

Investigation of the resonance-assisted hydrogen bond in model β -diketones through localized molecular orbital analysis of the spin–spin coupling constants related to the O–H \cdots O hydrogen bond

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The resonance-assisted hydrogen bond (HB) phenomenon has been studied theoretically by a localized molecular orbital (LMO) decomposition of the spin–spin coupling constants between atoms either involved or close to the O–H \cdots O system of some β -diketones and their saturated counterparts. The analysis, carried out at the level of the second-order polarization propagator approximation, shows that the contributions in terms of LMO to the paramagnetic spin orbital and the spin dipolar Ramsey terms proof the importance of the delocalized π -electron structure supporting the idea of the existence of the resonance-assisted HB phenomenon. The LMO contributions to the Fermi contact term indicate mainly the presence of the HB that may or not be linked to the π -electrons. Copyright © 2014 John Wiley & Sons, Ltd.

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Introduction

The large number of experimental and theoretical studies on hydrogen bonds (HBs) published in recent years reflects their importance for processes, which are crucial for life such as the stabilization of biological structures, enzyme catalysis in biological environments, and also for processes of technological interest.^[1–7] Among the numerous HBs known, the O–H \cdots O is of particular interest for biochemistry as it plays a central role in the stabilization of biomolecular structures and transition states in the course of the enzymatic reactions.^[8–18]

This particular HB is considered strong when the R(O,O) distance is slightly smaller than 2.5 Å.^[2,19] In this case, the stabilization energy can vary between 15 and 40 kcal/mol², and usually, the hydrogen is located in a more equidistant position between the oxygens. Another characteristic of such a strong HB is a displacement of the ^1H NMR chemical shift of 16–20 ppm^[20] as well as a decrease of the IR $\nu(\text{O–H})$ stretching frequencies up to 2560 cm⁻¹.^[20,21]

From a theoretical point of view, these types of HBs were analyzed using techniques such as the natural bond orbital analysis developed by Reed and Weinhold,^[22] the atom in molecule analysis by Bader,^[23] and, more recently, the noncovalent interactions approach by Johnson *et al.*^[24] Within the first procedure, one interprets the HB in terms of the charge-transfer stabilization energy, which is proportional to the HB strength,^[25] within the second, one characterizes it by the type of bond critical points.^[26,27] Furthermore, for conjugated systems, the ‘charge transfer’ phenomenon can be used also as a criterion for the way a π -system is delocalized over the whole molecule.^[25] Finally, the noncovalent interactions approach detects noncovalent interactions in real space, based on the electron density and its derivatives. In this procedure, the sign of the second electron-density Hessian eigenvalue is used to

provide the type of interaction (negative for hydrogen bond), and its strength can be derived from the density on the noncovalent interaction surface.

Model compounds such as β -diketones are widely used in such theoretical studies, in particular, its simplest representative the malonaldehyde (Fig. 1).^[28] These molecules are characterized by a neutral conjugated system and a very short (from 2.3 to 2.4 Å) intramolecular O–H \cdots O HB, where the donor and acceptor are connected through conjugated double bonds.^[29]

To explain this observation, Gilli *et al.*^[20,21] proposed the resonance-assisted HB phenomenon (RAHB) model in which the strength of the HB is related to the π electronic delocalization of the keto-enol group O=C–C=C–O–H, which induces partial charges of opposite signs on the oxygens. This causes a displacement of the hydrogen toward the keto oxygen atom, leading to a decrease of the energy of the system.

Therefore, the RAHB model can be considered as a feedback mechanism that keeps a partial charge over the oxygen, neutralizing the enlargement of the polarization due to the mesomeric effect by moving the proton toward the opposite side.^[21,30]

Since the seminal work by Gilli *et al.*,^[21] where they introduced the idea of RAHB mechanism, a large amount of works were published during several years, which invoke such concept to elucidate different phenomena related to structural chemistry.^[31–41] Although none of them goes beyond this model in trying to explain

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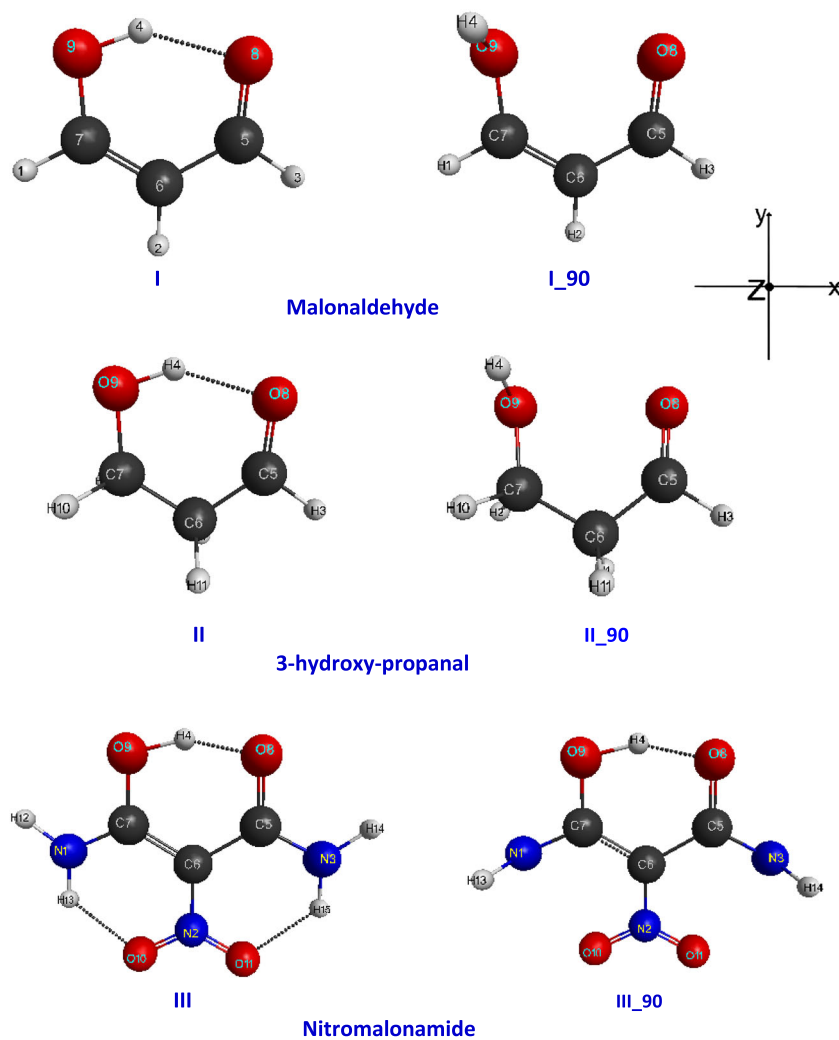


