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Magnetic descriptors of hydrogen bonds in malonaldehyde and its derivatives

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The nature of the hydrogen bond, HB, as such is still unknown, though few of its most fundamental features has been uncovered during the last decades. At the moment it is possible to get reliable results of few of its broadest properties, like magnetic properties. They could give new insights about the physics underlying the strength and features of HBs.
In this article we analize the electronic origin of NMR spectroscopic parameters of malonaldehyde, MA, and some substituted MAs. These substituted MAs are such that the H-bond are assisted by one of the two phenomena: resonance assisted, RAHB or charge assisted, CAHB. We have studied the dependence of those parameters with two of the main factors which most contribute to both phenomena, the geometrical and the electronic factors, and found out how can they be used to characterize the RAHB or the CAHB by means of reliable theoretical calculations.
We show that, in the set of compounds analyzed here: i) the shielding of the proton of the H-bond can be used as a measure of the strength of the HB, and ii) the relation between contact and non-contact mechanisms of J-couplings between donor and acceptor atoms is a reliable descriptor of whether the H-bond is resonance assisted or charge assisted.

1 Introduction

The hydrogen bonds, HB, are among the most ubiquitous and interesting bonds in Nature. They can be considered as the strongest of all noncovalent interactions though the weakest of covalent ones.[1] This is related with the fact that, at the moment, there is no consensus about what the HBs are.[2–6]

There are also several research programs to uncover how can the magnetic properties be related with the main characteristic of them. In a recent article Weinhold and Roger proposed some criteria to better summarize the current understanding of H-bonding and, from them, make progressive refinements of its definition.[7] They divided most of descriptors of H-bonding in a) Structural and spectroscopic, and b) Theoretical and computational. One of the aims of this article is to contribute to improve the use and understanding of descriptors included in a).

Hydrogen bonds are generally described as electrostatic interactions with partly covalent character.[8,9] The electrostatic interactions occurs between the partially positively charged hydrogen atom and the opposing partially negatively charged hydrogen acceptor atom which is an electronegative atom such as nitrogen or oxygen.

One of the important factors that strengthen the HB is the resonance assistance mainly produced by the π-electronic framework. This fact was described by a model first proposed by Gilli and collaborators,[10,11] who called it resonance assisted hydrogen bonding, RAHB. They stated that, in this case "*the interplay between hydrogen bonds and (...) heteroconjugated systems can strengthen remarkably the hydrogen bond itself*".

The RAHB should have a very important role as a conducting force in processes like the synthesis and coordination of organic compounds.[12–14] It is also involved in the activation of covalent bonds and synthetic transformations.[14,15]

One early interpretation for the RAHB model was proposed by Gilli and collaborators by studying the HOCR=CR−CR=O molecular fragments. They have found that the RAHB can be described as a resonance synergetic process between the extended conjugation effect (meaning the delocalization of π-electronic framework) and one HB that belongs to the system, which is so strengthened.[10,11,16]

Another interpretation for RAHB is that the delocalization of the π electronic framework contribute to the HB by making the proton acceptor more negative and the proton donor more positive. This results in a stronger electrostatic interaction, and thus, the shortening of the HB distance which strengthen the hydrogen bond.[10,11,17–19]

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Resonance in the π-electronic framework influence the intramolecular HB by reducing its distance, and also providing an additional stabilizing component to the net bonding energy. On the other hand the interactions through the σ-electronic framework plays an important role in the enhancement of the HB strength in malonaldehyde, though not by resonance assistance in the sense of an interplay between σ charge transfer and π polarization; σ- and π-electronic frameworks seems to contribute independently from each other.[4]

Very often one find misunderstandings of the concepts of resonance-assisted and charge-delocalized assisted. Studying intermolecular RAHB in dimers of carboxylic acids and amides, and intramolecular RAHB in malondialdehyde and its substituted derivatives Grabowski and coauthors have shown that one should be very careful when considering the origin of HB stabilization. They found that in their compounds the HB are charge-delocalized assisted rather than resonance assisted.[20]

Charge assisted hydrogen bonds, CAHB, in which donors and acceptors have an ionic character that reinforce the electrostatic character of the HB, are another phenomenon that influence the HB. Although CAHBs have been recognized for decades, their use in network design, particularly for "crystal engineering" has grown substantially in the past decade. The evidence suggests that CAHB introduce extraordinary robustness to molecular networks that reflects a combination of strong intermolecular forces and structural compliance, thus facilitating design of organic solid-state materials.[21]

Few years ago we stated that the contributions of two non-contact mechanisms to NMR J-couplings,[22] *i.e.* Spin-dipolar, SD, and paramagnetic spin orbital, PSO, are valid sensors for studying the resonance phenomenon. We considered the values of J^{PSO}(O-O) and J^{SD}(O-O) in malonaldehyde, MA, nitromalonaldehyde, NMD, and nitromalonamide, NMA, to do it. It was clearly shown that their large values are related with the RAHB.[23]

As a continuing research program on these matters we were interested to find out a likely relationship among the CAHB phenomenon and the NMR spectroscopic parameters. Given that the RAHB is related with electronic mechanisms of J-couplings that are mainly transmitted by the π-electronic framework, we conjectured that the CAHB phenomenon should be related with the Fermi-contact, FC, mechanism.

Our main concern is here to give new understandings about the importance of σ- and π-electronic frameworks in order to characterize the different type of H-bonds. We shall show what electronic mechanisms of the NMR J-couplings are more involved on both, RAHB and CAHB type of H-bonds. We focused our studies on malonaldehyde, MA, and a set of substituted MAs. We have been previously working with them and found that they fulfill the necessary conditions for pursuing our main concern: to know whether the J-coupling mechanisms are related with the above mentioned types of HBs. In other words, we shall answer the inquire about whether the NMR spectroscopic parameters can or cannot be applied as faithful descriptors of H-bonds.[23]

Another aim of this work is related with the analysis of geometric factors that may influence the HBs. We shall show how to distinguish between electronic effects and geometric effects, and the fact that the CAHB is very much influenced by geometric factors, though this is not the case for the RAHB.

We shall also show that there is a relationship between the electronic mechanisms that contribute to the NMR J-coupling and the shieldings of the hydrogen atom that belongs to the HB.

In the next section we describe some characteristics of the two types of HBs that shall be treated in some detail afterwards; what some authors had found and propose as resonance-assisted H-bonds and charge-assisted H-bonds. We shall then expose few descriptors of H-bonds and its relationship with the NMR spectroscopic parameters. The models and theoretical level used for calculations are given in Section 3, and then its application to a selected set of molecular compounds in order to get a deeper understanding about the NMR spectroscopic parameters as descriptors of the RAHB and the CAHB. The main conclusions are given in Section 5.

2 Some features and types of H-bonds

We shall sketch in this section few of the most common features of HBs, and especially those related with RAHB and CAHB. They were first suggested by Gilli and coauthors,[10,12,16,24,25] who introduced the electrostatic-covalent hydrogen-bond, ECHB. It has the following characteristics:

- Weak HBs are electrostatic interactions that become more covalent as they are strengthen.
- Strong HBs are covalent bonds of three-center-four electron type.
- The strongest HB should be symmetric and homonuclear, because only in those cases there are two resonant forms with the same energy which can effectively be mixed (according to the valence-bond theory).

