

Hydrogen Bonds

A Critical Check for the Role of Resonance in Intramolecular Hydrogen Bonding

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Abstract: Although resonance-assisted H-bonds (RAHBs) are well recognized, the role of π resonance in RAHBs is controversial, as the seemingly enhanced H-bonds in unsaturated compounds may result from the constraints imposed by the σ skeleton. Herein the block-localized wave function (BLW) method, which can derive optimal yet resonance-quenched structures with related physiochemical properties, was employed to examine the correlation between π resonance and the strength of intramolecular RAHBs. Examination of a series of paradigmatic molecules with RAHBs and their saturated analogues showed that it is inappropriate to compare a conjugated system with its saturated counterpart, as they may have quite different σ frameworks. Nevertheless, com-

parison between a conjugated system and its resonance-quenched (i.e., electron-localized) state, which have identical σ skeletons, shows that in all studied cases, π resonance unanimously reduces the bonding distance by 0.111–0.477 Å, strengthens the bonding by 40–56%, and redshifts the D–H vibrational frequency by 104–628 cm⁻¹. Furthermore, there is an excellent correlation between hydrogen-bonding strength and the classical Coulomb attraction between the hydrogen-bond donor and the acceptor, which suggests that the dominant role of the electrostatic interaction in H-bonds and RAHBs originates from the charge flow from H-bond donors to acceptors through π conjugation.

Introduction

Owing to the current research endeavors in the fields of biological systems, nanoparticles, and innovative materials, significant interest in weak noncovalent interactions has been steadily growing, as these interactions are the driving forces behind protein folding, molecular self-assembly, and electron transfer. As a consequence, new kinds of interactions such as halogen bonds and tetrel bonds have been identified and analyzed. Among the noncovalent and directional interactions, however, H-bonding is the most important and ubiquitous.^[1] In the past decades, a number of strong and unconventional H-bonds, such as charge-assisted H-bonds (CAHBs),^[2] low-barrier H-

bonds (LBHBs),^[3] dihydrogen-bonds (DHBs),^[4] and resonance-assisted H-bonds (RAHBs)^[2a,5] have been recognized, and consequently it has been found that the strength of H-bonding can range from less than 1 to 40 kcal mol⁻¹.^[1f] Considering the wide range of bonding strength, Desiraju argued that H-bonding is an interaction without borders,^[6] whereas Steiner pointed out that an H-bond is composed of electrostatic, covalent, and dispersion contributions in variable weights.^[1f]

Among the new kinds of H-bonds, RAHBs may have received the most attention, both experimentally and computationally. The proposal of RAHBs originates from the observation of the crystal structures of β -diketo enols by Gilli and co-workers in the late 1980s, who ascribed the shortened H-bond distance to resonance.^[2a,5,7] In the instance of β -diketone enols, the intramolecular H-bond (IMHB) in which the donor (hydroxyl group) and acceptor (carbonyl oxygen atom) are connected through π -conjugated double bonds is enhanced by the resonance and results in the shortening of O...O distances (2.39–2.44 Å, as opposed to 2.7–3.0 Å in H-bonds without π conjugation).^[2a] This H-bond shortening is accompanied by lengthening of the hydroxyl group with a decrease of its vibrational frequency and abnormal downfield ¹H NMR chemical shift.^[5a] Extensive computational studies have been performed since the proposal of the RAHB concept, and most of them focused on the correlation among geometrical parameters and magnetic or spectroscopic properties. While the concept of RAHB highlights the cooperativity between π -electron delocalization and H-bonds,^[8] the growing interest in protein folding and computational simulations and engineering of proteins and DNAs requires a better understanding of the nature of IMHBs (includ-

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ing RAHBs), which so far is quite divergent. This echoes the controversy over the nature of H-bonds, which continues to be the subject of studies.^[9] H-bonds can be either purely electrostatic,^[1c,d,10] of partial covalent nature,^[4e,11] or even dispersive,^[1f] and current consensus is that H-bonds are predominantly electrostatic with minor covalent character.^[7a] For RAHBs, π -electron delocalization results in effective mixing of resonance forms, and is responsible for very strong H-bonds with low energy-barrier height for the proton-transfer reaction. For the instance of malonaldehyde (**1** in Figure 1), which is a prototypi-

