

NMR Spectroscopic Parameters of Molecular Systems with Strong Hydrogen Bonds

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A series of closed H-bonded molecules that have (or not) delocalized bonds were studied. The dependence of both NMR spectroscopic parameters σ and J -couplings, and also the energy stability of such molecules with H-bond strength, were analyzed. The selected basic geometrical structure was that of malonaldehyde. From its full optimized geometry, the corresponding geometry of 3-OH propanal was obtained, fixing either the $d(\text{O}-\text{O})$ distance or a more extended local geometry and then optimizing the other part of the whole structure. Nitromalonaldehyde and nitromalonamide were also studied because they should have stronger H-bonds and their basic structure is also malonaldehyde. The last one also has electronic effects that may be varied by rotating the amino groups. By doing this it is possible to show that the effects on acidity of donors are more important than the equivalent effects on the basicity of acceptors. It is also shown that J -couplings that involve atoms close to the H-bond have important noncontact contributions that must be included in order to reproduce total J values. Noncontact contributions are more important than the Fermi contact (FC) one for $J(\text{O}-\text{O})$ in malonaldehyde. In nitromalonamide all three terms, FC, paramagnetic spin-orbital, and spin-dipolar are of the same order of magnitude when both amino groups are rotated. This does not happen for its planar configuration. Nuclear magnetic shielding of the hydrogen belonging to the H-bond is quite sensitive to it. The magnetic behavior of such hydrogen atom is modified when it is part of a closed H-bonded molecule. Then a relationship between the H-bond strength with the paramagnetic contributions of the shieldings of both atoms, C and O of the donor substructure, was obtained. We have found a cubic correlation between $\sigma^p(\text{C})$ of the C–O donor bond with $\sigma(\text{H})$ of the H-bonded hydrogen. It is observed that both the noncontact J -coupling contributions and shieldings on atoms belonging to the donor substructure, give a clear evidence about the presence of the resonance phenomenon in the model compounds that have been studied, malonaldehyde, nitromalonaldehyde, and nitromalonamide.

1. Introduction

During the past few years NMR spectroscopic parameters, J and σ , were applied to get new insights on some special features of hydrogen bonds. Most of them have been reviewed recently^{1–3}

A few years ago, we studied the proton transfer mechanism for Schiff bases⁴ and cooperativity effects on linear $(\text{CNH})_n$ and $(\text{NCH})_n$ chains⁵ applying DFT/B3LYP⁶ and SOPPA⁷ theoretical schemes. In the case of Schiff bases, an inflection point was obtained when each NMR spectroscopic parameter was expressed as a function of $d(\text{N}-\text{H})$ and also when the correlation between both parameters was depicted. The analysis of these (cubic) functions showed whether the proton was bounded to the oxygen, to the nitrogen atom, or shared by both atoms. In line with these findings, it was possible to predict the position of the proton in the bridge. On the other hand cooperativity (global) effects were observed on intermolecular J -couplings of linear chains. Such couplings were largely dependent on the number of molecules in the chain.

Coupling constants and proton chemical shifts are very sensitive to resonance effects. The study of a likely relationship between J and σ with the resonance-assisted hydrogen bond (RAHB) mechanism of Gilli and coauthors⁸ is then a good challenge for getting theoretical support (or rejection) for such phenomenon. The RAHB mechanism was proposed to explain the appearance of strong and very strong H-bonds in conjugated neutral molecular systems. The key model system to which this mechanism was applied is malonaldehyde for which the strength of the hydrogen bond is linked to the resonance in the keto–enol system. On the basis of the last of their models on H-bonds, the so-called electrostatic-covalent hydrogen bond model (ECH-BM) Gilli and Gilli have proposed that weak H-bonds are electrostatic in nature but become increasingly covalent when increasing its strength, very strong bonds being essentially three-center-four-electron covalent bonds.^{9,10} This is qualitatively explained by the consideration that two valence bond (VB) resonance forms, $\Psi_{\text{COV}1}(-\text{O}-\text{H}\cdots\text{O}=\text{C})$ and $\Psi_{\text{COV}2}(-\text{O}^-\cdots\text{H}-\text{C}=\text{O}^+)$, are allowed to become identical and therefore isoenergetics through the connection of the two O atoms by the π -conjugated system. The H-bond strength is related with ΔPA , the difference between proton affinities of both the H-bond

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donor and acceptor atoms. One of their conclusions was that the length of the H-bond can be roughly predicted by the unique knowledge of the nature of the organic molecule containing an homonuclear O—H...O H-bond, which is in line with Gilli's model, applying Bader's atoms in molecules, the AIM approach.¹¹ Pakiari and Eskandari have shown that the H-bond in the closed form of 3-hydroxypropenal is more covalent than such H-bond in linear 3-hydroxypropenal.

One important point about the RAHB mechanism is that its influence on both VB resonance forms makes them become isoenergetics. So systems like malonaldehyde should be characterized by a large degree of charge delocalization and symmetry of the keto—enol group.

Madsen et al.¹² have studied the topology of the intramolecular H-bond in benzoylacetone by both X-ray and neutron diffraction experiments and also by the analysis of electron densities from Baders AIMs approach.¹³ They found out that (a) the hydrogen of the H-bond is asymmetrically placed between the two oxygens in the keto—enol part of the molecular structure, and (b) there are high formal charges on both the oxygens and the enol hydrogen. They concluded that the H-bond has partly covalent and partly electrostatic contributions and introduced a proposal of a slight modification of the original neutral RAHB mechanism to include a positive charge on the hydrogen of the H-bond and a negative charge on both oxygens of the O—H...O bond. A similar study on nitromalonamide confirmed that the enolic hydrogen has an asymmetric position between the two oxygen atoms.¹⁴ Geometrical structures of several derivatives of malonaldehyde with symmetrized structures were also analyzed by Hargis et al.¹⁵ They found out that nitromalonamide has the shortest $d(\text{O}—\text{O})$ distance. In a recent article Gilli and coauthors have introduced another feature for H-bond systems. Two kinds of cooperativity effects can occur, σ -bond and π -bond cooperativity or anticooperativity. The π -bond cooperativity should be the driving force that controls the RAHB mechanism.¹⁶ In a previous article, the RAHB mechanism was also coined π -bond cooperativity effect.¹⁷

On the basis of the assumption that H-bonds are electrostatic or arise mainly due to the σ -electronic framework, Alkorta and coauthors^{18,19} and then Sanz and coauthors^{20,21} have raised some doubts about the very existence of the RAHB mechanism. They focused on the analysis of NMR spectroscopic parameters on a number of saturated and unsaturated compounds: malonaldehyde, its diaza derivatives, and their saturated counterparts. They concluded that the NMR J -coupling and the hydrogen chemical shift of the H-bond, $J(\text{O}—\text{O})$ and $\delta(\text{H})$, respectively, do not reflect any evidence of such mechanism. They considered only the Fermi contact (FC) mechanism in their J -coupling calculations. This restriction was based on previous works of Del Bene and coauthors on $J(\text{X}—\text{X})$ across hydrogen bonds.^{22,23}

Recent further works were published by Sanz and coauthors.^{24,25} They searched for the reason why the strength of the H-bond is higher on keto—enol-like systems. They suggest in ref 24 that the enhanced strength of the intramolecular hydrogen bond (IMHB) in tropolone, aminotropone, and aminotropimine as compared with their saturated counterparts are primarily due to the much higher intrinsic basicity (acidity) of the H-bond acceptor (donor) groups in the unsaturated compounds. In their last article on this subject, they found that formylformimidic acid exhibits a IMHB much stronger than that of malonaldehyde. This fact was rationalized as due to the simultaneous enhancement of the intrinsic acidity (basicity) of the H-bond donor (acceptor), when the carbon atom is replaced by a nitrogen atom. This fact is an step forward of a previous work published by

Grabowski who found that "The existence and strength of an X—H...Y H-bond depend on the Lewis acidity of X-H bond and on the Lewis basicity of Y center."²⁶

The NMR spectroscopic parameters are the best magnetic properties to test this open question. Theoretical calculations and the analysis of NMR spectroscopic parameters give deep insights on the electronic mechanisms and structure of molecular systems. Still there are a controversy on whether the existence of indirect J -coupling through H-bonds may be considered as a probe of a certain degree of covalency of the corresponding H-bonds. In the review article recently published by Krivdin and Contreras,² they analyzed previous works on this subject and concluded that transmissions of J -couplings through H-bonds are possible even if the covalency is very low or does not exist.

