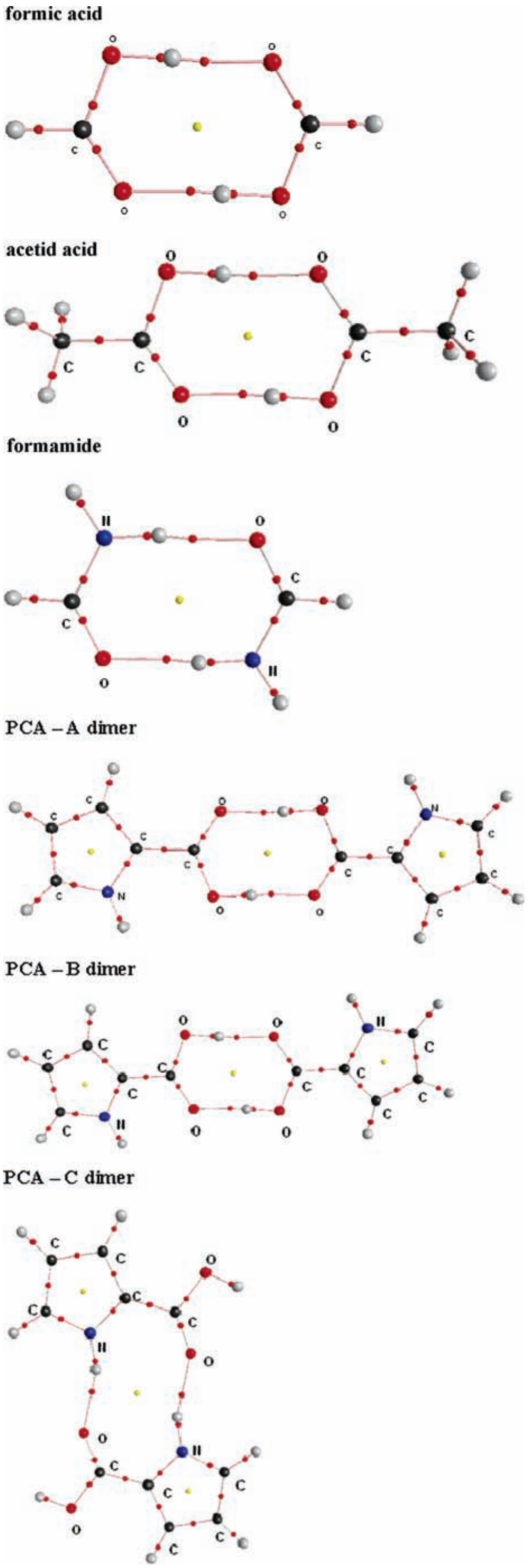

Figure 1. Molecular graphs of the systems investigated here. Big circles correspond to attractors attributed to nuclei (only non-hydrogen atoms are labeled) and small circles to critical points, bond critical points (BCPs), and ring critical points (RCPs).

The total MP2 interaction energy of a dimer can be expressed as follows:[27,28]

$$\Delta E^{\mathrm{MP}2} = \sum_{i=0}^{2} \epsilon_{\mathrm{MP}}^{(i)} = \Delta E^{\mathrm{HF}} + \epsilon_{\mathrm{MP}}^{(2)} \tag{1}$$

ΔE^{HF} is the interaction energy obtained in the supermolecular approach from the restricted Hartree–Fock (RHF) energies of the subsystems, whereas the $\epsilon_{\mathrm{MP}}^{(2)}$ term encompasses the electron correlation corrections to this interaction calculated accordingly. The Hartree–Fock interaction energy can be further partitioned into the Heitler–London and delocalization components.

$$\Delta E^{\mathrm{HF}} = \Delta E^{\mathrm{HL}} + \Delta E_{\mathrm{del}}^{\mathrm{HF}} \tag{2}$$

The Heitler–London interaction energy encompasses the first-order electrostatic interactions between monomers and the associated Heitler–London exchange repulsion.[29] The delocalization component assembles collectively the effects associated with the relaxation of the electronic densities of monomers restrained by the Pauli Exclusion Principle.[30] Because the Heitler–London wave function is obtained as an antisymmetrized Hartree product of the monomer wave functions, the corresponding alterations of the electron density distributions of the interacting subsystems are related solely to the small rotations of their orbitals. Therefore one can visualize the redistribution of the electronic densities of the interacting subsystems corresponding to the delocalization component, by plotting the interaction induced difference density, which can be obtained as a difference between the total RHF electronic density of the complex and the appropriate density distributions of the isolated monomers.

