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CLOPPA Analysis of the Molecular Polarizability and the Energy of Strong Intramolecular Hydrogen Bonds: Resonance Assisted?

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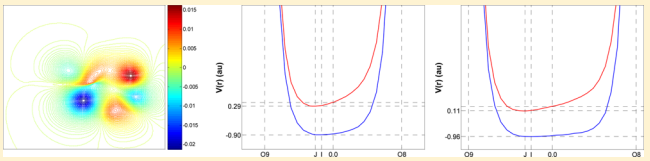
ABSTRACT: The contributions from localized orbitals within the polarization propagator approach (CLOPPA) method is applied to investigate the influence of the π system on the polarizability of the intramolecular hydrogen bond of malonaldehyde, in order to address if this linear response property provides evidence for the existence of the resonance assisted HB (RAHB) mechanism. On the same grounds, this influence on the energy of the hydrogen bond and the potential energy curve of the proton are also evaluated. Results obtained seem to confirm that the π system delocalizes on the hydrogen bond region, and this effect of delocalization is partially responsible for the unusual strength of this intramolecular hydrogen bond.



INTRODUCTION

It is well-known that hydrogen bonding plays a fundamental role in many physical, chemical, and biochemical phenomena. Thus, it has received considerable attention, both from experimental and theoretical points of view. Despite the widespread interest and the vast literature on the subject, the ultimate nature of hydrogen bonds (HBs) is not yet fully characterized, mainly because it is not due to a single interaction but covers a wide range of them.[1] Therefore, there may be very different HBs, with a broad range of strengths, from very weak HBs (from 1 to 4 kcal/mol) to strong ones (from 15 to more than 40 kcal/mol).[2] In the early times, HBs had been characterized as a proton shared by two electronegative atoms[3] (i.e., by two electron pairs[4]), thus suggesting an electrostatic nature. However, this kind of description does not stand for the great variety of moieties, which nowadays have been recognized as HBs,[5−10] and therefore, this pure electrostatic picture has been replaced by a combination of both electrostatic and covalent contributions.[1] On the basis of experimental grounds, Gilli and co-workers have proposed a qualitative electrostatic-covalent HB model (ECHBM),[11−15] which relates the HB strength with the main character of the bond, such that a weak HB is mainly electrostatic in nature, and its covalent character increases with increasing strength. Gilli et al. suggested[14] that the covalent contribution to the HB increases as the difference of the proton affinities of the donor and the acceptor, ΔPA, or, similarly, of the acidity constant, ΔpK_a, are closer to zero, and this limit is indicative of a very strong and symmetrical HB. According to this model, and taking into account structural and spectroscopic data, these authors proposed a classification of very strong HBs by four specific molecular patterns. Among them, the so-called "resonance assisted HB" (RAHB) mechanism has been proposed[11−15] to explain the unusual strength of intra- or intermolecular HBs in conjugated neutral molecular systems. It is considered as a π-bond cooperative effect,[16] wherein the strength of the HB is due to the delocalization of the π system on the HB region. However, there is still no unanimous opinion on whether this mechanism is responsible for the atypical strength of this type of HBs. A large amount of theoretical studies have addressed this issue from different perspectives and applying many diverse tools, with contradictory results and conclusions. In addition to those proposed by Gilli et al., which were also used by several authors,[8,9,17] other studies have suggested various descriptors of the strength of the HB and have sought to correlate them with the degree of delocalization of the π system on the HB region. Among them, those provided by the quantum theory of atoms in molecules (QTAIM)[18] seems to be among the most common and powerful ones. Topologycal parameters of this method are used as descriptors of the strength of both inter- and intramolecular HBs[1,8,9,19−22] in which a RAHB mechanism is assumed. Other used tools are the natural bond orbitals theory (NBO),[20,23−25] the electron localization function method (ELF),[19,26,27] the extended transition state-natural orbitals for chemical valence (ETS-NOCV) density analysis method,[25] geometrical parameters,[1] and the use of Hammett substituent constants[28] to describe the electronic properties of RAHB.[29] NMR properties, in particular, chemical shifts and $^{2h}J_{XY}$ coupling constants, were also examined[30−34] to determine if these properties provide evidence of the RAHB mechanism. Some of these methods lead to a positive view of the subject, that is, there is a significant correlation between the resonance effect and the strength of the HB,[17,21,22,27,29,33,35,36] while for others, no evidence of the RAHB mechanism is found,[19,24,25,30−32] and the strength is explained as an effect of the σ skeleton.

In principle, two main topics should be taken into account to determine the feasibility of the proposed RAHB mechanism. On one hand, a first issue to consider is if there is an actual effect of delocalization of the π system onto the HB fragment. This issue could be addressed by finding a molecular property that can account for changes when the π system is delocalized. On the other hand, the second issue is to determine whether

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the interaction of this delocalized π system with the HB moiety increases its strength. Despite all proposed descriptors, perhaps the most valid criterion for evaluating the HB strength should be the HB energy or, more exactly, the potential interaction energy of the proton in the HB region.[1,9,20] The energy of an intermolecular HB is usually calculated as the difference between the energy of the complex and that of the monomers.[1,25,27] This method is not applicable to an intramolecular HB and the standard method to evaluate its energy is to calculate the difference between the energy of the closed conformation (i.e., for which the intramolecular HB exists), and that of the open one, i.e., that which is obtained by rotating the X−H bond 90° or 180°.[21] However, as it was previously discussed, this method gives only an approximate estimation of the HB energy,[9,21−23] as other additional effects are neglected, like, for instance, the repulsion of the lone pairs of the donor and acceptor atoms in the open conformation,[9,22] due to their unfavorable relative position. Therefore, it has been concluded that this energy difference cannot be a reliable descriptor of the HB strength.[23] Alternative procedures have been put forward, for example, relating the energy of the intramolecular HB with the internal rotation barrier of the donor and/or of the acceptor groups,[37] or with the two-center shared electron number (SEN approach).[34] In addition, different schemes to decompose the electronic energy are used,[8,22,25,34] finding that the charge transfer term prevails over the others. However, in some cases of strong HBs,[8] the polarization interaction energy is even more important than the charge transfer one.

