Research Article

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Hydrogen bonds assisted by π-electron delocalization – the influence of external intermolecular interactions on dimer of formic acid

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MP2 and DFT calculations with the use of 6-311++G(d,p) basis set were carried out to study formic acid dimer as well as this species interacting with additional Lewis acids such as HF, Li^+ and Na^+. These Lewis acids were positioned near carbonyl or hydroxyl oxygen atoms and their influence on geometrical and other parameters of formic acid dimer was analysed. Additionally the 'quantum theory of atoms in molecules' (QTAIM) was applied as well as the 'natural bond orbitals' (NBO) method. Numerous correlations between geometrical, QTAIM and energetic parameters were found. It was found that π-electron delocalization is not always connected with the enhancement of H-bond strength.

Keywords: MP2 method; DFT method; carboxylic acids; formic acid; hydrogen bond; quantum theory of atoms in molecules; natural bond orbitals method; π-electron delocalization; double proton transfer process

INTRODUCTION

Carboxylic acids are one of the most often investigated kind of species since these compounds are important in numerous chemical and biochemical processes. The influence of substituent effects on carboxylic acids, the acidity of these compounds, hydrogen bonds (H-bonds) between carboxylic groups as well as the double proton transfer processes in dimers of carboxylic acids are examples of topics often undertaken in numerous studies.[1,2]

Particularly, the topics connected with H-bonds in dimers of carboxylic acids seem to be very interesting. It was found that centrosymmetric dimers of carboxylic acids are very common in crystal structures of organic compounds.[2] For these systems the eight-membered ring exists (as shown in Scheme 1 of formic acid dimer) with the inversion center within the ring. According to the Etter graph terminology [3] this is a very well-known $R_2^2(8)$ motif of the following bonds and contacts: [C═O. . .H—O—C═O. . .H—O—C]. Such motifs containing two proton donors and two proton acceptor centers and also containing eight connections (bonds and contacts) are very often in crystal structures, not only of carboxylic acids but also of amides and the other compounds. It is worth mentioning that the centrosymmetric dimers of carboxylic acids exist in crystals of propionic acid and more complex aliphatic acids as well as in crystals of benzoic acid and its derivatives. However such dimers are not known for crystals of acetic acid and formic acid, only fluoro and chloro derivatives of acetic acid form centrosymmetric dimers in crystals.[2] On the other hand formic and acetic acids form centrosymmetric dimers in the gas phase.

Numerous effects existing in dimers of carboxylic acids were investigated early on [1] and continuations of these studies endure by nowadays. These are: the mesomeric effect of carboxylic group, proton transfer and double proton transfer processes and disorder existing often in crystals of carboxylic acids.[4] The latter effect was analysed early on and the existence of dynamic as well as orientational disorder were discussed extensively.[2] This should be mentioned that mesomeric and both kinds of disorder effect existing in crystals of centrosymmetric dimers of carboxylic acids lead to similar changes of geometry of carboxylic groups and to similar changes of H-bonds.[5]

This is very important that H-bonds of carboxylic acids may be attributed to relatively strong ones since they posses characteristics of interactions which are partly covalent in nature.[6] The decomposition scheme of interaction energy [7] as well as the quantum theory of atoms in molecules (QTAIM) [8,9] were applied to analyse H-bonds of carboxylic acids. It was found that the delocalization interaction energy term is meaningful for dimers of carboxylic acids and that this term is comparable to the electrostaic interaction energy.[6] Besides the QTAIM studies also indicated that H-bonds of dimers of carboxylic acids are classified as strong ones.[10]

It seems that special characteristics of H-bonds of carboxylic acids are connected with the π-electron delocalization within the mentioned above eight-membered ring. Such delocalization may lead to the equalization of C—O and C═O bonds of carboxylic group; it is connected with the idea of so-called resonance assisted hydrogen bonds (RAHBs).[11,12] RAHBs were analysed

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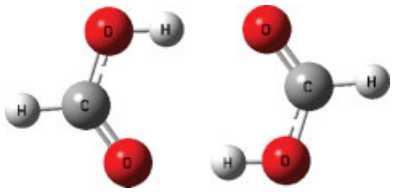


Scheme 1.

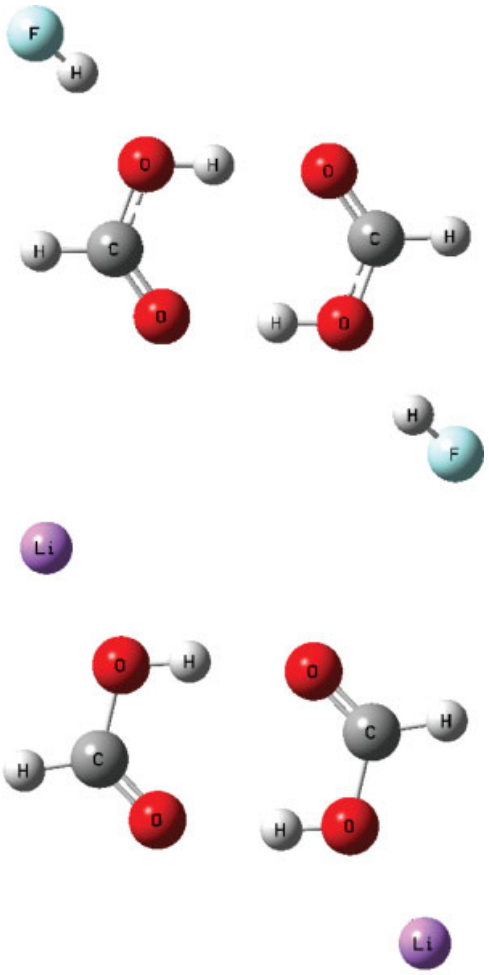
extensively for intramolecular H-bonds of malonaldehyde, its derivatives and the other numerous systems. It was stated that RAHBs may be detected for systems containing conjugated single and double bonds since for such systems π-electron delocalization influences H-bonds, that is, it causes their enhancement. It was also pointed out that also intermolecular RAHBs may exist for such moieties as dimers of carboxylic acids, amides and dimers of DNA bases. However it is worth mentioning that RAHB concept was criticized in recent studies. It was shown that H-bond strength for the systems usually attributed to RAHBs is not connected mainly with π-electron delocalization but rather with the properties of the σ single bond skeleton.[13,14] However it was also calculated that roughly 20–30% of the H-bond energy is connected with the π-electron delocalization and 70–80% with the energy attributed to the closure of quasi-ring by H-bond formation.[15]

There are the other studies which are not in line with the RAHB model. For example, the interaction of the oxygen carbonyl atom in malonaldehyde with the additional Lewis acid leads to the π-electron delocalization but also to the weakening of H-bond and not to its strengthening. This was found for intramolecular H-bonds of malonaldehyde and its derivatives which were usually attributed to RAHBs.[16] Such influence of external Lewis acids was also analysed for intramolecular N—H. . .O H-bonds leading to the similar findings.[17]

The aim of this study is to analyse the dimer of formic acid and the influence of external agents on this dimer. For the mentioned analyses *ab initio* and DFT calculations were performed as well as QTAIM[8,9] and NBO[18] theories were applied. However the main part of analyses is to characterize systems which are usually attributed to intermolecular RAHBs.