Because the electrostatic constituent of the Heitler–London interaction energy can be obtained from the standard polarization perturbation theory as a first-order term $\epsilon_{\mathrm{el}}^{(10)}$,[31] the exchange effects can be estimated simply as a difference between these two components.[14]

$$\epsilon_{\mathrm{ex}}^{\mathrm{HL}} = \Delta E^{\mathrm{HL}} - \epsilon_{\mathrm{el}}^{(10)} \tag{3}$$

The electron correlation $\epsilon_{\mathrm{MP}}^{(2)}$ term can also be further partitioned.[16,32] This term incorporates the second-order dispersion interaction, $\epsilon_{\mathrm{disp}}^{(20)}$, due to the intermolecular Coulomb electron correlation effects[33] and the electron correlation corrections to the Hartree–Fock components. The dispersion and the correlation correction to the first-order electrostatic interaction including relaxation effects,[34,35] $\epsilon_{\mathrm{el,r}}^{(12)}$, are evaluated directly, whereas the remaining electron correlation corrections are collectively gathered in the exchange-delocalization component, $\Delta E_{\mathrm{ex-del}}^{(2)}$, of which the main contribution is due to the electron correlation corrections to the $\epsilon_{\mathrm{ex}}^{\mathrm{HL}}$ component.

$$\Delta E_{\mathrm{ex-del}}^{(2)} = \epsilon_{\mathrm{MP}}^{(2)} - \epsilon_{\mathrm{el,r}}^{(12)} - \epsilon_{\mathrm{disp}}^{(20)} \tag{4}$$

A more detailed description of this partitioning scheme can be found in our previous papers.[36,37] Although any partitioning scheme has to be to some extent arbitrary, it was demonstrated that this particular approach based on the Møller–Plesset perturbation theory combined with the symmetry adapted perturbation theory, is capable of providing the rigorous, quantitative, and physically meaningful description of intermolecular forces.[28,38,39]

TABLE 1: Alteration of the Selected Geometrical Parameters (Å) Due to the Process of Complexation, the H···O Distances (Å) and the Binding Energies Corrected for BSSE (kcal/mol), and the Results Obtained within the MP2/6-311++G(d,p) and MP2/Aug-cc-pVDZ (Bold Values) Levels of Theory[a]

dimer	$\Delta r_{\mathrm{O-H(N-H)}}$	$\Delta r_{\mathrm{C=O}}$	$\Delta r_{\mathrm{C-O(N)}}$	$r_{\mathrm{H\cdots O}}$	E_{HB}
$(HCOOH)_2$	0.021	0.016	0.029	1.726	−6.6
	0.027	**0.018**	**0.033**	**1.680**	**−7.0**
					(−7.6)
$(CH_3COOH)_2$	0.023	0.017	0.032	1.705	−6.1
	0.033	**0.019**	**0.036**	**1.672**	**−7.2**
					(−7.9)
$(HCONH_2)_2$	0.013	0.013	0.018	1.901	−5.6
	0.019	**0.015**	**0.017**	**1.840**	**−6.7**
					(−7.1)
$(C_4H_4NCOOH)_2$-A	0.028	0.019	0.036	1.657	−7.9
	0.033	**0.020**	**0.040**	**1.631**	**−8.2**
$(C_4H_4NCOOH)_2$−B	0.026	0.019	0.031	1.670	−7.4
	0.031	**0.020**	**0.034**	**1.647**	**−7.5**
$(C_4H_4NCOOH)_2$−C	0.008	0.007	0.001[b]	1.879	−6.3
	0.000	**0.008**	**0.001**[b]	**1.837**	**−6.2**

[a] For the binding energies the MP2/aug-cc-pVTZ results (in parentheses) are also included. [b] C–N(H) bond within the pyrrole ring.