The aim of this work is, therefore, to address the aforementioned issues by means of (i) the analysis of the molecular polarizability of the HB moiety and its changes due to the presence of the π system, in order to determine if this property can account for the degree of delocalization of the π system on the HB region; and (ii) the calculation of the energy of the HB fragment, in order to assess the influence of the π system on it.

The question whether there is a connection between the π electron delocalization and a response property like the molecular polarizability was dealt with before,[38] with nearly negative results. It was concluded that there is not a definite correlation between aromaticity and polarizability, and only the out-of-plane component could perhaps serve as indicative of a relative aromatic character within sets of related systems. In spite of this disappointing conclusion, in previous papers,[39−41] it was shown that, not the bulk property, but its decomposition into local contributions arising from different molecular fragments could provide insight into the underlying interactions inside the electronic cloud. Thus, it seems that this kind of analysis might be useful to assess the influence of the π system in the HB region.

The contributions from localized orbitals within the polarization propagator approach (CLOPPA) technique[42−44] appears as a convenient method to deal with these issues, as it is a useful tool to identify the electronic mechanisms operating in a given phenomenon in terms of localized molecular orbitals (LMOs). It was implemented at the ab initio level for the theoretical analysis of NMR spin−spin couplings[7,45−48] and the static molecular polarizability tensor,[39,41] although the same scheme can be used for any second-order molecular property. It is noteworthy that the very idea of defining a molecular fragment with LMOs could also be applied for calculating first-order properties; in particular, the energy associated to a molecular fragment could be evaluated in this way.

The present article is organized as follows. In first place, a brief account of the inner projections of the polarization propagator (IPPP)-CLOPPA method is presented, applied to the molecular polarizability tensor. Also, a method for estimating the energy of a fragment and the interaction energy within the fragment in terms of LMOs is introduced; in particular, it is applied to calculate the HB energy and the potential energy of the proton in the HB moiety. Numerical results of the analysis of the molecular polarizability and the energy of the intramolecular HB of the malonaldehyde molecule are presented in the results and discussion section. Interesting features, which complement and give a new insight to previous studies, are found.

IPPP AND CLOPPA METHODS

Molecular Polarizability Tensor. The IPPP and the CLOPPA methods are useful tools to identify the electronic mechanisms operating in a given phenomenon in terms of LMOs. It can be applied to any second order response property. In particular, the method, applied to the analysis of the molecular polarizability tensor was described previously[39−41] and it is implemented at the RPA level of approximation. For the sake of comprehension, the main ideas are briefly outlined.

Within the polarization propagator (PP) formalism at the RPA level, the static polarizability tensor can be written as[49]

$$\vec{\alpha} = -2 \sum_{ia \le jb} {}^1P_{ia,jb} \times [\langle a^*|\vec{x}|i\rangle\langle b^*|\vec{x}|j\rangle + \langle b^*|\vec{x}|j\rangle\langle a^*|\vec{x}|i\rangle] \quad (1)$$

where i,j (a,b) indices stand for occupied i,j (vacant a^*,b^*) molecular orbitals (MOs) of a Hartree−Fock (HF) reference state, ${}^1P_{ia,jb} = -({}^1A - {}^1B)^{-1}_{ia,jb}$ is the singlet part of the PP matrix, connecting virtual excitations $i \rightarrow a^*$ and $j \rightarrow b^*$. $\langle a^*|\vec{x}|i\rangle$ and $\langle b^*|\vec{x}|j\rangle$ are the matrix elements of the dipole operator $\vec{x}$ between an occupied and a vacant MO. These last elements are called perturbators.

In the CLOPPA method, the polarizability tensor $\vec{\alpha}$ is rewritten in terms of LMOs, by applying to the PP matrix elements and to the perturbators a convenient unitary transformation from canonical HF MOs to occupied and vacant LMOs, separately. These LMOs are obtained in such a way that they represent chemical functions like bonds, lone pairs, and atomic inner shells, and their corresponding anti-LMOs (anti-bonds, anti-lone pairs, etc). It must be taken into account that the prefix "anti" followed by the name of an occupied LMO is used here to designate those vacant orbitals localized using the same criteria as their occupied counterparts, and it indicates a spatial location of the vacant LMOs. The localization technique used in this work is Engelmann's, applied in an iterative way, as it was described previously.[42] The formal expression of $\vec{\alpha}$ in terms of LMOs, eq 1, is not altered, but i,j indices now stand for occupied LMOs, and a,b indices stand for vacant LMOs. However, it must be noted that the similarity between both equations is only formal, as the expression of the elements of the PP in terms of LMOs change from their expression in terms of canonical MOs, when applying the above-mentioned unitary transformation. From this transformation, the rs Cartesian component of the polarizability tensor ($r,s = x,y,z$) arising from a chosen molecular fragment can be obtained by restricting the sum to the subset of LMOs that define this fragment, i.e., the local subspace:[39,41]

$$\alpha^{\mathrm{L},rs}_{\mathrm{CLOPPA}} = -2 \sum_{ia \le jb}^{\mathrm{local}} {}^1P_{ia,jb} \times [\langle a^*|x_r|i\rangle\langle b^*|x_s|j\rangle + \langle b^*|x_r|j\rangle\langle a^*|x_s|i\rangle]$$

$$\alpha^{\mathrm{L},rs}_{\mathrm{CLOPPA}} = \sum_{ia\le jb}^{\mathrm{local}} \alpha^{rs}_{ia,jb} \quad (r, s = x, y, z) \tag{2}$$

