



Resonance assisted hydrogen bonds in open-chain and cyclic structures of malonaldehyde enol: A theoretical study



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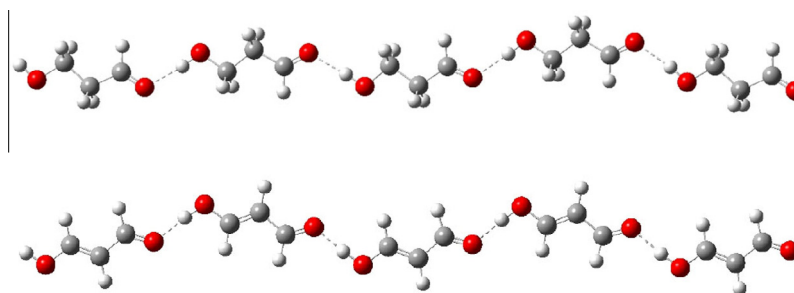
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HIGHLIGHTS

- Open-chain and cyclic structures of malonaldehyde enol were compared.
- Catemers up to 9 monomers have been calculated.
- Bader QTAIM analysis was used to understand the structures.
- NMR properties, ¹H chemical shifts and ²h_{JO} coupling constants, were analyzed.

GRAPHICAL ABSTRACT



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ABSTRACT

In 1989 Gilli, Bellucci, Ferretti and Bertolasi introduced the notion of Resonance Assisted Hydrogen Bonding (RAHB) one of the most fruitful concepts in structural chemistry. After reviewing our previous contributions to this topic, the present work analyzes theoretically this concept especially in non-cyclic structures. Geometries, electron densities and Laplacian at the bond critical points, cooperativity through many body interaction energies, deformation energies as well as NMR properties (chemical shifts and ²h_{JO} coupling constants) are used for the discussion.

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1. Introduction

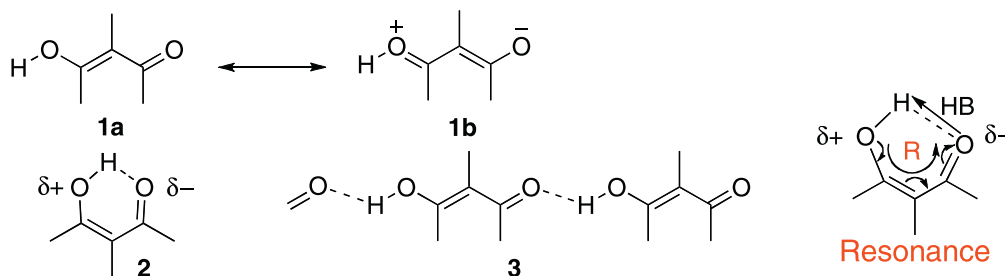
Resonance Assisted Hydrogen Bond (RAHB) has been and still is one of the most successful structural concepts. Introduced in 1989 by Gilli, Bellucci, Ferretti and Bertolasi it has been cited near 650 times [1], and a series of subsequent papers on the same topic by this group were cited more than 100 times each [2–7]. Besides,

Gastone and Paola Gilli published a book where this topic is reviewed [8]. The standard definition of RAHB is “A class of strong or very strong hydrogen bonds which cannot be accounted for by electric charges or steric hindrance, but is due to the fact that the neutral donor and acceptor atoms are connected by a system of π -conjugated double bonds; such a bond has been referred to as RAHB (resonance-assisted hydrogen bonding)” [3].

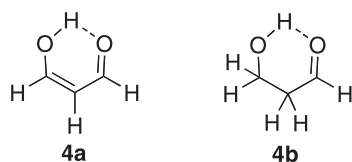
To understand the subsequent discussion we will slightly adapt some sentences from the 1989 paper [1]: “In this paper such methods ... are applied to the -diketone fragment in its enol form **1** ... with the aim of understanding what happens to the fragment geometry when it is perturbed by intramolecular, **2**, or intermolec-

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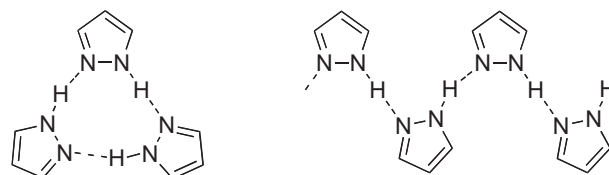
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Scheme 1. The main structures of Gilli's first paper.