Figure 1. Molecular models.

this mechanism, except perhaps Madsen *et al.*,^[42,43] who introduced a slight modification to the original neutral RAHB mechanism that allowed the presence of partial charges also on the H of the O–H...O system, instead of being zero as in the original model. Such modification reveals the existence of a partial positive charge on hydrogen and partial negative charges on both oxygens.

Despite the original success of Gilli's model, several studies have raised some doubts about the very existence of the RAHB during the last years.^[44–51] Therefore, further attempts are necessary to investigate the influence of the π system on the HB region.

In recent years, the NMR parameters such as J-couplings were widely applied to provide a new comprehension of HB.^[52–54] This is possible because of the high sensitivity of the J-couplings to small variations of the electron density in different regions of the studied molecule, which allows a deeper insight in the electronic mechanisms and structures of the molecular systems.

Hence, for instance, the paramagnetic spin orbital (PSO) and the spin dipolar (SD) contributions to the isotropic J-couplings are related to the π -electronic structure of the molecules. However, their relation with the conjugation is not yet clear. Cremer and collaborators^[55] suggested that for C–C bonds, the absolute value of the PSO and SD contributions to $^1J(\text{C}–\text{C})$ can reflect the π -character of such bond. Some other works^[56,57] have

suggested that the long-range J-couplings are strictly related to these two mechanisms that would allow one to obtain J-couplings to distances of a few nanometers.

There are several procedures to decompose the J-couplings into contributions from localized molecular orbitals (LMOs).^[58–75] Using a method, which allows a σ – π separation, one could identify contributions from the π cloud to the J-coupling between atoms either involved or close to HB in systems with possibly a RAHB and thereby confirm or reject such hypothesis.

The main aim of this work is thus to find evidence for the existence or absence of the RAHB mechanism in the enoles of the β -diketones throughout the study of the J-couplings using LMO within the second-order polarization propagator approximation (SOPPA).^[76–79] In the comparison of malonaldehyde with its saturated analogue, 3-hydroxy-propanal, we concentrate on the couplings, which are sensitive to a possible interaction between the HB and the π -conjugated system. In previous works,^[51,80] it was seen that $^2J(\text{O}–\text{O})$ coupling constant in malonaldehyde has significant values for three of the four Ramsey terms, the PSO, the SD, and the Fermi contact (FC) term. We compare therefore the LMO contributions to the PSO, SD, and FC terms of spin–spin coupling constants between atoms either involved or close to the O–H...O system in malonaldehyde, 3-hydroxy-propanal, and nitromalonamide.

Computational details

The geometrical structures studied in this work (Fig. 1) were determined at the DFT/B3LYP/6-311++G** level of theory.^[81,82] The structure of malonaldehyde (**I**) was obtained, optimizing the whole molecule without restrictions (full geometrical optimization). Then 3-hydroxy-propanal (**II**) was optimized in the plane defined by the O–H⋯O HB geometry, keeping fixed the basic structure of malonaldehyde, which means that the distances $d(\text{O}–\text{O})$, $d(\text{O9}–\text{H4})$, $d(\text{C5}–\text{O8})$ and the angles $\text{O9}–\text{H4}–\text{O8}$, $\text{H4}–\text{O8}–\text{C5}$, $\text{H4}–\text{O9}–\text{C7}$, $\text{O9}–\text{C5}–\text{H3}$ are the same as those for structure **I**. Compounds **I_90** and **II_90** were derived from **I** and **II**, respectively, by rotation of the O–H bond by 90° around the C–O bond, keeping all other variables unmodified. For nitromalonamide (**III**), a full geometrical optimization procedure was applied, whereas compound **III_90** was obtained from **III** by rotation of the amino groups by 90° around the N–C bonds. The xy -plane is chosen as the plane of the molecules as shown in Fig. 1. Geometry optimizations were performed using the Gaussian 03 program package.^[83]

The theory of indirect nuclear spin–spin coupling constants (SSCC)^[84] and of different computational methods for calculating them has been described extensively in the literature.^[54,85–87] However, one should mention that there are four contributions to the SSCC: the FC and the SD, which come from the interaction of the nuclear magnetic moments with the spin of the electrons; and the diamagnetic spin orbital and the PSO, which are due to the interaction of the nuclear spins with the orbital angular momentum of the electrons.

It is known that the FC term is dominant in the couplings of saturated compounds,^[54] whereas in non-saturated compounds with double or triple bonds, the SD and PSO terms acquire considerable importance that can mean larger values than for the FC term.^[88–90]

Calculations of the SSCC were performed at the SOPPA level as implemented in the Dalton code^[91] and described in the work of Packer *et al.*,^[78] using LMOs. The correlation-consistent polarized valence basis sets or cc-pVXZ ($X = \text{D}, \text{T}$) of Dunning and collaborators were employed.^[92,93]

The localization procedure is realized by first solving the Hartree–Fock equations in Dalton and then localizing the orbitals according to the Pipek–Mezey localization scheme.^[94] Afterwards, the Møller–Plesset correlation coefficients and the solution vectors to the SOPPA equations were obtained using the LMOs instead of canonical molecular orbitals (CMOs). This implies that the non-diagonal Fock matrix in the LMO basis has been approximated by the diagonal Fock matrix in canonical orbitals. To obtain the contribution of each occupied LMO to the spin–spin coupling constants, equation 9 of the work of Zarycz and Aucar⁹⁵ was applied. As described in this reference, the procedure differs from that implemented by Sauer and Provasi within Hartree–Fock and DFT.^[74,75] Hence, the calculations using LMOs in the present work give only approximated results. However, as will be discussed in the next section, the difference between results obtained with canonicals and LMOs is small enough to justify this approximation.