Those authors suggested that there are three ways for strengthening the HB, meaning: donating or withdrawing an electron (CAHB [-]) or (CAHB [+]), or by delocalization of a π-type electron (RAHB). This last type of HB is related with multiple π-type bonds, which are simple bonds interspersed with multiple bonds (conjugation). This kind of interaction was coined by Jeffrey as a cooperative effect of π-type.[26]

2.1 Few descriptors of the strength of H-bonds

Based on energy criteria it is not easy to find a well defined separation between what HBs are and other bonding interactions, like van der Waals or covalent bondings. Such a diffuse separation also appears for the strength of the so called weak, moderate and strong HBs.[1]

It is usually accepted that strong HBs have short bond lengths. In those cases the donor-acceptor distances (X$\cdots$Y) are between 2.40Å and 2.55Å, being the extreme cases known as short and strong HBs (SSHBs) and low barrier HBs (LBHBs) respectively, because they belong to systems that have only one potential well for the proton transference.

Even though one can use the energy stabilization of conjugated systems that contain intramolecular HBs as a measure of the HB

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strength, there are very few methods available to calculate the energy of the HB. The main difficulty strives on the fact that one cannot find two molecular structures that differs only on the position of the HB though maintaining fixed all other properties.[3,27,28]

What one usually do, to get the strength of HBs, is to calculate the energy difference between the closed configuration that include the HB and the open configuration where the HB is broken. This cannot give accurate values when some additional effects are not estimated (meaning, effects that appears due to the rotation of the O-H group). In this work we considered the open configuration of the molecule as obtained by rotating in 90° the X−H bonding with respect to the C−X bonding though clumping all other parts of the molecular structure.

Given that the hydrogen bond distances r_{OH} and r_{HO} cannot be varied independently, *i.e.* they are correlated, q_1 should also be correlated with q_2, being q_1 a measure of the asymmetry of the HB and q_2 the distance between the donor X–H and the acceptor H–X along the HB. They were first proposed by Limbach and collaborators.[29]

Then, applying our own model to calculate the HBs energy we shall be able to consider its dependence with those geometric parameters which are defined as,

$$q_1 = \frac{1}{2}\left(r_{OH} - r_{HO}\right)$$

$$q_2 = r_{OH} + r_{HO}$$

Several works by Limbach and collaborators have also shown that the chemical shifts of donor and acceptor atoms and the bond order of HBs can be correlated with q_1 and q_2.[30–32] Still recently it was pointed out that the distance between the oxygens, d(O–O), is not a good descriptor of the strength of HBs because both oxygens tend to stay closer each other due to steric effects.[33]

2.2 Resonance assisted hydrogen bonds, RAHB

A number of recent theoretical[4,7,23,34–36] and experimental publications[37,38] devoted to study the nature of the RAHB shows the importance of this phenomenon. It was also applied to describe intermolecular interactions in systems which contain fragments of DNA[39–41] and proteins.[42]

Some authors consider that the RAHB arises from the delocalization of the π-electronic framework which produce an increasing of the negative charge on the acceptor group of the HB. As a consequence the donor group increases its positive charge and so it produce a large electrostatic interaction, which in turn shorten the distance of the HB and this increases its strength.[43–46]

The electronic origin of the RAHB is under continuous debate. Celia Fonseca and collaborators studied the redistribution of the σ and π-electronic framework associated with the HB formation in MA and its saturated derivatives.[4] They found that the flow on the π-electronic framework are consistent with the existence of RAHB following the Lewis structure; meaning that the charge of the donor group becomes more positive and the charge of the acceptor group more negative when the HB is established. This effect is only found in the non-saturated system, making the shortening of the distance among the donor and acceptor atoms. This fact introduce an extra mechanism that stabilize the bonding energy. Furthermore, σ-type orbitals play an important role in strengthening the interaction, though the contribution of the σ-framework and the π-framework to that strengthening of the HB are independent each other.[4]

2.3 Charge assisted hydrogen bonds, CAHB

CAHB is another HB that is considered strong by Gilli's classification. In order to get such a bond it is necessary that the hydrogen atom of the HB be in a single potential wall which means that the distance of the HB must be short.

CAHBs are also known as ionic or low-barrier hydrogen bonds.[13,16,24,25,47 48–50] The latter designation accounts for the low potential-barrier height for the proton transfer process between the donor and acceptor atoms. As will be seen later on, the presence of the charge increases considerably their strength, making them to fall into the category of moderate (4-15 kcal/mol) or strong (15-40 kcal/mol) hydrogen bonds.[26] It is known that the CAHBs control a great variety of processes involving molecules with groups exhibiting acid-base properties. For example, in solution they are responsible for the molecular self-assemblies into clusters, growing to ionic crystals.[48] Due to the strength and directionality of the CAHB, this type of noncovalent interaction has an impact on the synthesis of coordination compounds, crystal engineering, etc.[51] In most cases, due to the additional electrostatic interactions involved, CAHBs are stronger in comparison to normal hydrogen bonds.

On the other hand, the CAHB, viz. interactions of the X(+)-H···Y(-) type with the X-H donor being a cation and the Y acceptor being an anion, constitutes a particularly powerful tool used in the synthesis and design of new compounds.[12,14,15]

2.4 NMR spectroscopic parameters

NMR is one of the major techniques used to learn about the structure, dynamics and interactions between biomolecules.[52]

Even though the protein structures can be determined at atomic resolution by NMR techniques, its incomparable strength lies in its sensing of subtle changes in a given chemical environment of the nuclei as a result of intrinsic conformational dynamics, solution conditions, and binding interactions. These facts can be recorded at atomic resolution, without explicit structure determination, and then incorporated with static structures or molecular dynamics simulations to produce a complete biological picture.[52]

In complexes with intermolecular HBs, saturated molecules with intramolecular HBs, unsaturated and saturated molecules in which the HB has been broken, and unsaturated molecules with intramolecular N-H···N or O-H···N hydrogen bonds, the NMR J-coupling is dominated by the FC term. This fact may indicate that the main transmission of the nuclear-spin coupling is across the HB.[53] Thus, in those molecular systems the dominant term is the FC one which depends on *s*-electron densities. On the other hand, in the hydrogen-bonded unsaturated molecules, carboxylic acids, and trans-glyoxal, the PSO term is the main one, which depends on non-s, predominately *p*-electron densities.[54] It is worth

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to highlight that the contact contribution to J-couplings are related with the electronic density in the zone close to the coupled nuclei, and the non-contact contributions arises when π-type electrons are involved.[22]

Are coupling constants sensitive to the presence of RAHBs? In a previous paper some of us have stated that the RAHB can be characterized by the PSO and SD mechanisms of J-couplings between donor and acceptor atoms in a HB.[23] The large non-contact contributions to some J-couplings together with some shieldings in MA, NMD and NMA can be explained resorting to an electronic mechanism that is influenced by the RAHB. In that work it was not analysed whether the contact mechanism of J-couplings could be related with CAHB bonding.

In Refs. 34,55–57 some doubts have been raised about the very existence of the RAHB mechanism. Their authors focused on the analysis of NMR spectroscopic parameters on the following 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(O-O) and δ(H), respectively, do not reflect any evidence of such mechanism. In fact they considered only the FC mechanism in their J-coupling calculations. Thus, these data do not enable one to provide an unambiguous answer to our main concern about whether coupling constants can be used to confirm the presence of an intramolecular RAHB.[53]

Still in Ref. 55 it was pointed out that in MA and its diaza derivatives, the HBs are stronger than in their unsaturated counterparts due to the influence of the σ-electronic framework. Such framework would make that the donor and acceptor atoms are closer in this case than in the equivalent saturated compounds. And also, Alkorta *et. al.* have shown in a recent article that ^{2h}J(O-O) for similar unsaturated molecules have greater absolute values than the J-couplings for the corresponding saturated molecules.[53] Thus one could use ^{2h}J(O-O) as a parameter from which it is possible to differentiate between intramolecular HBs in the corresponding, unsaturated and saturated molecules. Therefore they are sensitive to the presence of RAHBs in the unsaturated molecules. For the unsaturated molecules ^{2h}J(X-Y) is dominated by the PSO term, while in the saturated molecules it is dominated by the FC term. Thus, the electronic mechanisms involved in the NMR J-coupling are very different for saturated and unsaturated molecules containing intramolecular HBs.