Scheme 2. The first model used in our approach.



Scheme 4. Pyrazole cyclamers (a trimer as example) and catemers (a tetramer is represented).

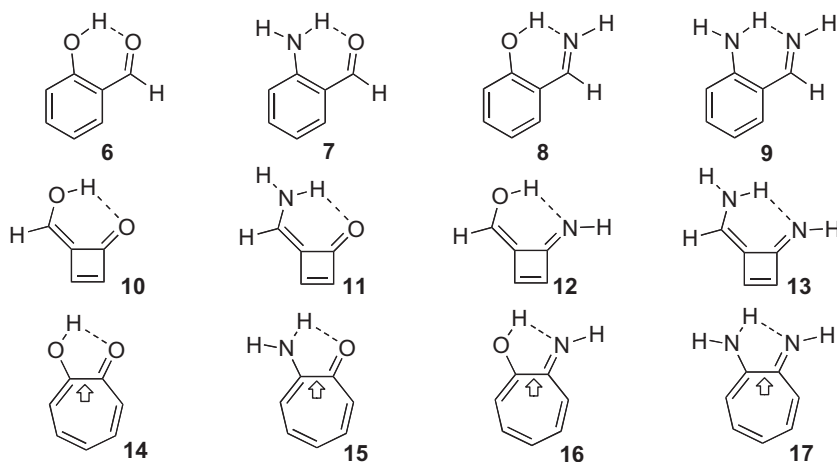
ular, **3**, hydrogen bonding.” Their graphical scheme of the RAHB model is depicted in Scheme 1. Some authors have particularly stressed the aromatic character of cyclic structures **2** [9].

We have devoted five papers to the subject of RAHBs using two approaches. The first one, based in our expertise in the calculation of spin–spin coupling constants (SSCCs) [10–15] was used to analyze the structure of molecules where the RAHB concept applies, such as the enol of malonaldehyde **4a** (Scheme 2).

We compared the conjugated **a** structures of the ring-closed malonaldehyde enol (**4a**) [16,17]. We calculated at the EOM-CCSD level [10–15] the SSCC of **4a** and **4b** finding that they depend on the O–O distance but not on the conjugation. The same outcome was reached using the ^1H chemical shifts of the proton involved in the HB. The main problem with this approach is that EOM-CCSD calculations are limited to small molecules; besides the Fermi contact term (FC) was used as an approximation to the total SSCC [10–15].

The second one was to extend the skeleton of β -diketones and related compounds to other molecules, such as those represented in Scheme 3, containing rings of different sizes (the saturated counterparts are not represented). In this second approach no SSCC were calculated.

In the case of the phenyl series **6–9** [18], the aromatic compounds have much strong IMHB that the saturated homologues, but if a constrained geometry was used for the saturated compounds, that is, a geometry having all the non-hydrogen atoms in the same position as in the conjugated molecule, then their HBs are similar or even stronger than those of the aromatic analogues. In the case of cyclobutenones **10–13** and their corresponding saturated cyclobutanones, due to the fact that the ring strain is less severe in the saturated compounds, the IMHB is weaker in the unsaturated series [19]. In both series we conclude that the decisive term was the σ -skeleton. The last paper we published [20], reports the study of tropolone **14** and its nitrogenated derivatives **15–17**. These compounds have the interesting property that, although conjugated, the single bond marked by an arrow in Scheme 3 does not play any role in the conjugation, being limited to bring the functional groups together. Another peculiarity is that both the saturated and unsaturated systems have a coplanar HB. The conjugation enhances the acidity of the OH (NH) and the basicity of the O=C (N=C) although there is no cyclic conjugation. Some small acyclic compounds (three carbon atoms) were studied but not the open-ring 7-hydroxyhepta-2,4,6-trienal ($\text{O}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{OH}$, two H atoms more than



Scheme 3. The second model used in our approach.

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