The interaction energy decomposition scheme was implemented[40] in the GAMESS quantum chemistry package.[41] The interaction difference density maps were obtained by adopting the modified version[42] of the MOLDEN program.[43] The atoms in molecules analysis was performed utilizing the AIM 2000 package.[44] All the remaining calculations have been carried out with the use of the Gaussian 98[45] and Gaussian 03[46] quantum chemistry packages.

Results and Discussion

Analysis of the Structural Parameters and the Binding Energies. The carboxylic acid dimers, as mentioned in the Introduction, could be classified as systems with the resonance-assisted intermolecular H-bonds. Hence, well-known and simple formic acid and acetic acid dimers are analyzed here. The formamide dimer is also included as the one with the heteronuclear N–H···O hydrogen bonds. Such bonds are expected to be weaker than O–H···O bonds occurring in carboxylic acids, due to the difference between the proton affinities (PA) of the H-bond donor and acceptor atoms. Moreover, an intuitive reasoning leads to the conclusion that there is also less effective mixing of the X–H···Y ⇔ X···H–Y tautomeric forms than in the case of homonuclear systems (X–H···X ⇔ X···H-X).[9] Also the three forms of PCA dimers previously analyzed by us both experimentally (IR spectra and X-ray crystal structure) and theoretically are investigated here (Figure 1).[47] Indeed, it was found that the O–H···O bonds formed through carboxylic groups in the PCA dimers are much stronger than the N–H···O bonds of the C form of the dimer. Furthermore, the H-bonds in the centrosymmetric A and B forms of PCA dimers were found to be considerably stronger than in the centrosymmetric formic acid dimer.[47b] Such a situation is almost certainly connected with the influence of the pyrrole aromatic ring.

All of the aforementioned statements and assumptions concerning the intermolecular RAHBs require more thorough studies, and this is the aim of our investigations here. First of all the results of the optimizations including selected geometrical parameters, obtained at the MP2/6-311++G(d,p) and MP2/aug-cc-pVDZ levels of theory, are presented in Table 1. The changes in the geometry of the carboxylic groups caused by the process of complexation are reported together with the

H···O intermolecular distances and the H-bond energies corrected for BSSE. Table 1 contains the energies of single H-bonds that constitute half of the binding energies because two (N)O—H···O connections are equivalent by symmetry. In the case of the formamide dimer, the changes of the corresponding bonds are shown, namely the N—H proton donating bond and the C—N and C═O bonds. One can see that the greatest changes occur for the A and B dimers of PCA. In the case of those complexes, the H···O contacts are the shortest, and the H-bonds are the strongest. The geometrical changes and the binding energies for the formamide and the C dimer of PCA are much smaller than in the A and B PCA dimers. The H-bond energy in the formamide dimer estimated at the MP2/aug-cc-pVDZ level of theory is equal to 6.7, whereas in the case of the A dimer of PCA it amounts to 8.2 kcal/mol. The observed changes of the geometrical parameters due to complexation are in line with other findings concerning similar systems that have been reported previously. For instance, the correlation between the elongation of the proton donating bond and H-bond strength is well-known;[1] this is also observed here (Table 1). The similar relationships between geometrical parameters based on the theoretical results and supported by the NMR studies were found for N—H···O and N—H···N bonds.[48]