COMPUTATIONAL DETAILS

The calculations were carried out with Gaussian03[19] sets of code using the standard 6-311++G(d,p) basis set[20] and MP2 method.[21] These calculations were performed on centrosymmetric dimer of formic acid and related systems. The latter are also centrosymmetric systems containing formic acid dimer and Lewis acid species situated near carbonyl or hydroxyl oxygen atoms, these are: Li^+, Na^+ ions and HF molecule. To keep the inverse symmetry for these systems, two Lewis acid moieties were situated at both equivalent O-centers – hydroxyl or carbonyl ones. Scheme 2 presents the systems with Lewis acid species at O-hydroxyl atoms while Scheme 3 presents the systems containing Lewis acids at O-carbonyl centers. The complexes containing Na^+ ions are not shown in Schemes since they are very similar to those containing Li^+ ions. The additional calculations were performed for monomer of formic acid and for that monomer with Lewis acid moiety attached to the O-hydroxyl or O-carbonyl center. For all species analysed here

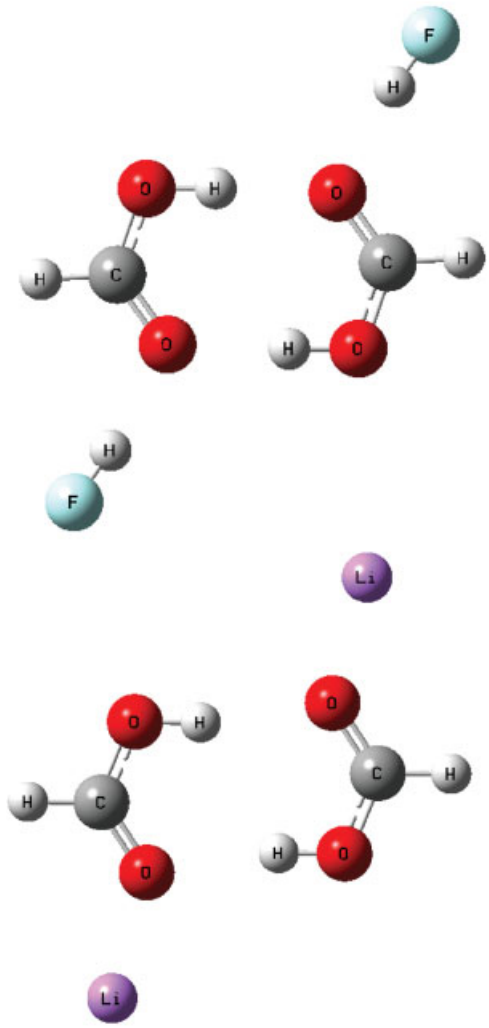


Scheme 2.

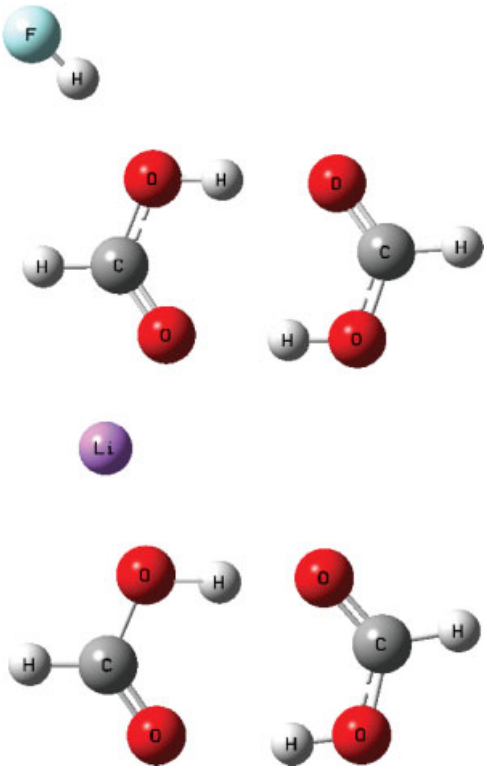
geometries were optimized and the final systems correspond to minima since no imaginary frequencies were found. Additional calculations were performed for transition states corresponding to the O—H. . .O ⇔ O. . .H—O double proton transfer reaction. For the latter transition states one imaginary frequency corresponding to 'the double movement of protons' approximately along O. . .O lines was detected.

Owing to the calculations performed on the species described above it is possible to explain the influence of external agents on the formic acid dimer and particularly on the H-bonds of the latter moiety. Non-centrosymmetric systems were also considered here; that is, formic acid dimer with the additional single Lewis acid moiety (Li^+, Na^+, HF) situated in the neighbourhood of O-hydroxyl oxygen (Scheme 4).

The QTAIM[8,9] is also applied and the characteristics of bond critical points (BCPs) are analysed in terms of the following properties: the electron density at the critical point (ρ_C), its Laplacian ($\nabla^2\rho_C$) and the total electron energy density at this critical point (H_C). For the latter value its components are also usually analysed: the potential electron energy density (V_C) and the kinetic electron energy density (G_C). Figure 1 presents the molecular graph derived from the QTAIM theory of the TS of the double proton transfer process for HCOOH dimer affected by hydrogen fluoride Lewis acid. Figure 1 also presents the electron density map of this system with the gradient paths included.



Scheme 3.



Scheme 4.

There is the well-known relationship resulting from the virial theorem between Laplacian and energetic properties of BCP:

$$1/4(\nabla^2\rho_C) = 2G_C + V_C \text{ and } H_C = G_C + V_C \quad (1)$$

AIM2000 programme[22] was used to perform QTAIM calculations.