Applying the NMR spectroscopic parameters it was observed that some chemical shifts in molecular complexes undergo remarkable changes when HBs are formed; therefore, they can indicate the presence of this interaction.[58] On the other hand it was found a linear correlation between δ(H) and the distances d(O-O) and d(H$\cdots$O) in homonuclear HBs bonds like O-H$\cdots$O.

In previous works we have used σ(H) as sensor of strong HBs. We have found that, in those cases where σ(H) is smaller than 20 ppm the HB will be strong.[23] Furthermore, the electronic mechanisms of the J(X-Y) couplings can be used as descriptors for establishing the way the HB interaction is strengthened. Given that the FC mechanism is sensitive to the electron-nucleus interaction at the site of the nuclei, the *s*-character of both coupled nuclei enhance it and that interaction is mainly propagated through the σ-electronic framework.[22] On the other hand, SD and PSO mechanisms of J-couplings depends on the π electronic framework, and have a direct link with extended conjugation.[59]

In this article we assume that the electronic mechanisms that are behind the transmission of J-couplings in HB-containing molecules can be used as sensors which may clear up if RAHB or CAHB are underway in those systems.

3 Molecular models and computational details

As mentioned in Section 1 we have taken MA as the compound of reference, and from it some substituted MA and few related compounds. The dependence of selected magnetic descriptors with both, geometric and electronic effects are analysed by using theoretical molecular models which also permit us to introduce geometrical restrictions to separate geometrical effects of the electronic effects.

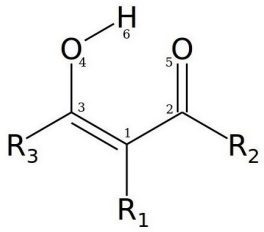
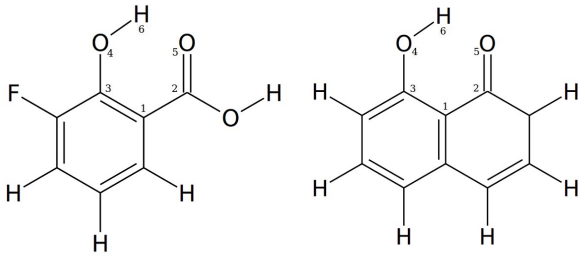


Fig. 1 Scheme of malonaldehyde and its substituents which are given in Table 1

In Figure 1 we show the scheme of the eight substituted MA used in this work, whose labels are given in Table 1. In Figure 2 we show the scheme of salicylic acid and naphthalene. Greek letters α, β and γ denote substituents positions on MA. Latin letters *a*, *b* and *c* denote the rotation of substituents by 90 degree at positions R_1, R_2 and R_3, respectively.



(a) Compound IX **(b)** Compound X

Fig. 2 Schemes of Salicylic acid (IX) and naphthalene (X).

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Table 1 Compounds based on the structure of substituted malonaldehyde of Fig.1

Compound	R_1	R_2	R_3
I	H	H	H
II_α	NO_2	H	H
II_γ	H	H	NO_2
$II_{\beta\gamma}$	H	NO_2	NO_2
III	H	NH_2	NH_2
IV	NO_2	NH_2	NH_2
V	BH_2	NH_2	NH_2
VI_α	F	H	H
VI_β	H	F	H
VI_γ	H	H	F
$VI_{\alpha\beta\gamma}$	F	F	F
VII_α	COOH	H	H
VII_γ	H	H	COOH
VIII	H	OH	OH

The nomenclature that will be used in Section 4.4 is as follows. Molecular compounds tagged as IV/G-1, IVbc/G-1, IVb/SP y IVbc/SP denote geometrical constraints related with compound IV, the nitromalonamide (NMA). The compound labeled as IV/G-1 has the same basic geometry as MA but include the substituents corresponding to NMA. The compound IVbc/G-1 is similar to the previous one but including a rotation of 90 degrees of the substituents R_2 and R_3. Then, compounds IVb/SP and IVbc/SP are obtained rotating R_2 y R_3 after optimizing the geometry of the NMA compound. SP means a restriction of type single-point.

Geometrical optimizations and calculations of NMR properties were performed at DFT/B3LYP level of theory.[60,61] According to previous studies one can obtain results of J(XY) couplings that should be in accord with experimental values using this functional.[62] It was also found that for HB-containing molecular systems that level of theory is enough to get reliable magnetic shieldings.[63]

All calculations were performed using the DALTON suite of programs.[64] In the case of geometry optimization the 6-311++g(d,p) basis set was used,[65–68] though the calculations of NMR spectroscopic parameters were performed with cc-pVTZ basis set.[69,70] In order to obtain gauge-invariant values of nuclear magnetic shieldings we calculated them with GIAO-London orbitals.[71–73]

4 Results and discussion

We first analyze results of geometric parameters and the energy of intramolecular HBs that belongs to the set of molecules shown in Figs. 1 and 2, and then the behavior of NMR spectroscopic parameters that give information about the magnetic nature of their H-bonds

4.1 Bond energy and strength of HB

The strength of HBs were obtained as mentioned in Section 3. We take the difference between the energies of the *closed* and *open* configurations that do contain the intramolecular HB. This last one is obtained by rotating 90 degrees the O−H bond with

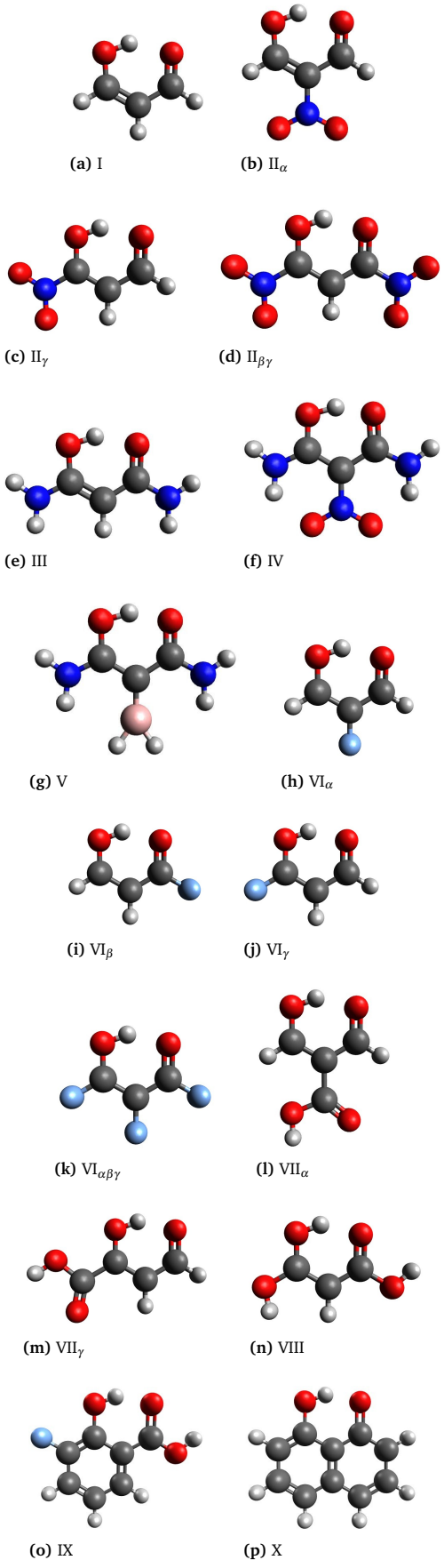

Fig. 3 Set of compounds analyzed without geometrical constraints.