The paramagnetic spin-orbital (PSO) and spin-dipolar (SD) noncontact terms of J -couplings are related with the π -electronic structure of the system. They have an still unclear relationship with the conjugation of molecular systems. Cremer and coauthors have suggested that the absolute value of the sum of PSO and SD can reflect the π -character of a given C—C bond.²⁷ Nonvanishing long-range couplings are strictly related with such electronic mechanisms that cause the transmission of J -couplings through distance of the order of nanometers.^{28,29} One of the aims of this article is to show how the noncontact contributions to J -couplings can be used to characterize the RAHB phenomenon.

We assume here that the hydrogen bond is not only electrostatic in nature. In line with this, we stress another important point. Gilli's original formulation of RAHB mechanism and its extension given by Madsen et al. are mostly based on the influence of the system of conjugated double bonds on the H-bonds. Some authors have also mentioned the effect of a charge flow through the system of conjugated double bonds³⁰ and the existence of a feedback mechanism that drives the charges in the ring toward symmetry.¹² We could then ask about the nature of this charge flow. From the arguments and schemes they used to explain such a mechanism they assumed that there should be a resonant charge flow on the keto—enol structure but a different charge flow on the O—H...O bond. Another aim of this work is to show that the above-mentioned charge flow modifies the magnetic response of the hydrogen belonging to the H-bond. There should arise a charge flow that would include both electronic skeletons, that is, σ and π . This flow would change the magnetic properties of a given hydrogen (and its closer atoms) when it participates in an H-bond belonging to a closed ring molecule.

The overall goal of our work is to show that the analysis of both NMR spectroscopic parameters, J and σ , can be used to elucidate whether the RAHB mechanism is present or not in a given H-bonded molecular frame. They are objective parameters that may be used to identify such an elusive mechanism. Even though each of the different components of both parameters are not accessible by experiments, they are well-established theoretically and the total value of such spectroscopic parameters are measurable quantities.

This article is organized as follows. In the next section, we give a short presentation of the most used theoretical methods to estimate H-bond's strength and a theoretical relationship between NMR spectroscopic parameters with electronic conjugation. Computational details that also include geometrical optimizations and the way we obtain chemical shifts are then given and results are shown in Section 4. We show there in some detail the main findings of this work. Finally some concluding remarks are given in Section 5.

2. Methods to Estimate the Strength of the H-bond

Our study is strongly related with the way the likely RAHB phenomenon that appears in malonaldehyde and related compounds would modify both NMR spectroscopic parameters, J and σ . They are sensitive to conjugation and so may be used to check the existence of the RAHB phenomenon.

Different schemes to detect the presence and characterize the nature of H bonds were developed: geometrical and energetic criteria, the analysis of topological parameters, and the application of spectroscopic methods. We start this section with the methods mostly used by theoreticians and then we shall consider the NMR spectroscopic parameters.

2.1. Stabilization Energy, AIM, and NBO Schemes. The estimation of the stabilization energy of intramolecular H-bonds in conjugated systems can be used as a parameter for measuring its strength. There are few schemes to calculate it,³¹ though there is an intrinsic difficulty when the stabilization energy related with the intramolecular H-bond is calculated; it is not possible to find two structures that differ only in an H-bond, while the other effects remain identical.^{26,32} One usual way to get such H-bond strength is through the calculation of the difference between the energies of closed (H-bonded) and open (non-H-bonded) configurations. The rotated angle of the X–H proton-donating bond in the open configuration is usually of 180° around the X–C bond, though it might be of 90° as in our case. The main point to consider in these cases is the application of the same procedure to the whole set of molecules considered.

In terms of stabilization energy H-bonds are usually classified as strong (>15 kcal/mol), moderately strong (4–15 kcal/mol), and weak (<4 kcal/mol).¹⁷

There are two other well-known techniques to characterize the strength of the H-bond interaction. They are the natural bond order analysis (NBO) developed by Weinhold³³ and the atom in molecule analysis (AIM) of Bader.³⁴ Within the first of these procedures, one interprets the H-bond in terms of charge transfer stabilization energy, which is proportional to the H-bond strength,³⁵ and within the second by the type of bond critical points (BCP). Some criteria were proposed to characterize H-bonds based on the AIM theory.^{36,37} Furthermore, for conjugated systems the “charge transfer” phenomenon can be used also as a criterion to obtain how the π -system is delocalized over the whole molecule.³⁵

Pakiari and Eskandari¹¹ analyzed topological parameters such as electron density, its Laplacian, kinetic energy density, potential energy density, and energy density at the BCP with Bader’s AIM theory for the H-bond of malonaldehyde. They also studied the charge transfer energies based on NBO analysis. They found that these H-bonds are partially electrostatic and partially covalent in nature.

2.2. NMR Spectroscopic Parameters. The nonrelativistic theory for the tensorial spectroscopic parameters of NMR, J and σ was first developed by Norman Ramsey.³⁸ He proposed four electronic mechanisms as a source for J -couplings and two for magnetic shieldings. Each mechanism has its origin in a different kind of interaction between nuclear spins and electrons. The indirect J -coupling takes into account the interaction of a given nuclear magnetic moment (say M) with its surrounding electrons that are transmitted to the whole molecule but have a finite perturbation that modifies the interaction between the electrons and the other nuclear magnetic moment (say N) of interest. Given that such electron–nucleus interactions depends on the spin and the position of the electrons, or depends on the current flow of them close to the coupled nuclei, J -couplings will give precise local and global information of the electronic

structure of the molecule in which one is interested. For shieldings, such information is more localized though it will also have the influence of the near surrounding of the molecule to the shielded nucleus. Several reviews were recently devoted to its description and understandings.^{2,39–41}

The scalar (the trace of the tensor) J -coupling between nuclei M and N can be written from Ramsey’s theory as a sum of four terms

$$J_{MN} = J_{MN}^{\text{FC}} + J_{MN}^{\text{SD}} + J_{MN}^{\text{PSO}} + J_{MN}^{\text{DSO}} \quad (1)$$

The first two terms are electron-spin dependent. The perturbative Hamiltonian corresponding to the FC term depends on the electron–nucleus interaction at the site of both coupled nuclei. So it gives a measure of the s-character on both coupled atoms. Its transmission mostly involves the σ -skeleton. So in saturated compounds, J -couplings are dominated by the FC term. In unsaturated compounds, the FC arises from an exchange σ – π mechanism. So the transmission of such FC interaction is also possible through the π -skeleton. In conjugating systems, its transmission is through hyperconjugative ($\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$) interactions.²

The SD term is originated in the extended magnetic fields outside of the coupled nuclei. In this case, the p_x orbitals are mainly involved. The electronic delocalization is important for transmitting SD contributions and also FC.