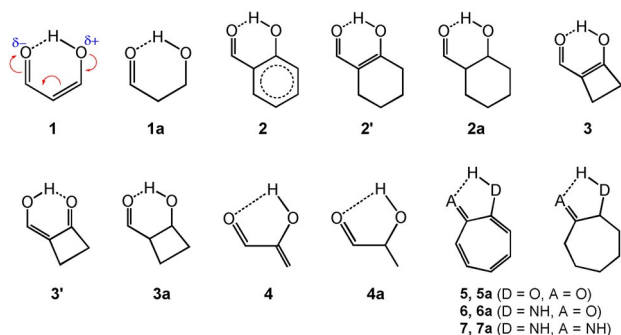


Figure 1. Molecules with IMHBs studied in this work.

cal enolone and has been extensively studied both experimentally and theoretically, the ground state can be treated as a linear combination of two tautomeric forms (enol-keto and keto-enol).^[5b,8a,12] This explanation implies a remarkable covalent nature of RAHB, like other very strong H-bonds. Indeed, Gilli and co-workers provided a general explanation of RAHB within their electrostatic covalent H-bond model (ECHBM),^[7a] which states that weak H-bonds are electrostatic in nature but their covalent character increases with increasing bond strength.

Interestingly, as Sanz et al. claimed, the stronger IMHBs in unsaturated compounds compared to their saturated analogues does not necessarily mean that there is a RAHB phenomenon, as this may simply result from the constraints imposed by the σ skeleton.^[13] This reminds us of the controversies over the existence of C–H...O H-bonding, as the seemingly short distances may originate from overall crystal stacking and are thus better labeled as van der Waals interaction,^[14] or whether there is any H-bonding between *ortho*-hydrogen atoms in planar biphenyl.^[15] Alkorta et al. also computed magnetic properties, which are quite sensitive to conjugation, as a probe for the RAHB phenomenon and found that neither the spin–spin coupling constants nor the proton chemical shifts provide clear evidence for the existence of RAHBs, and the enhanced stability of IMHBs in unsaturated compounds comes from the σ skeleton, which allows the oxygen atoms to be in closer proximity than in the saturated analogues.^[16] Mo and Beck investigated the mechanism of synergistic interplay between π delocalization and H-bonding interactions using an energy-decomposition scheme and showed that the enhanced interactions are mostly due to classical dipole–dipole (i.e., electrostatic) attraction, as resonance redistributes the electron

density and increases the dipole moments in interacting parts.^[17] However, we note that this work focused on intermolecular rather than intramolecular H-bonding, and the latter differs from the former, irrespective of whether the concerned H-bond is coupled with π conjugation or not.

In this work, we critically examined the impact of π conjugation on IMHBs by comparing the structural and spectral changes on quenching the resonance in the very same conjugated systems. This is achieved with the block-localized wave function (BLW) method,^[18] which is the simplest variant of ab initio valence bond (VB) theory^[19] and can self-consistently derive the wave function for an strictly electron localized (usually the most stable resonance) state. Góra et al. also employed a variant of ab initio VB theory, called complete active space VB (CASVB),^[20] in the exploration of resonance stabilization in RAHB systems and found that the resonance effects are negligible.^[21] However, the use of delocalized orbitals in their VB computations necessarily means that any particular VB structure is contaminated by all others, and consequently the resonance stabilization is underestimated. Importantly, the BLW method has ability to optimize geometries with computed spectroscopic and magnetic properties, and the computational data can be scrutinized and justified by experiments with model systems.

Results and Discussion

We studied a series of exemplary IMHB systems **1–7** together with their saturated counterparts **1a–7a** (Figure 1). Table 1 lists the major results.

Malonaldehyde (**1**) may be the iconic example for the concept of RAHB. In **1**, the π resonance shifts the electrons from the less electronegative hydroxyl oxygen atom to the more electronegative carbonyl oxygen atom through the central carbon–carbon double bond, and this leads to additional positive charge on the hydroxyl group and additional negative charge on the carbonyl group. These opposite additional charges generate additional (enhanced) electrostatic attraction. This attraction seems to be the cause of the much shorter H-bond distance (see Table 1). In accordance, the O–H vibrational frequency is notably redshifted by 638 cm^{−1} with reference to methanol (3842 cm^{−1}) or malonaldehyde itself with the OH group flipped out (3843 cm^{−1}) at the same level of theory. With the BLW method, the resonance is strictly turned off, and geometry optimization results in a greatly stretched OH...O distance, from 1.703 to 2.068 Å, and the O–H vibrational frequency drops to 3765 cm^{−1}, that is, redshifted by only 77 cm^{−1} compared with methanol. This comparative study with regular DFT and BLW methods clearly shows that the RAHB phenomenon in malonaldehyde is truly caused by the π resonance and has nothing to do with the σ framework. For its saturated analogue **1a**, the H-bond is even shorter than in the electron-localized state of **1**, and this further confirms the significant role of π resonance in malonaldehyde. The comparison between the BLW geometry of **1** and the DFT geometry of **1a** also suggests that the saturated analogue is more flexible for the formation of the IMHB in terms of varying the dihedral angles of