A further insight into the changes of the properties of the interacting species due to complexation may be possible if one analyzes the shifts in their electron density distributions. In the case of typical hydrogen bond formation, a certain fraction of the electronic cloud transfers from the proton acceptor to the donating molecule. Moreover, some rearrangements of the charge density within the confines of monomers occur as well.[49] To avoid the arbitrariness of choosing one of the available population analysis schemes and their limitations, the interaction difference densities were plotted. The isodensity maps obtained for the studied complexes are shown in Figure 2. As was mentioned in the Computational Details, the visible redistribution of the electronic densities of monomers can be attributed essentially to the delocalization effects, i.e., $\Delta E_{\mathrm{del}}^{\mathrm{HF}}$ interaction energy component. The blue contours in Figure 2 represent the areas where the electron density diminished as a result of the H-bond formation, whereas the red contours enclose regions where the accumulation of the electron density occurred. One can see that the density rearrangement after complexation is different in the case of O—H···O bond formation than for N—H···O bond formation. This result parallels findings that the interactions were found to be considerably stronger in the former dimers with the homonuclear H-bonds. Because the dimers considered are centrosymmetric, both connected molecules are equivalent; hence, both are uncharged. Such a situation does not correspond to any electron density transfer from one molecule to another; only the changes within the regions may be considered. Additionally, in all studied complexes each monomer behaves as proton donor and acceptor at the same time. One can see a similar rearrangement of the electron density for the analyzed species (Figure 2). The regions of loss of the electron density are concentrated at the positions of the atoms of the proton donating bonds (O—H and N—H). The same applies to the double proton accepting C═O bond, because there is a loss of density for it as well.

The gain of the electron density is observed at the position of the oxygen atom in the C═O bond, the single proton donating bond (O—H and N—H) and also the single C—O bond of the carboxylic groups or the corresponding N—C bond of the formamide dimer. The only exception is the C dimer of PCA where the accumulation of the electronic density due to H-bond formation takes place almost exclusively at the N—H bond and the oxygen atom position of the C═O bond. Interestingly, there is no visible charge transfer from the pyrrole rings into the region of the carboxylic groups for the PCA dimers. Hence, there must be yet another reason, not connected with the redistribution of the electronic densities due to the presence of pyrrole rings, why the H-bonds of the A and B dimers are stronger than the H-bonds in the acetic and formic acid dimers. However, the picture connected with the reorganization of the electron charge density supports nicely the features of the intermolecular RAHB