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respect to the plane of the compound with no other modification of its geometry. If the O−H bond were rotated 180 degrees and then the resultant geometry were optimized, one would not get the actual energy for the HB formation. In such a case some other effects like sterics shall be included.

Table 2 Dependence of parameters q_1, q_2, HB-energy and σ(H), with substituents. All values are given in Angstroms, kcal/mol and ppm, respectively

Compound	q_1	q_2	HB-energy	σ(H)
I	-0.35	2.70	24.67	17.13
II_α	-0.33	2.66	27.10	16.58
II_γ	-0.31	2.65	21.11	16.30
$II_{\beta\gamma}$	-0.41	2.80	15.31	19.45
III	-0.27	2.58	28.53	15.77
IV	-0.17	2.45	36.70	12.59
V	-0.19	2.48	37.38	12.53
VI_α	-0.39	2.76	20.01	19.60
VI_β	-0.43	2.82	19.80	20.38
VI_γ	-0.23	2.55	28.78	13.80
$VI_{\alpha\beta\gamma}$	-0.40	2.78	14.73	20.89
VII_α	-0.31	2.65	28.32	15.73
VII_γ	-0.34	2.69	22.35	17.01
VIII	-0.31	2.64	24.53	17.24
IX	-0.39	2.74	16.09	20.36
X	-0.22	2.52	33.89	13.19

In Table 2 we show the parameters q_1 and q_2, together with the bond energies and magnetic shieldings of the protons that belongs to the HB. One can see that the energy of the HBs strongly depends on the separation between the donor atom and the acceptor atom, meaning that when q_2 is increased the bonding becomes weaker. This is a typical behavior of low-barrier H-bond (LBHB).

According to Jeffrey these systems have strong H-bonds because their estimated energy is between 15 to 40 kcal/mol. Nitromalonamide and its analogue, that contains boron (compounds IV and V) are the strongest in our study. It is worth to mention that q_1 has the lowest absolute values, meaning that its HBs tend to be symmetric. The same happens for compound X. All this is in accord with the proposal of Grabowski about the SSHB,[1] being observed in Fig. 5 that the symmetry of compounds increase as the HB energy is increased.

In Figs. 4 and 5 we show the dependence of the H-bond energy with the values of q_1 and q_2. There is a good lineal dependence in both cases, being $R^2 = 0.93$. We did not include all compounds because in some of them it is not possible to rotate the O−H bond adequately. When the O−H is rotated, an strong interaction between the LPs of the oxygen atom 4 and the R_3 substituent do appears in compounds II_γ and $VI\gamma$ (see Figs. 3c and 3j). At the same time the hydrogen that belongs to the O−H bond also interact with the same substituents. As a consequence of all this the estimated energy of HB cannot be related with the above mentioned way of getting it because it include in this cases another interactions that cannot be avoided.

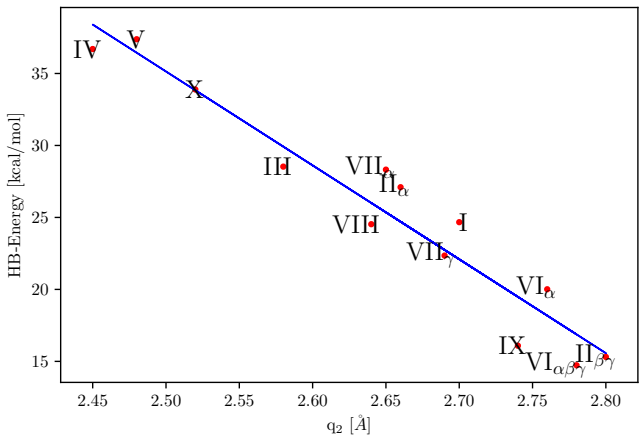

Fig. 4 Dependence of the H-bond energy with q_2 for most of studied compounds . The lineal fitting has $R^2 = 0.93$.

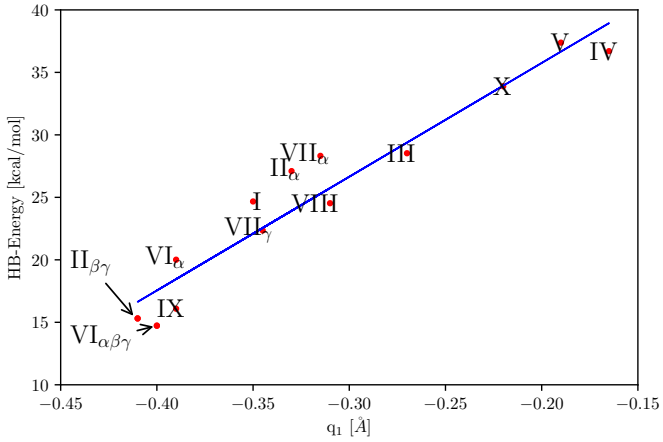

Fig. 5 Dependence of the H-bond energy with q_1 for most of studied compounds. The lineal fitting has $R^2 = 0.93$.

It was previously found that the values of σ(H) in strong HB should be less than 20 ppm; this is what was obtained in most of our compounds, as shown in Table 2, though it is not the case for compounds VI_β, $VI_{\alpha\beta\gamma}$ and IX. These results are in line with the estimated energy of compounds of Table 2 and have a similar behavior of the parameter q_2; meaning that the magnetic shielding is inversely proportional to the HB energy.

We want to highlight the importance of the position of the substituents in the substituted MA. When the atom of fluor (highly electronegative) is involved, the hydrogen bond is weakened or strengthened depending on where the fluor is inserted. When the substituent R_2 (which is in the opposite position with respect to the OH bond) is F it produce the highest value of σ(H). On the other side, when the substituent R_3 is F the σ(H) becomes much lower than that of the MA (compound I) making that the strength of the HB be increased.

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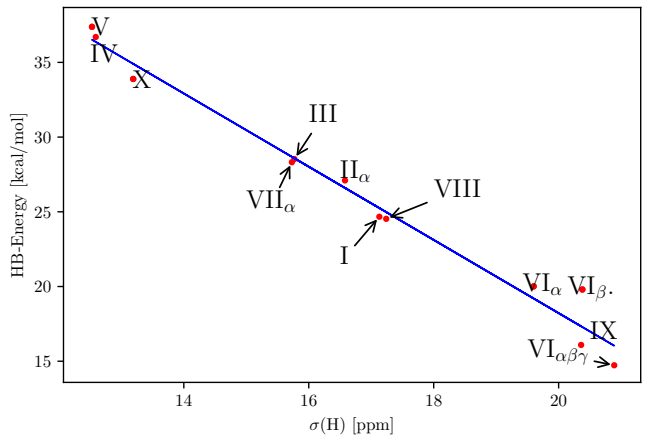

Fig. 6 H-bond energy vs σ(H). The linear fitting has $R^2 = 0.98$. In those H-bonds where the shielding is smaller the H-bond energy is larger. The strongest H-bond belongs to compounds IV, V and X because substituents work like electronic density attractor leaving the proton deshielded.