Although all LMOs involved in the sum of eq 2 belong to the local fragment, it must be noted that ${}^1P_{ia,jb}$ depends on all LMOs of the molecule, and thus, each $\alpha^{rs}_{ia,jb}$ term contains the indirect influence of the whole molecule on the fragment under consideration. The strictly local contribution of a local fragment, that is, the contribution which strictly arises from the chosen fragment can be obtained by means of the IPPP approach.[42,43] Within this method, the strictly local polarizability is calculated as in eq 2, but the PP matrix is inner projected onto the local subspace. This projected propagator ${}^1W$ is used in the calculation, instead of the whole PP matrix:

$$\begin{aligned}\alpha^{\mathrm{L},rs}_{\mathrm{IPPP}} &= -2 \sum_{ia\le jb}^{\mathrm{local}} {}^1W_{ia,jb} \times [\langle a^*|x_r|i\rangle\langle b^*|x_s|j\rangle \\ &\quad + \langle b^*|x_r|j\rangle\langle a^*|x_s|i\rangle] \\ \alpha^{\mathrm{L},rs}_{\mathrm{IPPP}} &= \sum_{ia\le jb}^{\mathrm{local}} \alpha^{\mathrm{L},rs}_{ia,jb} \quad (r, s = x, y, z)\end{aligned} \tag{3}$$

Bearing in mind the preceding discussion, the indirect influence of the rest of the molecule on the polarizability of a certain local fragment can be quantified by the difference between eqs 2 and 3 as

$$\begin{aligned}\alpha^{\mathrm{ind},rs} &= \sum_{ia,jb}^{\mathrm{local}} \alpha^{\mathrm{ind},rs}_{ia,jb} \\ &= \sum_{ia,jb}^{\mathrm{local}} (\alpha^{rs}_{ia,jb} - \alpha^{\mathrm{L},rs}_{ia,jb}) \\ &\equiv \alpha^{\mathrm{L},rs}_{\mathrm{CLOPPA}} - \alpha^{\mathrm{L},rs}_{\mathrm{IPPP}}\end{aligned} \tag{4}$$

$\alpha^{ind,rs}$ shows to what extent the rest of the molecule contributes indirectly to the polarization of the fragment.

Proper LMOs Polarizabilities and Mutual Polarizabilities. Taking into account that, within ab initio calculations, there are several vacant LMOs that can be ascribed to each type of local fragment, four-indices terms appearing in eqs 2 and 3 are more conveniently defined as[39,41]

$$\alpha^{rs}_{ia,jb} = \sum_{\substack{\alpha\in' a' \\ \beta\in' b'}}^{\mathrm{local}} \alpha^{rs}_{i\alpha,j\beta} \tag{5}$$

where α (β) represent vacant LMOs of the a^* (b^*) type. Each term $\alpha^{rs}_{ia,jb}$ involves at most two occupied and two types of vacant LMOs and indicates to what extent the a^*-type vacant LMOs contribute to the polarization induced in the i occupied LMO by the effect of intramolecular interactions, when the j occupied LMO is coupled with the b^*-type vacant LMOs by the external field. Therefore, each term gives a measure of the efficiency of such involved LMOs in transmitting the polarization of the electronic cloud induced by the external perturbation.

Within this approach, it is convenient to define two-indices contributions for a given pair of occupied LMOs i and j, by summing over the whole set of vacant LMOs:[41]

$$\alpha^{rs}_{ij} = \sum_{a,b} \alpha^{rs}_{ia,jb} \tag{6}$$

As it was previously shown,[41] these terms can be interpreted as the s component of the induced dipole on the i occupied LMO (per unit field), due to the field created by the polarization of the j LMO in the presence of an external electric field $\vec{E}_r = E_r\hat{x}_r$:

$$\alpha^{rs}_{ij} = \frac{1}{E_r}[\langle\tilde{i}|x_s|\tilde{i}\rangle - \langle i|x_s|i\rangle] \tag{7}$$

where $|\tilde{i}\rangle$ is the modified occupied i LMO due to the polarization of the j LMO. Terms of this type are called mutual polarizabilities.

In the same way, if $i = j$, eq 6 represents the s component of the dipole moment (per unit field) of the LMO i induced by the r component of the external field $\vec{E}$, i.e., the rs polarizability component of the occupied i LMO.[41] These α^{rs}_{ii} terms will be referred to as proper LMO polarizabilities. Both mutual and LMO polarizabilities represent local properties within the molecule, and they provide a local picture of the distortion of the electronic system owing to an external field. Therefore, this local description seems to be adequate to account for the effect of nonuniform electric fields on the molecular electronic distribution, such as the effect of the field of a given molecular group over another molecular fragment.

Energy of a Molecular Fragment. Likewise, the total energy of a molecular fragment can be evaluated in terms of LMOs. It can be calculated by projecting the Fock operator onto the subset of occupied LMOs that define the fragment (correcting the double counting of bielectronic energies by subtracting the adequate terms), plus the nuclear potential energy. Explicitly

$$\begin{aligned}E_{\mathrm{frag}} &= \sum_{i\in\mathrm{frag}} [2\sum_{k}^{N/2} \langle i|k\rangle\varepsilon_k\langle k|i\rangle - \sum_{j\in\mathrm{frag}} (2\langle ij|ij\rangle - \langle ii|jj\rangle)] \\ &\quad + \frac{1}{2}\sum_{n}^{M\in\mathrm{frag}} \sum_{m\neq n} V_{nm}\end{aligned} \tag{8}$$

where subindices (i,j) designate those LMOs that span the molecular fragment, while k runs for canonical MOs; ε_k are orbital energies corresponding to canonical MOs, $\langle ij|ij\rangle$ and $\langle ii|jj\rangle$ stand for the Coulomb and exchange integrals, respectively, calculated between LMOs of the molecular fragment, and $(n,m = 1,...,M)$ are the M nuclei of the chosen fragment. It should be noted that this definition of the energy takes also into account the interaction of the fragment with the electrons of the rest of the molecule.