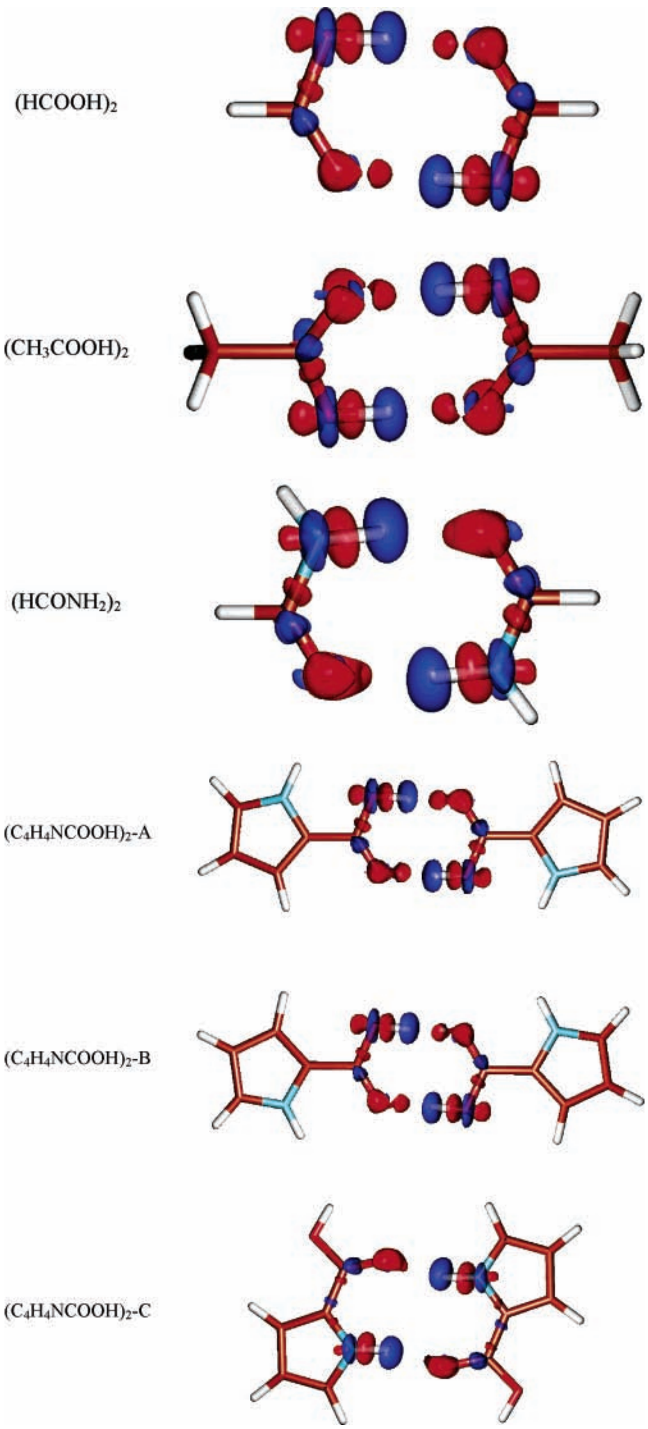

Figure 2. Interaction difference density maps of the studied systems. Red designates an increase in the electron density caused by the intermolecular interactions, whereas blue indicates a related decrease of the electron density. The isodensity contours were plotted for ±0.002 electron/bohr^3.

TABLE 2: Characteristics of H···O BCP for the Complexes Investigated Here[a]

dimer	ρ_{BCP}	$\nabla^2\rho_{BCP}$	G_{BCP}	V_{BCP}	H_{BCP}	ρ_{RCP}
$(HCOOH)_2$	0.0401	0.1293	0.0348	−0.0374	−0.0026	0.0076
	0.0449	**0.1522**	**0.0391**	**−0.0401**	**−0.0010**	**0.0079**
	(0.0476)	(0.1002)	(0.0373)	(−0.0495)	(−0.0122)	(0.0080)
$(CH_3COOH)_2$	0.0424	0.1336	0.0369	−0.0404	−0.0035	0.0081
	0.0460	**0.1545**	**0.0401**	**−0.0416**	**−0.0015**	**0.0083**
	(0.0488)	(0.1009)	(0.0381)	(−0.0510)	(−0.0129)	(0.0083)
$(HCONH_2)_2$	0.0275	0.0966	0.0228	−0.0215	0.0013	0.0043
	0.0324	**0.1084**	**0.0261**	**−0.0251**	**0.0010**	**0.0048**
	(0.0334)	(0.0934)	(0.0268)	(−0.0303)	(−0.0035)	(0.0050)
$(C_4H_4NCOOH)_2$-A	0.0478	0.1422	0.0418	−0.0480	−0.0062	0.0083
	0.0509	**0.1636**	**0.0448**	**−0.0487**	**−0.0039**	**0.0084**
$(C_4H_4NCOOH)_2$−B	0.0463	0.1409	0.0406	−0.0460	−0.0054	0.0084
	0.0489	**0.1605**	**0.0430**	**−0.0458**	**−0.0028**	**0.0083**
$(C_4H_4NCOOH)_2$−C	0.0259	0.1065	0.0241	−0.0216	0.0025	0.0032
	0.0294	**0.1146**	**0.0262**	**−0.0238**	**0.0024**	**0.0032**

[a] The electron density, its Laplacian, kinetic energy density, potential energy density, and the electron energy density at BCP are given. Additionally, the electron density at RCP is included (all values in au). The results obtained at the MP2/aug-cc-pVDZ and the MP2/aug-cc-pVTZ levels of theory are indicated by bold type and parentheses, respectively. The remaining results were obtained at the MP2/6-311++G(d,p) level of theory.

systems. The elongation of the C=O bond and the shortening of the C−O bond due to complexation could be connected with the loss and the gain of their electron density, respectively.

