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π-Electron delocalisation for intramolecular resonance assisted hydrogen bonds

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ABSTRACT: π-Electron delocalisation for the intramolecular resonance assisted hydrogen bonds (IRAHBs) is analysed here. The investigation is based on MP2/6-311++G** calculations as well as on the results derived from the Bader theory. The Mulliken analysis of the change in natural population atomic charges for the IRAHB systems shows that there is a transfer of the electron charge from the —$R_1C{=}CR_2$—CR_3 region into the —O—H...O= hydrogen bond. The results of calculations also show that the strength of IRAHBs depends mainly on the process of the π-electron delocalisation. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: π-electron delocalisation; resonance assisted hydrogen bonds; intramolecular hydrogen bonds; *ab initio* calculations; Bader theory

INTRODUCTION

The intramolecular hydrogen bond (H-bond) has been subject of many investigations,[1,2] and a great deal of effort devoted to studies on the strength of such bonds.[3,4] There are many differences in the nature of intermolecular and intramolecular H-bonds. It is worth mentioning that H-bond energy may be obtained using theoretical approaches such as *ab initio* or DFT calculations: it is calculated as a difference in energy of the complex on one hand and of the energies of monomers on the other.[5]Such an approach is not possible for intramolecular H-bonds and there is no the direct way to calculate H-bond energy for them.[4]

Special attention is often given to strong intramolecular H-bonds and the so-called resonance assisted hydrogen bonds (RAHBs) are often studied.[6] A lot of RAHBs have been found among the crystal structures of β-diketone enols. For such systems there is π-electron delocalisation of the O=C—C=C—OH keto–enol group. According to the statements of Gilli and coworkers[6] such π-electron delocalisation is responsible for the changes of the geometry of the skeleton building up the spacer between the H-bond donor and acceptor.

Conformations of malonaldehyde and its simple derivatives containing the intramolecular H-bonds are examples of RAHBs (Scheme 1). The following geometrical changes are observed for RAHBs:

- the equalization of the lengths of bonds: C—O and C=O
- the equalization of the lengths of bonds: C—C and C=C
- the elongation of the O—H bond as it is known for typical H-bonds, and the shortening of the H...O distance.

In extreme cases the H atom is moved into the middle of the O...O distance and d1–d4; d3–d2 differences in bond lengths tend to zero.

The O—H...O intramolecular resonance assisted hydrogen bonds (IRAHBs) have been investigated extensively. However, other types of IRAHBs have been also studied, such as N—H...O, O—H...N, O—H...S, S—H...O: e.g. the N—H...O ⇔ N...H—O proton transfer process for the crystal structures of chromone derivatives have been studied both experimentally and theoretically;[7] high-level *ab initio* calculations on the intramolecular H-bond in thiomalonaldehyde have been performed[8] since it is an example of the enol-enethiol equilibrium: O—H...S ⇔ O...H—S; the substituent effects on the strength of the intramolecular H-bond in thiomalonaldehyde have been also studied.[9] Among calculations on the RAHBs those concerning malonaldehyde[10,11] and its derivatives[12,13] have often been carried out. There is a very interesting case of benzoylacetone for which the results of very low temperature X-ray and neutron diffraction studies are known; [14] those authors also performed the topological analysis of the experimental charge density.

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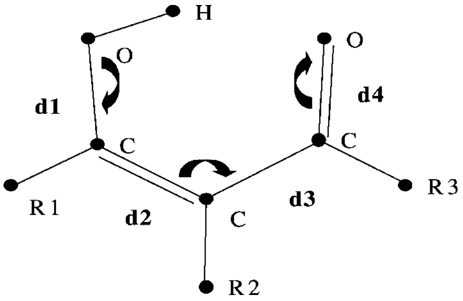
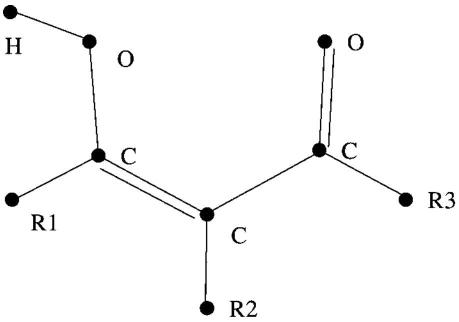


Scheme 1. Conformations of malonaldehyde and simple derivatives containing intramolecular H-bonds



Scheme 2. Open conformations of malonaldehyde and simple derivatives

It has been pointed out that for the hydrogen bonds that are resonance assisted the π-electron delocalisation is greater and hence the equalization of C—C, C=C and C—O is greater, C=O bond lengthens and thus the H…O distance is shorter. At short H…O distances the effective coupling between two covalent and one ionic valence bond (VB) structures leads to the so-called low barrier H-bonds.[15,16]