Table 1. Key optimized bond lengths [Å], stretching vibrational frequencies [cm⁻¹], and intramolecular H-bonding energies [kJ mol⁻¹] at the B3LYP/6-311 + G(d,p) level of theory.

Species	Method	R_{A-H}	R_{DH}	R_{CA}	R_{A-D}	$\tilde{\nu}_{DH}$	ΔE_{HB}
1	DFT	1.703	0.997	1.238	2.589	3204	53.8
	BLW	2.068	0.967	1.202	2.867	3765	27.9
1a	DFT	1.880	0.967	1.210	2.745	3723	24.8
	DFT	1.768	0.984	1.228	2.641	3416	46.2
2	BLW	1.999	0.966	1.201	2.823	3765	27.2
	DFT	1.648	1.000	1.241	2.552	3122	61.7
2'	BLW	2.000	0.967	1.203	2.817	3750	32.7
	DFT	2.187	0.966	1.210	2.880	3779	10.0
2a	DFT	2.154	0.979	1.233	3.102	3580	31.2
	BLW	2.631	0.965	1.202	3.300	3810	17.1
3	DFT	2.154	0.977	1.218	2.981	3604	30.5
	BLW	2.547	0.965	1.189	3.316	3808	17.1
3a	DFT	2.074	0.968	1.213	2.827	3741	15.3
	DFT	2.122	0.972	1.214	2.684	3679	25.6
4	BLW	2.233	0.966	1.198	2.778	3783	15.4
	DFT	2.108	0.970	1.208	2.683	3714	23.1
5	DFT	1.816	0.989	1.246	2.497	3387	52.9
	BLW	2.100	0.967	1.200	2.678	3765	23.4
5a	DFT	1.974	0.972	1.217	2.595	3674	31.2
	DFT	2.048	1.013	1.242	2.539	3531/3710	(47.9) ^[a]
6	BLW	2.264	1.001	1.198	2.668	3669/3804	(20.1) ^[a]
	DFT	2.151	1.016	1.214	2.648	3503/3594	(22.7) ^[a]
6a	DFT	2.026	1.015	1.301	2.532	3505/3706	(61.7) ^[a]
	BLW	2.232	1.002	1.261	2.658	3657/3801	(27.9) ^[a]
7	BLW	2.232	1.002	1.261	2.658	3657/3801	(27.9) ^[a]
	DFT	2.148	1.016	1.274	2.660	3492/3583	(30.9) ^[a]

[a] Values predicted with the correlation shown in Figure 4.

the hypothetical six-membered ring (see Figure 1). In other words, at least in malonaldehyde, the σ framework is unfavorable for the IMHB compared to its saturated counterpart.

At this point it would be helpful to estimate the strength of the IMHB in malonaldehyde. However, unlike intermolecular H-bonds, which can be easily evaluated through a supramolecular approach, difficulties linger in the proper evaluation of the strength of IMHBs. Hence, a few approximate approaches have been proposed,^[9c, 22] and among them the simplest and most effective one is to rotate the OH group about the O–C single bond by 180° from its H-bonding position and take the resulting energy variation as the H-bond energy.^[23] Notably, Wang et al. further compensated the steric effect involved in the rotation process, which is derived from a model system in which the H-bond donor is substituted by a methylene group.^[22c, 24] Here we simply used the rotation approach^[23] to estimate the H-bond strength in malonaldehyde. On flipping the hydroxyl group out, DFT computations show that the energy of malonaldehyde increases by 53.8 kJ mol⁻¹ (Table 1). However, if we strictly localize the π electrons, the energy change is only 27.9 kJ mol⁻¹. This value is very close to the energy change in the saturated analogue **1a** (24.8 kJ mol⁻¹). Thus, consistent with the geometrical changes, resonance nearly doubles the H-bonding strength in malonaldehyde. Moreover, there is a negative hyperconjugative interaction from the methylene group to the carbonyl group in **1a**. If this hyperconjugation effect is quenched, the OH...O distance would be slightly stretched from 1.880 Å in Table 1 to 1.915 Å but still much

shorter than the distance in the electron-localized state of **1** (2.068 Å).

