



On the performance of resonance assisted hydrogen bond theory in malonaldehyde derivatives



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ABSTRACT

According to the resonance assisted hydrogen bond (RAHB) theory, the π -electron delocalization (π -ED) promotes the intramolecular hydrogen bond (IMHB). Since the relation between the IMHB and π -ED are not well known, in the present work, the linear correlations between the descriptors of π -ED and estimated IMHB energies were systematically investigated. In this regard, the significance of π -ED in chelated forms of the benchmark systems by various descriptors, such as λ , λ' , HOMA, NICS, PDI, ATI, FLU and FLU π were evaluated. On the other hand, the IMHB energy of RAHB units by some adopted models, such as RRM, RBM, GCM, IRM and OCM are estimated. Furthermore, we explored all of the possible linear correlations between the π -ED indices and various IMHB energies to judge about the performance of RAHB theory. According to our results, it was found that there are great linear correlations between the RRM, RBM and GCM than IRM and OCM methods with some of the π -electron delocalization indices;

RRM: $\lambda' > \text{FLU} > \lambda > \text{HOMA} > \text{FLU}\pi \approx \text{ATI} > \text{PDI} > \text{NICS}(1) > \text{NICS}(0)$
 RBM: $\lambda' > \lambda > \text{HOMA} > \text{FLU} > \text{FLU}\pi > \text{ATI} > \text{PDI} > \text{NICS}(1) > \text{NICS}(0)$
 GCM: $\lambda' \approx \text{HOMA} > \lambda > \text{PDI} > \text{FLU} > \text{FLU}\pi > \text{NICS}(1) > \text{ATI} > \text{NICS}(0)$.

Surprisingly, the bond order factor of Gilli (λ'), which introduced similar to λ , has the best linear relationship with the IMHB energies. Consequently, the linear coefficients between the RRM, RBM and GCM energies with HOMA, λ and λ' descriptors are in agreement with the RAHB theory.

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1. Introduction

It is well known that non-covalent interactions play a central role in all aspects of physical science [1]. The hydrogen bond is one of the most important categories of non-covalent interactions and it is not surprising that many attempts, experimentally or theoretically, have been made to describe the nature of hydrogen bonds [2–6]. According to the systematic investigation of structural and spectroscopic data Gilli and coworkers was classified the hydrogen bonds to different categories: resonance assisted hydrogen bonds (RAHBs), charge assisted hydrogen bonds (\pm CAHBs) and low barrier hydrogen bonds (LBHBs) [7]. The resonance assisted hydrogen bond (RAHB) is a special type of hydrogen bonds that benefits from a resonance phenomenon in the molecular framework and classified to the inter and intramolecular cases [7]. The X-ray and spectroscopic data of β -dicarbonyl compounds indicate that with shortening of O–H...O distance, the chemical

shift of enolic proton $\delta(\text{OH})$ increased and O–H stretching frequency decreased. According to these data, the authors suggested that the resonance process, through the π -conjugated double bonds, can be stabilizing the cis enol forms of these compounds and assist the hydrogen bond.

Over the years, the RAHB model has become a widely accepted and applied to understand the nature of hydrogen bonding in a broad range of benchmark systems, especially for O–H...O hydrogen bond in malonaldehyde and its derivatives [8–12]. However, in the past decade Yanez et al. have published a series of papers and questioning the validity of RAHB idea [13–16]. They investigated a vast selection of compound, such as β -dicarbonyl and β -enaminone, and concluded that there is no evidence of resonance assisting to intramolecular hydrogen bonds. Because of controversies in physical origin of the intramolecular resonance assisted hydrogen bonded systems, in the present study we decide to perform a comprehensive theoretical study about the RAHB systems in malonaldehyde derivatives. The main goals of this study are as follows:

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- Evaluation of the π -electron delocalization, by various descriptors
- Examination of the halogen substitutions effects on the π -electron delocalization
- Estimation of the IMHB energies of benchmark systems, by some adopted models
- Assessment of the performance of RAHB theory according to the linear correlations between the π -ED descriptors and IMHB energies.

2. Computational methods

In the present study, all of the computations were performed by Gaussian 03 series of programs [17]. First, the geometry optimizations and vibrational frequencies calculations were carried out at MP2/6-31++G(d,p) level of theory. Then, estimation of IMHB energies of model compounds were estimated by related rotamers method (RRM), rotational barrier method (RBM), geometry corrected method (GCM), isodesmic reaction method (IRM) and open-close method (OCM) [18–22]. The optimized structures were used to obtain the appropriate wave function files for AIM and NBO analyses. The nature of the intramolecular hydrogen bond was studied using the AIM theory of Bader by mean of AIM2000 [23] software and the natural bond orbital's (NBO) analysis was performed using the NBO package included in Gaussian 03 suite of program [24]. Finally, the π -electron delocalization of RAHB rings were evaluated by the bond order factor of Gilli (λ'), the geometrical factor of Gilli (λ) [25], the harmonic oscillator model of aromaticity (HOMA) [26], the nucleus independent chemical shift (NICS) [27], the para delocalization index (PDI) [28], the average two center index (ATI) [29], the aromatic fluctuation index (FLU) [30], and the π -fluctuation aromatic index (FLU π) [31]. In this study, the R_{opt} , α , and δ_{ref} for evaluation of HOMA and FLU indices are calculated at MP2/6-311++G(d,p) level of theory. Moreover, the bond orders of λ' factor of Gilli, were calculated using the Wiberg bond indices included in NBO analysis.