The natural bond orbitals (NBO) method is also applied here,[18,23] however the B3LYP/6-311++G(d,p) level of approximation is used to carry out NBO calculations; in this case the single point calculations were performed for the geometries optimized at the mentioned earlier MP2/6-311++G(d,p) level.

RESULTS AND DISCUSSION

Geometrical parameters

Tables 1 and 2 present geometrical parameters of the systems containing two formic acid molecules (dimer with two H-bonds) and the systems containing one formic acid molecule. These are OH bond lengths, H...O distances as well as C═O and C—O bond lengths. One can observe interesting dependencies and relationships. For example, the C═O and C—O bond lengths for isolated formic acid are equal to 1.205 and 1.348 Å, respectively, while these lengths for formic acid dimer amount to 1.221 and 1.319 Å. This is a very well known effect observed early on.[2] It was explained by the existence of mesomeric effect of carboxylic group and also by the π-electron delocalization within the eight-membered ring of the dimer. Such delocalization leads to the lengthening of C═O double bond and shortening of C—O single bond and also causes the enhancement of O—H...O H-bonds. And really, it was detected that H-bonds of carboxylic acids may be classified as rather strong and partially covalent in nature.[6]

The results of Tables 1 and 2 show that for all systems analysed the equalization of C—O and C═O bonds is greater for dimers than for the corresponding monomeric forms – this comparison concerns HCOOH monomer interacting with Lewis acid and HCOOH dimer interacting with two equivalent Lewis acid moieties. The external Lewis acid agents also influence carboxylic groups, if such agents are situated near carbonyl oxygen thus it leads to the lengthening of C═O bond and the shortening of C—O bond. However if the Lewis acid moiety interacts with the hydroxyl oxygen center thus it results in the lengthening of C—O bond and shortening of C═O bond. Thus the interaction of Lewis acid with carbonyl oxygen causes the reverse effects if compared with the interaction of Lewis acid with the hydroxyl oxygen. If one assumes that O...O (or H...O) distance roughly reflects the strength of hydrogen bonding thus the results concerning complexes with HF molecules show (Table 1) that HF near carbonyl oxygen centers causes the equalization of CO bonds on one hand and to the weakening of H-bonds on the other hand.

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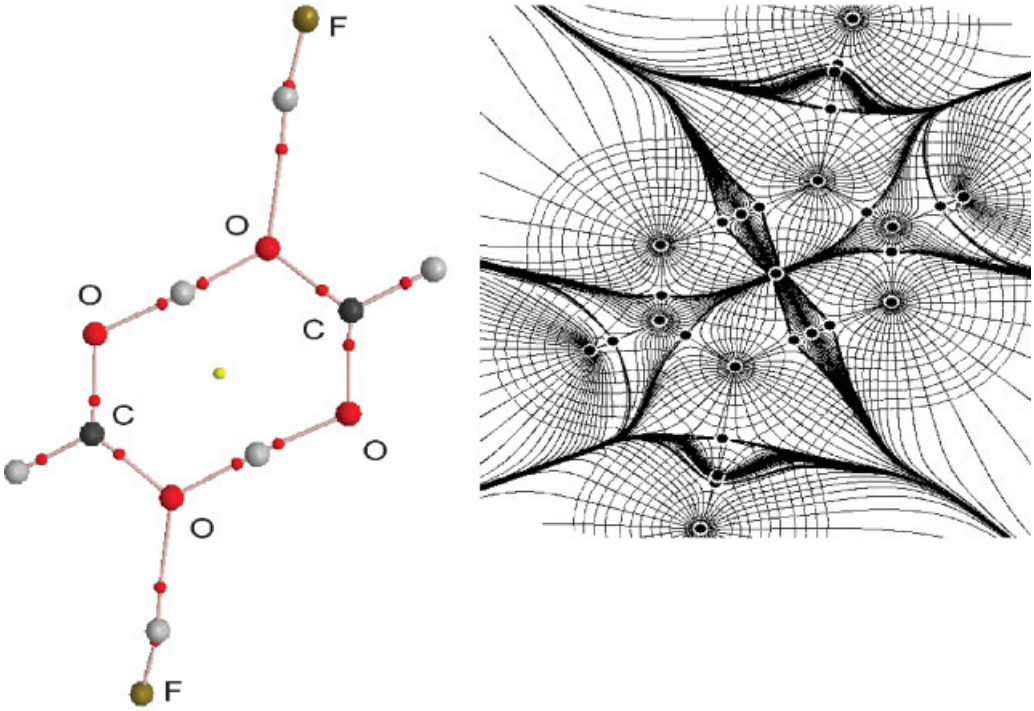

Figure 1. The molecular graph of the transition state of the double proton transfer process of $(HCOOH)_2 \ldots (HF)_2$ system, big circles correspond to attractors (nuclei positions) while small circles to critical points, right, the contour electron density map with the gradient electron density paths indicated (orientation the same as for molecular graph)

Table 1. Geometrical parameters (in Å) of the systems analysed here, OH bond lengths, H. . .O and O. . .O distances as well as C═O and C–O bond lengths are included

Complex	OH	H. . .O	O. . .O	C═O	C–O
CD	0.99	1.727	2.716	1.221	1.319
CD-TS	1.201	1.201	2.400	1.265	1.265
CD-HF/OH	0.993	1.699	2.691	1.217	1.331
CD-HF/CO	0.989	1.74	2.729	1.23	1.307
CD-HF-TS	1.187	1.215	2.401	1.254	1.278
CD-Li/OH	0.989	1.787	2.772	1.202	1.376
CD-Li/CO	0.979	1.985	2.956	1.243	1.297
CD-Li-TS	1.19	1.22	2.408	1.241	1.304
CD-Na/OH	0.99	1.753	2.742	1.208	1.357
CD-Na/CO	0.983	1.851	2.829	1.238	1.303
CD-Na-TS	1.198	1.209	2.405	1.249	1.29
AS-HF/OH	0.997	1.658	2.656	1.216	1.331
AS-HF	0.986	1.762	2.747	1.222	1.318
AS-Li/OH	1.038	1.468	2.501	1.202	1.368
AS-Li	0.979	1.907	2.874	1.232	1.307
AS-Na/OH	1.018	1.535	2.547	1.206	1.357
AS-Na	0.981	1.878	2.851	1.231	1.309

There are following designations: CD – centrosymmetric dimer, AS – assymetric system, in the case of assymetric systems two non-equivalent H-bonds are considered, one with the external agent situated at hydroxyl oxygen atom and the second one without external influences (weaker one), TS – transition state corresponding to the double proton transfer process, HF, Na^+ and Li^+ designate external agents influencing on formic acid dimer, OH and CO indicate the external agents are situated at hydroxyl or carbonyl groups, respectively.