Such a behavior is shown in Fig. 6. We observe that the fitting line is much better than that obtained for q_1 and q_2, which indicate that one can obtain a good estimate of the HB energy by using the magnetic shielding of the proton belonging to the HB. This is a remarkable finding because it is not possible to get the bonding energy by experiments and, to our knowledge, such a correlation was never mentioned before for intramolecular H-bondings. In the case of intermolecular interactions, an interesting relationship between the magnitude of the changes in the chemical shift tensor induced by intermolecular interactions and the strengths of the intermolecular interactions was found by Marek and coauthors for crystalline forms of barbituric acid.[74]

4.2 NMR J-couplings as descriptors of HB

In this section we shall show the behavior of the underlying electronic mechanisms of J-couplings in our set of HB-containing molecules and whether they can be used as descriptors of the strength of HBs. In Table 3 we include the most important J-couplings for all planar configurations shown in Fig. 1. For MA (compound I), the contribution of non-contact terms for J(O-O) are larger than that of the FC term. So we assume that there is a RAHB in this case because the transmission of the magnetic perturbation is mostly performed through the π-electronic framework.

The main contribution to J(O_4-H_6) arises from the FC mechanism (-54.85 Hz), which means that magnetic interactions between nuclear spins of O_4 and H_6 atoms are mainly transmitted through the σ-electronic framework. In line with this, the analysis of J(C_3-O_4) shows that the contribution of the FC mechanism is also larger than the PSO one in this coupling (21.65 Hz vs 9.17 Hz, respectively). On the other hand, the main mechanism for J(C_2-O_5) is PSO, which is larger than the FC one (18.15 Hz vs 13.12 Hz). This is an expecting behavior due to the nature of the covalence bond between C_2 and O_5.

Table 3 Calculated J(XY) couplings for plain configurations shown in Fig. 1. Values are given in Hz

	I	II$_\alpha$	II$_\gamma$	II$_{\beta\gamma}$	III	IV	V
J(O_4-H_6)							
FC	-54.85	-54.42	-56.18	-59.47	-55.30	-46.07	-48.64
SD	0.12	0.10	0.16	0.06	0.33	0.25	0.28
PSO	-5.74	-5.04	-5.20	-6.55	-4.51	-2.43	-2.93
DSO	-0.44	-0.47	-0.54	-0.52	-0.56	-0.67	-0.63
Total	-60.91	-59.83	-61.77	-66.47	-60.03	-48.92	-51.91
J(O_5-H_6)							
FC	5.97	6.33	6.07	4.45	6.51	4.41	5.23
SD	-0.13	-0.27	-0.17	0.02	-0.26	-0.32	-0.34
PSO	2.44	2.39	2.62	2.01	1.90	1.71	1.71
DSO	-0.66	-0.69	-0.70	-0.67	-0.78	-0.86	-0.83
Total	7.63	7.75	7.82	5.81	7.37	4.93	5.77
J(O_4-O_5)							
FC	2.48	2.93	3.17	1.21	5.30	9.08	8.05
SD	3.45	2.75	3.87	3.20	0.92	0.67	0.55
PSO	5.74	4.78	5.94	3.96	1.92	0.85	0.82
DSO	0.00	0.01	0.01	0.01	0.01	0.02	0.01
Total	11.68	10.46	12.98	8.39	8.15	10.62	9.44
J(C_2-O_5)							
FC	13.12	12.53	12.69	3.40	11.98	12.22	12.94
SD	-0.72	-1.01	-0.99	-2.15	-0.36	-0.22	-0.32
PSO	18.15	18.66	18.50	14.75	11.29	11.00	11.95
DSO	-0.07	-0.08	-0.07	-0.11	-0.13	-0.14	-0.13
Total	30.49	30.10	30.12	15.89	22.78	22.85	24.44
J(C_3-O_4)							
FC	21.65	20.71	15.10	13.75	14.44	13.50	14.45
SD	1.32	1.06	1.68	1.63	0.21	0.17	0.14
PSO	9.17	10.77	8.87	8.66	7.09	8.74	9.35
DSO	-0.10	-0.11	-0.15	-0.15	-0.14	-0.16	-0.14
Total	32.04	32.43	25.50	23.89	21.59	22.26	23.80

When the nitro group is in position R_1 (compound II$_\alpha$), the strength of the RAHB is lowered. In this case the PSO component of J(O_4-O_5) is still larger than that of the FC one (4.78 Hz vs 2.93 Hz), meaning that its J-coupling is transmitted mainly through the π-electronic framework. Furthermore the SD component (2.75 Hz) is close to the FC one which means that such substituent donate electrons to the σ-electronic framework and withdraw them from the π-electronic framework, though not enough to eliminate the RAHB.

When the NO_2 group is in position R_3 (compound II$_\gamma$), the substituted MA recover the RAHB. The nitro group does not withdraw electrons from the π-electronic framework in this position, though it donate electrons on the σ-electronic framework of the HB. This last effect makes that the FC component grows from 2.48 Hz to 3.17 Hz when it is compared with that of compound I. Lastly, when substituens NO_2 are in positions R_2 and R_3 (compound II$_{\beta\gamma}$), the main mechanism that contribute to the HB is the RAHB.

Let us analyse now what happens when two amino groups are included in MA (compound III). In this case the RAHB is not found because the FC contribution to J(O_4-O_5) is larger than the addition of SD and PSO contributions (the FC increases $\simeq$ 2 Hz). The total value of this J-coupling is one order of magnitude smaller than that of compound I, which means that the substituents withdraw electrons from the π-electronic framework and donate them to the σ-electronic framework, making that the RAHB mechanism be replaced by the CAHB mechanism. This behavior is opposite to the behavior found in compound II$_{\beta\gamma}$, where

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the presence of NO_2 in the same position of amino groups in compound III modified the way the HB was strengthened.

In order to learn more about the complementary effect due to the groups NH_2 and NO_2, we included both of them to MA as shown in Fig. 3f. In this case the RAHB vanish because both substituents withdraw electrons from the π-electronic framework. We have seen that just including the NH_2 groups the resonance is eliminated, due to the substitution with NO_2 is not enough. So the presence of substituents NH_2 is much more important than the groups NO_2 because they are able to change the mechanisms that strengthen the HB.

When the group BH_2 is included in position R_1 instead of the nitro group (see Fig. 3g), the results of J-couplings are similar to those analyzed above for NMA. So the HB has a similar behavior and is of CAHB type. This means that the group BH_2 has an equivalent influence on NMR spectroscopic parameters as the group NO_2.

We have also analyzed the behavior of J(N-O) of the lower intramolecular HBs of compound IV (the HB between the hydrogens of groups NH_2 and the oxygen atoms of the group NO_2). We found that the contribution of the FC term is larger than that of the SD and PSO terms in both cases. This implies that there is no RAHB in those H-bonds, as one may expect, because there is no extended conjugation. So there are different HBs within the same compound that have completely different characteristics.

4.3 Complementary study of J(O_4-O_5) in compounds VI, VII, VIII, IX and X

Once we have shown that the J-couplings between donor and acceptor oxygen atoms are good descriptors of intramolecular HBs, we continuous showing results of calculations of that parameter for compounds VI to X.