In a similar way, the potential energy of the H proton in the HB moiety, $V_{\mathrm{HB}}(H)$, is evaluated as

$$V_{\mathrm{HB}}(H) = \sum_{n}^{M\in\mathrm{HB}} V_{\mathrm{H}n} + \sum_{i\in\mathrm{HB}} \langle i|V_{\mathrm{He}}|i\rangle \tag{9}$$

RESULTS AND DISCUSSION

In order to settle on the feasibility of the RAHB proposed mechanism, the molecular polarizability and the electronic energy of the intramolecular hydrogen bond of the malonaldehyde molecule are analyzed. Malonaldehyde is chosen as a model compound as it was one of the first molecules in which this type of mechanism was described as responsible for the strength of its hydrogen bond (HB).[11,20,24,30−33] The xy-plane is chosen as the plane of the molecule. The geometric structure of malonaldehyde is taken from ref 33, where a full theoretical optimization of the structure was performed with the cc-pVXZ ($X = D, T$) basis set. Three different cases are considered (see Chart 1): I) the distance

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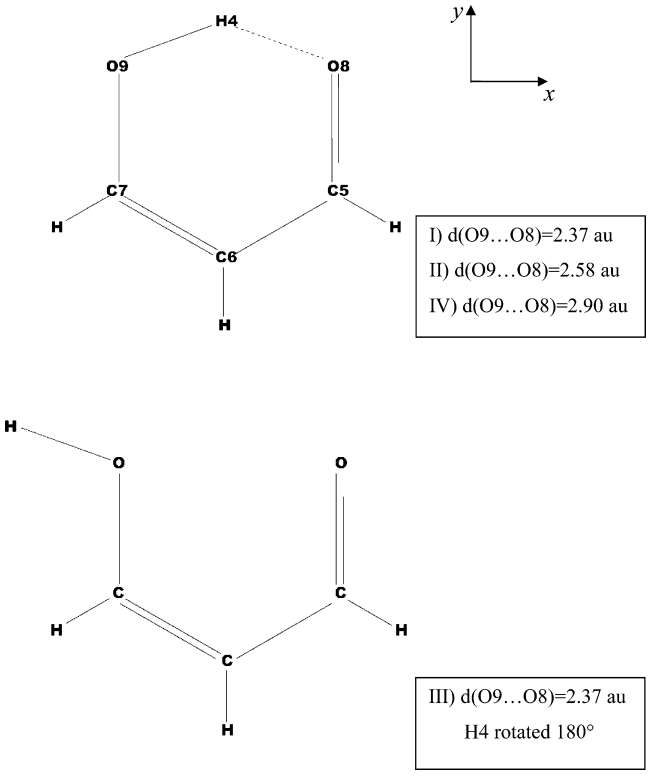
Chart 1



between both oxygen atoms of the hydrogen bond is taken as in ref 33, d(O9···O8) = 2.37 Å, II) d(O9···O8) = 2.58 Å, and III) the same structure as I, considering an open conformation, that is, with the hydrogen atom of the hydrogen bond (H4) rotated 180°. In some calculations, a fourth structure, IV, is taken into account, where the d(O9···O8) = 2.90 Å. Therefore, in molecule I, there is an intramolecular hydrogen bond; in II, the HB is weakened; while in III and IV, the hydrogen bond is broken. Calculations were performed at the RPA[49] level by means of the SYSMO[50−52] program. CLOPPA and IPPP analysis of polarizabilities and electronic energy were carried out by means of a modified version of the SYSMO program. The atomic orbital basis set used is Pol.Sadlej (10s6p4d,6s4p)−[5s,3p2d,3s,2p].[53] It is worth mentioning that Sadlej basis sets were specially designed for accurate calculation of polarizabilities.

The localization procedure was extensively explained previously;[41,46−48] therefore, only a few aspects are commented here, due to their relevance in this work. The notation used to identify occupied and vacant LMOs obtained by the localization procedure is depicted in Table 1. Only occupied and vacant LMOs localized in the HB zone and the π system are considered, as the influence of this latter system on the strength of the HB is to be assessed. In the case of the open conformation, compound III, although there is not, strictly speaking, an HB zone, the same LMOs as in the other conformations are taken into account, and for that reason, they are also referred as HB LMOs or LMOs localized in the HB zone. Considering the notation of Table 1, the LMOs localized in the HB zone for all conformations are occupied S(O8), S(O9), LP_{xy}(O8), LP_z(O9), and O9−H4, and their respective vacant LMOs. Unless explicitly stated, these vacant LMOs localized in the HB zone are joined together and indistinctly referred to as HB* LMOs. Among them, as it was found before,[46−48] there are several vacant LMOs localized in the whole hydrogen bond moiety. This kind of

Table 1. Labeling of the LMOs

	occupied LMOs	vacant LMOs
(anti)inner shell of atom X	S(X)	S(X)*
σ-(anti)bond between X and Y	X−Y	X−Y*
π-(anti)bond between X and Y[a]	π(X−Y)	π(X−Y)*
(anti)lone pair of atom X oriented in μ (μ = x,y,z) direction	LP_μ(X)	LP_μ(X)*
σ-bridge vacant LMOs		HBσ*
π-bridge vacant LMOs		HBπ*

[a]When no atoms are indicated, it is referred to the whole π system.

LMOs are called bridge vacant LMOs, σ or π. It is noteworthy that this type of LMOs arises from canonical MOs of low orbital energies. As it was shown before,[46−48] they are physically significant in the hydrogen bond formation.