Results

As mentioned in the Introduction, the RAHB refers to an interaction between an HB and the electrons of conjugated double bonds that link the acceptor and donor of the HB, in a manner that

the π -structure of the carbon skeleton affect the HB and vice versa. Thus, in this work, we study the Ramsey terms of the SSCC related to the formation of the intramolecular HB O–H⋯O and the possible influence on it of the conjugation of the π structure in malonaldehyde and its saturated counterpart (3-hydroxy-propanal) as well as the nitromalonamide (Fig. 1). For doing so, we use LMO for calculating such couplings, as described in the Conclusions Section.

In order to proof the reliability of our localization scheme, we list in Table 1 the results for the four Ramsey contributions to the SSCCs and its isotropic value for compounds represented in Fig. 1 with and without the localization procedure, employing the cc-pVTZ basis set and with CMOs using the cc-pVTZ-J basis set,^[56] optimized for J-coupling. It is seen that, in general, the agreement between the cc-pVTZ and cc-pVTZ-J basis set results is very good for the PSO and SD contributions, and the pattern of J-couplings are alike. Major differences are observed for the FC terms, as could be expected. However, as we will see later on, the most important contributions for the study are the SD and PSO term, which are almost identical in both basis sets. Thus, considering the results obtained with CMO and LMO and the same basis set, i. e. cc-pVTZ, it is observed that the largest differences are for the FC term of ^1H (O9–H4) in the structures **I_90** and **II_90**, which are, respectively, 4.41 and 4.11 Hz, i. e. 8.22% and 8.55% of deviation. Therefore, it is apparent that the approximation to the Fock matrix is good enough to reproduce the results obtained using CMOs, in particular, as the variation of the FC term does not play an important role in the analysis of this coupling as we can see in the following text.

The spin–spin coupling constant for oxygen^[96–111] has received less attention than the more common cases of H, C, N, P, and F, as the only magnetic isotope of the oxygen is the ^{17}O with a natural abundance of 0.037% and a nuclear spin of $I = 5/2$ that implies a quadrupole moment, which is responsible of the broadening of the NMR line widths. Therefore, only relatively large coupling constants can be measured. Hence, it is not surprising that we could not find an experimental measurement of ^1J ($^{17}\text{O}–^{17}\text{O}$). However, our theoretical values are close to those calculated at DFT level of theory and with equation-of-motion coupled cluster singles and doubles calculations in the CI-like approximation in previous works.^[47,80]

More studies refer to the one bond $^1\text{J}(\text{X}–^{17}\text{O})$ where X is a nucleus without quadrupole relaxation. However, the determination of ^1J (H– ^{17}O) in water molecules must be carried out under slow chemical exchange conditions.^[97] Concerning the particular case of ^1J ($^{17}\text{O}–^1\text{H}$), Sergeyev and coworkers^[112] assigned an experimental value of 32.0 Hz to this coupling constant in acetylacetone. In their study, and in agreement with other investigations,^[113,114] Sergeyev *et al.* suggest that the hydroxylic proton migrate rapidly, in the NMR time scale, between the oxygens, and therefore, the measured value can be considered as the average value corresponding to the delocalization of the proton in the O–H⋯O region. Hence, taking the theoretical values of the ^1H (O9–H4) and ^1H (O8–H4) shown in Table 1 for structure **I**, and following the procedure indicated by Berger *et al.*,¹¹¹ we obtain 38.7 Hz for the average values of ^1H ($^{17}\text{O}–\text{H}$). Moreover, for the tautomeric form of compound **I**, the ^1H (O9–H4) is close to the one obtained experimentally^[112] for methyl ester of salicylic acid and the ortho-hydroxy-acetophenone (~79 Hz). Therefore, the value of this coupling could be used for determining the position of the proton in the HB as performed for the Schiff bases derived from salicylic aldehydes using the value of ^1H (N–H).^[115]

On the other hand, for compound **I**, the calculated value of $^1\text{J}(\text{C5}–\text{O8})$ is 28.11 Hz, whereas the distance $R(\text{C5}–\text{O8})$ is 1.32 Å,

Table 1. The four Ramsey contributions and the isotropic spin–spin coupling constants for the nuclei involved in the intramolecular H-bond of malonaldehyde, 3-hydroxy-propanal, and nitromalonamide[†] at SOPPA/cc-pVTZ level and using CMO (LMO) [Hz]