Table 2. Geometrical parameters (in Å) of the systems investigated here, OH, C═O and C–O bond lengths included, the single formic acid molecule interacting with Li^+, Na^+ or HF, M designates one HCOOH molecule within the system, the other designations are the same as in Table 1

Species	OH	C═O	C–O
M	0.969	1.205	1.348
M-HF/OH	0.970	1.200	1.364
M-HF/CO	0.970	1.213	1.334
M-Li/OH	0.974	1.183	1.424
M-Li/CO	0.972	1.231	1.302
M-Na/OH	0.973	1.188	1.403
M-Na/CO	0.971	1.225	1.312

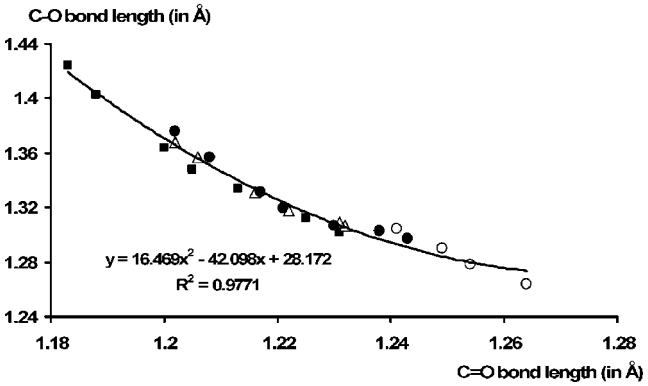

Figure 2. The dependence between C–O and C═O bond lengths (in Å), the second order polynomial relationship corresponds to all species presented, full squares correspond to the species containing one formic acid molecule, full circles to centrosymmetric species, empty circles to transition states of the double proton transfer reaction, empty triangles correspond to assymetric (non-centrosymmetric moieties)

There were similar observations for intramolecular O—H. . .O and N—H. . .O H-bonds that the Lewis acid interacting with C═O bond enhances π-electron delocalization but weakens the strength of H-bond.[16,17] This is not in agreement with the RAHB model[11,12] where it was pointed out that the bond lengths equalization connected with π-electron delocalization leads to the enhancement of H-bond strength. On the other hand Table 1 shows that the hydrogen fluoride moiety acting on O-hydroxyl center causes the lengthening of C—O bond, shortening of C═O bond and enhancement of H-bond strength. However the other Lewis acids (Na^+ and Li^+) situated at hydroxyl oxygen cause differentiation of CO bonds for centrosymmetric formic acid dimer but do not enhance H-bond strength. It may be connected with the electrostatic repulsion of equivalent HCOOH. . .Na^+ (or Li^+) positively charged moieties what leads to the enlargement of O. . .O distance. To check if such electrostatic repulsion is responsible for the weakening of H-bonds the 'asymmetric complexes' were also analysed here. This is the formic acid dimer interacting with the single Li^+, Na^+ and HF moieties positioned near one of O-hydroxyl atoms (as shown in Scheme 4). One can see the meaningful strength enhancement of the corresponding hydrogen bond and the differentiation of CO bonds of the corresponding carboxylic group. On the other hand the other O—H. . .O H-bond of the same complex is much weaker than H-bonds of the centrosymmetric formic acid dimer not involved in any additional interactions.

There is the other interesting finding concerning monomers of formic acid interacting with Lewis acids, those situated in the neighbourhood of carbonyl oxygen and those located near hydroxyl oxygen atom, the corresponding results of Table 2 show that for all such systems there are only slight changes of O—H bond length. However the Lewis acid influence is reflected in the changes of C—O and C═O distances. As it was described above the Lewis acid at hydroxyl oxygen causes the elongation of C—O bond and consequently the shortening of C═O bond length (as shown in Table 2). If the Lewis acid interacts with carbonyl oxygen atom thus the elongation of C═O bond and the shortening of C—O bond are observed. All these observations are in line with the bond valence sum rule – one of the main relations of the so-called bond valence model (BV model).[24,25] Briefly summarizing some of statements of that model one may say that the additional contact of any covalent bond causes its weakening and the loss of covalency of that bond is compensated by the additional contact. Hence the Lewis acid interaction with carbonyl oxygen has to be connected with the lengthening and weakening of C═O bond. There is no meaningful change of O—H bond for species containing one formic acid molecule since there are no additional intermolecular contacts with hydrogen atoms – thus there are changes of C—O and C═O bonds. The lengthening of O—H bond is observed only for species containing two formic acid molecules since in such cases there are additional contacts for H-atoms (O—H. . .O H-bonds).

Table 1 also presents the geometrical parameters of transition states corresponding to the double proton transfer processes. For these systems the CO bond equalization (both CO bonds are equal or nearly so) corresponds to the strongest H-bonds (the shortest O. . .O distances). Figure 2 presents the correlation between C═O and C—O bond lengths. This relationship is well fitted by the second order polynomial, correlations are much better if the sub-samples are considered.