Influence of the π System on the HB Polarizability. In Table 2, the main components, the averaged in-plane value and the averaged total value of the HB polarizability tensor in compounds I, II and III, are displayed, taking into account (i) only the contribution of the HB LMOs and (ii) the contribution of the HB LMOs, plus the total π system. As the HB lies in the xy-plane, the in-plane averaged polarizability and the xx and yy components are analyzed in depth. From this Table, it can be seen that, although the in-plane averaged polarizability of the fragment is smaller in compound I than in II, the contribution of the π system, $\Delta\alpha$, is larger for compound I than for compound II. The former can be explained taking into account that the length of the considered fragment is larger in II than in I (as the polarizability depends on the spatial length), while the latter fact shows that the π system contributes to increase the polarizability of the hydrogen bond. In contrast, the contribution of the π system to the in-plane polarizability is larger in III than in I, and this fact seems to be indicating that the π system does not contribute more particularly to the fragment when an HB is present. However, this global upshot could be misinterpreted and deserves further analysis. It can be rationalized taking into account the effect of the π system on the polarizability of each LMO of the HB moiety. In Table 3, this effect is depicted. The polarizability of the occupied LMOs O9−H4, LP_{xy}(O8), and LP_z(O9) are shown for compounds I and III, calculated including in the subspace (i) the occupied LMO and the HB* vacant LMOs and (ii) the same LMOs as in (i), plus the whole π system (occupied and vacant LMOs). In the latter case, the LMO polarizability is calculated as

$$\alpha_{\mu\mu} = \alpha_{\mu\mu}(i, i) + \alpha_{\mu\mu}(i, j) \quad \mu = x, y, z$$

where i = LMO (O9−H4, LP_{xy}(O8), or LP_z(O9)), and j = π(C−C), π(C−O), that is, by adding the mutual polarizabilities of the LMO with the π system, to the proper polarizability of the LMO. It is relevant to mention that the polarizability of other LMOs of the HB fragment (σ lone pairs and cores) is scarcely affected by the π system. When comparing the effect of the π system in the in-plane averaged polarizability, $\langle\alpha_{xy}\rangle$, it is observed that this effect is different for each LMO of the HB moiety. Thus, the interaction with the π system drastically decreases the O9−H4 in-plane polarizability, most of all in the x direction, (which is approximately the HB direction), while it slightly increases this value in III. The effect is similar and negative for LP_{xy}(O8), while it is large and positive for LP_z(O9) in both compounds, though it is more pronounced in I than in III.

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Table 2. Main Components, Averaged in-Plane Value $\langle\alpha_{xy}\rangle$ and Averaged Total Value $\langle\alpha\rangle$ of the HB Polarizability Tensor on Compounds I, II, and III; All Values in au

compound I						
LMOs	LMO*s	α_{xx}	α_{yy}	α_{zz}	$\langle\alpha\rangle$	$\langle\alpha_{xy}\rangle$
HB[a]	HB*	7.7971	2.2877	5.0337	5.0395	5.0424
HB + π[b]	HB* + π*	6.4671	7.4500	6.1275	6.6815	6.9586
$\Delta\alpha$[c]		−1.3300	5.1623	1.0938	1.6420	1.9162
compound II						
LMOs	LMO*s	α_{xx}	α_{yy}	α_{zz}	$\langle\alpha\rangle$	$\langle\alpha_{xy}\rangle$
HB[a]	HB*	8.3219	2.2622	4.9518	5.1786	5.2921
HB + π[b]	HB* + π*	6.9911	7.2554	6.2004	6.8156	7.1233
$\Delta\alpha$[c]		−1.3308	4.9932	1.2486	1.6370	1.8312
compound III						
LMOs	LMO*s	α_{xx}	α_{yy}	α_{zz}	$\langle\alpha\rangle$	$\langle\alpha_{xy}\rangle$
HB[a]	HB*	7.9227	2.6101	4.7158	5.0829	5.2664
HB + π[b]	HB* + π*	8.8895	7.4429	6.0557	7.4627	8.1662
$\Delta\alpha$[c]		0.9668	4.8328	1.3399	2.3798	2.8998

[a]Only the contribution of the occupied and virtual HB LMOs are considered. [b]Contribution of the HB LMOs, plus the total π system. [c]Contribution of the π system: difference between contributions defined in footnotes b and a.

Table 3. Main Components, Averaged in-Plane Value $\langle\alpha_{xy}\rangle$, and Averaged Total Value $\langle\alpha\rangle$ of the HB Polarizability Tensor on Compounds I and III for the Occupied LMOs of the HB O9−H4, LP$_{xy}$(O8) and LP$_z$(O9). All Values in au

O9−H4		I				
LMOs	LMO*s	*xx*	*yy*	*zz*	$\langle\alpha(xy)\rangle$	$\langle\alpha\rangle$
O9−H4	HB*	2.3566	0.7185	0.4802	1.5376	1.1851
O9−H4 + π[a]	HB* + π*	0.2900	0.5163	0.8571	0.4032	0.5545
$\Delta\alpha$		−2.0666	−0.2022	0.3769	−1.1344	−0.6306
		III				
LMOs	LMO*s	*xx*	*yy*	*zz*	$\langle\alpha(xy)\rangle$	$\langle\alpha\rangle$
O9−H4	HB*	2.4705	0.7708	0.4494	1.6207	1.2302
O9−H4 + π[a]	HB* + π*	2.7983	0.7901	0.8941	1.7942	1.4942
$\Delta\alpha$		0.3278	0.0193	0.4447	0.1736	0.2639
LP$_{xy}$(O8)		I				
LMOs	LMO*s	*xx*	*yy*	*zz*	$\langle\alpha(xy)\rangle$	$\langle\alpha\rangle$
LP$_{xy}$(O8)	HB*	2.8651	0.7731	0.4614	1.8191	1.3665
LP$_{xy}$(O8) + π[a]	HB* + π*	1.6286	0.8301	1.4526	1.2294	1.3038
$\Delta\alpha$		−1.2365	0.0570	0.9912	−0.5898	−0.0628
		III				
LMOs	LMO*s	*xx*	*yy*	*zz*	$\langle\alpha(xy)\rangle$	$\langle\alpha\rangle$
LP$_{xy}$(O8)	HB*	3.1153	0.8695	0.3445	1.9924	1.4431
LP$_{xy}$(O8) + π[a]	HB* + π*	2.3742	0.8046	1.4673	1.5894	1.5487
$\Delta\alpha$		−0.7411	−0.0649	1.1228	−0.4030	0.1056
LP$_z$(O9)		I				
LMOs	LMO*s	*xx*	*yy*	*zz*	$\langle\alpha(xy)\rangle$	$\langle\alpha\rangle$
LP$_z$(O9)	HB*	0.5468	0.3454	4.1741	0.4461	1.6888
LP$_z$(O9) + π[a]	HB* + π*	2.6721	5.5666	3.5715	4.1194	3.9367
$\Delta\alpha$		2.1253	5.2212	−0.6026	3.6733	2.2480
		III				
LMOs	LMO*s	*xx*	*yy*	*zz*	$\langle\alpha(xy)\rangle$	$\langle\alpha\rangle$
LP$_z$(O9)	HB*	0.5395	0.3854	3.9335	0.4625	1.6195
LP$_z$(O9) + π[a]	HB* + π*	2.6874	5.1951	3.3452	3.9413	3.7426
$\Delta\alpha$		2.1479	4.8097	−0.5883	3.4788	2.1231