	FC	SD	PSO	DSO	ISO
² _J (O8-O9) I	2.84 (2.76) [3.71]	2.42 (2.72) [2.40]	5.58 (5.73) [5.54]	0.01 (0.01) [0.00]	10.85 (11.21) [11.66]
² _J (O8-O9) I_90	2.78 (2.66) [3.33]	1.15 (1.28) [1.14]	3.22 (3.22) [3.22]	0.1 (0.01) [0.01]	7.17 (7.17) [7.71]
¹ _J (O9-H4) I	-65.00 (-63.93) [-79.67]	0.30 (0.35) [0.19]	-5.76 (-5.85) [-5.09]	-0.41 (-0.41) [-0.40]	-70.87 (-69.84) [-84.97]
¹ _J (O9-H4) I_90	-53.62 (-49.21) [-70.32]	0.09 (0.20) [0.01]	-11.79 (-11.96) [-11.13]	-0.38 (-0.38) [-0.38]	-65.70 (-61.35) [-81.82]
¹ _J (O8-H4) I	5.24 (6.03) [5.87]	-0.19 (-0.19) [-0.17]	2.35 (2.40) [2.28]	-0.65 (-0.65) [-0.66]	6.75 (7.59) [7.32]
¹ _J (O8-H4) I_90	-0.40 (-0.41) [-1.21]	0.09 (0.06) [0.09]	-0.06 (-0.05) [-0.07]	-0.02 (-0.02) [-0.02]	-0.40 (-0.42) [-1.21]
¹ _J (C7-O9) I	17.59 (18.11) [16.87]	1.03 (1.35) [1.06]	8.27 (8.72) [8.11]	-0.07 (-0.07) [-0.09]	26.82 (28.11) [25.95]
¹ _J (C7-O9) I_90	18.37 (19.12) [17.07]	0.27 (0.44) [0.31]	3.91 (4.07) [3.89]	-0.07 (-0.07) [-0.09]	22.47 (23.56) [21.19]
			3-hydroxy-propanal		
² _J (O8-O9) II	1.55 (1.43) [2.03]	0.07 (0.07) [0.08]	-0.77 (-0.83) [-0.78]	0.1 (0.01) [0.01]	0.86 (0.68) [1.33]
² _J (O8-O9) II_90	2.65 (2.53) [2.95]	0.2 (0.02) [0.02]	-0.25 (-0.28) [-0.25]	0.1 (0.01) [0.01]	2.43 (2.28) [2.74]
¹ _J (O9-H4) II	-53.25 (-51.10) [-70.87]	0.38 (0.46) [0.27]	-7.23 (-7.40) [-6.59]	-0.45 (-0.45) [-0.39]	-60.55 (-58.50) [-77.59]
¹ _J (O9-H4) II_90	-48.11 (-43.99) [-60.27]	0.17 (0.30) [0.10]	-11.12 (-11.29) [-10.51]	-0.32 (-0.32) [-0.32]	-59.38 (-55.31) [-71.00]
¹ _J (O8-H4) II	6.25 (7.06) [7.34]	-0.68 (-0.71) [-0.66]	0.91 (0.94) [0.84]	-0.64 (-0.64) [-0.66]	5.84 (6.65) [6.87]
¹ _J (O8-H4) II_90	0.19 (0.20) [0.20]	-0.04 (-0.04) [-0.04]	0.00 (0.00) [-0.01]	-0.03 (-0.03) [-0.03]	0.13 (0.13) [0.13]
¹ _J (C7-O9) II	23.47 (25.77) [21.50]	-1.50 (-1.57) [-1.43]	-2.10 (-2.13) [-2.05]	-0.09 (-0.09) [-0.11]	19.77 (21.98) [17.91]
¹ _J (C7-O9) II_90	21.69 (23.28) [19.90]	-1.67 (-1.74) [-1.60]	-1.77 (-1.80) [-1.76]	-0.09 (-0.09) [-0.10]	18.16 (19.66) [16.44]
			Nitromalonamide		
² _J (O8-O9)					
III	10.15 (10.33)	0.56 (0.58)	0.81 (0.80)	0.02 (0.02)	11.54 (11.72)
III_90	6.82 (7.13)	2.10 (2.18)	5.78 (5.66)	0.02 (0.02)	14.71 (14.98)

[†] Between square brackets are calculations with CMO at SOPPA/cc-pVTZ-J level.

[†] Basis set for nitromalonamide: cc-pVTZ for O8, O9, C5, C6, C7, and H4 and cc-pVDZ for N1–N3, O10, and O11; and a minimal basis set constituted by only one s-type orbital with coefficient 1.159 for H12–H15.

just in between the distance of a single bond (1.43 Å) and of a double bond (1.23 Å) and therefore with partial character of a double bond, whereas the experimental value reported^[99] for the double bond of the acetone is 22 Hz, which agrees quite well with our calculations.

In the following text, we will discuss our results in light of the decomposition in LMO, first for malonaldehyde and 3-hydroxypropanal and then for nitromalonamide.

Structures I, II, I_90, and II_90

$^2J(O8-O9)$

Table 2 collects the most important contributions obtained with LMOs to the FC terms for $^2J(O8-O9)$ coupling constant in structures **I**, **II**, **I_90**, and **II_90**. The most important finding is that for the two structures, where there is an HB, i. e. **I** and **II**, the dominant contributions are the $\sigma(O9-H4)$ and the lone-pair (LP) SPy(O8). The former almost vanishes for the two structures where the HB is broken, i. e. **I_90** and **II_90**, whereas the latter diminishes 55% when going from **I** to **I_90** and 35% going from **II** to **II_90**.

Moreover, the total FC coupling of the compound **I** is a ~40% larger than the corresponding in compound **II**, whereas the rotated structures show a difference of only ~0.2 Hz. In both cases, such difference arises from the LP-SPy(O8) contribution, while the $\sigma(O9-H4)$ contributes with the same value to each pair. This implies that the LP-SPy(O8) reinforces the FC when the molecule has conjugated π -orbitals in it, which may be due to a hyperconjugative interaction of type LP $\rightarrow \pi^*$, where π^* is the antibonding of a π bonding orbital.^[116]

Table 2. LMO decomposition of the FC term to $^2J(O8-O9)$ [Hz] for structures **I**, **II**, **I_90**, and **II_90**

Localized orbitals [†]	I	II	I_90	II_90
C(O8)	-0.60	-0.04	0.50	0.22
C(O9)	-0.82	-1.93	-0.01	0.63
LP-SPxy(O9)	-0.76	-0.38	0.62	0.58
[LP-SPyz(O9)]				
$\sigma(C5-O8)$	-0.25	-0.16	-0.02	-0.06
$\sigma(O9-H4)$	2.28	2.27	0.05	0.09
$\sigma(C7-O9)$	-0.14	-0.04	-0.10	-0.02
LP-SPy(O8)	3.04	1.85	1.37	1.19
Sum	2.76	1.57	2.42	2.63

[†] Between brackets is the LMO of the rotated structures (**I_90** and **II_90**).

It is remarkable that the contributions of the core orbitals, C(O8) and C(O9), are more symmetric in compound **I** than in **II**, showing a good agreement with the fact that the electronic distribution is more symmetric in **I** than in **II** because of the π electronic delocalization of the former. Furthermore, the sum of both core orbitals goes from -1.42 Hz for **I** to 0.49 Hz for **I_90** and from -1.97 Hz for **II** to 0.85 Hz for **II_90**. These changes help to counteract the reduction suffered by $\sigma(O9-H4)$ and LP-SPy(O8) contributions when passing from the planar to the open structures.