Table 4 Total values of J(O_4-O_5) and their contributing mechanisms for malonaldehyde with high electronegative substituents. All values are given in Hz

	I	VI_α	VI_β	VI_γ	$VI_{\alpha\beta\gamma}$	VII_α	VII_γ	VIII	IX	X
FC	2.48	1.69	0.90	5.41	1.71	3.33	2.52	4.02	1.87	7.20
SD	3.45	3.97	1.81	2.76	1.79	2.85	4.08	1.06	0.92	0.67
PSO	5.74	4.99	2.89	5.10	2.45	5.25	6.20	2.16	1.79	1.49
DSO	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.01	0.01	0.01
Total	11.68	10.65	5.62	13.30	5.96	11.45	12.81	7.26	4.60	9.38

In Table 4 we observe that for the four fluorine substituted MAs the extended conjugation is the more important mechanism; this indicate the presence of RAHB. The atomic fluorine in any of R positions withdraws electrons from the π-electronic framework, though it is not enough to make null the RAHB. When fluorine atom is in position R_3 it also donate electrons to the σ-electronic framework in such a way that the FC mechanism is highly improved for J(O_4-O_5). Then the HB is strengthened by two mechanisms: charge assisted and conjugation. When instead of fluorine one include chlorine the behavior is quite similar.

Using carboxilic group as substituent a new behavior do appears: when COOH is in position R_3 (compound VII_γ) an small addition of electrons is donated to the π-electronic framework, increasing the resonance. This fact is observed by analizing PSO and SD contributions to J(O_4-O_5); they increase their values as compared with those of compound I. On the other hand, when the substituent is in position R_1 there is an increase of electron density of the σ-electronic framework though not enough to change the way the HB is strengthened. In both cases the H-bond is mostly given by a RAHB mechanism.

The analysis of compound IX shows that it has a weak HB that can be described by the shielding of the proton, which is 20.36 ppm (see Table 2). The J(O_4-O_5) is weakened and does not have any mechanism that strengthen the HB. On the other hand naphthalene (compound X) has a well defined CAHB mechanism because of the high FC contribution to the J(O_4-O_5). A similar behavior occurs in di-hydroxy-malonaldehyde (compound VIII).

4.4 Effects of rotation of substitutens and geometrical restrictions on spectroscopic parameters.

The next step in our research about the use of NMR spectroscopic parameters to know about the electronic mechanisms that affect the H-bonds, is to learn about the influence of geometrical effects on J-couplings of NMA to which we impose different geometrical constraints. Our aim was to quantify the substitutent effects with independence of geometric effects.

In Table 5 we observe that the estimated HB energy is sensitive to both, the rotation of the substituents and the way the geometry of the molecular system is optimized after that rotation. When the NO_2 group in position R_1 is rotated, the value of the HB energy goes down to a value of energy that is close to that of MA (compound I). This means that the strength of the HB related with the substituent in R_1 is very important for the stabilization of the whole system, and so, for the strengthen of the intramolecular O−H···O H-bond. On the other hand, when the NH_2 groups are rotated independently the value of the energy goes down, even though such energy is larger when the rotation of the substituent is performed in position R_2.

When one uses the same geometry of compound I in compound IV (model IV/G-1), the value of the HB energy of compound IV is close to that of compound I, though the strengthening of the intramolecular O–H ... O HB is due to CAHB (it arises from the analysis of J(O_4-O_5)). This shows that electronic effects due to the presence of substituents are more important than geometrical effects.

Table 5 Dependence of HB-energy (given in kcal/mol) and σ(H) (given in ppm) with geometrical constraints

	IV	IVa	IVb	IVc	IV/G-1	IVbc/G-1	IVb/SP	IVbc/SP
HB-energy	36.70	26.47	33.42	36.39	26.62	-	35.63	34.87
σ(H)	12.59	16.67	13.17	12.92	18.86	17.68	12.28	12.33

Geometrical structures of models IVb/SP and IVbc/SP are obtained by *single point* calculations. There are no optimizations of geometries after the rotation of substitutens in compound IV. With these studies we wanted to know how important are geometric effects on both, the H-Bond energies and the J-couplings.

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Under these constraints we observe that when the group NH_2 at position R_2 is rotated, no change in the HB energy do appears. This effect is opposite to what happen when the geometry of the whole compound is optimized after the rotation of the substituent (compound IVb). This means that geometrical effects are not as important as electronic effects on the strength of HB energies. This is also observed when both NH_2 groups are rotated; change in the HB energy is not important and such energy is higher than that of compound IVb.

Results in Table 5 show that the influence of geometrical constraints on σ(H). Its behavior is in accord with that of the energy, meaning that when the energy of the HB increases, σ(H) decreases and viceversa.

The effect of geometrical constraints on J-couplings are shown in Table 6. When the substituent NH_2 is rotated in position R_3 (compound IVc), the value of the FC contribution to $J(O_4\text{-}H_6)$ is smaller than its value for the planar configuration (-42.35 Hz vs -46.07 Hz), but its PSO contribution does not change. This means that there is an smaller contribution of the σ-electronic framework to that J-coupling. On the other hand for the $J(O_4\text{-}O_5)$ coupling the contribution of the FC mechanism decrease but the PSO and SD increases, meaning that the π-electronic framework has a higher influence when the substituent is rotated. Still the resonance is not recovered because the addition of PSO and SD contributions give a value that is smaller than that of the FC one. The rotation of NH_2 in position R_3 makes an important increase of the contribution of the π electronic density to the $J(C_3\text{-}O_4)$ coupling, because the PSO contribution increase one order of magnitude with respect to its value in the planar configuration. The FC contribution increase a little bit (1 Hz), meaning that there is an small increase of the influence of the σ-electronic structure to the $J(C_3\text{-}O_4)$ coupling.

The PSO contribution to $J(C_2\text{-}O_5)$ does not change too much, though its FC contribution is lowered due to an smaller contribution of the σ-electronic framework to that J-coupling. This is something one should expect because a rotation of NH_2 in its position should not modify $J(C_2\text{-}O_5)$.

When the substituent NH_2 in position R_2 is rotated (compound IVb), the FC contribution to $J(O_4\text{-}H_6)$ is larger than its contribution in the planar configuration (-48.67 Hz vs -46.07 Hz). This implies that the rotation of NH_2 enforce the coupling through the σ-electronic framework. On the other hand the behavior of J(O-O) is similar to the case where the substituent NH_2 is rotated in position R_3; meaning that the rotation reduce the influence on that J-coupling of the σ-electronic framework but increase the influence of the π-electronic framework. The PSO and SD contributions increase one order of magnitude compared with the planar configuration. Furthermore the FC contribution to $J(C_3\text{-}O_4)$ goes down a little with respect to the planar configuration (12.93 Hz vs 13.50 Hz) and the contribution of the PSO mechanism does not change. In the case of $J(C_2\text{-}O_5)$ the FC term diminish (from 12.22 Hz to 9.69 Hz) and the PSO increase (from 14.48 Hz to 11.00 Hz). This means that the effect of the rotation of NH_2 at position R_2 reduce the influence of the σ-electronic framework to $J(C_2\text{-}O_5)$ and improves the influence of the π-electronic structure.

When the two NH_2 groups are rotated simultaneously (compound IVbc/SP), the influence of substituents on the π-electronic framework vanish. This fact is known due to the components of J(O-O) are quite similar to that of the compound II.