Both spin–orbital mechanisms are electron spin-independent and arise due to orbital currents induced in the electronic system. The PSO term depends on two electronic angular momentum operators. Therefore, for couplings between nuclei different from H the PSO mechanism arises from both p_σ and p_π orbitals. The diamagnetic spin–orbital (DSO) term is of first order. This means that such a term is obtained as the ground-state average of its perturbative Hamiltonian. This operator has the same functional form as the corresponding term for the nuclear shielding. They differ in the fact that the PSO term depends on two electron–nucleus distant operators but the diamagnetic term of σ depends on one of such operators and the distant operator to the gauge origin. The DSO is large at positions of high density and is usually much smaller than the PSO.

PSO and SD terms are dominant when π -skeleton is important for transmission of nuclear spin information. Cremer and coauthors have suggested that the absolute value of the sum between PSO and SD reflects the increasing π -character of the C–C bond in the following set of molecules: ethane, ethene, and ethyne.^{42,43} This sum gives also a numerical value that reflects the mixed single–double bond character of the C–C bonds in benzene. In the case of F–F long-range couplings,²⁸ the noncontact terms are by far the most important.

As Figure 1 shows for malonaldehyde with and without H-bond, it would only be a resonance if an extended conjugation appears on the keto–enol region. In other words, there would not be resonance if there is no single–double intermediate C7–O9 bond. In this case (malonaldehyde), a resonance would appear if two equivalent structures with π -bonds bonding different atoms are necessary to describe the whole electronic structure of the molecule. So in the case of a broken H-bond as in the bottom line of Figure 1 there is no need for two equivalent structures for describing the electronic system and then there would not be important contributions of PSO or SD terms to $J(\text{O}–\text{O})$.

Our main working hypothesis is based on the consideration that the values of $J^{\text{PSO}}(\text{O}–\text{O})$ and $J^{\text{SD}}(\text{O}–\text{O})$ are valid sensors

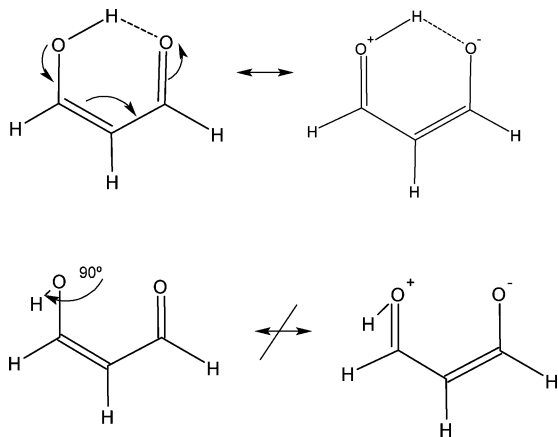


Figure 1. Conjugation diagram for malonaldehyde.

for the resonance phenomenon. As was previously shown for C–C and F–F couplings, the existence of conjugation is the underlying mechanism that makes the PSO and SD contributions so important. In our case, such a mechanism should be a resonance or an extended conjugation. Then if there is a resonance the PSO and SD terms should be \geq than the FC term.

Ramsey's expression of scalar nuclear magnetic shieldings, σ , is divided in two terms, paramagnetic and diamagnetic. The last term is never measured directly. In experiments, one usually measures what is known as the chemical shift of a given nucleus, by comparing the resonance of the same nucleus in that compound of interest with its resonance in an arbitrary reference compound.⁴⁴ The relationship between both parameters belonging to a given nucleus, X, is

$$\delta(X) = \frac{\sigma_{\text{ref}} - \sigma}{1 - \sigma_{\text{ref}}} \quad (2)$$

Given that $\sigma_{\text{ref}} \ll 1$, one can set the denominator equal to one.

On the other side, from theoretical models one usually calculate the nuclear magnetic shieldings. There are several accurate methods to calculate J and σ . It was shown that one must include electron correlation in order to obtain accurate shielding tensors in molecules with multiple bonds.⁴⁵ This is specially so for magnetic shieldings of ^{15}N and ^{17}O . It is known that the correlation contributions are relatively small for carbons involved in single bonds while they are considerably larger for multiply bonded carbons, especially when they are bonded to nitrogen or oxygen atoms.⁴⁶ A similar statement is applied for J coupling calculations.^{40,47,48} Several schemes were developed to include electron correlation. The implementations of the density-functional theory, DFT⁴⁹ show that the choice of the exchange-correlation functional is critical. Our recent study on Schiff bases⁴ shows that calculations of $^1J(\text{NH})$ and shieldings of N with the semiempirical hybrid B3LYP⁶ functional give close results to experiments and also to that of the second-order polarization propagator approach, SOPPA.⁷

3. Computational Details

Our DFT shielding calculations were performed employing both, gauge-including atomic orbitals (GIAO)/London orbitals to guarantee origin-independence.⁵⁰ Geometry optimization was performed with the Gaussian 03 suite of programs⁵¹ and all calculations of NMR spectroscopic parameters were performed with the DALTON suite of programs.⁵² We worked mostly with

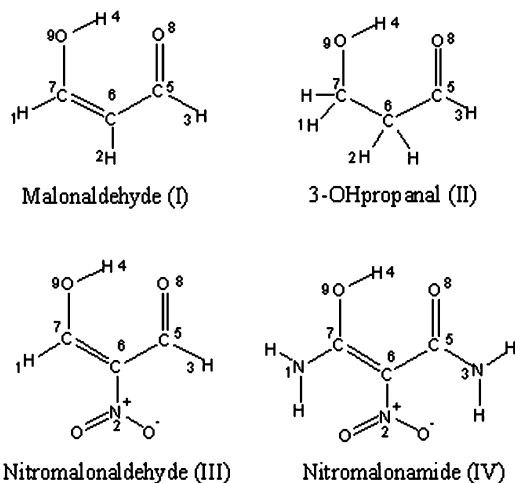


Figure 2. Basic molecular structures analyzed.

standard correlated-consistent basis set of Dunning and collaborators; the correlation-consistent polarized valence basis sets or cc-pVXZ (X = D, T)⁵³ and their improvements via the flexibility in the outer valence region (augmented-cc-pVXZ, X = D, T)⁵⁴ or their improvement via the flexibility in the core region (cc-pCVXZ, X = D, T).⁵⁵

Chemical shift of H and C in malonaldehyde were calculated as

$$\begin{aligned} \delta^{\text{TMS}}(\text{H}) &= 30.84 - \sigma(\text{H}) \\ \delta^{\text{TMS}}(\text{C}) &= 188.1 - \sigma(\text{C}) \end{aligned} \quad (3)$$

being 30.84⁶¹ and 188.1⁶² the experimental absolute values of such nuclei in TMS. In the case of nitromalonamide, we applied the alternative though equivalent expression

$$\delta^{\text{TMS}}(\text{X}) = \delta^{\text{TMS}}(\text{X, Met}) + \delta^{\text{Met}}(\text{X}) = \delta^{\text{TMS}}(\text{X, Met}) + \sigma^{\text{Met}}(\text{X}) - \sigma(\text{X}) \quad (4)$$

where $\delta^{\text{TMS}}(\text{X, Met})$ is the chemical shift of the X atom in methyl with respect to TMS and $\delta^{\text{Met}}(\text{X})$ is the chemical shift of the X atom with respect to methyl. The first value is taken from experiment and the second from calculations. Experimental values for the chemical shift of C and H in methyl with respect to TMS are $\delta^{\text{TMS}}(\text{H, Met}) = 0.23$ ppm and $\delta^{\text{TMS}}(\text{C, Met}) = -2.1$ ppm.⁶³

We started our procedure of geometry optimization with a full geometrical optimization of malonaldehyde. Then the 3-OH propanal was optimized as a planar geometry with two differences, (a) keeping only $d(\text{O}-\text{O})$ of structure I fixed and then optimizing the remaining molecular structure, IIa; and (b) the same as in (a) but keeping the basic structure of malonaldehyde fixed, which means $d(\text{O}-\text{O})$, $d(\text{O9}-\text{H4})$, and the angle $\text{O9}-\text{H4}-\text{O8}$, IIb. A similar procedure was applied for both nitromalonaldehyde and nitromalonamide. All geometry optimizations were performed at DFT/B3LYP/6-311++G** level of approach. All optimized geometrical structures are given as Supporting Information.