Topological Parameters and Decomposition of the Interaction Energy. The Bader theory is a powerful tool not only to characterize the electronic properties of the considered species but also to have a better understanding of the nature of the intermolecular interactions.[50] The characteristics of the bond critical point (BCP) (the electron density at BCP) and its Laplacian ($\nabla^2\rho_{BCP}$) reveal the nature of the interactions. When ρ_{BCP} is large, this indicates the concentration of the electronic charge ($\nabla^2\rho_{BCP} < 0$). When ρ_{BCP} is small, this implies the depletion of the electronic charge in the internuclear region ($\nabla^2\rho_{BCP} > 0$). The former case is an indication of sharing of the electronic charge density between both nuclei, which defines the covalent (polar) bond. The latter is observed for interactions between the closed-shell systems such as ionic interactions, van der Waals interactions, or hydrogen bonds. The energetic properties of BCPs are also very useful for analyzing atom−atom connections and interactions. The electronic energy density H_{BCP} of the charge distribution may be expressed as

$$H_{BCP} = G_{BCP} + V_{BCP} \tag{5}$$

where G_{BCP} is a local one-electron kinetic energy density and V_{BCP} is the local potential energy density. The relation between the Laplacian and the components of the local energy density H_{BCP} is given by the following equation (in atomic units).

$$\frac{1}{4}\nabla^2\rho_{BCP} = 2G_{BCP} + V_{BCP} \tag{6}$$

The sign of the Laplacian at a specific point in space determines whether the negative potential energy or the positive kinetic energy is in excess of the virial ratio amounting to 2. In the regions where the Laplacian is negative, the potential energy dominates, whereas in the regions where its sign is positive the kinetic energy prevails.

The electron density at BCP correlates well with the H-bond energy and the geometrical descriptors of the H-bond strength.[51] Similarly, good relationships were observed between the H-bond energy and the other topological parameters such as the Laplacian of the electron density at the BCP of the H···Y contact (Y designates the proton acceptor), and the corresponding H_{BCP}, G_{BCP}, and V_{BCP}.[52] One can see such dependencies for the species analyzed here. Figure 1, as was mentioned in the previous section, presents the molecular graphs of the studied complexes. For all the H···O connections there are bond paths and corresponding bond critical points. Therefore the first topological criterion of the existence of hydrogen bonding is fulfilled.[53] Table 2 presents the results of the calculations at the following levels of theory: MP2/6-311++G(d,p), MP2/aug-cc-pVDZ, and MP2/aug-cc-pVTZ. The single H···O contacts are considered as corresponding to the single hydrogen bonds, because for binding energies the two equivalent H···O interactions should be taken into account. Table 2 reveals that the values of the electron density at H···O BCP (ρ_{BCP}) for formic acid, acetic acid, and the A and B configurations of PCA are much greater than for the formamide dimer and the C configuration of PCA. According to the next criteria of Koch and Popelier,[53] concerning the existence of H-bonds, the electron density and its Laplacian for the H···Y contact within the X−H···Y H-bond should have a relatively high value. Both parameters for closed-shell interactions as H-bonds are positive and should be within the following ranges: 0.002−0.040 au for the electron density and 0.020−0.150 au for its Laplacian. One can see that in the case of H···O contacts considered here these criteria are fulfilled.

It is worth mentioning that for the linear-trans water dimer the counterpoise corrected binding energy, estimated at the MP2/6-311++G(d,p) level of theory, is equal to −4.45 kcal/mol. The respective electron density at H···O BCP amounts to 0.023 au, whereas its Laplacian to 0.091 au. One can see that all of the values of the electron density at H···O BCP outweigh the corresponding value for the water dimer and the same applies to the Laplacian. It is well-known that for some of the very strong RAHBs the Laplacian values are negative, indicating the covalent nature of the interactions. However, it was also pointed out that if the Laplacian is positive and the density of the electronic energy at BCP (H_{BCP}) is negative, then the interaction is only partly covalent in nature.[52d,54] The results reported in Table 2 reveal that in the case of systems in which one expects resonance-assisted hydrogen bonds to be formed, the H_{BCP} values are negative. For the formamide dimer as well as for the C configuration of PCA, the H_{BCP} values are positive at the MP2/6-311++G(d,p) and MP2/aug-cc-pVDZ levels of theory, although at the MP2/aug-cc-pVTZ level of theory the H_{BCP} value for the formamide dimer is also negative. Thus one can expect that for strong and very strong resonance-assisted hydrogen bonds the partly covalent character of the H···Y interaction is probably their distinct characteristic.