The aim of the present study is to investigate the nature of π-electron delocalisation for RAHBs. The studies are based on results of *ab initio* calculations and on the Bader theory.[17]

METHODS OF CALCULATION

The calculations have been performed using the Gaussian 98 program.[18] The split valence 6-311++G(d, p) basis set was used in calculations, which includes d and p polarisation functions on heavy and hydrogen atoms, respectively, and diffuse shells.[19,20] The inclusion of the diffuse functions within the basis sets is very important for investigations concerning H-bonds.[5] Correlation energy has been considered by means of the second-order Møller–Plesset perturbation theory.[21] Strictly speaking, the geometry of the malonaldehyde and its simple derivatives have been optimised at the MP2/6-311++G** level of theory.

The wave functions being resulting from the above *ab initio* calculations were further applied in terms of the Bader theory[17] and to find bond critical points (BCPs) and ring critical points (RCPs). The characteristics of these critical points such as the electron densities and their Laplacians, are used to describe the intramolecular H-bonds. Calculations to derive the topological parameters of the Bader theory were performed with the use of the AIM2000 program.[22]

RESULTS AND DISCUSSION

π-Electron delocalisation

The sample of malonaldehyde and its simple fluoro-and chloro-derivatives optimised at the MP2/6-311++G** level of theory is analysed here. The mono fluoro- and chloro-derivatives are considered where F or Cl may be a R1, R2 or R3 substituent. In additional, the sample analysed here is slightly extended since the malonaldehyde derivative with the OH group as the R3 substituent (Scheme 1) is also considered. The emphasis in this study is put on the distributions of charges on atoms and the consequences of such distributions.

The changes of the geometry of RAHB systems are the result of π-electron delocalisation which is usually explained in terms of electron transfer (Scheme 1). It is well known that, for the intermolecular H-bonds, there is the transfer of the electron charge from the proton-donating molecule to the proton acceptor.[5] For example, for the linear (*trans*) dimer configuration of water there is the transfer of 18 m$\bar{e}$ from the proton-donating water molecule to the accepting one due to the complexation; this result was obtained from the calculations performed at MP2/6-311++G** level of theory.

The H-bond energy for the intramolecular system may be estimated only roughly. The procedure often used is to calculate the difference in energy between the closed conformation for which the intramolecular H-bond exists and the open conformation obtained from this after the rotation of O—H bond 180° around C—O (single) bond.[11,23] The rotation really breaks the H-bond but other effects come into play, such as the unfavourable approach of the lone pairs of the two oxygen atoms.[23] Scheme 2 presents the open conformation. The detailed analysis of that way of the calculation of intramolecular H-bond energy has been presented before[24,25] and it has been pointed out that the difference mentioned above cannot be accepted as a reliable estimate of the H-bond strength. A procedure of estimation of intramolecular H-bond energy based on utilizing barriers of the donor and/or of the acceptor groups was recently proposed and tested successfully.[25]

There is the question whether the electron transfer for the RAHB systems is of the same nature as that one known for intermolecular H-bonds. For intermolecular H-bonds we observe the electron transfer as an effect of the complexation, whereas for intramolecular H-bonds

Table 1. The changes of atomic charges (in me) for the change of the open conformation into the closed conformation

R1, R2, R3	Δq[O(H)]	Δq[H]	Δq [O(=)]	Δq [OH]	Δq [C(R1)C(R2)C(R3)]
H, H, H	−53	37	−68	−16	84
H, F, H	−42	20	−82	−22	104
H, Cl, H	−45	37	−78	−8	86
H, H, F	−25	9	−56	−16	72
H, H, Cl	−23	18	−65	−5	70
F, H, H	−55	70	−80	15	65
Cl, H, H	−81	89	−74	8	66
H, H, OH	−40	22	−59	−18	77