4. Results and Discussion

All structures analyzed are shown in Figure 2. They all have in common the $\text{O}-\text{H}\cdots\text{O}$ bond. To consider the influence of the $\text{O}-\text{O}$ distance and the local geometrical structure on the

TABLE 1: H-Bond Energies for All Compounds in Units of kcal/mol^a

	compounds				
	I	IIa	IIb	III	IV
H-bond rot 90°	24.80	6.13	7.29	27.28	37.39
H-bond rot 180°	16.92	7.53	9.80		
N ₁ C ₇ and H-bond rot 90°					40.92
N ₃ C ₅ and H-bond rot 90°					36.23
N ₁ C ₇ , N ₃ C ₅ and H-bond rot 90°					39.47

^a H-bond energies are obtained from the difference between the stabilization energy of the open configuration (H-bond rotated 90 or 180°) and the stabilization energy of the closed configuration.

strength of the H-bond we have worked with both fully optimized and partially optimized geometries as described in the last section. The structures with a broken H-bond were considered through the O–H rotation of 90 and 180° of model compounds I and II and only through rotation of 90° for model compounds III and IV.

4.1. H-bond Energies. In Table 1 we show H-bond energies for all compounds of Figure 2 obtained applying the procedure outlined in the first paragraph of Section 2.1. The computed strength of H-bonds in both compounds II (IIa and IIb) is larger when the H-bond is rotated 180° compared with results for H-bond rotated 90°. For malonaldehyde, this happens when the H-bond is rotated 90°. This means that the structure of compounds II are more stable when the H-bond is rotated 90° though that of compound I is more stable when the H-bond is rotated 180°. One way to get an understanding of this fact is through its analysis with localized orbitals. When the O₉–H₄ bond in compound I is in the molecular plane (when there is a H-bond or when that bond is rotated 180°), there is an overlapping between one of the O₉ LPs and the π -bond of C₆ and C₇. This overlapping is minimized when the O₉–H₄ bond is rotated 90° out of molecular plane. Then this stabilization is due to an extended overlap that resembles the RAHB as arising from an extended conjugation within the keto–enol substructure. For compounds II, this does not happen because such overlapping is not possible. All this is in line with previous works of Gilli et al.^{8,59}

Applying previous definition of the H-bond strength from its stabilization energy,¹⁷ the H-bond of compounds II can be considered as moderately strong but that of malonaldehyde and nitromalonamide should be very strong. The strength of the H-bond increase in the following order: $E_{\text{HB}}(\text{II}) < E_{\text{HB}}(\text{I}) < E_{\text{HB}}(\text{III}) < E_{\text{HB}}(\text{IV})$. Then one may consider that the extended conjugation follows such pattern of increase.

One interesting molecular system is nitromalonamide (IV). For this system, the H-bond strength is the highest when N₁C₇ bond is rotated 90° and such strength is the lowest when the bond N₃C₅ is rotated 90°. So the H-bond strength is not the lowest for the planar arrangement. To understand which is the source of such behavior, we analyze the likely effect on the electron density on both donor and acceptor oxygens when one stops the introduction of π -electrons on the general framework of the planar configuration of malonaldehyde. If one reduces the amount of π -electrons on the donor (its acidity will increase), it will enforce the H-bond. On the other hand, the reduction of π -electrons on the acceptor (its basicity falls down) will make the H-bond weaker. In our case, when the N₃C₅ bond is rotated 90° there will be less π -electrons on the basic structure of malonaldehyde and so there will be less π -electrons on the O₈, which means that the basicity of such oxygen will fall down. In this case, the strength of the H-bond will fall down. As seen

in Table 1, the H-bond energy goes from 37.39 to 36.23 kcal/mol. On the other hand, if the N₁C₇ bond is rotated it will primarily increase the acidity of O₉ and so the strength of the H-bond. This is observed in the energy because it increase to 40.92 kcal/mol. The variation of the H-bond strength is not symmetric showing that the effect on the donor is larger than that on the acceptor.

On the other hand, as shown by Buemi⁶⁰ when the NO₂ system is rotated 90° such strength (22.98 kcal/mol) becomes lower than that for planar configuration (37.39 kcal/mol). It shows that when H-bonds of the lower bridge are broken by rotating the NO₂ group, the resulting system is less stable than the planar system due to effects of the extended conjugation.

4.2. Effects of Extended Conjugation (Resonance) on J and σ . Calculated NMR spectroscopic parameters for model compounds I and II are given in Table 2 and Table 3. We first investigated the basis set dependence of magnetic shieldings considering three basis sets, (i) cc-pVTZ, (ii) aug-cc-pVTZ for all atoms, and (iii) the best one which has aug-cc-pCVTZ for both C₅ and O₈ and cc-pVTZ for all other atoms. The general trends are the same with independence of the given basis set. References for the shielding of H and C are that of TMS, $\sigma(\text{H}) = 30.84$ ppm⁶¹ and $\sigma(\text{C}) = 188.1$ ppm.⁶² Our results are close to experiments for malonaldehyde, $\delta(\text{H}_4)^{\text{exp(ours)}} = 13.99$ (13.88) ppm⁵⁶ and $\delta(\text{C}_5)^{\text{exp(ours)}} = 181.3$ (202.30) ppm.⁵⁷ The experimental value for $\delta(\text{C}_5)$ correspond to an equivalent carbon in phenylmalonaldehyde. We are not aware of experimental measurements for compound I.

Calculations for compounds I and II show that H₄ is less shielded when the H-bond is stronger, or in other words given that for malonaldehyde H₄ is less shielded than for 3-OH propanal the H-bond is stronger in compound I compared with compound II. What would be the case if we still freeze the basic structure of compound I but modify the substituents? We will show below that using $\sigma(\text{H}_4)$ as a sensitive parameter one observes that the H-bond becomes still stronger for compounds III and IV.

When the bond O₉–H₄ is rotated 90° (it means when the H-bond breaks down), $\sigma(\text{H}_4)$ of both compounds I and II becomes closer. Quite a similar trend is observed for shieldings of atoms O₈ and O₉. Indeed O₈ is much more affected than O₉ and variations of shieldings on compound I are larger than that on compound II when the H-bond is broken.

As shown in Table 3 for the J -couplings of O₈–O₉ of compound I, both PSO and SD terms are larger than the FC term. Couplings between oxygen atoms have quite similar FC contributions in compounds I and IIa but the other paramagnetic terms, SD and PSO, have completely different contributions. We find that the total value of $J(\text{O}_8\text{–O}_9)$ for planar malonaldehyde is one order of magnitude larger than such coupling for 3-OH propanal even though the FC contributions are close each other. We find that $J^{\text{PSO}}(\text{O}_8\text{–O}_9) > J^{\text{SD}}(\text{O}_8\text{–O}_9) > J^{\text{FC}}(\text{O}_8\text{–O}_9)$ in malonaldehyde. This behavior is modified only for the noncontact terms when the H-bond is rotated 90°, though the PSO terms continuous being little larger than the FC one. These are remarkable findings.