QTAIM parameters

The Bader theory (QTAIM) was also applied here to deepen the nature of the analysed interactions, that is, H-bonds. The QTAIM theory was often applied before for the analyses of H-bonded systems.[26,27] It was indicated very often that the electron density at the H. . .Y BCP is a good measure of H-bond strength of X—H. . .Y system.[28] The shorter H. . .Y distance corresponds to the stronger H-bond and in consequence is characterized by the greater electron density at the corresponding H. . .Y BCP. This is also in force for the complexes analysed here. Figure 3 shows the dependence between H. . .O distance and the electron density at BCP, not only H. . .O intermolecular contacts of O—H. . .O bridges are included but also the contacts for transition states and O—H proton donating bonds of carboxylic groups. One can see the continuity of H. . .O interactions, starting from closed-shell interactions, next are those of TSs and there are covalent bonds. Figure 3 also contains the H. . .O distances corresponding to F—H. . .O H-bonds, the latter are very well fitted to the other H. . .O/O—H distances. Table 3 presents the characteristics of F—H. . .O systems. The latter continuity was earlier observed also for H. . .O interactions,[29] for H. . .H contacts[30] and early on for H. . .F ones.[31] There is also the continuity of covalent bond

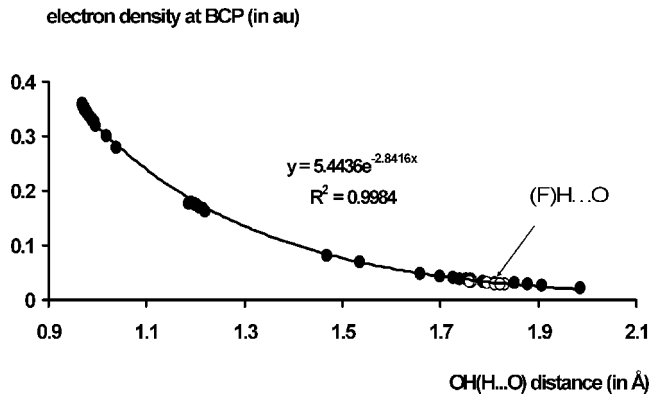

Figure 3. The exponential relationship between H...O (and O–H) distance (and bond length) – in Å, and the electron density at the corresponding BCP (in au), the (F)H...O contacts are also included (designated by empty circles)

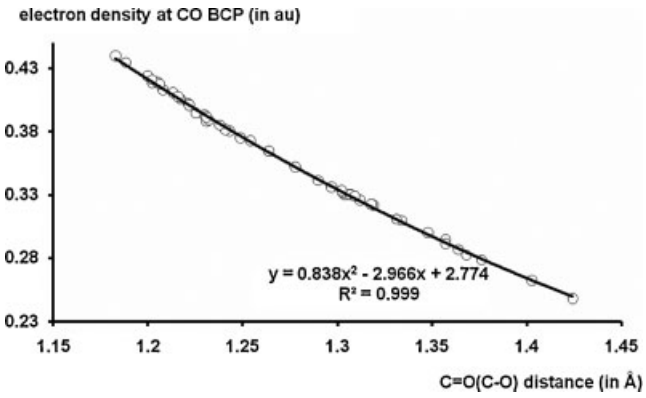

Figure 4. The dependence between C–O (C═O) bond length (in Å) and the electron density at the corresponding BCP (in au)

Table 3. F–H bond lengths and H...O distances (in Å) of F–H...O H-bonds, designations of species are the same as in Tables 1 and 2, the electron density at the corresponding H...O BCP is also included (in au)

System	F–H	H...O	ρ_C
CD-HF/OH	0.925	1.832	0.0278
CD-HF/CO	0.929	1.764	0.0343
CD-HF-TS	0.927	1.795	0.0311
AS-HF/OH	0.926	1.811	0.0294
M-HF/OH	0.925	1.822	0.029
M-HF/CO	0.93	1.759	0.0343

For monomer HF molecule the H–F bond length amounts to 0.917 Å.

interactions for single and double bonds – Fig. 4 presents the relationship between C═O/C—O bond length and the electron density at the corresponding BCP. There are longer C—O bonds included, shorter C═O ones as well as CO bonds of transition states where full (or nearly so) equalization of bonds takes place.

Tables 4 and 5 contain the BCPs' characteristics of OH bonds and H...O contacts (Table 3 presents the electron densities at BCPs of (F)H...O contacts). MP2/6-311++G(d,p) results are included. It is worth mentioning that for H...O contacts the characteristics indicate interactions of the broad strength range. Positive values of Laplacians usually indicate non-covalent interactions. And almost all H...O contacts analysed posses positive Laplacians, except of those corresponding to the transition states. Rozas, Alkorta and Elguero[32] suggested that the Laplacian as well as the total electron energy density at H...Y BCP (as shown in Eqn 1) should both be used as criteria to

Table 4. QTAIM parameters of O–H bonds and H...O contacts of dimers of formic acid (in au), designations of complexes are the same as in Table 1

Complex	OH BCP					H...O BCP				
	ρ_C	$\nabla^2\rho_C$	G_C	V_C	H_C	ρ_C	$\nabla^2\rho_C$	G_C	V_C	H_C
CD	0.3265	−2.3255	0.0671	−0.7156	−0.6485	0.0399	0.1289	0.0347	−0.0372	−0.0025
CD-TS	0.1702	−0.3239	0.0951	−0.2711	−0.1760	0.1702	−0.3239	0.0951	−0.2711	−0.1760
CD-HF/OH	0.3211	−2.2836	0.0659	−0.7027	−0.6368	0.0426	0.1338	0.0371	−0.0408	−0.0037
CD-HF/CO	0.3274	−2.3431	0.0661	−0.718	−0.6519	0.0384	0.127	0.0337	−0.0356	−0.0019
CD-HF-TS	0.1758	−0.396	0.0942	−0.2873	−0.1931	0.1628	−0.2575	0.0941	−0.2526	−0.1585
CD-Li/OH	0.3246	−2.328	0.0633	−0.7086	−0.6453	0.0325	0.1161	0.0287	−0.0285	0.0002
CD-Li/CO	0.3397	−2.4428	0.0665	−0.7437	−0.6772	0.0222	0.0765	0.0176	−0.0161	0.0015
CD-Li-TS	0.1752	−0.4047	0.0917	−0.2846	−0.1929	0.1591	−0.2318	0.093	−0.2439	−0.1509
CD-Na/OH	0.3249	−2.3186	0.0652	−0.7101	−0.6449	0.0361	0.1236	0.0319	−0.0328	−0.0009
CD-Na/CO	0.3343	−2.3925	0.0871	−0.7324	−0.6453	0.0304	0.1015	0.0251	−0.0249	0.0002
CD-Na-TS	0.172	−0.3546	0.0931	−0.2749	−0.1818	0.165	−0.2783	0.0942	−0.2579	−0.1637
AS-HF/OH	0.3156	−2.2274	0.0664	−0.6897	−0.6233	0.0474	0.1409	0.0412	−0.0473	−0.0061
AS-HF	0.3303	−2.3626	0.069	−0.7246	−0.6556	0.0364	0.1221	0.0316	−0.0327	−0.0011
AS-Li/OH	0.2751	−1.7641	0.0739	−0.5888	−0.5149	0.0792	0.1576	0.0662	−0.093	−0.0268
AS-Li	0.3393	−2.4514	0.0658	−0.7444	−0.6786	0.0252	0.0925	0.0214	−0.0197	0.0017
AS-Na/OH	0.2956	−1.9861	0.0721	−0.6408	−0.5687	0.0667	0.1598	0.0572	−0.0744	−0.0172
AS-Na	0.337	−2.4306	0.0657	−0.7391	−0.6734	0.0272	0.0978	0.0231	−0.0218	0.0013