we can detect the changes between the open conformation and the closed one. Table 1 shows such changes in natural population atomic charges for selected atoms of the sample considered here. We see the following changes for all of molecules: the increase of the electron density for both oxygen atoms, and its decrease for the hydrogen atom within the O—H...O bond. This is in line with the mechanism known for intermolecular H-bonds; there is the transfer of the electron density from the hydrogen atom to the oxygen acceptor. However, if we consider the O—H donating bond as a whole, there is also an increase of the electron density for this group. There are only two exceptions (Table 1): for derivatives for which R1 = F or Cl there is a decrease of the electron density of the OH group. This may be explained in the following way. Fluorine and chlorine are the electron-withdrawing substituents and hence the transfer of the electron density from CC bonds is not to the O—H...O region but to these substituents. This would be true for both forms—open and closed. However, if we compare the densities of the F and Cl atoms in these conformations, we see that the increase of the electron density for the closed conformation is 22 and 33 mē for fluorine and chlorine derivatives, respectively. This may be the reason why the R1 electron-withdrawing substituents cause the corresponding RAHBs to belong to the strongest H-bonds. In other cases of malonaldehyde derivatives there is the transfer of electrons from the C(R1) = C(R2)—C(R3) region to the O—H...O region. Table 1 shows the decrease of the electron density in the region of carbon atoms. The situation is similar to that of the intramolecular resonance assisted dihydrogen bonds for which[26] in almost all cases considered there is the increase of the electron density for each of atoms of $O—H^{+\delta}\ldots{}^{-\delta}H$ bond.

A similar interpretation may be achieved if we consider the integrated atomic charges[27] derived from the Bader theory.[17] For example, for the results of malonaldehyde, there are the following changes of these charges after the change of the open conformation into the closed one; Δq(O—) = −57 mē, Δq(H) = 55 mē, Δq(O═) = −36 mē. It means that there is an increase of the electron density for both oxygen atoms of the O—H...O bond and a decrease of this density for the hydrogen atom, also and that there is the loss of the electron density of 38 mē for the remaining part of the molecule (the $R_1C—CR_2 = CR_3$ fragment).

H-bond strength

There are problems with the exact estimation of the H-bond energy for intramolecular systems like those investigated here. It has been pointed out that the difference between the energy of the closed conformation and the open one (hereafter abbreviated as $E_{C—O}$) does not correspond to the H-bond energy since various additional effects disturb the real H-bond interaction.[24,25] However there are the other descriptors of the H-bond strength. Among them there are the topological parameters derived from the Bader theory.[17] For the X—H...Y H-bond, where X—H is the proton-donating bond and Y is an accepting centre, the electron density of the H...Y bond critical point ($\rho_{H\ldots Y}$) seems to be a good descriptor of the H-bond energy.[28,29] It was found that $\rho_{H\ldots Y}$ correlates with the H-bond energy for different samples of systems; however this correlation is better for homogeneous cases.[30]

For the case of malonaldehyde derivatives considered here, the linear correlation coefficient for the dependence between $\rho_{H\ldots O}$ and $E_{C—O}$ is 0.887; this strongly supports the statement that $E_{C—O}$ is not a good descriptor of the H-bond strength. However other parameters which may be treated as H-bond strength measures correlate well with $\rho_{H\ldots O}$. For example, the linear correlation coefficients for dependencies O—H bond length versus $\rho_{H\ldots O}$ and H...O distance versus $\rho_{H\ldots O}$ are 0.995 and 0.993, respectively. This is also in line with the earlier studies since it was pointed out that $\rho_{H\ldots Y}$ may be treated as a good measure of the hydrogen-bonding strength not only for intermolecular H-bonds but also for intramolecular ones.[9,11] Recent studies by Sanz and co-workers show such a dependence for X...H...Y intramolecular systems where X = O,S and Y = Se,Te.[31]

The changing of the open conformation into the closed one may be considered to consist of two stages. The first stage is the rotation of the O—H bond 180° around the C—O single bond, hence obtaining of the closed conformation (Scheme 1). The second stage is connected with changes of the geometry of the system due to the

Table 2. The differences in energies between conformations (in kcal mol^{-1}); %res corresponds to the percentage contribution of $|E_C\text{-}E'|$ within $|E_{C—O}|$

R1, R2, R3	$\lvert E_{C—O}\rvert$	$\lvert E'-E_O\rvert$	$\lvert E_C-E'\rvert$	%res
H, H, H	12.15	9.41	2.74	22.53
H, F, H	9.73	7.43	2.31	23.70
H, Cl, H	10.83	8.61	2.22	20.49
H, H, F	9.14	7.04	2.10	22.99
H, H, Cl	9.24	7.12	2.12	22.94
F, H, H	13.47	9.26	4.21	31.25
Cl, H, H	12.49	8.67	3.82	30.56
H, H, OH	11.12	8.76	2.35	21.17