It is also interesting to observe the behavior of the following couplings: C₅–O₈ with C₇–O₉ and C₅–C₆ with C₆–C₇. When the H-bond of malonaldehyde is rotated 90°, $J^{\text{FC}}(\text{C}_7\text{–O}_9)$ does not change its value but the noncontact terms are reduced in a half. This is also observed for nitromalonamide (see below) but does not happens for compound II where the noncontact terms are not modified when the H-bond is rotated and the FC increases but not by much. There is a positive shift of

TABLE 2: Magnetic Shieldings in ppm Calculated at DFT-B3LYP Level of Theory with Different Basis Sets^a for the Main Nuclei of Compounds I and II

		planar						O ₉ -H ₄ rot 90°					
		C ₅	C ₆	C ₇	H ₄	O ₈	O ₉	C ₅	C ₆	C ₇	H ₄	O ₈	O ₉
I	pT	-14.2	77.9	7.9	17.2 ^b	-197.7	146.8	-13.6	61.0	10.3	28.8	-397.0	200.9
	apT	-15.2	76.4	7.5	17.1	-193.3	144.5	-15.0	59.8	9.9	28.6	-384.8	199.2
	◇	-20.8	76.7	7.5	17.1	-199.2	142.7	-20.4	59.8	9.6	28.7	-394.4	199.2
IIa	pT	-30.3	140.9	119.0	24.9	-315.6	324.8	-20.3	137.7	120.6	31.2	-395.3	299.1
	apT	-31.4	140.2	119.2	24.6	-307.4	318.0	-21.8	136.8	120.4	30.9	-384.6	293.2
	◇	-37.8	140.1	119.2	24.7	-318.8	318.6	-27.8	136.8	120.2	31.1	-397.2	297.2
IIb	pT	-37.9	139.0	124.5	23.7	-320.3	312.9	-28.0	136.4	125.5	30.1	-412.7	280.6
	apT	-39.0	138.5	124.7	23.4	-311.3	307.2	-29.5	135.6	125.3	29.8	-400.8	275.5
	◇	-45.5	138.3	124.8	23.6	-323.3	308.0	-35.7	135.5	125.4	30.0	-414.0	279.2

^a pT means that all nuclei have the same cc-pVTZ basis set; apT means that all nuclei have aug-cc-pVTZ basis set and ◇ means that C₅ and O₈ have aug-cc-pCVTZ basis set and all other nuclei have a pT basis set. ^b From ref 19, $\sigma(\text{H}) = 18.34$ ppm when $d_{\text{OO}} = 2.6$ Å. In our case $d_{\text{OO}} = 2.59$ Å.

TABLE 3: Contributions of the Three Paramagnetic NMR *J* Coupling Mechanisms for Several Coupled Nuclei of Compounds I and II (All Values in Hz)

	planar				O ₉ H ₄ rot 90°			
	FC	SD	PSO	total	FC	SD	PSO	total
I								
<i>J</i> (O ₈ -O ₉)	2.46 ^a	3.47	5.73	11.68	2.78	1.47	3.03	7.29
<i>J</i> (C ₅ -O ₈)	13.26	-0.73	18.16	30.61	15.24	-2.09	20.88	33.96
<i>J</i> (C ₇ -O ₉)	21.80	1.34	9.16	32.21	22.09	0.54	4.80	27.32
<i>J</i> (C ₅ -C ₆)	60.46	0.43	-4.30	56.84	59.96	0.91	-3.01	58.11
<i>J</i> (C ₆ -C ₇)	86.35	1.86	-7.65	80.79	91.79	3.64	-9.12	86.53
<i>J</i> (O ₈ -H ₄)	5.98	-0.13	2.44	7.63	-0.49	0.04	-0.05	-0.52
<i>J</i> (H ₁ -H ₄)	12.70	-0.07	3.51	11.74	3.07	-0.02	2.04	2.80
<i>J</i> (H ₃ -H ₄)	0.15	0.04	1.29	-0.27	0.08	0.00	1.37	-0.22
IIa								
<i>J</i> (O ₈ -O ₉)	2.11	0.10	-0.71	1.50	2.93	0.02	-0.20	2.76
<i>J</i> (C ₅ -C ₆)	32.15	0.52	-2.54	30.38	33.33	0.57	-2.21	31.94
<i>J</i> (C ₆ -C ₇)	26.23	1.25	0.07	27.78	31.42	1.21	-0.02	32.83
<i>J</i> (O ₈ -H ₄)	6.33	-0.69	1.05	6.00	0.14	-0.04	0.03	0.08
<i>J</i> (H ₃ -H ₄)	-0.25	0.00	1.22	-0.62	-0.04	0.00	1.31	-0.34
IIb								
<i>J</i> (O ₈ -O ₉)	1.18	0.05	-1.14	0.09	2.53	0.00	-0.35	2.20
<i>J</i> (C ₅ -O ₈)	12.81	-1.79	20.64	31.60	14.54	-2.39	21.01	33.10
<i>J</i> (C ₇ -O ₉)	29.29	-1.51	-1.58	26.10	27.00	-1.72	-1.34	23.83
<i>J</i> (C ₅ -C ₆)	39.12	0.44	-2.93	36.89	40.06	0.51	-2.55	38.27
<i>J</i> (C ₆ -C ₇)	35.01	1.11	-0.22	36.14	39.03	1.08	-0.30	40.05
<i>J</i> (O ₈ -H ₄)	7.18	-0.73	0.88	6.69	0.17	-0.05	0.00	0.09
<i>J</i> (H ₃ -H ₄)	-0.44	0.00	1.30	-0.84	-0.02	-0.01	1.33	-0.33

^a From ref 19, $J^{\text{FC}} = 3.5$ Hz.

$J^{\text{PSO}+\text{SD}}(\text{C}_5-\text{C}_6)$ being $J^{\text{FC}}(\text{C}_5-\text{C}_6)$ almost constant. $J(\text{C}_6-\text{C}_7)$ changes also in a different way because the FC and SD terms becomes more positive and PSO more negative. These variations may be related with changes in the conjugation of the π -electron system. Given that the theoretical contribution (see ref 42) of the PSO term for $J(\text{C}-\text{C})$ on C_2H_4 (C_2H_6) [C_2H_2] is close to -13 Hz (-0.03 Hz) [9 Hz] and its equivalent contribution of the SD term is close to 4.6 Hz (1.4 Hz) [14 Hz] one may infer that both bonds, C₅-C₆ and C₆-C₇ in malonaldehyde have an important π -character. On the other hand, when rotating the O₉-H₄ bond in the model compound II only the FC mechanism is modified for $J(\text{C}_6-\text{C}_7)$. There are no significant variations of all four mechanisms of $J(\text{C}_5-\text{C}_6)$.

If one looks for couplings that contain hydrogen atoms one would expect that noncontact terms would be vanishingly small. The FC and SD coupling mechanisms of $J(\text{O}_8-\text{H}_4)$ for malonaldehyde and 3-hydroxypropanal (IIa) have comparable values and the contribution of the PSO mechanism is larger for malonaldehyde. When the O₉-H₄ bond is rotated all such

contributions goes down being then close to zero. This finding is enforced by the analysis of H₃-H₄ couplings. In this case $J^{\text{PSO}} > J^{\text{FC}}$ (one order of magnitude larger). The DSO contributions are also of the order of the PSO though negative. $J(\text{H}_1-\text{H}_4)$ have large contributions of the FC and PSO terms for malonaldehyde that goes down when the H-bond is broken.