Table 6 Effects of geometrical constraints on J(XY) couplings. All values are given in Hz

	IV	IVa	IVb	IVc	IV/G-1	IVbc/G-1	IVb/SP	IVbc/SP
$J(O_4\text{-}H_6)$								
FC	-46.07	-56.50	-48.67	-42.35	-57.29	-43.97	-45.22	-41.79
SD	0.25	0.31	0.21	0.07	0.24	0.12	0.22	0.07
PSO	-2.43	-4.48	-2.65	-2.82	-5.57	-5.45	-2.23	-2.55
DSO	-0.67	-0.57	-0.65	-0.63	-0.52	-0.51	-0.67	-0.62
Total	-48.92	-61.26	-51.76	-45.73	-63.15	-49.80	-47.90	-44.89
$J(O_5\text{-}H_6)$								
FC	4.41	6.52	6.51	6.64	5.34	6.01	5.84	7.66
SD	-0.32	-0.26	-0.55	-0.31	-0.31	-0.25	-0.58	-0.46
PSO	1.71	1.87	1.97	2.25	1.55	2.31	1.92	2.65
DSO	-0.86	-0.80	-0.85	-0.86	-0.73	-0.72	-0.85	-0.82
Total	4.93	7.33	7.08	7.73	5.85	7.34	6.33	9.02
$J(O_4\text{-}O_5)$								
FC	9.08	5.41	6.68	6.47	2.69	0.37	6.97	4.89
SD	0.67	0.92	1.31	1.31	0.49	2.27	1.31	2.83
PSO	0.85	1.89	2.66	2.64	0.76	4.34	2.67	5.72
DSO	0.02	0.01	0.02	0.02	0.01	0.01	0.02	0.02
Total	10.62	8.24	10.67	10.44	3.96	6.99	10.97	13.46
$J(C_2\text{-}O_5)$								
FC	12.22	11.98	9.69	10.96	8.10	7.12	11.33	9.94
SD	-0.22	-0.40	-0.99	-0.36	-0.52	-1.94	-0.99	-1.49
PSO	11.00	11.01	14.48	11.42	11.41	16.16	14.84	15.72
DSO	-0.14	-0.14	-0.13	-0.14	-0.14	-0.13	-0.14	-0.14
Total	22.85	22.45	23.04	21.87	18.84	21.20	25.04	24.03
$J(C_3\text{-}O_4)$								
FC	13.50	14.23	12.93	14.58	13.69	15.48	12.97	14.11
SD	0.17	0.26	0.15	0.56	0.12	0.49	0.14	0.45
PSO	8.74	7.04	8.74	10.95	7.05	9.76	8.89	11.18
DSO	-0.16	-0.16	-0.16	-0.15	-0.16	-0.16	-0.16	-0.15
Total	22.26	21.37	21.66	25.94	20.69	25.58	21.84	25.60

If the substituent NO_2 is rotated in position R_1 (compound IVa), the FC contribution to the $J(O_4\text{-}H_6)$ is increased with respect to the planar configuration (-56.50 Hz vs -46.07Hz). This means that such rotation enhance the contribution of the σ-electronic framework to that J-coupling. At the same time there is an small increase of the PSO contribution, meaning the increasing involvement of the π-electronic framework. On the other hand, the behavior of the influence of the rotation of NO_2 on $J(O_4\text{-}O_5)$ is different; the FC contribution (5.40 Hz) diminish when the substituent NO_2 is rotated but its decrease is smaller (6 Hz) when both NH_2 substituents are rotated separately. Besides, for the π-electronic structure the behavior is opposite; the rotation of NO_2 does not improve the coupling $J(O_4\text{-}O_5)$ through the π-electronic structure as much as its increase due to the rotation of any of NH_2 substituents. The contributions of PSO and SD to that coupling is increased when any of NH_2 substituents rotate (PSO = 2.6 Hz and SD = 1.3 Hz) but its increase is lower when the NO_2 substituent is rotated (PSO = 1.8 Hz and SD = 0.9 Hz).

The couplings $J(C_3\text{-}O_4)$ and $J(C_2\text{-}O_5)$ are little modified when the NO_2 substituent is rotated with respect to the planar configuration. The FC component of $J(C_3\text{-}O_4)$ increase around 0.7 Hz which indicate that there is an increase of the contribution due to the σ-electronic framework. The PSO contribution diminish in almost 2 Hz, meaning that the rotation reduce the contribution due to the π-electronic framework. One can then rationalize the effect of rotating the NH_2 substituent by considering that, in this case, the LP is not any longer involved in the π-electronic framework, and so its withdrawing effect is diminished. When

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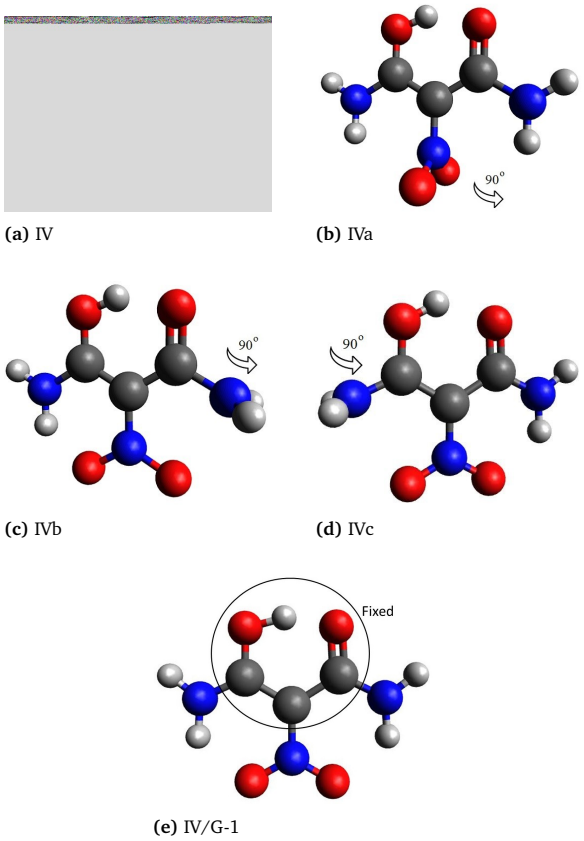
both NH_2 substituents are rotated such effect is removed and the electronic effects that are involved in MA (compound I) appears again. Furthermore, when the NO_2 substituent is rotated there is no modification of the π-electronic framework to which the nitrogen LPs of the substituent NH_2 belongs; then the electronic effects observed in NMA are still working.

In order to quantify the purely electronic effects that the substituents introduce on MA, we reoptimized the geometry of substituted malonaldehydes considering the basic geometrical structure of MA as fixed (see the scheme of Fig. 7e). In addition one can also learn about the geometric effects on J-couplings.



(a) IV **(b)** IVa **(c)** IVb **(d)** IVc **(e)** IV/G-1

Fig. 7 Geometrical constraints used in nitromalonamide.

In Table 6 one can see that $J(O_4\text{-}H_6)$ of model IV/G-1 have an important increase in its value compared with the fully optimized geometry of compound IV (-63.15 Hz vs -48.92 Hz). The electronic origin of that increasing is the variation in the FC mechanism which change from -46.07 Hz to -57.29 Hz, meaning that geometrical effects diminish the FC contribution in around 10 Hz. The PSO contribution does not have important variations so that geometrical effects contribute with around 3 Hz to such mechanism on $J(O_4\text{-}H_6)$.

In the case of $J(C_2\text{-}O_5)$ the FC contribution does vary: from 12.22 Hz to 8.10 Hz in the model IV/G-1, though PSO term does not vary much. The value of $J(C_3\text{-}O_4)$ is also similar in both cases though its PSO contribution vary in around 1.5 Hz with respect to the fully optimized geometry.

The coupling between both oxygens, $J(O_4\text{-}O_5)$, is the one that suffer the largest variations. It changes from 10.62 Hz in compound IV to 3.96 Hz in compound IV/G-1. Again the FC is the most sensitive mechanism to geometrical constraints. It changes from 9.08 Hz to 2.69 Hz in those compounds. What is more important is the fact that there is no modification of the mechanism that strengthen the HB, the CAHB. This enforce the fact that the RAHB does not only depends on the geometry (which is related with the extended conjugation) but also on the electronic effects related with the substituents. When the basic geometry of NMA is fixed to that of MA, the FC contribution to $J(O_4\text{-}O_5)$ is approximately the same as in MA; as is well known the FC mechanism is dependent on the geometry. On the contrary the PSO and SD mechanisms give different values in both compounds. So that that non-contact contributions depend on the electronic structure but not much on the geometry. A similar behavior is found for the coupling $J(O_4\text{-}H_6)$.