If the central C–C double bond in malonaldehyde conjugated with other π components, we would expect a reduction of its conductivity from the hydroxyl group to the carbonyl group. This is reflected in *o*-hydroxybenzaldehyde (**2**), in which the central C–C double bond is part of a benzene ring, which would prefer cyclic six π electrons due to the aromatic stability.^[13b] As a consequence, the H-bonding in **2** is weaker than that in **1**, as evidenced by the H-bond distances (1.703 versus 1.768 Å), strengths (53.8 versus 46.2 kJ mol⁻¹), and O–H vibrational frequencies (3204 versus 3416 cm⁻¹). With the deactivation of resonance except for the cyclic aromaticity, as we treat the benzene ring as one block, we observe similar trends to those found in the localized states of **1**, except that the OH...O distance is a little shorter in localized **2** (1.999 Å) than in localized **1** (2.068 Å). This should be ascribed to the rigidity of the benzene ring. To verify this assumption, we also studied the reference molecule 2-hydroxy-1-cyclohexene-1-carboxaldehyde (**2'**), in which the H-bond is even shorter (1.648 Å) than in **1** (1.703 Å) and, accordingly, the bond strength is higher (actually, the highest in all systems studied in this work). Once the π conjugation is disabled, however, the H-bond is stretched to 2.000 Å, the same as in localized **2**. Thus, the comparison between **1** and **2** shows that the σ framework does have an impact on IMHBs, but the impact is very limited compared to the resonance effect. Furthermore, the σ impact may favor (e.g., in **2**) or disfavor (e.g., in **1**) the H-bond. The saturated analogue of both **2** and **2'** is **2a**, which exhibits a much weak H-bond, as shown by the bonding distance, the O–H vibrational frequency, and the bonding strength. In fact, unlike **1**, the H-bond in saturated analogue **2a** is longer than that in the electron-localized state of **2** or **2'**, which indicates that the σ skeleton in unsaturated **2** alone is more favorable to intramolecular H-bonding than in its saturated analogue **2a**.

Enols of derivatives of cyclobutene have been provided as evidence that the strength of IMHBs is dictated by the constraints imposed by the σ skeleton, namely, the four-membered ring.^[13a] Here we studied 2-hydroxy-1-cyclobutene-1-carboxaldehyde (**3**) together with its tautomer **3'** and their saturated counterpart 2-hydroxy-cyclobutanecarboxaldehyde (**3a**). At the B3LYP/6-311 + G(d,p) level of theory, **3'** is more stable than **3** by 17.1 kJ mol⁻¹, due to the Mills–Nixon effect, which favors the tautomer with the double bond external to the ring.^[13a] The IMHBs in both tautomers **3** and **3'** are actually very similar by any measure, though their strengths are much lower than those in **1** and **2**. Interestingly, we observed an inconsistency between H-bonding distance and strength in **3** and **3'**. Compared with **1a**, the H-bonding distances in **3** and **3'**, both of which have a value of 2.154 Å, are much longer than that in **1a** (1.880 Å), but the bonding strengths are higher (31.2 and 30.5 versus 24.8 kcal mol⁻¹). We suspect that this results from the enhanced electrostatic attraction and charge transfer due to the π resonance. To verify this assumption, we restrained the movement of π electrons and recomputed the H-bonding strengths at the DFT optimal geometries. The H-bonding strengths dramatically decrease to only 3.0 and

5.0 kJ mol⁻¹ for **3** and **3'**, respectively. Alternatively, we examined the Mulliken partial charges on the bonding H and O atoms in **3** and **3'** versus those in **1a**. While the charges on the hydrogen atoms are quite similar (0.281, 0.268, and 0.275 e in **3**, **3'** and **1a**, respectively), we observe enhanced negative charges on the carbonyl oxygen atoms in **3** and **3'** (−0.355 and −0.384 e, respectively) compared with **1a** (−0.277 e). Thus, in the cases of **3** and **3'**, it is the σ skeleton that restrains the approach of the carbonyl oxygen and hydroxyl hydrogen atoms, as otherwise the strong electrostatic attraction would shorten the H-bond distance. In other words, the σ framework restricts rather than assists the formation of a stronger IMHB in **3** and **3'**. To appreciate the strong electrostatic attraction resulting from the π conjugation, we plotted the electron-density difference (EDD) maps for **3** and **3'**, which correspond to the difference between the DFT and BLW electron densities and show the movement of electron density due to the π resonance (Figure 2).