TABLE 3: Interaction Energy Components (kcal/mol) for the Investigated Molecular Complexes[a]

dimer	$\epsilon_{el}^{(10)}$	ϵ_{ex}^{HL}	ΔE_{del}^{HF}	$\epsilon_{el,r}^{(12)}$	$\epsilon_{disp}^{(20)}$	$\Delta E_{ex-del}^{(2)}$	Δ_E^{HF}	$\epsilon_{MP}^{(2)}$	Δ_E^{MP2}
$(HCOOH)_2$	−30.1	30.0	−14.3	1.5	−7.1	6.4	−14.5	0.9	−13.6
$(CH_3COOH)_2$	−32.2	32.3	−15.2	1.3	−7.7	6.9	−15.0	0.5	−14.5
$(HCONH_2)_2$	−23.4	19.8	−8.5	1.3	−5.6	4.3	−12.1	0.0	−12.1
$(C_4H_4NCOOH)_2$-A	−36.7	37.6	−18.6	1.9	−9.0	7.7	−17.7	0.6	−17.1
$(C_4H_4NCOOH)_2$−B	−34.8	36.1	−17.3	1.6	−8.8	7.5	−16.0	0.3	−15.7
$(C_4H_4NCOOH)_2$−C	−19.9	16.1	−6.9	1.6	−6.3	3.3	−10.7	−1.4	−12.1

[a] The results were obtained at the MP2/6-311++G(d,p) level of theory.

Table 2 collects also the electron densities at the ring critical points created due to the double H-bond formation. The ring critical point (RCP) is a point of minimum electron density within the ring surface and a maximum on the ring line.[53b] For example, in the case of benzene due to symmetry constraints, the RCP lies at the center of the ring. In the absence of symmetry, the RCP can be found anywhere inside the ring. It was pointed out that the electron density at RCP often correlates with the H-bond energy for the samples of the related systems with intramolecular H-bonds.[10a] This also holds for the sample analyzed here where RCPs are created due to the existence of double H-bonds between the investigated species.

Table 3 reports the interaction energy components for the investigated molecular complexes. The decomposition of the interaction energies was performed according to the scheme described in the preceding section. It is possible to summarize the following findings. The first-order Heitler−London interaction energy term is close to zero for formic acid and acetic acid dimers as well as for the A and B configurations of the PCA dimers. It is because the first-order electrostatic interaction energy term is quenched by the exchange repulsion energy. In the case of the remaining systems bound by considerably weaker H-bonds, the electrostatic energy outweighs the exchange energy and hence, the first-order HL energy term is weakly attractive. One can also observe greater stabilization from the dispersion energy in the case of O−H···O hydrogen bonds. There are also other differences between the homonuclear and heteronuclear double H-bonds investigated here. In the case of the former, the delocalization energy term is dominant and is about 2 times greater than for the latter. In fact, the compensation between the major correlation interaction energy components, namely, the dispersion and exchange-delocalization, makes the delocalization component the only significant interaction energy term. These findings are in line with the results of calculations performed on the formic acid dimer by Iwata et al. within the multiconfigurational SCF formalism in the STO-3G(d) basis set.[55] However, these results seem to be treated carefully nowadays due to the size of the basis set applied. The authors have found that in the ground state, the charge transfer (CT) and polarization (PL) energy terms are the most important attractive contributions to the intermolecular interaction energy of this system. They have applied yet another interaction energy partitioning technique, namely, the Kitaura−Morokuma scheme, adapted to the multiconfigurational wave functions.[56] In this scheme, the sum of CT and PL components correspond to the delocalization energy term considered here.