Table 5. QTAIM parameters of O-H bonds of monomers of formic acid (in au), designations of species analysed are the same as in the previous tables

Complex	ρ_C	$\nabla^2\rho_C$	G_C	V_C
M	0.3543	−2.4962	0.0742	−0.7724
M-HF/OH	0.3508	−2.4873	0.0712	−0.7643
M-HF/CO	0.3527	−2.5028	0.0719	−0.7695
M-Li/OH	0.3436	−2.4517	0.0677	−0.7483
M-Li/CO	0.3478	−2.5092	0.0663	−0.7599
M-Na/OH	0.3465	−2.458	0.0698	−0.7542
M-Na/CO	0.3497	−2.5081	0.0683	−0.7636

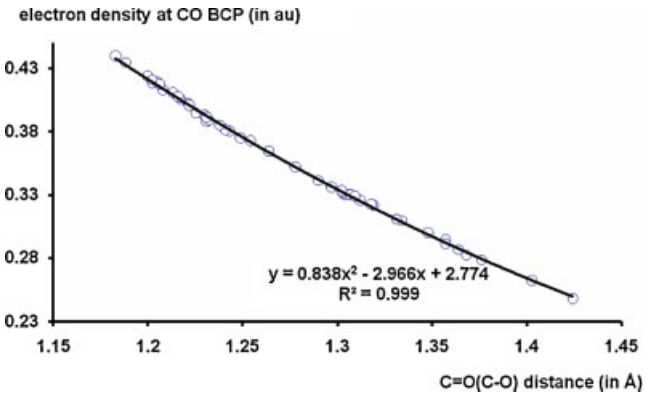

Figure 5. The dependence between H. . .O (OH) distance (in Å) and the total electron energy density at the corresponding BCP (in au)

characterize hydrogen bonding. They proposed for weak and medium H-bonds that both $\nabla^2\rho_C$ and $H_C > 0$; for strong H-bonds it is: $\nabla^2\rho_C > 0$ and $H_C < 0$, while for very strong ones both $\nabla^2\rho_C$ and $H_C < 0$. The latter H-bonds are usually classified as covalent in nature. H_C is negative if $|V_C| > G_C$, thus Table 4 indicates that for almost all H. . .O interactions H_{BCP}'s are negative. It was pointed out that such interactions may be classified as being at least partly covalent in nature.[33] Figure 5 presents the dependence between H. . .O (OH) distance and the total electron energy density at the corresponding BCP (H_C), three kinds of interactions (covalent, partly covalent and closed-shell interactions) are nicely indicated here.

The decomposition scheme of the interaction energy was earlier applied to analyse carboxylic acids and it was found that for this class of compounds H-bonds are characterized by the meaningful contribution of the delocalization interaction energy term.[6] For typical H-bonds the electrostatic interaction energy term is the most important attractive one and next, the other attractive contributions may be important but usually much less than electrostatic energy.[34] For H-bonds of carboxylic acids the delocalization energy is competitive to electrostatic term. It was generally concluded that the delocalization is attributed to covalent character of H-bond interaction.

Energetic dependencies and NBO results

Table 6 presents energies of some of systems investigated here. These are those for which the proton transfer process was analysed: formic acid dimer and centrosymmetric species containing Lewis acid moieties in the proximity of O-carbonyl or O-hydroxyl centers. It was pointed out early on that the influence of external agents may decrease the potential barrier height for the double proton transfer process in dimers of carboxylic acids. Particularly such decrease was explained for the crystal structures of carboxylic acids.[35,36] For the species analysed here there is such decrease for agents acting on O-hydroxyl center, while for Lewis acid positioned near carbonyl bond there is the increase of the potential barrier height. Table 6 also shows that the systems with Lewis acids at O-carbonyl centers are characterized by lower energies if compared with the

Table 6. Energies (in hartrees) of selected systems analysed here, the energies containing ZPVE terms are also included (in hartrees), the differences in energies (in kcal/mol) are presented – between the transition state and the considered system in minimum and also the differences between both configurations corresponding to the double proton transfer process (in kcal/mol), such differences containing ZPVE term are also shown; designations of species analysed are the same as in the previous tables

Complex	Energy	Energy + ZPVE	Energy difference	Energy difference (ZPVE included)
CD	−378.747745	−378.676802	8.84[a]	4.95[a]
CD-TS	−378.733664	−378.668908	0[b]	0[b]
CD-HF/OH	−579.324190	−579.228577	7.11[a]	3.73[a]
CD-HF/CO	−579.328872	−579.232277	10.04[a]	6.05[a]
CD-HF-TS	−579.312865	−579.222634	2.94[b]	2.32[a]
CD-Li/OH	−393.217078	−393.144177	7.89[a]	4.62[a]
CD-Li/CO	−393.225788	−393.151704	13.36[a]	9.35[a]
CD-Li-TS	−393.204504	−393.136808	5.47[b]	4.72[b]
CD-Na/OH	−702.054206	−701.982420	8.35[a]	4.83[a]
CD-Na/CO	−702.058498	−701.985929	11.05[a]	7.04[a]
CD-Na-TS	−702.040892	−701.974716	2.69[b]	2.20[b]

[a] The difference in energy between the transition state and the considered system in minimum.
[b] The difference in energy between both configurations corresponding to the double proton transfer process (in kcal/mol).