It is known that when going from **I** to **I_90** (Fig. 2), there is neither conjugation nor overlapping between the LMOs LP-SPz(O9) and $\pi(C7-C6)$, which implies that the resonance is broken and that the delocalization of the π -cloud diminishes. Therefore, it seems to be reasonable that the FC terms of the rotated compounds tend to be more alike to each other.

As stated previously in this section, the FC term of the $^2J(O8-O9)$ coupling of compounds **I** and **II** is mainly determined by the contributions LP-SPy(O8) and $\sigma(O9-H4)$, whereas the main contributions of the compound **I_90** are LP-SPy(O8) (55.0%), LP-SPyz(O9) (24.9%), and C(O8) (20.1%); and for compound **II_90**, the main contributions are LP-SPy(O8) (45.4%), C(O8) (8.4%), C(O9) (24.0%), and LP-SPyz(O9) (22.1%).

The main LMO contributions to the SD term of the $^2J(O8-O9)$ for structures **I**, **II**, **I_90**, and **II_90** are collected in Table 3. It is seen that only the structures **I** and **I_90** have no negligible contributions, which means that according to previous studies in unsaturated compounds,^[88-90] there is a π -structure involved in the coupling pathway of the coupled nuclei. The malonaldehyde (**I**) corroborates such affirmation because the main contributions to the SD term of the $^2J(O8-O9)$ coupling involve the π -orbitals [$\pi(O9-C7)$, $\pi(C7-C6)$,

Table 3. LMO decomposition of the SD term to $^2J(O8-O9)$ [Hz] for structures **I**, **II**, **I_90**, and **II_90**

Localized orbitals [†]	I	II	I_90	II_90
LP-SPxy(O9) [LP-SPyz(O9)]	0.16	0.02	0.09	~0.0
$\sigma(O9-H4)$	0.37	0.04	0.14	~0.0
LP-Pz $>$ $\pi(O9-C7)$ [LP-Px(O9)]	0.64	-0.03	0.34	0.01
$\pi(C5-O8)$	0.54	-0.01	0.19	~0.0
LP-Px(O8)	0.76	0.07	0.41	0.01
$\pi(C6-C7)$ [‡]	0.19	—	0.04	—
Sum	2.66	0.09	1.21	0.02

[†] Between brackets is the LMO of the rotated structures (**I_90** and **II_90**).

[‡] The LMO $\pi(C6-C7)$ does not exist for **II** and **II_90**.

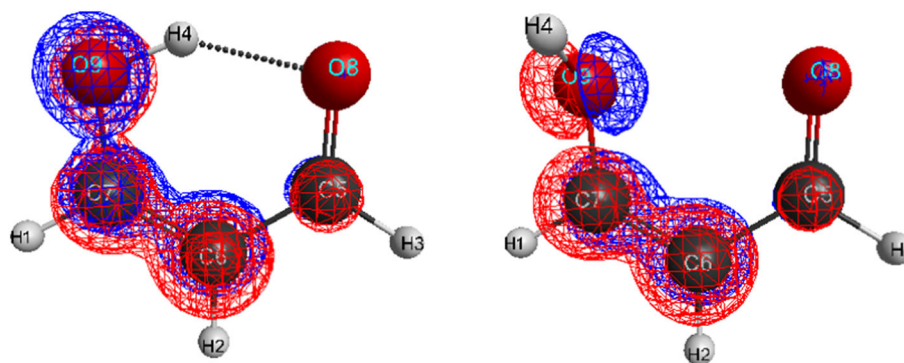


Figure 2. Representation of the $\pi(C5-O8)$ and LP-SPz(O9) LMOs for compound **I** (left) and **I_90** (right).

and $\pi(\text{C5-O8})$] that contribute with $\sim 51.5\%$ and the p -type LP-Px(O8) that contributes with $\sim 28.6\%$. All these contributions decrease drastically when the HB is broken, in the **I_90** structure, producing a reduction of more than 50% in the coupling. As a consequence of the overlapping between the LP-Pz(O9) and the orbital $\pi(\text{C7-C6})$ in structure **I** (Fig. 3), the LP-Pz(O9) acquire a π -character that also means an extension of the π conjugation through the carbonate structure that links the donor and acceptor of the HB, which coincide with the π -conjugation phenomenon described by Gilli *et al.*^[21] Obviously, in compound **II**, this cannot happen because there is no possibility of such overlapping. These different features of the LP-Pz(O9) in the unsaturated and saturated structures are reflected in the fact that its contribution for the former is 25%, whereas for the latter is almost zero.

Moreover, when the HB is broken, the π -type contributions diminish more than a 60% as well as the $\sigma(\text{O9-H4})$, whereas the LP contributions of the p -type decrease as much as 46%. All these changes together cause a reduction of about 50% of the SD term, what demonstrate that such contribution is sensitive to the presence of the extended conjugation, which is broken up in **I_90**. For **I_90**, the p -type LPs are responsible of $\sim 70\%$ of the coupling. It is important to remark that, at the contrary of what happens with compound **I**, all the contributions to the SD term for compound **II**, including $\pi(\text{C5=O8})$, are negligible. The coupling in structure **I** is not uniquely determined by the σ skeleton of the molecule, which implies that the J-coupling between the atoms involved in the HB makes apparent that the structure of the conjugated double bonds modify the characteristics of the HB in structure **I**.

As can be observed in Table 1, the value of the PSO term of $^2J(\text{O8-O9})$ is nearly zero for structures **II** and **II_90**, whereas for structure **I**, it is almost as large as the sum of the FC and SD terms and therefore responsible for $\sim 50\%$ of the coupling. In Table 4, the most relevant LMO contributions to the PSO term of the structures **I**, **II**, **I_90**, and **II_90** are displayed. These are the same as those seen for the SD term, although they behave differently.