3. Results and discussions

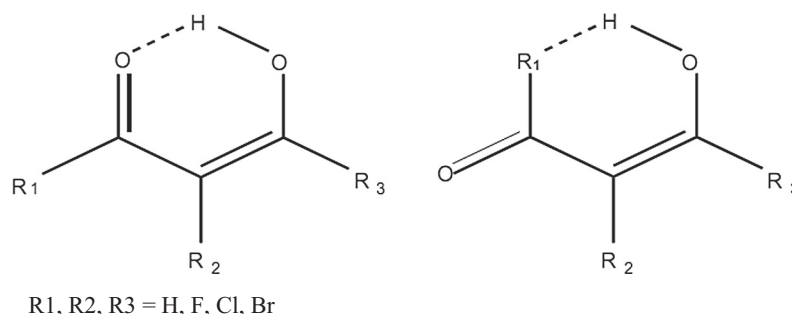
In the current study, the chelated enol forms of malonaldehyde (MA) and its halogenated derivatives have been considered, a set of benchmark structures. In these compounds, three different sites (H atoms) are available for halogen substitution, but one site is excluded. This exception is because of the limitation of the RRM procedure; if we replace the H atom in R1 position by a halogen atom an additional O—H...X hydrogen bond will be formed after rotation around C—C bond, which perturb the IMHB energies (Scheme 1). So, substitution of halogen in R1 position intended just for evaluating the π -ED descriptors, and in the IMHB energies discussion was omitted. As mentioned, in the first part of our study the π -electron delocalization of RAHB systems by various

descriptors was evaluated. In the second part, the IMHB energies of model compounds are estimated by some usual methods; RRM, RBM, CAM, IRM and OCM.

3.1. π -electron delocalization

The π -electron delocalization is one of the most controversial concepts in theoretical and computational chemistry. The influences of this phenomenon on the various properties of molecules such as electronic energies, molecular structures, tautomeric compositions, reactivity of molecules and magnetic properties are frequently discussed and analyzed, especially in full delocalized or aromatic cases [32–34]. Since the aromaticity is not a physical observable; it is usually evaluated by some related molecular properties. Beside the aromatic systems, the partial delocalization of π -electrons in a wide variety of systems is observed. The most intriguing case of this kind, RAHB systems, is extensively investigated [35–38]. The cis enol forms of malonaldehyde and its derivatives are a set of simplest RAHB systems with effective coupling between the IMHB and partial π -electron delocalization. Indeed, a RAHB ring cannot be considered as a aromatic ring, however, partial delocalization of π -electrons, partial equalization of bond lengths, planarity, and extra stability of RAHB ring in malonaldehyde derivatives are reported. Similar to aromatic cases, one can suppose that the significance of partial delocalization can be also evaluated by some of their indices. Therefore, in the present study beside the bond order factor (λ') and geometrical factor of Gilli (λ), a set of geometrical, magnetic and electronic based indices, such as HOMA, NICS(0), NICS(1), PDI, ATI, FLU and FLU π , were examined to quantify the quasi-aromatic character of RAHB systems and their results are gathered in Table 1. Finally, it should be mentioned that these indicators are not explicit criteria of RAHB rings and only utilized for illustration of similarities between aromatic and quasi-aromatic systems.

The geometrical parameters are a rich source of data about the π -electron delocalization. In a RAHB system, π -ED tends to equalize the analogous single and double bonds. The HOMA is a geometrical based index, which directly related to the bond equalization and lies in the range 0–1. In other words, the RAHB rings with full delocalization/localization of π -electrons have maximum (1)/minimum (0) values of HOMA. Furthermore, Gilli [25] proposed the λ index to estimate the resonance process. Although, the λ values of RAHB systems are in good concordance with the π -ED, but this factor can only be applied for RAHB rings with the similar hetero atoms, such as MA. Evidently, in the RAHB systems with different hetero-atoms, the evaluation of the π -ED by λ index doesn't lead to accurate results. This problem was overcome by choosing λ' indicator of π -ED, by Gilli and coworkers [39]. They evaluated the π -ED of hetero-RAHB rings in terms of Pauling bond order, or more exactly bond number, n . According to their statement, the electron delocalization of the two sub-fragments are defined as



Scheme 1. The molecular structure of malonaldehyde derivatives.

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