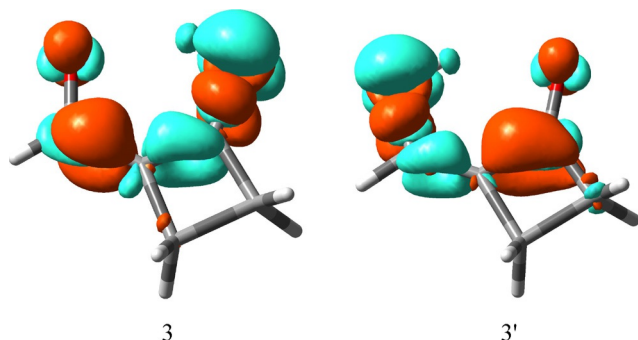


Figure 2. EDD isosurface maps with an isovalue of 0.003 a.u. showing the movement of electron density due to π conjugation in **3** and **3'**. The orange/cyan color indicates increasing/decreasing electron density.

With deactivation of the π resonance, the molecular structures of **3** and **3'** would relax with increased H-bonding distances, which are actually beyond the normal range of H-bonds with distances between the hydrogen and the acceptor longer than 2.5 Å. Nevertheless, still we observe significant bonding strengths (17.1 kJ mol⁻¹ for both **3** and **3'**), though the values are only half of those in fully delocalized molecules. These increased H-bonding strengths compared with the values at the DFT optimal geometries but with resonance deactivated (3.0 and 5.0 kJ mol⁻¹ for **3** and **3'**) highlight the Pauli repulsion between the carbonyl and hydroxyl groups in the latter geometries. The saturated counterpart of **3** and **3'** exhibits a shorter H-bond distance yet a lower bonding strength. This confirms the quite different σ skeletons in the conjugated **3** and **3'** and their saturated form **3a**.

2-Hydroxy-2-propanal (**4**) is also an example of framework constraint, as the IMHB is in an unfavorable orientation. Indeed, DFT optimization shows that the H-bond distance reaches 2.122 Å, and the O–H vibrational frequency is redshifted by only 163 cm⁻¹ with reference to methanol (3842 cm⁻¹). On flipping the hydroxyl group out of the bonding region, the H-bond strength becomes merely 25.6 kJ mol⁻¹. In fact, all the

data for **4** are quite close to those of its saturated reference 2-hydroxy-2-propanal (**4a**), as shown in Table 1. As the resonance strengths in **4** and **1** are expected to be comparable and their adiabatic resonance energies are 127.6 and 158.3 kJ mol⁻¹, respectively, disabling the conjugation in **4** similarly stretches the H-bond by 0.111 Å to 2.233 Å, and reduces the H-bonding strength to 15.4 kJ mol⁻¹. We expect that disabling the hyperconjugation effect in **4a** would lead to similar results.