The most important contribution to the PSO term are $\sigma(\text{O9-H4})$ with 1.22 Hz and LP-Px(O8) with 2.61 Hz, which represent almost the 71% of the total, whereas the π -type orbital contributes with 1.08 Hz, which is almost as large as the same contributions to the SD term (Table 3). As in the case of the SD term, it should be stressed that the contributions $\sigma(\text{O9-H4})$ and LP-Px(O8) are very close to zero in compound **II**, which shows that the π structure of compound **I** influences the PSO term, increasing its value in this case. Moreover, when going from **I** to **I_90**, the LP-Pz(O9) in **I** becomes LP-Px(O9) in **I_90**, and its contribution increases $\sim 100\%$ respect its value in **I** but does not compensate the general decrease

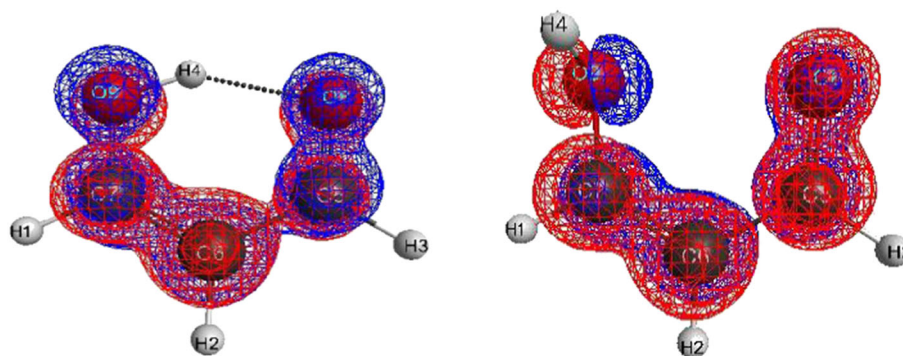


Figure 3. Representation of the π structure in **I** (left) and **I_90** (right).

Table 4. LMO decomposition of the PSO term to $^2J(\text{O8-O9})$ [Hz] for structures **I**, **II**, **I_90**, and **II_90**

Localized orbitals [†]	I	II	I_90	II_90
LP-SPxy(O9) [LP-SPyz(O9)]	0.51	-0.04	0.07	~ 0.0
$\sigma(\text{O9-H4})$	1.22	-0.20	0.12	~ 0.0
LP-Pz- > $\pi(\text{O9-C7})$ [LP-Px(O9)]	0.61	-0.20	1.24	0.01
$\pi(\text{C5-O8})$	0.33	-0.10	0.10	~ 0.0
LP-Px(O8)	2.61	-0.31	1.52	0.01
$\pi(\text{C6-C7})^\ddagger$	0.14	—	0.03	—
Sum	5.42	-0.86	3.08	0.02

[†] Between brackets is the LMO of the rotated structures (**I_90** and **II_90**).

[‡] The LMO $\pi(\text{C6-C7})$ does not exist for **II** and **II_90**.

of the other ones. Thus, for **I_90**, the p -type LPs are responsible for the coupling.

The detailed analysis of the FC, SD, and PSO terms of $^2J(\text{O8-O9})$ shows a marked difference between the HB in structures **I** and **II**, manifesting that the main difference between them is due to the presence of the conjugated system in **I**.

The three terms analyzed up to here corroborate that for **I_90**; the LPs contribute most to each of them as suggested by Alkorta *et al.*^[47]

$^1J(\text{O9-H4})$

For the FC term of the $^1J(\text{O9-H4})$ coupling the main LMO contribution for all compounds is by far the $\sigma(\text{O9-H4})$, as expectable (Table 5), and it determines the final value and sign of the couplings.

The contributions LP-SPxy(O9) [LP-SPyz(O9)] and $\sigma(\text{C7-O9})$ themselves are different for each structure, but in all cases, they diminish the absolute value of the coupling as they are always positive for the different structures. Thus, the contribution LP-SPxy(O9) in **I** is twice as large as in **II**, and when the HB is broken the LP-SPyz(O9) contributions for the different compounds becomes similar to each other. On the other side, the orbital $\sigma(\text{C7-O9})$ contributes in a similar fashion in each structure, i.e. it is not sensitive to the formation or not of the HB.

The core contribution C(O9) is more important in structures **II** and **II_90** than in **I** and **I_90**. Moreover, in the former compounds, it is positive, whereas in the latter, its sign is negative.

Noteworthy, is that in **II** the LMOs $\sigma(\text{C7-H2})$ and $\sigma(\text{C7-H10})$ contribute symmetrically to the coupling, and its sum is almost equivalent to contribution $\sigma(\text{C7-H1})$ in **I**. Such symmetry is broken in **II_90**.

Table 5. LMO decomposition of the FC term to ${}^1J(\text{O9-H4})$ [Hz] for structures **I**, **II**, **I_90**, and **II_90**

Localized orbitals [†]	I	I_90	II	II_90
C(O9)	-2.01	-0.37	10.05	5.18
LP-SPxy(O9) [LP-SPyz(O9)]	9.72	11.64	4.97	14.68
$\sigma(\text{O9-H4})$	-78.68	-66.87	-71.00	-67.89
$\sigma(\text{C7-O9})$	4.49	4.65	3.27	3.24
$\sigma(\text{C7-H1})^\ddagger$	1.49	0.08	—	—
$\sigma(\text{C7-H2})^\ddagger$	—	—	0.59	1.36
$\sigma(\text{C7-H10})^\ddagger$	—	—	0.59	-0.53
LP-Px(O8)	1.26	-0.07	0.60	-0.05
$\pi(\text{C6-C7})^\ddagger$	0.01	1.64	—	—
Sum	-63.72	-49.31	-51.53	-43.49

[†] Between brackets is the LMO of the rotated structures (**I_90** and **II_90**).

[‡] The LMOs $\pi(\text{C6-C7})$ and $\sigma(\text{C7-H1})$ do not exist for **II** and **II_90**, whereas LMOs $\sigma(\text{C7-H2})$ and $\sigma(\text{C7-H10})$ do not exist for **I** and **I_90**.

When the HB is broken, the absolute value of the total FC term diminishes ~23.0% in malonaldehyde and ~14.0% in 3-hydroxypropanal, respectively, which is a consequence of that the main contribution, $\sigma(\text{O9-H4})$, becomes more similar to each other in both structures, **I_90** and **II_90**, with a difference of less than 1 Hz. Besides, the contribution of such bond decreases 15% going from **I** to **I_90** and only a 4.4% going from **II** to **II_90**. For the rotated structures, the difference in the FC term comes mainly from the difference between the LP-SPyz(O9) contributions, which is about 20%. Moreover, the breaking of the HB in **I_90** makes the $\sigma(\text{C7-H1})$ contribution negligible as the LP-Px(O8), a behavior which is not observed in the $\sigma(\text{C7-H2})$ and $\sigma(\text{C7-H10})$ contributions corresponding to **II_90**.