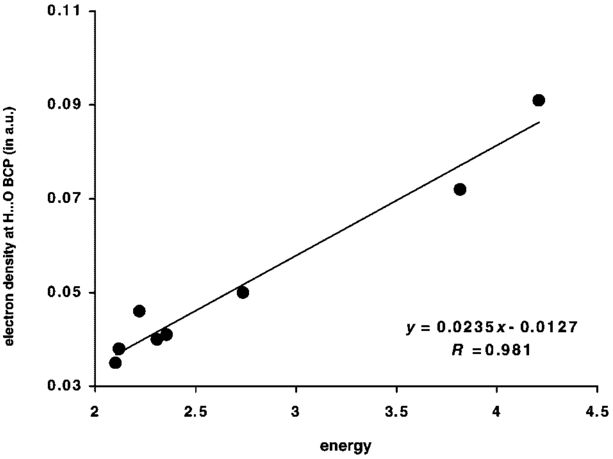


Figure 1. The dependence between the energy responsible for π-electron delocalisation (in kcal mol^{-1}) abbreviated as $|E_C-E'|$ and the electron density at H…O bond critical point

process of the π-electron delocalisation. Strictly speaking, the first stage is the closing of the system without the change of the other geometrical parameters and the second stage is the changing of the geometry. E_O corresponds to the open conformation energy, the energy of the closed conformation without the changing of the geometry is designated as E' and the energy of the most stable conformation existing after closing of the system and the change of the geometry is designated as E_C. Hence the modulus of $E_{C—O}$ energy $|E_{C—O}|$ consists of two terms, $|E'-E_O|$ and $|E_C-E'|$, the first one being the result of the closing of the system and the second one being the result of the change of the geometry after the closing of the system. These terms are included in Table 2. It is very interesting that, for every system, the first term connected only with the closing of the system is approximately three times greater than the second term. In additional, $|E'-E_O|$ does not correlate with $\rho_{H...O}$—the linear correlation coefficient is 0.641; the situation is similar for correlation between $E_{C—O}$ and $\rho_{H...O}$. However $|E_C-E'|$ correlates with $\rho_{H...O}$ and $R = 0.981$; Fig. 1 shows this dependence. These results show that, for the RAHBs, the H-bond energy depends mainly on the π-electron delocalisation.

The λ-parameter has been introduced[6,12] to describe the resonance for the RAHB systems such those considered here (Scheme 1);

$$\lambda = (1 - |Q|/Q_0) \tag{1}$$

where; $Q = (d_1 - d_4) + (d_3 + d_2)$; $Q_0 = 0.320$. Q_0 was obtained from the standard bond distances: $d_1(C-O) = 1.37$Å, $d_2(C{=}C) = 1.33$ Å, $d_3(C—C) = 1.48$ Å, $d_4C{=}O) = 1.20$ Å. According to the statements of Buemi[12] $\lambda = 1$ and $\lambda = 0$ correspond to the fully π-delocalised and to the fully π-localised structures respectively.

Another parameter describing the resonance within such systems as RAHBs is introduced here. If we consider the differences between the corresponding C—O, C═O and C—C, C═C bonds for the open conformation thus we can write;

$$\begin{aligned} \Delta d_1^o &= d_3^o - d_2^o \\ \Delta d_2^o &= d_4^o - d_1^o \end{aligned} \tag{2}$$

and the d-values of Eqn. (2) correspond to those presented in Scheme 1 but for the open conformation. Precisely similar equations may be written for the closed conformation;

$$\begin{aligned} \Delta d_1^c &= d_3^c - d_2^c \\ \Delta d_2^c &= d_4^c - d_1^c \end{aligned} \tag{3}$$

Hence the resonance parameter describing the changes connected with the change of the open conformation into the closed one may be defined.

$$\Delta_{rp} = 1/2\left[\left(\Delta d_1^o - \Delta d_1^c\right)/\Delta d_1^o + \left(\Delta d_2^o - \Delta d_2^c\right)/\Delta d_2^o\right] \tag{4}$$

This resonance parameter refers to the changes between two conformations (Schemes 1 and 2) while the λ-parameter considers the differences between the reference system with single and double C—C and C═O bonds not perturbed by any kind of delocalisation and the analysed system with the intramolecular H-bond. It is worth mentioning that, for the open conformation, there is also the π-electron delocalisation, although not so strong as for the closed system.[11] Δ_{rp} is zero if there is no difference between the closed and the open conformation; it is unity if there is the full equalisation of C═O, C—O and C—C, C═C bonds. Hence the physical meaning of Δ_{rp} parameter is similar to the meaning of λ.