Finally, we studied tropolone (**5**), aminotroponeimine (**7**), and their intermediate form 2-aminotropone (**6**) with unsaturated seven-membered rings, in addition to their saturated analogues. Interestingly, the amino groups in **6** and **7** are coplanar with the conjugated rings, but in their saturated analogues they are pyramidal, and consequently the H-bond donor and acceptor are not coplanar. These systems have been analyzed by Sanz et al., who showed that the concerned IMHBs are much stronger than those of their saturated analogues and the enhancement comes from “the much higher intrinsic basicity and acidity of the hydrogen-bond acceptor and donor groups”, which are not related to the π resonance.^[13c] Much like **4**, there is no direct π conjugation from the donor group DH to the acceptor group A in these systems. However, the H-bonding strength in **5** is comparable to the bonding energy in malonaldehyde (**1**), though the H-bond distance is a little longer, while the heteroatomic internuclear distance is shorter. With localization of π -electron pairs, the H-bond distance is significantly stretched to 2.100 Å, comparable to that in the electron-localized structure of **1** (2.068 Å). Accordingly, the H-bonding is greatly weakened to 23.4 kJ mol⁻¹ (by 56%), and the OH vibrational frequency is blueshifted by 378 cm⁻¹. The saturated analogue **5a** exhibits a normal IMHB with a strength of 31.2 kJ mol⁻¹ and H-bond distance of 1.974 Å. We note that the H-bond in **5a** is slightly stronger than that in the resonance-disabled form of **5**, as both the geometrical parameters and OH vibrational frequency show. This discrepancy is primarily due to the weak hyperconjugative interaction from the methylene group to the carbonyl group. For **6** and **7**, we were unable to estimate the H-bond strengths using the flipping approach, but both the structural parameters and vibrational frequencies similarly endorse the role of π resonance in their IMHBs. We agree with the hypothesis by Sanz et al. that there is enhanced basicity of the H-bond acceptor and/or the enhanced acidity of the H-bond donor in **5–7** compared with their saturated counterparts,^[13c] but here we demonstrate that these enhancements along with the enhanced H-bond originate from the π resonance.

To identify the possible correlations among various structural and spectral parameters, we focused on the type of OH...O H-bond in systems **1–5**, and considered their electron-delocalized and electron-localized structures, along with their saturated counterparts **1a–5a**. Often, an H-bond is characterized by the H-bond distance, but we found that the correlation between the H-bond strengths and distances is very poor (Figure 3A). For the H-bond donor (hydroxyl group), good correlation between its bond length and the stretching vibrational frequency is expected. Indeed, an excellent correlation is observed (Figure 3B). In fact, the H-bond donor itself is an excellent indica-

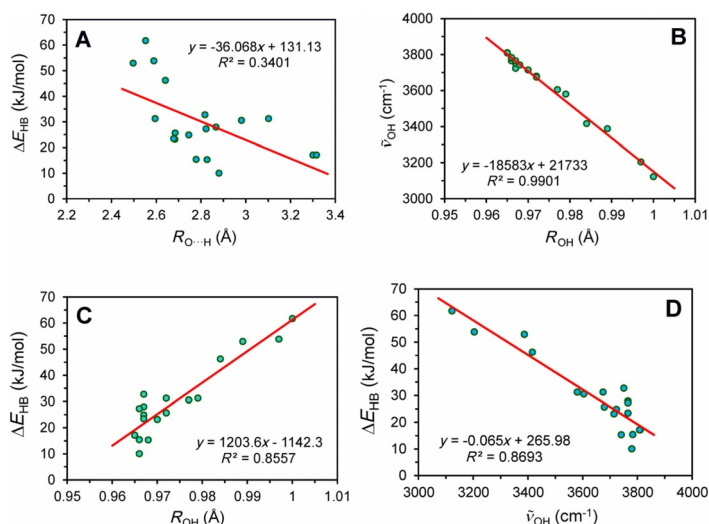


Figure 3. Correlations among H-bond strength ΔE_{HB} , H-bond distance $R_{\text{O}\cdots\text{H}}$, the distance R_{OH} , and the stretching vibrational frequency ν_{OH} of the hydroxyl group in the $\text{OH}\cdots\text{O}$ H-bonds in systems 1–5.

tor for the H-bond strength. Figures 3C and D show the good correlations of the bond strength with the bond length and the stretching vibrational frequency of the hydroxyl group.

As it is generally believed that electrostatic attraction plays the primary role in H-bonds, we used the Mulliken charges on the H-bond donor and acceptor to estimate the electrostatic energy [Eq. (1)] and explore its correlation with the H-bond strength in systems 1–5.

$$E_{\text{ele}} = \frac{q_{\text{O}}q_{\text{H}}}{R_{\text{O}\cdots\text{H}}} \quad (1)$$

In fact, the changes of the charges with the π resonance switched on and off also reflect the changes of the intrinsic basicity and acidity of the H-bond acceptor and donor groups. As Figure 4 shows, there is good linear relationship between the Coulomb electrostatic energy and the H-bond strength. However, we note that all energy components (except maybe the dispersion-energy term) contributing to the total bonding strength increase with increasing bonding strength.^[25] To visualize the change of the electrostatic energy in an RAHB with the π resonance shut down, we plotted the electrostatic po-