[a]It is calculated by summing up the proper polarizability of the LMO and its mutual polarizability with the π occupied LMOs. See text for definition.

In order to understand how the π system influences the polarizabilities of the HB LMOs, Table 4 displays the proper and mutual polarizabilities with the π system of the HB LMOs. Only the *xx* component of polarizabilities are shown, as this component is that which almost corresponds to the HB direction. It is worth noting that, due to the σ character of the O9−H4 bond and the LP$_{xy}$(O8) lone pair, their proper polarizabilities are not affected at all by the π* system, as perturbators of this property are

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Table 4. *xx* Component, α_{xx}, of Proper and Mutual Polarizabilities with the π LMOs, of the Main LMOs of the HB Fragment; All Values in au[a]

i	*j*	I	II	III
O9−H4	O9−H4	2.3566	2.4434	2.4705
O9−H4	π(C−C)	−2.1572	−2.0503	0.2808
O9−H4	π(C−O)	0.0906	0.0372	0.0471
total		0.2900	0.4303	2.7984
LP_{xy}(O8)	LP_{xy}(O8)	2.8651	3.2610	3.1193
LP_{xy}(O8)	π(C−C)	−0.9645	−1.2033	−0.4403
LP_{xy}(O8)	π(C−O)	−0.2720	−0.3020	−0.3047
total		1.6286	1.7557	2.3743
LP_z(O9)	LP_z (O9)	2.5157	2.4413	2.4818
LP_z(O9)	π(C−C)	0.1420	0.2513	0.4717
LP_z(O9)	π(C−O)	0.0144	−0.0052	−0.0113
total		2.6721	2.6874	2.9422
LP_z(O9)	LP_z (O9)[b]	0.5468	0.5506	0.5395
LP_z(O9)	π(C−C)[b]	0.0066	0.0073	0.0096
LP_z(O9)	π(C−O)[b]	0.0109	0.0063	0.0046
total		2.6721	0.5643	0.5642

[a]Unless informed, all values are calculated taking into account the HB* and π* vacant LMOs. [b]Values calculated taking out the π* vacant LMOs from the subspace (only the HBπ* are considered).

null for virtual excitations $\sigma \rightarrow \pi^*$, as each electronic system, σ and π, can only be polarized in the *x* direction through virtual excitations to vacant LMOs of its own symmetry (the indirect influence of the π system through the PP is not significant in this case). Thus, proper polarizabilities of these σ-character LMOs are mainly due to virtual excitations LMO → HB*, and hence, they are quite similar in all compounds considered. On the other hand, π-character LP_z(O9) proper polarizability is due to virtual excitations LP_z(O9) → π* and LP_z(O9) → HBπ*. In fact, as it can be seen from Table 4, if π* vacant LMOs are excluded from the subspace, this proper polarization is reduced in a large amount.

Despite the differences among them, proper polarizabilities of LMOs within the HB moiety present quite similar values in all compounds considered; therefore, there is no evidence in them of a distinct behavior of the π system in the presence of a hydrogen bond.

As far as mutual polarizabilities α_{ij}^{rs} ($i \neq j$; $r,s = x,y,z$) are concerned, they carry information about interactions between the electronic distribution of *i* and *j* LMOs.[39,41] It is worth noting that the magnitude of mutual polarizabilities depends on the extent to which the two LMOs involved are polarizable. On the one hand, a more polarizable *i* LMO produces an internal field of larger magnitude; on the other hand, a more polarizable *j* LMO is more affected by this field, and therefore, its induced dipole is larger. Furthermore, the α_{ij}^{rs} sign indicates if the dipole moment induced in the *i* LMO, due to the field produced by the induced dipole moment on the *j* LMO, is parallel (positive) or antiparallel (negative) to that produced by the external field. Taking in mind these features, a most interesting fact can be rationalized. From Table 4, it can be seen that the low value of the *xx* component of the polarizability of the O9−H4 bond in I (and, therefore, of the in-plane averaged polarizability), as compared with the same value in III, is mostly due to the notably large, negative mutual polarizability between O9−H4 and π(C−C), which renders −2.1572 au in I, whereas it is only 0.2808 au in III. The analysis of these two values points out that a significant interaction between O9−H4 and π(C−C) is taking place in I, which is, comparatively, negligible in III. This interaction represents a direct cooperative effect of the π system, as defined in ref 39. Following the hints given above, this large value in I can only be due to two near-in space polarizable LMOs, while the negative sign would indicate that these two LMOs share a region in space where they are nearly parallel. This assertion also would explain the experimental finding that this type of hydrogen bond always shows an unusual downfield ^{1}H NMR chemical shift, that is, the proton is highly deshielded.[24] Therefore, it may be concluded that the π system delocalizes within the HB fragment, probably increasing the number and mobility of the electrons in this molecular region. This effect, in fact, could be ascribed to a resonance effect that closes the molecular ring and therefore should contribute to the HB strength. It can be seen that the same effect is observed for the remaining closed conformations considered, II (−2.0503 au) and IV (−0.7208 au), although this mutual polarizability decreases, as the distance between both oxygen atoms increases. It can be argued that the same conclusion could be applied to the π system in III, as the low positive value of the mutual polarizability could be due to the relative orientation of both LMOs. However, the analysis of the remaining mutual polarizabilities supports the former assertion. In fact, it can be seen from the (negative) value between LP_{xy}(O8) and π(C−C), which is two times larger (in absolute value) in I than in III, denoting again that π(C−C) extends more toward LP_{xy}(O8) in I than in III, and the larger values of LP_{xy}(O8)/π(C−O) and LP_z(O9)/π(C−C) in III than in I, which are a sign of a more local interaction in the former molecule. It can be concluded that, although there would be a delocalization of the π system in the open conformation,[9] III, this should be much weaker than in the closed conformation, I.