Let us see now what happens when the rotation of substitutens and the constraint of the basic geometry are implemented at the same time. When the NH_2 substituent is rotated though in a model with the MA geometry (model IVbc/G-1), the mechanisms PSO and SD are the main ones for $J(O_4\text{-}O_5)$ and the contribution of the FC mechanism is reduced when compared with what happens in NMA. It means that the rotation of the substituents enforce the transmission of the O-O coupling through the π-electronic structure and diminish the contribution through the σ-electronic framework. As a consequence the HB is again of RAHB type.

If one rotate the substituent NH_2 in the R_2 position one obtain similar effects in both, the optimized geometry of NMA and the IV/G-1 model (it is the NMA with the basic structure of MA). This is a remarkable finding, which again shows that the FC contribution highly depends on the geometrical structure of compounds without any dependence with the electronic structure, and the opposite happens for the non-contact mechanisms. If one now rotate both NH_2 substituents with the constraint that the basic geometry is that of MA (model IVbc/SP), the contributions to $J(O_4\text{-}O_5)$ are such that the HB is of RAHB type.

Table 7 Dependence of HB-energy and σ(H) with geometrical constraints for compound V. All values are given in kcal/mol and ppm, respectively

	V	Va	Vb	Vc
HB-energy	37.38	29.59	36.96	35.67
$\sigma(H)$	12.53	14.86	12.31	13.44

To make our analysis of geometric and electronic effects more complete we show, in Tables 7 and 8, results of calculated values of the NMR spectroscopic parameters and HB energy of compound V when substituents are rotated. The behavior of the HB energy is similar to what happens in compound IV; meaning that the rotation of the BH_2 makes the compound less stable (the HB energy decrease in around 10 kcal/mol). It is worth to mention that compound V does not have HB that involve the substitutent BH_2, which are very important in the stabilization of compound IV. As a consequence the rotation of groups BH_2 does not have

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any influence on the HB energy. As happens with the HB energy, the behavior of σ(H) when the proton belongs to the HB, is the same as that of compound IV.

Table 8 Dependence of the contributing mechanisms to J(XY) with geometrical constraints on compound V. All values are given in Hz

	V	Va	Vb	Vc
$J(O_4\text{-}H_6)$				
FC	-48.64	-54.15	-47.86	-45.70
SD	0.28	0.31	0.25	0.12
PSO	-2.93	-4.21	-2.74	-3.62
DSO	-0.63	-0.58	-0.62	-0.57
Total	-51.91	-58.63	-50.98	-49.77
$J(O_5\text{-}H_6)$				
FC	5.23	6.54	6.26	7.13
SD	-0.34	-0.18	-0.53	-0.33
PSO	1.71	1.78	1.90	2.12
DSO	-0.83	-0.81	-0.82	-0.81
Total	5.77	7.32	6.81	8.11
$J(O_4\text{-}O_5)$				
FC	8.05	5.31	6.64	5.31
SD	0.55	0.96	1.09	0.96
PSO	0.82	2.18	2.46	2.18
DSO	0.01	0.01	0.01	0.01
Total	9.44	8.71	10.22	8.47
$J(C_2\text{-}O_5)$				
FC	12.94	11.72	11.41	11.55
SD	-0.32	-0.27	-0.85	-0.51
PSO	11.95	11.28	15.25	12.47
DSO	-0.13	-0.13	-0.12	-0.13
Total	24.44	22.60	25.69	23.39
$J(C_3\text{-}O_4)$				
FC	14.45	14.75	13.65	16.10
SD	0.14	0.36	0.10	0.63
PSO	9.35	7.64	9.67	11.35
DSO	-0.14	-0.15	-0.14	-0.14
Total	23.80	22.61	23.27	27.94

In Table 8 it is observed that $J(O_4\text{-}O_5)$ has contributions from different electronic mechanisms that are similar to that of compound V. It means that the HB is still of the type CAHB after the rotation of substituents.

5 Concluding remarks

As a continuation of our research program that try to shed some light on the magnetic nature of H-bonds by using NMR spectroscopic parameters, we have studied the electronic mechanisms by which H-bonds are strengthened in malonaldehyde and some of its substituted derivatives. We used this time model compounds to also include in our analysis the effect of geometrical constraints.

We first propose one way to reliably calculate H-bond energies of the selected set of compounds. Then a highly linear correlation was found between parameters q_1 and q_2 and the estimated energy for the H-bond, which depends on the separation between the donor and the acceptor atoms. This dependence is such that when the distance q_2 increases, the bonding becomes weaker.

The two compounds that have the most strengthened HB of the present study are nitromalonamide and its analogous that contain boron (compounds IV and V, respectively). For these compounds we have found the lowest absolute values of q_1, showing that their H-bond tend to be symmetric. The same happens in compound X. These two findings are in line with previously published results, though to our knowledge, parameters q_1 and q_2 were never used in the way we used them here to evaluate the HB-energy.

On the other hand, the proton magnetic shielding, σ(H), of the proton that belongs to the HB is inversely proportional to the binding energy. A highly linear correlation was found, which indicates that reliable H-bond energies can be predicted by calculating the magnetic shielding of the proton. This is a remarkable result since it is not possible to directly measure the energy of the H-bonds. The value of the shielding of the proton that is involved in the H-bond give an estimation of the strength of the H-bond.

Malonaldehyde has a resonance-assisted H-bond whose estimated energy is 24.67 kcal/mol. The contributions of the SD and PSO electronic mechanisms (which are known to be dependent on the π-electronic framework) to the J(O-O) coupling are larger than the FC contribution. Gilli had suggested that the resonance in a H-bond could strengthen its intensity, though he did not mention how large such strengthening could be. When studying the nitromalonamide we found that its strength is 36.70 kcal/mol which is significantly larger than that of the un-substituted malonaldehyde. This fact is not related to an increase in the resonance effect but rather to a change in the way in which the intramolecular H-bond is strengthened. The analysis of the J(OO) coupling show that there is an increase of almost one order of magnitude of the FC component which must be due to the enforcement of σ-electronic framework to the J(O-O) coupling (the FC goes from 2.48 Hz to 9.08 Hz). This is an indication that the H-bond has a different magnetic nature when it belongs to the NMA molecule; in this case the H-bond is assisted by charge (CAHB).

In previous works we have shown that the RAHB is related with electronic mechanisms of J-couplings that are mainly transmitted by the π-electronic framework, and in this work we stated that the CAHB phenomenon is related with the Fermi-contact mechanism. The difference between contact and non-contact contributing mechanisms to J-couplings of donor and acceptor atoms in saturated compounds like the set analysed here, express whether the H-bond is resonance assisted or charge assisted. Then, one of our main findings is the fact that when the addition of SD + PSO contributions to J-couplings between donor and acceptor atoms belonging to a HB-containing molecule is larger than the contribution of the FC mechanism, the HB is of RAHB type; the opposite happens when the H-bond is of CAHB type

Another finding was the fact that the carboxylic group (COOH) was the only one substituent that little increase the π-electronic framework of the molecular system when it is in position R_3. This fact promote the extended conjugation and so increase the resonance effect.

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