The PSO term, on the other hand, is a 23% smaller in **II** compared with the value in **I**. This difference is only 6% in the opposite direction, when the HB is broken, i.e. between **I_90** and **II_90**. It is seen in Table 6 that the most important contribution is LP-Pz- $\pi(\text{O9-C7})$ [LP-Px(O9)] followed by $\sigma(\text{C7-O9})$ and not $\sigma(\text{O9-H4})$ as was the case for the FC term. Moreover, the contribution $\sigma(\text{O9-H4})$ is now positive in contrast to the other ones.

When going from **I** to **I_90**, the variation of the PSO term is ~104.4%, whereas going from **II** to **II_90** is ~52.6%, which implies a larger sensitivity or impact on the HB formation when such formation comes escorted by a resonant structure, validating the Gilli's model. In more detail, the larger variations arise from the LP-P(O9) with a 96%, LP-Sp(O9) with 108% and

Table 6. LMO decomposition of the PSO term to ${}^1J(\text{O9-H4})$ [Hz] for structures **I**, **II**, **I_90**, and **II_90**

Localized orbitals [†]	I	I_90	II	II_90
C(O9)	-0.95	-0.61	-1.40	-0.82
LP-SPxy(O9) [LP-SPyz(O9)]	-1.47	-3.06	-1.63	-2.59
$\sigma(\text{O9-H4})$	1.51	1.85	1.86	1.45
$\sigma(\text{C7-O9})$	-2.05	-3.62	-3.12	-3.62
LP-Pz- $\pi(\text{O9-C7})$ [LP-Px(O9)]	-3.48	-6.84	-3.63	-5.96
Sum	-6.22	-12.24	-7.66	-11.51

[†] Between brackets is the LMO of the rotated structures (**I_90** and **II_90**).

$\sigma(\text{C7-O9})$ with 76.6% for **I_90**, and the same contributions for **II_90** vary 64%, 58.9% and 16%, respectively.

${}^1J(\text{O8-H4})$

Another term sensitive to the presence or absence of the HB and the resonant structure is the PSO of the ${}^1J(\text{O8-H4})$ whose contributions are collected in Table 7. This term is in compound **I** about 2.6 as large as in compound **II** (Table 1). The main responsible for this change is the LP-Px(O8) contribution that is about four times larger in **I** than in **II** and almost vanishes for **I_90** (Table 7). Noteworthy is that the LP-Pz- $\pi(\text{O9-C7})$ [LP-Pz(O9)] contribution, although small in **I** (~14% of the total PSO), vanishes in **II**, which reinforces the idea of the influence of the resonant structure on the HB.

${}^1J(\text{C7-O9})$

The coupling ${}^1J(\text{C7-O9})$ has a FC term that is larger in **II** than in **I** (Table 1), whereas the contrary occurs for the PSO term. The SD term, on the other hand, has similar absolute values for both structures.

In Table 8 are shown the main LMO contributions that determine the PSO term in the structures **I**, **I_90**, **II**, and **II_90**. In all cases, the most important contribution is the corresponding to the bonded atoms, $\sigma(\text{C7-O9})$, which in **I** is more than four times the value in **II**. Such relation is approximately the same as the relation existing between the totals.

When the contribution of the LP-Pz(O9) is inspected in structures **I** and **II**, it can be seen that it has a difference in absolute value of three times in favor of **I**. This lone pair conjugates with the π

Table 7. LMO decomposition of the PSO term to ${}^1J(\text{O8-H4})$ [Hz] for structures **I**, **II**, **I_90**, and **II_90**

Localized orbitals [†]	I	II	I_90	II_90
C(O8)	-0.26	-0.22	-0.05	-0.04
$\sigma(\text{O9-H4})$	0.49	0.19	-0.02	-0.03
LP-SPy(O8)	0.35	0.28	0.03	0.02
LP-Pz(O9)- $\pi(\text{O9-C7})$ [LP-Pz(O9)]	0.30	0.02	-0.01	-0.04
LP-Px(O8)	1.35	0.33	-0.04	0.01
Sum	2.22	0.61	-0.09	-0.10

[†] Between brackets is the LMO of the rotated structures (**I_90** and **II_90**).

Table 8. LMO decomposition of the PSO term to ${}^1J(\text{C7-O9})$ [Hz] for structures **I**, **II**, **I_90**, and **II_90**

Localized orbitals [†]	I	II	I_90	II_90
LP-SPxy(O9)	0.47	-0.18	0.34	-0.24
$\sigma(\text{C6-C7})$	0.86	-0.35	0.28	-0.77
$\sigma(\text{C7-H1})$	0.63	-0.78	0.29	-0.57
$\sigma(\text{O9-H4})$	0.16	-0.32	0.28	-0.55
$\sigma(\text{C7-O9})$	4.90	1.05	2.98	1.03
LP-Pz- $\pi(\text{O9-C7})$ [17-LP-Px(O9)]	2.45	-0.65	0.21	-0.04
$\pi(\text{C6-C7})^\ddagger$	-0.69	—	-0.27	—
Sum	8.78	-2.01	4.11	-1.72

[†] Between brackets is the LMO of the rotated structures (**I_90** and **II_90**).

[‡] The LMO $\pi(\text{C6-C7})$ does not exist for **II** and **II_90**.

structure of the carbon skeleton in plane structures; nevertheless, when the HB is broken also the conjugation disappears. Therefore, such contribution almost vanishes, and the $\sigma(\text{C7-O9})$ diminishes markedly (~40%) for **I_90**; however, it is almost the same for **II** and **II_90**

Structures **III** and **III_90**

Finally, the influence of the π -structure for the formation of the HB in the β -diketones can be assessed discussing the $^{2\text{h}}\text{J}(\text{O8-O9})$ coupling in the equilibrium structure of the nitromalonamide (**III**), and the nitromalonamide with N1-C7 + N3-C5 rotated 90° (**III_90**) as shown in the Conclusion.