It is worth noting that, according to the preceding discussion, it can be expected the same behavior in each molecule where a resonant π system contributes to a HB moiety; that is, a drop of the polarizability of the X−H bond, due to its interaction with the π system, as in this case, the minimal energy configuration corresponds to antiparallel induced dipoles. It is worth noting that this feature is in agreement with results obtained by QTAIM in intermolecular HBs, in which it was observed a decrease of the polarization of the hydrogen as a result of complexation.[10]

In order to deepen this insight, Figure 1 depicts the difference between the π system density, calculated in I and in III:

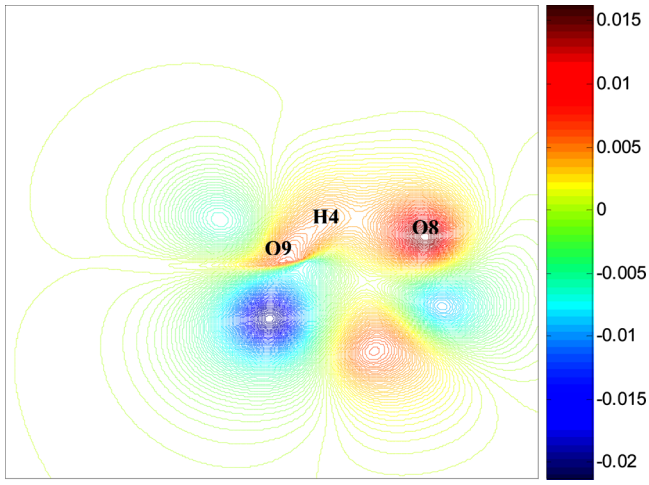

Figure 1. Difference between the π system density in the normal malonaldehyde (I) and the molecule with the H4 rotated 180° (III).

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$$\Delta\rho_\pi = \rho_\pi(\mathrm{I}) - \rho_\pi(\mathrm{III})$$

From the figure, it can be neatly observed how the π system is more delocalized over the region between both oxygen atoms in I than in III, giving a final support to conclusions obtained by means of the mutual polarizablities analysis.

HB Energy Analysis: Influence of the π System. In the preceding section, it is obtained that there is an effect of delocalization of the π system within the HB region, which could be ascribed to a resonance effect. This effect was shown to alter the polarizability of each LMO of the HB moiety and therefore the mobility of electrons. However, the remaining question is whether this delocalization effect actually contributes to increase the strength of the HB. In order to assess this question, the energy of the HB fragment is calculated (a) including only the occupied LMOs of the fragment and (b) the π system is also included, in order to analyze its influence on the HB energy. Table 5 displays the obtained results for all four compounds considered. It can be noted that, although the π system stabilizes the energy of the fragment in all cases, the energy diminishes more in the case of existing HB (compound I). Moreover, it is noticeable that, in cases II, III, and IV, where the HB is weakened or it does not exist, the contribution of the π system is very similar, despite the different conformation of the compounds. These facts should be, finally, indicative of a RAHB mechanism, contributing to the strength of the HB moiety.

Table 5. Electronic Energy of the HB Fragment

compound	E (au)[a]	E (au)[b]	ΔE
I	−142.717098	−124.211137	−18.505961
II	−143.102657	−125.128023	−17.974634
III	−143.010903	−125.087443	−17.923460
IV	−143.061528	−125.521633	−17.539895

[a]Calculated including the π system. [b]Calculated excluding the π system.

In order to deepen this insight on the influence of the π system, the potential energy curve of the proton in the HB moiety is calculated as in eq 9, along the line between both oxygen atoms, including the interaction of the proton with the π electrons and excluding it for the closed compounds I (Figure 2) and IV (Figure 3).

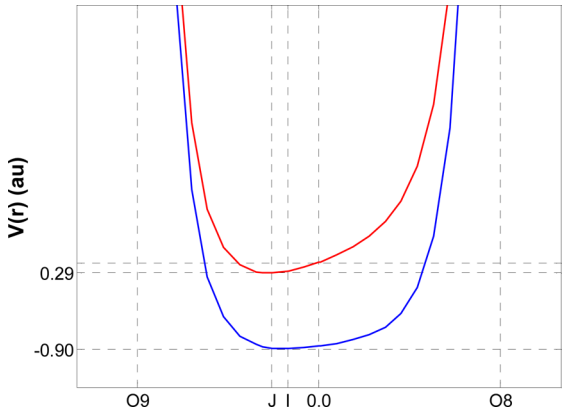

Figure 2. Energy potential well for the proton in the hydrogen bond of compound I, including and excluding the interaction with the π system. Energy values in au. Red, without including the π interaction; blue, including the π interaction. The points I and J correspond to the minima of both curves, respectively.

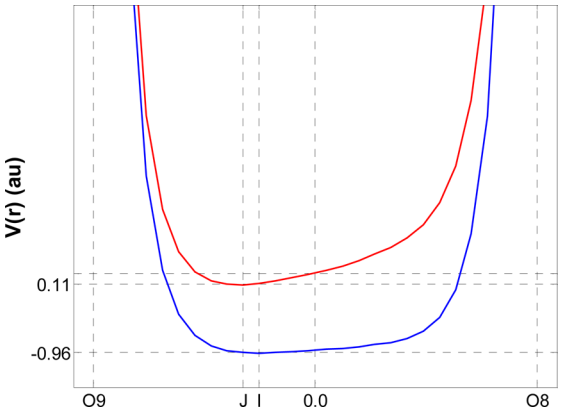

Figure 3. Energy potential well for the proton in the region between both oxygen atoms of compound IV, including and excluding the interaction with the π system. Energy values in au. Red, without including the π interaction; blue, including the π interaction. The points I and J correspond to the minima of both curves, respectively.