All these results may indicate the existence, though with small influence on *J* couplings, of a resonance mechanism. Then we decided to study some related systems that are known to have larger resonance effects. The chosen molecular systems were nitromalonaldehyde and nitromalonamide. We optimized their geometries, starting with the partial optimization of nitromalonaldehyde keeping frozen the basic structure of malonaldehyde and then we optimized the nitromalonamide (i) keeping the whole structure fixed but with $d(\text{C}_5-\text{N}_3)$ and $d(\text{C}_7-\text{N}_1)$ distances and (ii) optimizing the whole geometrical structure. The output have a clear difference on $d(\text{O}-\text{O})$, which is 2.589 (2.396) Å for nitromalonaldehyde (nitromalonamide) and for $d(\text{O}_8-\text{H}_4)$, which is 1.703 (1.392) Å for the same compounds. From these

TABLE 4: Nuclear Magnetic Shieldings σ for Model Compounds I, IIb, III, and IV at B3LYP/cc-pVTZ Level of Approach (All Values in ppm)

shielding of		C ₅	C ₆	C ₇	H ₄	O ₈	O ₉
malonaldehyde	σ^d	363.19	372.56	363.87	139.55	467.97	452.97
	σ^p	-377.39	-294.70	-355.96	-122.38	-665.62	-306.18
	σ	-14.20	77.86	7.91	17.16	-197.65	146.79
3-OH-propanal b	σ^d	374.40	368.349	373.70	140.76	467.93	462.68
	σ^p	-412.29	-229.34	-249.24	-117.03	-788.27	-149.77
	σ	-37.89	139.00	124.47	23.72	-320.34	312.91
nitromalonaldehyde	σ	-14.47	48.59	4.53	17.22	-196.09	148.33
nitromalonamide (optimized with restrictions)-weaker H-bond planar		13.74	72.39	14.85	18.92	19.73	178.47
N ₁ -C ₇ rot 90°		13.11	62.29	6.81	18.11	-0.16	91.32
N ₃ -C ₅ rot 90°		-0.59	68.12	13.23	18.75	-182.11	174.73
(N ₁ -C ₇ + N ₃ -C ₅) rot 90°		-3.06	60.04	4.38	17.74	-224.21	86.56
O ₉ -H ₄ rot 90°		17.32	66.11	15.08	27.78	-61.75	207.38
Nitromalonamide (full optimized)-stronger H-bond planar	σ^d	494.12	537.44	495.10	134.74	474.48	470.39
	σ^p	-485.62	-466.41	-488.39	-122.15	-429.50	-338.21
	σ	8.50	71.03	6.72	12.59	44.97	132.18
N ₁ -C ₇ rot 90°	σ^d	494.22	538.26	500.26	134.84	474.88	467.47
	σ^p	-486.02	-480.82	-507.70	-123.04	-439.51	-451.72
	σ	8.20	57.44	-7.44	11.80	35.37	15.75
N ₃ -C ₅ rot 90°	σ^d	499.52	538.21	495.28	134.68	-471.53	471.11
	σ^p	-508.23	-476.65	-489.44	-122.39	-607.10	-339.85
	σ	-8.71	61.56	5.83	12.29	-135.57	131.26
(N ₁ -C ₇ + N ₃ -C ₅) rot 90°	σ^d	499.40	538.96	500.17	134.74	-472.11	468.42
	σ^p	-509.99	-488.32	-509.50	-123.50	-630.18	-454.30
	σ	-10.59	50.64	-9.33	11.24	-158.07	14.12
O ₉ -H ₄ rot 90°	σ^d	495.76	536.56	500.76	25.75	478.42	469.23
	σ^p	-483.03	-472.93	-495.49	0.18	-551.60	-298.03
	σ	12.73	63.63	5.28	25.93	-73.18	171.19

results, one can say that the H-bond is stronger for nitromalonamide. In Table 4, it is observed that $\sigma(\text{H}_4)$ is larger in nitromalonaldehyde than in nitromalonamide with a full optimized geometrical structure.

Considering results of chemical shift calculations for the full optimized geometrical structure of nitromalonamide (which compares quite well with the corresponding experimental structure) given in Table 4, one observes that $\sigma(\text{O})$ and $\sigma(\text{C})$ are modified by the rotation of any of both nitrogen bonds, N₁-C₇ or N₃-C₅. The shielding on H₄ becomes two times larger when the H-bond is broken. The H-bond for this optimized structure is stronger than in the case of the optimized structure with restrictions based on nitromalonaldehyde and malonaldehyde. Shieldings of O₈, O₉, C₅, and C₇ are quite sensitive to the strength of the H-bond. If one looks for what happens on O₈, $\sigma(\text{O}_8)$ for the structure of nitromalonamide with restrictions is half of its value for the full optimized structure. When N₃-C₅ is rotated 90° $\sigma(\text{O}_8)$ suffer a very large variation which is larger on the weaker H-bonds.

If the electron surrounding to the hydrogen H₄ is largely dependent on the σ electrons it should be less affected when N₁-C₇ and/or N₃-C₅ are rotated 90°. In such a case, the π -electronic framework is strongly modified though the σ -electronic framework is not. Then $\sigma(\text{H}_4)$ should not change much if it depends only on the σ -skeleton. As observed in Table 4, H₄ is deshielded in almost the same amount for both the full

optimized and the partially optimized nitromalonamide although its absolute values are quite different. When any of both N-C bonds is rotated the π -skeleton is most affected. By rotating the N₁-C₇ bond, the strength of the H-bond becomes little higher; there is a shift of $\sigma(\text{H}_4)$ from 12.59 (planar) to 11.80 ppm (N₁-C₇ rotated). This variation may be due to a lowering of the electron density on the O₉ that increase its acidity. In terms of bond energy, it grows from 37.39 kcal/mol (planar) to 40.92 kcal/mol (N₁-C₇ rotated). On the other hand when the N₃-C₅ is rotated there is a very small variation of $\sigma(\text{H}_4)$, from 12.59 ppm to 12.29 ppm (rotated). In this last case, the lowering of the electron density on O₈ will diminish the strength of the H-bond, which means an increasing of the shielding. But the effect of stopping the introduction of π -electrons through the rotation of N₃-C₅ bond will operate on the whole π -skeleton, and so increasing also the acidity of O₉. Then it seems that the acidity conditions of the donor atom are more important than the basicity conditions of the acceptor atom on the strength of the H-bond.

On the other hand, when N₁-C₇ and N₃-C₅ are both rotated 90° the variation of $\sigma(\text{H}_4)$ is larger than the sum of its variations considering the rotation of N₁-C₇ or N₃-C₅ separately. This suggest that there may be a (weak) cooperativity effect. Gilli have observed that a π -bond cooperativity should be the driving force that controls the RAHB mechanism. From the analysis of the shielding on H₄ we may say that it may be true.

TABLE 5: Comparison between Experimental and Calculated Chemical Shift in Nitromalonamide (All Values in ppm)

	C ₅	C ₆	C ₇	H ₄
theor	179.7	119.3	181.5	18.8
exp	170.3 ^a	106.3 ^a	170.3 ^a	18.9 ^b

^a Taken from ref 64. ^b Taken from ref 65.

In Table 5, we show how good our results are with respect to experimental chemical shift for nitromalonamide. One should mention the small differences between $\delta(C_5)$ and $\delta(C_7)$ that are not observed in experiments and the quite a good reproduction of $\delta(H_4)$.

Regarding the statement “if the RAHB is a working mechanism there should be a charge flow through the conjugated system that drives charges into the ring (the whole ring)”,¹² this flow would have a different effect on each magnetic component of σ . It is worth to mention here that paramagnetic components of σ are related with spin-rotation constants.⁵⁸ In Table 4, we show the pattern that follow both components of shieldings of such atoms that may feel the charge flow mentioned above. For the special case of $\sigma(H_4)$, we observe that it acquired unusually large para and diamagnetic contributions when H₄ is involved in the H-bond. When the H-bond is broken (see the last line of Table 4) those contributions recover their usual values being the shielding in this case is mainly diamagnetic. It is important to highlight the fact that contributions for the shielding of hydrogen atoms located outside the ring (e.g., H₁, H₂, and H₃ for compounds I and II) are of the same order of magnitud as

their total values. As an example $\sigma(H_1)$ for compound I (IIb) have a diamagnetic component of -10.84 (23.23) ppm and a paramagnetic component of 35.02 (4.21) ppm.