Table 7. The energy connected with the electron charge transfer from lone pairs to the anti-bonding orbital of the proton donating bond (in kcal/mol), designations of species analysed are the same as in the previous tables

Complex	Energy
CD	23.22
CD-TS	183.57
CD-HF/OH	25.91
CD-HF/CO	20.3
CD-HF-TS	176.2
CD-Li/OH	17.12
CD-Li/CO	9.0
CD-Li-TS	178.02
CD-Na/OH	20.16
CD-Na/CO	14.9
CD-Na-TS	178.89
AS-HF/OH	30.81
AS-HF	19.86
AS-Li/OH	67.31
AS-Li	10.48
AS-Na/OH	51.09
AS-Na	12.2
F-H. . .O interaction	
CD-HF/OH	8.43
CD-HF/CO	13.24
CD-HF-TS	9.66
AS-HF	9.39
M-HF/OH	8.89
M-HF/CO	14.97

systems containing the same agents at O-hydroxyl centers. It is in line with the Leffler–Hammond rule[37,38] since the latter species of the higher energies are closer to transition states and consequently posses the stronger H-bonds. Such observations were detected previously for the systems with intramolecular H-bonds.[39]

The results confirm the statement that the lattice forces in crystals may influence on the proton transfer reaction and particularly may decrease the double proton transfer barrier height for centrosymmetric dimers of carboxylic acids. It should be pointed out that the lattice forces may influence the other effects and phenomena such as π-electron delocalization and dynamic disorder.

The NBO analysis was also performed here to deepen the nature of O—H. . .O H-bonds. Table 7 presents energies connected with the transfer of electronic charge within O—H. . .O bridges – from the *n*-lone pairs of oxygen acceptor center to the antibond σ^*_{OH} orbital of the proton donating bond. This is the second order energy lowering which in SCF MO theory may be expressed as

$$\Delta E^{(2)}_{n\sigma^*} = -2\frac{\langle n|F|\sigma^*\rangle}{\varepsilon_{\sigma^*} - \varepsilon_n} \quad (2)$$

where *F* is the Fock operator and $\varepsilon_{\sigma}{}^*$ and ε_n are NBO orbital energies. It is worth mentioning that this electron charge transfer and the corresponding lowering of energy are attributed to

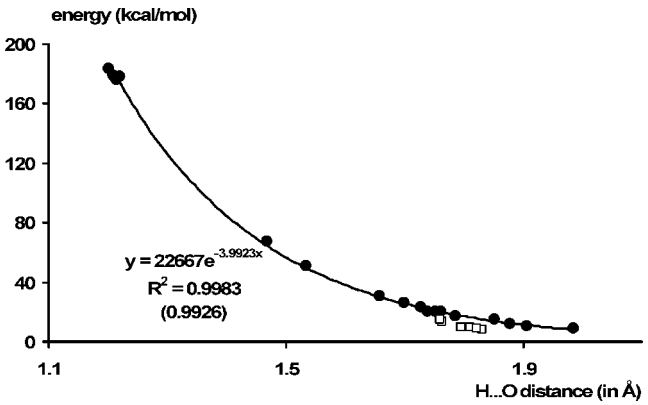

Figure 6. The dependence between H. . .O distance (in Å) and the energy (in kcal/mol) connected with charge transfer from the oxygen lone pairs to the anti-bonding O–H orbital, F–H. . .O are given for comparison (empty squares); R^2 given in parentheses was obtained after exclusion of transition states

hydrogen bond interactions. It was shown that if this part of energy is neglected during calculations thus the H-bonded systems are not created,[18] in other words the second order energy lowering is responsible for the existence of H-bonds.

Figure 6 presents the relationship between the H. . .O distance of O—H. . .O system and the energy expressed by Eqn 2. This is a very good exponential correlation, even the H. . .O interactions of F—H. . .O H-bonds (Fig. 6, empty squares) are well fitted to the exponential regression line (these H-bonds are not included in this regression). The latter relationship indicates that for stronger H-bonds of shorter H. . .O distances there is the greater electron transfer from the proton acceptor to the proton donating bond and the greater energy lowering connected with this process.

It is well known that the H-bond formation is connected with the lengthening of the proton donating X—H bond (except of the special case of so-called blue-shifting H-bonds). This lengthening is greater for stronger H-bonds. These early observations are confirmed by the correlation presented in Fig. 7 – between O—H bond length and the second order energy lowering (Eqn 2). Figure 8 shows the relationship between the electron density at H. . .O BCP and the energy expressed by Eqn 2. One can see that the latter energy may be useful as a good descriptor of H-bond

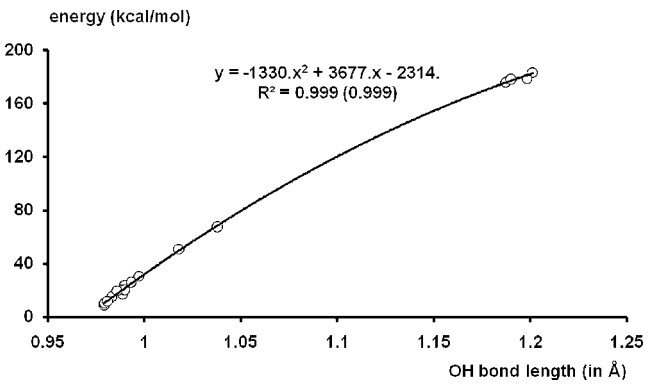

Figure 7. The dependence between O–H bond length (in Å) and the energy (in kcal/mol) connected with charge transfer from the oxygen lone pairs to the anti-bonding O–H orbital; R^2 given in parentheses was obtained after exclusion of transition states

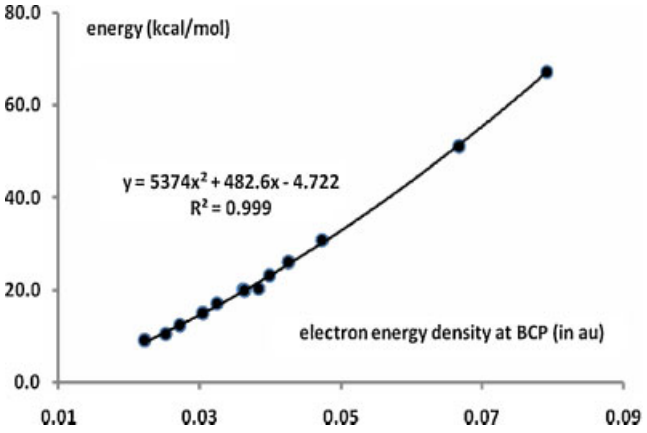

Figure 8. The dependence between the electron density at H. . .O BCP (in au) and the energy (in kcal/mol) connected with charge transfer from the oxygen lone pairs to the anti-bonding O–H orbital; transition states are not taken into account

strength since it well correlates with the other numerous parameters expressing the H-bond strength. The similar observations were presented recently for the intramolecular dihydrogen bonds[40] as well as for the complexes formed between guanidine and formate with RNA bases.[41]

CONCLUSIONS

The influence of external agents – Lewis acids – on the centrosymmetric dimer of formic acid was analysed here. It was found that Lewis acid acting on O-hydroxyl center increases the strength of the O—H. . .O hydrogen bond while this acid positioned near O-carbonyl atom decreases the strength of H-bond. In the latter case there is the greater π-electron delocalization resulting in the equalization of C═O and C—O bond lengths of carboxylic group. The latter observations are not in line with the so-called RAHB model.