It is worth mentioning that the difference in the interaction strength between the homonuclear resonance-assisted hydrogen bonds O−H···O and the heteronuclear N−H···O bonds correlates nicely with the H···O intermolecular distances. The same applies to the estimated interaction energy components. Figure 3 reveals the relationship between the main components of the interaction energy and the H···O distances for the whole sample of the analyzed species. One can see the two cases of heteronuclear N−H···O bonds with considerably greater H···O distances. For the O−H···O hydrogen bonds there are nice correlations between the magnitudes of the interaction energy components and the H···O distances. It seems that the same applies to the N−H···O bonds. However, there is not enough data to confirm such an assumption. Figure 3 indicates clearly that the attractive electrostatic energy term is compensated by the repulsive exchange energy term. The same effect can be observed regarding the dispersion and exchange-delocalization correlation energy terms. Therefore the stabilization from the delocalization energy term is the major component of the total interaction energy in these systems, whose magnitude increases with the decrease of the H···O distance.

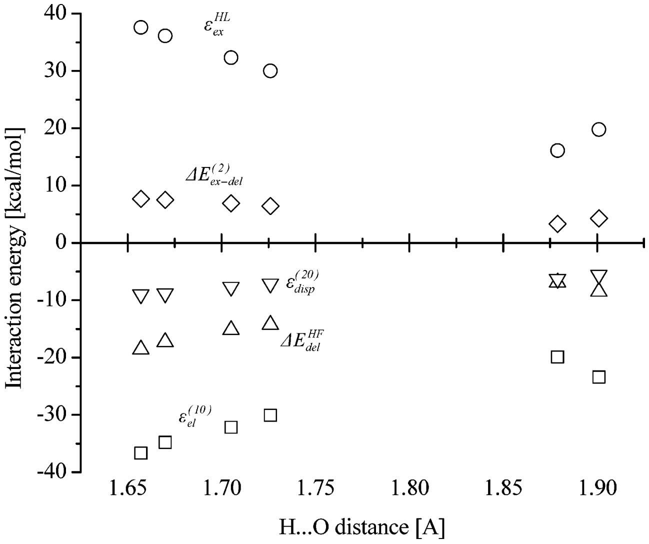

Figure 3. Dependence between the H···O intermolecular distance (Å) and the main interaction energy components (kcal/mol) for the investigated species.

There is still an issue that needs to be addressed. Why are the H-bonds stronger in the A and B dimers of PCA than in the dimers of formic and acetic acids? This phenomenon is most likely due to the greater delocalization energy contribution in the case of the PCA dimers, because the Heitler−London interaction energy term is close to zero in both cases. This is accompanied by the smaller H···O distances and greater equalization of the C−O and C═O bonds for the A and B dimers than for the remaining RAHBs considered here.

Summary

The intermolecular O−H···O and N−H···O resonance-assisted hydrogen bonds (RAHBs) were investigated here. The following distinct features characterize these systems.

1. The O−H···O systems are medium or even strong hydrogen bonds whereas the N−H···O H-bonds are characterized by a considerably weaker interactions.

2. The electronic energy density (H_{BCP}) at the H···O bond critical point is negative for the O−H···O systems, which means that they are partly covalent in nature. Such a situation does not occur in the case of the N−H···O hydrogen bonds.

3. The electrostatic energy term is compensated by the exchange repulsion energy and the same applies to the two major correlation energy components: the intermolecular dispersion and the exchange-delocalization. Hence, the delocalization energy term remains the most important attractive contribution to the interaction energy of the O−H···O double H-bonds. The delocalization interaction energy term increases with an decrease in the H···O distance. Therefore one may expect that the distinct feature of the strong RAHBs is the meaningful role of the delocalization energy.

4. The dispersion energy term for O−H···O H-bonded systems becomes increasingly more important if the H···O distance decreases. However, this interaction energy component is not as important as the delocalization energy.

Moreover, it was established that for the N−H···O H-bonded systems (the formamide dimer and the C dimer of the pyrrole-2-carboxylic acid) the electrostatic energy term is the most important attractive term similarly to the case of the conventional hydrogen bonds.

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