Table 3 shows Δ_{rp} values for the sample considered here together with the other geometrical parameters, such as the elongation of the O—H proton-donating bond and the elongation of the C═O proton-accepting bond after

Table 3. The geometrical parameters of malonaldehyde derivatives for the closed conformation (in Å); the elongations of OH, C═O bonds and the H...O distances are included, the values of the resonance parameter (Δ_{rp}) are also given

R1, R2, R3	OH	C═O	H...O	Δ_{rp}
H, H, H	0.031	0.020	1.687	0.339
H, F, H	0.023	0.018	1.776	0.278
H, Cl, H	0.026	0.019	1.717	0.308
H, H, F	0.018	0.017	1.825	0.237
H, H, Cl	0.020	0.021	1.793	0.261
F, H, H	0.083	0.033	1.449	0.627
Cl, H, H	0.056	0.027	1.540	0.471
H, H, OH	0.023	0.019	1.761	0.261

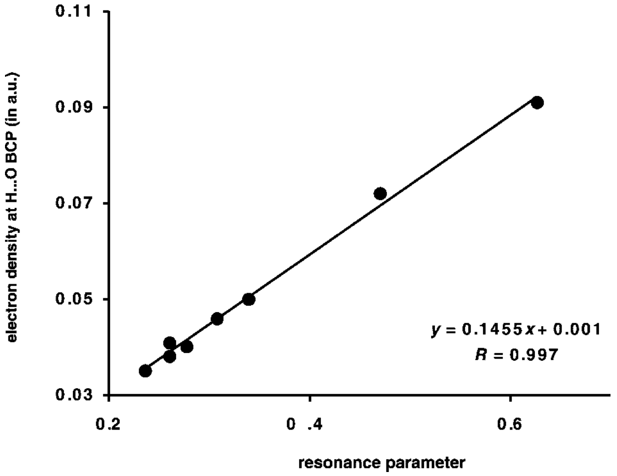


Figure 2. The correlation between the resonance parameter (Δ_{rp}) and the electron density at H...O bond critical point

the transfer from the open conformation to the closed one. The H...O distances for the intramolecular H-bonds are also included.

Δ_{rp} correlates well with $\rho_{H...O}$, with a linear correlation coefficient of 0.997 (Fig. 2). This means that the H-bond strength is mainly affected by the π-electron delocalisation, as was shown for energetic parameters. This statement is based on the results of calculations performed on the case of the strongly related systems and may not be fulfilled for other cases. For example, the dependence between the π-electron delocalisation and the H-bond strength was studied for the O—H...N bridges of the crystal structures of the Schiff bases.[32] Correlation between the energy and the delocalisation was not found. However the authors used the O...N distance as an approximate descriptor of the H-bond strength. The authors claimed that the O...N distance may be relatively easily deformed by crystal lattice forces and hence the correlation is not observed. As a measure of delocalisation the HOMA index[33,34] was applied.[32]

It is worth mentioning that there are not correlations between the charges analysed in the previous section and other topological, energetic or geometrical parameters. The only charge which correlates with the other parameters is the net atomic charge of the hydrogen atom within the O—H...O bond of the closed conformation. For example, there is correlation between this charge and $\rho_{H...O}$ the situation is the same for dependence between Δ_{rp} and this net atomic charge. Figure 3 presents this dependence for which the linear correlation coefficient is 0.970.

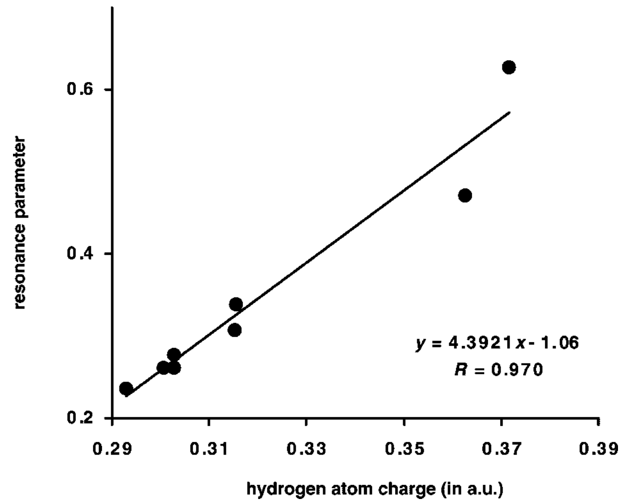


Figure 3. The dependence between the net hydrogen atomic charge (in a.u.) of the hydrogen within O—H...O bond and the resonance parameter (Δ_{rp})

CONCLUSION

The results of MP2/6-311++G** calculations show that, for the intramolecular resonance assisted H-bonds of malonaldehyde and its derivatives, there is a transfer of the electron charge from the $R_1C—CR_2=CR_3$ fragment of the molecule to the O—H...O H-bond. The part of the energy which is roughly responsible for the π-electron delocalisation correlates well with other parameters describing the H-bond strength, as for example the electron density at the H...O bond critical point.

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