The SD and PSO terms in structure **III** are small with values under 1 Hz, and the FC term determines the isotropic coupling, whereas in **III_90**, the FC decrease 30.1%, and the SD and PSO rise up to 3.8 and 7.1 times their values in **III**, i.e. both terms are similar to the corresponding contributions for structure **I**. If one considers the distance O–O, which is 2.589 Å for **I** and 2.396 Å for **III** and **III_90**, it can be seen that the SD and PSO terms do not depend on the donor–acceptor distance but on the π structure of the molecule. It differs notoriously from the behavior of the FC term, which the value in **III** is 3.7 times larger than its value in **I**. This is in complete agreement with a previous study^[80] at DFT level, where on changing the distance O–O by 0.2 Å in the structure **III**, the FC term triples its value, whereas the PSO and SD terms almost do not vary.

In Table 9 are shown the main LMO contributions to the FC term of the $^{2\text{h}}\text{J}(\text{O8-O9})$ coupling for structures **III** and **III_90**. The main contribution corresponds to the bond $\sigma(\text{O9-H4})$, followed by the LP-Pxy(O8). The contributions of the LP-SPxy-O8 and LP-SPxy(O9) compensate almost each other. When the HB is broken, the contributions LP-Pxy(O8) increases 1.36 Hz, and $\sigma(\text{O9-H4})$ diminishes 1.18 Hz in a manner that LP-Px(O8) becomes the most important in **III_90**.

In both structures, **III** and **III_90**, the most important contributions are the ones that conform the HB; and for the rotamer **III_90**, the LP-SPxy(O8) and LP-SPxy(O9) decrease, in absolute value, respect to the value in **III** but not in the same amount.

The most important LMO contributions of the SD and PSO terms for the $^{2\text{h}}\text{J}(\text{O8-O9})$ coupling are shown in Table 10. The dominant contributions for both structures are the LP-Px(O8) followed by the $\sigma(\text{O9-H4})$, whereas for **III_90**, there is a general increment of all contributions mainly because of the reinforcement of the resonance, which is restricted to the basic β -diketone structure $\text{O}=\text{C}-\text{C}=\text{C}-\text{O}-\text{H}$. In particular, the carbon skeleton [$\pi(\text{O9-C7}) + \pi(\text{C7-C6}) + \pi(\text{C5-O8})$] contributes with 0.55 Hz, i.e. ~25% of the total, which manifests that the SD term is stronger when the π

Table 9. LMO decomposition of the FC term to $^{2\text{h}}\text{J}(\text{O8-O9})$ [Hz] for **III** and **III_90**

Localized orbitals	III	III_90
S(O9)	1.32	0.25
S(O8)	0.03	−0.18
$\sigma(\text{O9-H4})$	5.97	4.79
$\sigma(\text{C5-O8})$	−0.38	−0.45
$\sigma(\text{C7-O9})$	−0.25	−0.35
LP-SPxy(O8)	2.97	0.45
LP-SPxy(O9)	−3.01	−1.88
LP-Pxy(O8)	3.87	5.23
Sum	10.53	7.87

Table 10. LMO decomposition of the SD and PSO terms to $^{2\text{h}}\text{J}(\text{O8-O9})$ [Hz] for **III** and **III_90**

Localized orbitals	SD		PSO	
	III	III_90	III	III_90
$\sigma(\text{O9-H4})$	0.25	0.58	0.21	1.63
LP-Pxy(O8-H4)	0.36	0.86	0.38	2.55
LP-SPxy(O9)	0.04	0.15	0.12	0.49
LP-Pz- $\pi(\text{O9-C7})$	−0.02	0.23	0.04	0.39
$\pi(\text{C7-C6})$	0.02	0.11	0.05	0.13
$\pi(\text{C5-O8})$	−0.02	0.21	0.03	0.29
Sum	0.62	2.13	0.82	5.47

delocalization throughout the carbon skeleton is more concentrated. Therefore, the SD term is strongly conditioned by the enlargement of the conjugation within the π orbitals and the lone pair of the main structure. The PSO term shows a behavior similar to the exposed earlier for the SD one.

Conclusions

We have studied the resonance-assisted HB phenomenon analyzing the main LMOs contributions of the spin–spin coupling constants between atoms either involved or close to the O–H \cdots O system using the SOPPA/cc-pVXZ (X=T,Z) level of approximation. The selected model compound for such analysis were malonaldehyde (**I**), 3-hydroxy-propanal (**II**), nitromalonamide (**III**), the rotamers **I_90** and **II_90** where the O–H \cdots O HB has been broken, and the rotamer **III_90** where the amino groups have been rotated 90° .

The main observations can be summarized as follows: the total FC term of the $^{2\text{h}}\text{J}(\text{O}–\text{O})$ depends more strongly on the distance d (O–O) than on the existence of the conjugated double bond that link the donor and acceptor of the HB, whereas the SD and PSO terms behave on the opposite fashion. Specifically, the analysis of these two terms reveals the influence of the π conjugated system on the HB and therefore provides evidence for the existence of the RAHB phenomenon.

The FC terms of the $^{2\text{h}}\text{J}(\text{O}–\text{O})$ tend to be more alike to each other in the rotated compounds **I_90** and **II_90** where the overlapping of the LMOs LP-SPz(O9) and $\pi(\text{C7-C6})$ does not exist, which on its side implies the breaking down of the resonance and the diminution of the π cloud delocalization.

In the structures with HB, the most important contributions for the FC term of $^{2\text{h}}\text{J}(\text{O}–\text{O})$ are given by the LMOs $\sigma(\text{O9-H4})$ and LP-SPx(O8), whereas for the PSO and SD, they are $\sigma(\text{O9-H4})$ and LP-Px(O8). For the structures without HB, the most important contributions are given by the LMOs of the s-type for the FC term and of the p-type for the SD and PSO, whereas the LMO $\sigma(\text{O9-H4})$ vanishes.

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