As was previously pointed out in the literature the strength of the H-bond goes up as $\sigma(H_4)$ goes down. For all compounds studied here, the paramagnetic component of such shielding follows this tendency. This is an indication that the electronic environment close to H₄ is more delocalized as the strength of its H-bond is increased.

The oxygens shieldings have similar values for their diamagnetic components but they suffer large variations on their paramagnetic components. σ^p is larger (lower) than σ^d for O₈ (O₉) in compounds I and II and also for nitromalonamide with N₃–C₅ rotated. For planar nitromalonamide and when the N₁–C₇ is rotated, such behavior is opposite for O₈.

If we analyze the effects of the extended conjugation on the paramagnetic component of $\sigma(O_9)$ and $\sigma(C_7)$, we observe that they become more positive as the strength of the H-bond goes down (from -454.30 to -149.77 ppm for $\sigma^p(O_9)$ and from -509.50 to -249.24 ppm for $\sigma^p(C_7)$). A completely equivalent trend is observed for $\sigma(H_4)$. For nitromalonamide, its values, from the smallest to the largest, are obtained when (a) N₁–C₇ and N₃–C₅ both rotated 90°, (b) N₁–C₇ rotated 90°, (c) N₃–C₅ rotated 90°, (d) planar, and then (e) compound I and (f) compound IIb. This behavior makes a lot of sense if we consider that the extended conjugation should have an influence on the substructure C₇–O₉–H₄. This pattern is not exactly the same when compared with that arising from energetic considerations (see Table 1). In Figure 3, we show a cubic correlation between the paramagnetic component of $\sigma(C_7)$ with $\sigma(H_4)$.

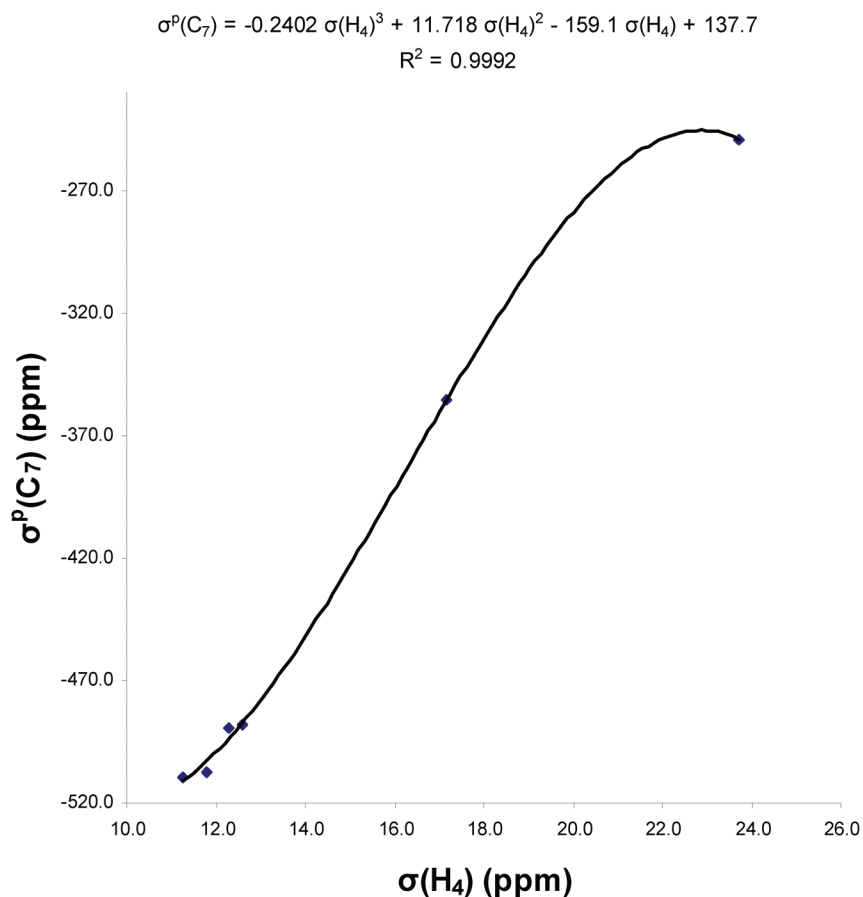


Figure 3. Correlation between $\sigma^p(C_7)$ and $\sigma(H_4)$.

TABLE 6: Contributions of the Three Paramagnetic NMR J Coupling Mechanisms for Several Coupled Nuclei of Nitromalonamide^a (All Values in Hz)

	optimized with restrictions				full optimized			
	FC	SD	PSO	total	FC	SD	PSO	total
Planar								
$J(\text{O}_8-\text{O}_9)$	2.85	0.51	0.80	4.17	9.47	0.65	0.75	10.90
$J(\text{C}_5-\text{C}_6)$	101.95	0.36	-3.33	99.43	91.42	0.36	-3.62	88.59
$J(\text{C}_6-\text{C}_7)$	135.76	0.61	-5.25	131.56	105.54	0.44	-4.78	101.63
$J(\text{C}_5-\text{O}_8)$	7.03	-0.34	11.20	17.75	12.48	-0.10	10.69	22.92
$J(\text{C}_6-\text{O}_8)$	0.60	-0.03	1.16	1.73	0.81	0.01	1.28	2.09
$J(\text{C}_7-\text{O}_9)$					14.06	0.19	8.40	22.50
O_9-H_4 rot 90°								
$J(\text{O}_8-\text{O}_9)$	2.82	0.11	0.14	3.10	6.16	0.05	-0.07	6.17
$J(\text{C}_5-\text{C}_6)$	102.78	0.43	-2.77	100.89	91.59	0.44	-2.74	89.72
$J(\text{C}_6-\text{C}_7)$	144.28	1.05	-6.08	139.69	114.79	0.92	-6.06	110.77
$J(\text{C}_5-\text{O}_8)$	7.86	-0.94	12.13	18.91	15.71	-0.92	12.21	26.87
$J(\text{C}_6-\text{O}_8)$	-0.79	0.04	0.70	-0.06	-1.31	0.07	0.66	-0.60
$J(\text{C}_7-\text{O}_9)$					15.63	-0.20	4.35	19.62
N_1-C_7 rot 90°								
$J(\text{O}_8-\text{O}_9)$	1.07	0.98	2.00	4.07	6.87	1.21	2.41	10.50
$J(\text{C}_5-\text{C}_6)$	97.00	0.41	-3.03	94.83	85.72	0.39	-3.37	83.16
$J(\text{C}_6-\text{C}_7)$	136.92	1.44	-6.74	132.05	106.92	1.08	-6.53	101.90
$J(\text{C}_5-\text{O}_8)$	7.13	-0.43	11.54	18.09	12.36	-0.17	10.94	22.98
$J(\text{C}_6-\text{O}_8)$	0.34	0.07	0.80	1.21	0.50	0.07	0.97	1.52
$J(\text{C}_7-\text{O}_9)$					15.39	0.34	11.38	26.95
N_3-C_5 rot 90°								
$J(\text{O}_8-\text{O}_9)$	1.15	1.01	2.09	4.26	7.01	1.22	2.42	10.67
$J(\text{C}_5-\text{C}_6)$	101.46	0.34	-4.32	97.92	91.64	0.42	-4.99	87.49
$J(\text{C}_6-\text{C}_7)$	130.95	0.54	-5.10	126.83	99.47	0.40	-4.62	95.67
$J(\text{C}_5-\text{O}_8)$	6.65	-1.32	15.22	20.42	12.27	-0.87	14.50	25.75
$J(\text{C}_6-\text{O}_8)$	-1.02	-0.12	2.12	0.98	-1.26	-0.21	2.48	1.01
$J(\text{C}_7-\text{O}_9)$					13.55	0.16	8.54	22.10
$\text{N}_1-\text{C}_7 + \text{N}_3-\text{C}_5$ rot 90°								
$J(\text{O}_8-\text{O}_9)$	0.06	2.17	4.21	6.46	5.16	2.54	5.28	13.00
$J(\text{C}_5-\text{C}_6)$	96.49	0.39	-3.91	93.42	86.15	0.40	-4.65	82.33
$J(\text{C}_6-\text{C}_7)$	132.05	1.29	-6.63	127.14	101.09	0.94	-6.40	96.04
$J(\text{C}_5-\text{O}_8)$	6.84	-1.66	15.97	21.01	12.29	-1.15	15.04	26.04
$J(\text{C}_6-\text{O}_8)$	-1.13	0.26	1.56	0.68	-1.52	0.11	1.97	0.56
$J(\text{C}_7-\text{O}_9)$					15.22	0.20	11.64	26.90