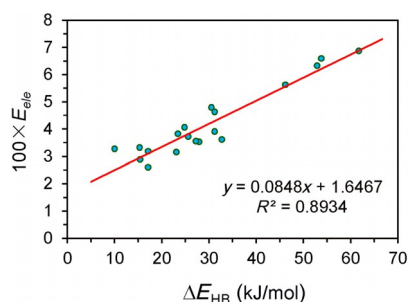


Figure 4. Correlation of the classical electrostatic energy E_{ele} between the H-bond donor (H) and acceptor (O) in the $\text{OH}\cdots\text{O}$ H-bonds in systems 1–5.

tential surfaces of selected molecules 1, 3, and 3' (Figure 5). Clearly, from the BLW (electron-localized) state to the DFT (electron-delocalized) state for a molecule with intramolecular RAHB, the boundary between the H-bond donor and acceptor becomes greener or even bluer, which suggests enhancement of the electrostatic attraction between the two groups.

As mentioned above, the H-bond strengths in 6 and 7 cannot be derived by the flipping approach. Given the good correlation between Equation (1) and the H-bond strength shown in Figure 4, we used the linear correlation to estimate the H-bonding energies in 6, 7, and their saturated counterparts. The projected H-bonding strengths in 6 and 7 are 47.9 and 61.7 kJ mol^{-1} , respectively, as opposed to 22.7 and 30.9 kJ mol^{-1} in their saturated counterparts. The comparison of 5–7 indicates that the strength of the IMHBs follows the order [donor, acceptor] = $[\text{NH}_2, \text{C}=\text{NH}] > [\text{OH}, \text{C}=\text{O}] > [\text{NH}_2, \text{C}=\text{O}]$.

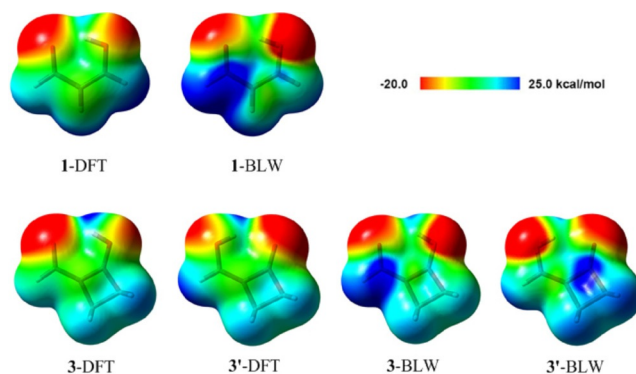


Figure 5. Electrostatic potentials on the 0.001 a.u. molecular surfaces of molecules 1, 3, and 3' computed at the B3LYP/6-311 + G(d,p) level of theory.

Conclusion

Ever since the proposal of the RAHB concept by Gilli et al. in the late 1980s,^[2a,5,7] there have been extensive studies to analyze and utilize the RAHB phenomenon. Yet there are disagreements over the nature of RAHB, as there is a possibility that the enhanced intramolecular H-bonding comes from the constraint of the σ skeleton. For instance, Yáñez and co-workers performed extensive computational studies on numerous examples and claimed that there is no evidence of RAHB effects.^[13,16,26] However, the use of a saturated analogue for an unsaturated system with RAHB is imperfect, as their σ frameworks are quite different. This is much like the proposals of isodesmic and homodesmotic model reactions in the study of aromaticity, in which reference molecules must be used. These reference molecules introduce unexpected effects and eventually seriously compromise the results.^[27] Indeed our present computations show that a σ skeleton may assist or constrain the IMHB if we simply compare the σ skeletons of a conjugated system and its saturated counterpart. The best reference

should be the molecule itself with the π conjugation disabled. According to the resonance theory, the resonance-disabled structure is actually a resonance structure and can be realized within the framework of VB theory.

As a variant of ab initio VB theory, the BLW method can clearly differentiate the σ frameworks of a conjugated system and its saturated counterpart, as it can derive optimal geometries with the π resonance quenched. In all exemplary cases studied in this work, we did not observe a single one in which the σ skeleton in the unsaturated form allows the H-bond donor and acceptor to be in closer proximity than in the saturated form. Significantly, with the conjugation turned off, the H-bond distance significantly stretches from 0.111 Å in 2-hydroxy-2-propenal (**4**) to 0.477 Å in 2-hydroxy-1-cyclobutene-1-carboxaldehyde (**3**), and is even longer than in the corresponding saturated analogue. In other words, resonance always assists the H-bonding by shortening the bond length, enhancing the bonding interaction, and redshifting the vibrational frequency.