These compounds were chosen because they correspond to the minimum and maximum distances between both oxygen atoms. In both compounds, a single well potential is obtained, both when including the interaction with the π system, as when it is excluded. However, it is worth noting that the interaction of the π system with the proton yields significant changes in the potential well, decreasing the potential energy and making it more symmetrical. In fact, it can be seen that the potential energy without the π interaction is neatly asymmetric, while its inclusion leads to a weakly asymmetric curve, with its minimum shifted to the midpoint between both oxygen atoms. Bearing in mind that the more symmetrical the potential, the stronger the H bond,[14] it can be concluded that the interaction of the π system with the proton contributes to strengthen the H bond. Although both closed compounds have these features in common, it can be seen that the effect of the π system is more marked in I than in IV. This fact can be observed in Figure 4, where the difference between the potential energy curves with and without

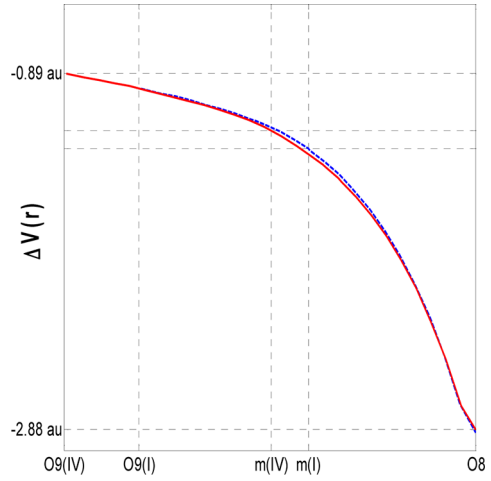

Figure 4. Difference between the potential energy including the interaction with the π system, $V_1(r)$, and excluding it, $V_2(r)$, for the proton in the region between both oxygen atoms, in compounds I and IV. Energy values in au. $\Delta V(r) = V_1(r) - V_2(r)$; red, compound IV; blue, compound I. The origin of the radial coordinate r is taken at the O8 position for both compounds. m(I) and m(IV) represent the position of the minimum of the potential well for compounds I and IV.

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the inclusion of the π system is displayed for both compounds considered. This difference represents the interaction potential energy between the π system and the H nucleus. It is worth noting that both curves almost match as the origin is taken on the O8 nucleus, showing that they mainly depend on the distance of the proton to its closest source of the π system, that is, the π(C5−O8) bond. Thus, it can be seen that, as the proton is placed further from the π(C5−O8) bond, the interaction energy decreases in absolute value. Therefore, as the proton equilibrium position in the HB zone is closer to O8 in compound I than in IV, the interaction with the π system is stronger, thus contributing more to deepen the potential well in the former than in the latter.

It is interesting to note that, being closed conformations, both compounds, I and IV, present different degrees of delocalization of the π system on the HB region, as it can be seen from the corresponding mutual polarizability values. However, although the delocalization is more marked in the former, this difference is not evidenced by Figure 4. This can be rationalized taking into account that, although the delocalized-onto-the-HB-region π system contributes to the potential energy, the difference in the degree of delocalization between both compounds is a much smaller effect that is screened by the interaction with the π system itself. Therefore, this degree of delocalization cannot be detected by means of a first order property like the potential energy, but with a second order property like mutual polarizabilities.

CONCLUDING REMARKS

In the present study, the influence of the π system on the electric dipolar molecular polarizability of the intramolecular hydrogen bond of malonaldehyde and several derived structure compounds is analyzed by means of the CLOPPA method. This influence on the energy of the HB and the potential energy curve of the proton are also evaluated. The focus was put on whether the analysis of these properties provides evidence for the existence of the RAHB mechanism.

As it was found elsewhere,[38] the analysis of the total value of each component of the polarizability tensor of the fragment does not reflect any evidence of a singular influence of the π system on the hydrogen bond moiety or any sign that could be attributed to a resonance effect. However, it is shown that this global upshot would be misleading and conveys conclusions that could be misinterpreted, and results require a further analysis. In fact, it is demonstrated that an in-depth analysis by decomposing the total polarizability in proper and mutual values leads to a qualitative and quantitative description of interactions in the HB zone. Thus, for example, the notably large, negative mutual polarizability between O9−H4 and π(C−C), although contributes to drop the total value of the O9−H4 polarizability, could be ascribed to a delocalization of the π system upon the HB region, and therefore, it reflects an effect of resonance, which should contribute to the HB strength. Moreover, it can be expected the same behavior in each molecule where a resonant π system contributes to a HB moiety; that is, a drop of the polarizability of the X−H bond, due to its interaction with the π system, as in this case, the minimal energy configuration corresponds to antiparallel induced dipoles.

The preceding results are highlighted by the analysis of the potential energy of the proton in the HB moiety, where the interaction of the π system with the proton yields significant changes in the potential well, decreasing the potential energy and making it more symmetrical. These effects show an actual strengthening of the HB due to the presence of the π electrons in the HB environment.

To summarize, about the question "is this strong HB resonance assisted?", the presented results lead to state that the HB is actually assisted by a resonance effect, as it is shown that (a) the π system delocalizes within the HB fragment, and therefore, this effect, in fact, could be ascribed to a resonance effect that closes the molecular ring; and that (b) there is an intense interaction of the π system with the proton (as it is evidenced by mutual polarizabilities), which actually contributes to the strength of the HB, as it can be observed from the potential energy curves. However, despite being a major factor, what cannot be surely stated is whether this resonance effect is the only determining factor of the unusual strength of the HB. This fact, indeed, would deserve further future analysis.

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Notes

The authors declare no competing financial interest.

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