Numerous correlations between geometrical, topological – derived from QTAIM theory and energetic parameters were found here. It was found that the second order energy lowering connected with the charge transfer from the lone pairs of acceptor of proton to the anti-bonding orbital of the proton donating bond is a very good descriptor of H-bond strength.

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REFERENCES

[1] H. A. Staab, *Einführung in die Theoretische Organische Chemie*, Verlag Chemie, Weinheim/Bergstr, **1959**.
[2] L. Leiserowitz, *Acta Crystallogr.* **1976**, *B32*, 775.
[3] M. C. Etter, *Acc. Chem. Res.* **1990**, *23*, 120.
[4] J. Bernstein, M. C. Etter, L. Leiserowitz, *The Role of Hydrogen Bonding in Molecular Assemblies in Structure Correlation*, (Eds: H. -B. Bürgi, J. D. Dunitz) VCH, Weinheim, **1994**.
[5] S. J. Grabowski, T. M. Krygowski, *Acta Crystallogr.* **1985**, *C41*, 1224–1226.
[6] R. W. Gora, S. J. Grabowski, J. Leszczynski, *J. Phys. Chem. A* **2005**, *109*, 6397–6405.
[7] G. Chałasiński, M. M. Szczęśniak, *Chem. Rev.* **2000**, *100*, 4227–4252.
[8] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, **1990**.
[9] Eds: C. Matta, R. J. Boyd, *Quantum Theory of Atoms in Molecules: Recent Progress in Theory and Application*, Wiley-VCH, **2007**.
[10] S. J. Grabowski, W. A. Sokalski, E. Dyguda, J. Leszczynski, *J. Phys. Chem. B* **2006**, *110*, 6444–6446.
[11] P. Gilli, V. Bertolasi, V. Ferretti, G. Gilli, *J. Am. Chem. Soc.* **1994**, *116*, 909.
[12] G. Gilli, P. Gilli, *J. Mol. Struct.* **2000**, *552*, 1.
[13] I. Alkorta, J. Elguero, O. Mó, M. Yáñez, J. E. del Bene, *Mol. Phys.* **2004**, *102*, 2563.
[14] I. Alkorta, J. Elguero, O. Mó, M. Yáñez, J. E. del Bene, *Chem. Phys. Lett.* **2002**, *411*, 411.
[15] S. J. Grabowski, *J. Phys. Org. Chem.* **2003**, *16*, 797.
[16] S. J. Grabowski, *Pol. J. Chem.* **2007**, *81*, 607–611.
[17] S. J. Grabowski, *J. Mol. Struct. (Theochem)* **2007**, *811*, 61–67.
[18] F. Weinhold, C. Landis, *Valency and Bonding*, Cambridge University Press, Cambridge, **2005**.
[19] 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, J. A. Pople, *Gaussian 03, Revision B.03*, Gaussian Inc., Pittsburgh, PA, **2003**.
[20] M. J. Frisch, J. A. Pople, J. S. Binkley, *J. Chem. Phys.* **1984**, *80*, 3265.
[21] C. Møller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618–622.
[22] AIM2000 designed by Friedrich Biegler-König, University of Applied Sciences, Bielefeld, Germany.
[23] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926.
[24] I. D. Brown, *Acta Crystallogr.* **1992**, *B48*, 553–572.
[25] S. J. Grabowski, T. M. Krygowski, Advances in Quantitative Structure Property Relationships. in *Molecular Geometry as a Source of Chemical Information – Applications of the Bond Valence – Bond Number Models, Vol. 3*, Elsevier Science B. V., Amsterdam, **2002**, 27–66.
[26] P. L. A. Popelier, *Atoms in Molecules. An Introduction*, Pearson, London, Great Britain, **2000**.
[27] L. Sobczyk, S. J. Grabowski, T. M. Krygowski, *Chem. Rev.* **2005**, *105*, 3513–3560.
[28] I. Alkorta, I. Rozas, J. Elguero, *Chem. Soc. Rev.* **1998**, *27*, 163.
[29] S. J. Grabowski, W. A. Sokalski, J. Leszczynski, *J. Phys. Chem. A* **2006**, *110*, 4772–4779.
[30] S. J. Grabowski, W. A. Sokalski, J. Leszczynski, *Chem. Phys.* **2007**, *337*, 68–76.
[31] E. Espinosa, I. Alkorta, I. Rozas, J. Elguero, E. Molins, *Chem. Phys. Lett.* **2001**, *336*, 457.
[32] I. Rozas, I. Alkorta, J. Elguero, *J. Am. Chem. Soc.* **2000**, *122*, 11154.
[33] D. Cremer, E. Kraka, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 627.
[34] S. J. Grabowski, W. A. Sokalski, *J. Phys. Org. Chem.* **2005**, *18*, 779–784.
[35] S. Hayashi, J. Umemura, S. Kato, K. Morokuma, *J. Phys. Chem.* **1984**, *88*, 1330.
[36] S. J. Grabowski, T. M. Krygowski, *Chem. Phys. Lett.* **1988**, *151*, 425–4427.
[37] J. E. Leffler, *Science* **1953**, *117*, 340.
[38] G. S. Hammond, *J. Am. Chem. Soc.* **1955**, *77*, 334.
[39] S. J. Grabowski, M. Małecka, *J. Phys. Chem. A* **2006**, *110*, 11847–11854.
[40] I. Alkorta, J. Elguero, S. J. Grabowski, *J. Phys. Chem. A.* **2008**, *112*, 2721–2727.
[41] I. Rozas, I. Alkorta, J. Elguero, *Org. Biomol. Chem.* **2005**, *3*, 366.