We further used the point charges on the H-bond donor and acceptor to derive the classical electrostatic energy and showed that it has a good correlation with the H-bond strength. This linear correlation not only indicates the primary role of the electrostatic interaction in H-bonding, but also makes it clear that the enhanced H-bonding comes from the charge flow from the H-bond donor to the acceptor through the π conjugation,^[1d,26] and our BLW computations thus confirm the existence of the RAHB phenomenon.

Experimental Section

BLW method

Molecular orbital (MO) theory assumes that all electrons are in MOs that are extended (delocalized) to the whole system, whereas valence bond (VB) theory starts from localized atomic orbitals to build Lewis (resonance) structures and describes a conjugated system with several resonance structures.^[19d] Each resonance structure can be defined with a Heitler–London–Slater–Pauling (HLSP) function [Eq. (2)] in which M_L is the normalization constant, \hat{A} is the antisymmetrizer, and $\varphi_{2i-1,2i}$ is a bond function composed of non-orthogonal orbitals ϕ_{2i-1} and ϕ_{2i} (or a lone pair if $\phi_{2i-1} = \phi_{2i}$) [Eq. (3)]. In Equation (3) α and β are electron spin states.

$$\Psi_L = M_L \hat{A} (\phi_{1,2} \phi_{3,4} \cdots \phi_{2n-1,2n}) \quad (2)$$

$$\phi_{2i-1,2i} = \hat{A} \{ \varphi_{2i-1} \varphi_{2i} [\alpha(i)\beta(j) - \beta(i)\alpha(j)] \} \quad (3)$$

As such, the final wave function for an adiabatic state is a linear combination of several important VB functions and the resonance effect is quantified by the energy difference between the most stable resonance structure and the adiabatic state. To lower the computational costs involved in Equation (2) and combine the advantages of both MO and VB theories, we proposed the BLW method, in which a BLW corresponds to a unique electron-localized diabatic state (usually the most stable resonance state).^[18b,c,28] The fundamental assumption is that all electrons and primitive basis functions χ_{μ} can be divided into k subgroups (blocks), and each MO is block-localized and expanded in only one block. Assuming that there are m_i bases and n_i electrons for block i , we can

express block-localized MOs for this block as Equation (4) in which C is a coefficient that is optimized in a variety of ways.

$$\phi_j^i = \sum_{\mu=1}^{m_i} c_{\mu}^i \chi_{\mu}^i \quad (4)$$

Subsequently, the BLW for a closed-shell system is defined by using a Slater determinant as in Equation (5) in which Φ_k is the successive product of occupied orbitals in block k .

$$\begin{aligned} \Psi^{BLW} &= \det \left[(\phi_1^1)^2 (\phi_2^1)^2 \cdots (\phi_{n_1/2}^1)^2 \cdots (\phi_1^i)^2 \cdots (\phi_{n_i/2}^i)^2 \cdots (\phi_1^k)^2 \cdots (\phi_{n_k/2}^k)^2 \right] \\ &= \hat{A} [\Phi_1 \Phi_2 \cdots \Phi_k] \end{aligned} \quad (5)$$

Orbitals in the same subspace are subject to the orthogonality constraint, but orbitals belonging to different subspaces are nonorthogonal. The BLW method is available at the DFT level of theory with geometry-optimization and frequency-computation capabilities.^[18c,28] The major difference between the BLW method and many other ab initio VB methods such as CASVB^[20] lies in the definition of one-electron orbitals. In the BLW method, orbitals as shown in Equation (4) are strictly localized on blocks (functional groups or atoms), while in CASVB all orbitals are expanded with all basis functions and thus delocalized over the whole system.

Computational details

Standard B3LYP DFT calculations with the 6-311+G(d,p) basis set were performed throughout this work, as this level of theory has been assessed for IMHBs and shown to give comparable results to MP2/6-311+G(d,p).^[13b,c] All computations were performed with the GAMESS software,^[29] into which the BLW code was ported by us. The comparison of the geometrical parameters and vibrational frequencies computed with the standard B3LYP and BLW-DFT methods reveals the impact of the resonance on both the structures and energetics of molecules with intramolecular RAHBs.

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Conflict of interest

The authors declare no conflict of interest.

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