^a Basis set for nitromalonamide: cc-pVTZ for O_8 , O_9 , C_5 , C_6 , C_7 , and H_4 ; cc-pVDZ for N_1-N_3 , O_{10} and O_{11} , and minimal for $\text{H}_{12}-\text{H}_{15}$

We should expect a larger influence of the RAHB mechanism on J -couplings for model compounds III and IV as compared with what would happen for model compounds I and II. The FC contribution of $J(\text{O}_8-\text{O}_9)$ for nitromalonamide is very dependent on $d(\text{O}_8-\text{O}_9)$ and the local geometry, but both SD and PSO are not. This is observed for the planar configuration in Table 6. On the other hand, the contribution of the SD (PSO) term is doubled (multiplied by 4) when any of the bonds N_1-C_7 or N_3-C_5 are rotated 90° and is larger than 4 (≈ 8) times when both bonds N_1-C_7 and N_3-C_5 are rotated 90° simultaneously. Simultaneous rotation produces a larger effect on noncontact terms than what is obtained from the summation of each of both rotations separately. On the other hand when the H-bond is broken, the SD and PSO contributions becomes almost zero and the FC term still has a contribution which is comparable with that of the planar structure. This is also a remarkable finding that is in line with our previous discussion on $\sigma(\text{O})$ and $\sigma(\text{H}_4)$.

There are some other couplings in nitromalonamide that are also important for our analysis. One of them is $J(\text{C}_7-\text{O}_9)$. The largest PSO contribution is found when both N-C bonds are rotated. That value (11.64 Hz) is close to the PSO contribution when only N_1-C_7 bond is rotated. Its smallest contribution is found when the H-bond is 90° out of plane. This is in line with its behavior in compounds I and II.

It is also observed that $|J(\text{C}_6-\text{C}_7)| > |J(\text{C}_5-\text{C}_6)|$ in all different unsaturated structures that we analyzed. For saturated com-

pounds IIa and IIb in their planar configuration such relation is opposite being the couplings close each other.

5. Concluding Remarks

We have studied a series of compounds for which the RAHB phenomenon, if it does exist, could be largely enough to modify in a specific way the electronic structure of such compounds. The basic structure analyzed was malonaldehyde. Geometrical differences were treated in such a way to avoid its effects on the final conclusions. We started with the analysis of the stabilization energy of the molecules for both H-bond configurations, closed and opened, and then we studied the likely relationship between the modification of the localization of molecular orbitals for conjugated systems with NMR spectroscopic parameters.

Malonaldehyde is more stable energetically when the O_9-H_4 H-bond is in the molecular plane, as compared with its electronic energy when such bond is rotated 180° . This last molecular structure is also more stable than that with the O_9-H_4 bond rotated 90° . This stabilization behavior is opposite to that in the 3-OH propanal and is more evident when both geometries are closer (I with IIb). We can explain it by considering the overlapping between one of the O_9 LPs and the π -skeleton; this overlap is the highest when the H-bond is not rotated. When the H-bond is rotated 180° , there is less overlap and finally the

lowest overlapping appears when O_9-H_4 bond is rotated 90° . This fact would mean that malonaldehyde is more stable due to an extended conjugation. The H-bond energies are higher in two cases (H-bond rotated 90 and 180°) than the H-bond energies in the corresponding (planar) 3-OH propanal structures. In our analysis, all other electronic effects (like electrostatic) are not modified and do not intervene in the following conclusion: the stabilization energy is higher when the molecular system has an extended conjugation that involves an H-bond. In such a case, the molecule cannot be described with a unique Lewis structure, or in other words the concept of resonance must be introduced.

The analysis of the total hydrogen shielding of the H-bond, $\sigma(H_4)$ shows that it is lower for malonaldehyde compared with 3-OH propanal. Two different geometrical structures of these last systems were analyzed where only the distance $d(O-O)$ corresponding to malonaldehyde molecule was kept fixed. For them, $\sigma(H_4)$ varies less than 1 ppm showing that such distance may be important but the other local geometrical parameters are not. The J -coupling analysis of compounds I and II shows that $J(O-O)$ couplings have a large contribution from noncontact terms for malonaldehyde, being they are of the same order of magnitude and sign as the FC term. A similar behavior is found in nitromalonamide when both amino groups are rotated. In the planar configuration of nitromalonamide, the noncontact terms are much smaller than the FC term. Noncontact contributions to $J(C_7-O_9)$ are also quite sensitive to the presence of H-bonds. So one should include all four terms in the calculation of J -couplings when a closed H-bond system is considered. The relative weight between the contact and noncontact contributions are very sensitive to the local electronic environment. All these facts are remarkable findings. In line with this finding, $J(O_8-H_4)$ has a relative large PSO contribution for malonaldehyde (three times smaller for IIb) in its planar configuration that becomes vanishingly small (also in IIb) when the H-bond is rotated 90° . If the through-space were its transmission mechanism, there would not be large PSO contributions.

From energetic considerations, nitromalonamide and nitromalonamide have strong H-bonds. The energetic analysis of nitromalonamide shows that modifications of the π -skeleton have an strong influence on the stability of the whole molecule and then on the strength of the H-bond. When the amino groups are in a planar configuration they are π -electron donors. When both or any of them are rotated this effect is canceled. The analysis of the effects of rotations of such groups shows that the electronic effects on the acidity of the donor atoms are more important than the electronic effects on the basicity of the acceptor atoms.

Analyzing the effects of the extended conjugation on the paramagnetic component of $\sigma(O_9)$ and $\sigma(C_7)$ on the whole set of molecules studied here it was observed that they become more positive as the strength of the H-bond goes down. A completely equivalent trend was observed for $\sigma(H_4)$ being its values, from the smallest to the largest, correspond to nitromalonamide with (a) N_1-C_7 and N_3-C_5 both rotated 90° , (b) N_1-C_7 rotated 90° , (c) N_3-C_5 rotated 90° , (d) planar, and then (e) compound I and (f) compound IIb. This pattern is not exactly the same when compared with that arising from energetic considerations (see Table 1). Still the difference is only with respect to two structures of compound IV (of the order of 2 kcal/mol) and so does not modify the analysis done for compounds I and II.

The hydrogen atom that is one of the most important elements in the H-bonds we analyzed does modify its usual magnetic

response found in other nonresonant molecular structures. Both, its dia and paramagnetic components becomes unusually large.

The large noncontact contributions to some J -couplings ($J(O-O)$, $J(O_9-C_7)$, $J(C_6-C_7)$, and $J(C_6-C_5)$) and also the trends of some shieldings ($\sigma(O_9)$, $\sigma(C_7)$, and $\sigma(H_4)$) in malonaldehyde, nitromalonamide, and nitromalonamide can be explained resorting to an electronic mechanism that is affected by both extended electron conjugation or resonance and cooperativity. Such a mechanism may be the previously proposed RAHB.

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Supporting Information Available: Additional tables and figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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