

Theoretical Study of Heteroatom Resonance-Assisted Hydrogen Bond: Effect of Substituent on π -delocalization

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ABSTRACT: *The concept of Resonance Assisted Hydrogen Bond (RAHB), which usually occurs in β diketons, has a remarkable role in chemistry. These molecules, which contain heteroatom particularly O and N, are species with biological interest in protein folding and DNA pairing. Therefore, the amplification of hydrogen bonds strength by substituents may be important in life sciences. In the current research, we have shown that the nature of hydrogen bond in the enol form of heteroatom RAHB systems has partial covalent and electrostatic character. Nonetheless, the strength of hydrogen bonds increases by means of three different groups of substituents, which cannot be attributed to the contributions of resonance structures. Parameters such as bond ellipticity, π delocalization indices and bond equalizations cannot help to prove the effect of conjugation on the strength of hydrogen bond in RAHB systems. It is shown by NBO that the primary and secondary hyperconjugative charge transfer caused by substituents help to amplify this type of hydrogen bond. We showed that the existence of π -conjugation is necessary only for transformation of electron from substituents to the hydrogen bond as an acceptor of electrons. The strength of RAHB has a rather good correlation with the distance between of two non-connected heteroatoms O and N according to reference [62].*

KEY WORDS: *Heteroatom RAHB, QTAIM, NBO, Resonance assisted hydrogen bond, π -delocalization*

INTRODUCTION

Hydrogen bonding, which was suggested by Huggins [1], Latimer & Rodebush [2] for first the time, is one of the most important interactions in chemical and biochemical reactions which occurs generally in aqueous and polar environments. This concept was cited by Lewis [3] in 1923 in his book on valence theory as "Bivalent Hydrogen". Since then, many books [4-9], reviews [10, 11] and various articles have appeared about hydrogen bonding. Hydrogen bond is considered as having a significant non-covalent interaction involving a polarized proton

donor (HX) and a high electronic density field (Y) which is generally formed by atoms containing lone pair orbital or π electrons [12, 13].

Due to the importance of hydrogen bond in natural science, many researchers have devoted their attention to study different aspects of this interaction. Their attempts relate particularly to the crucial roles played by H-bond in biological systems, such as molecular recognition that could be a basis for the creation of life [14-17], formation of higher order structure of peptides and nucleic acids

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and biochemical processes, specially enzymes catalyzed ones [18, 19]. Very strong hydrogen bonds are among the most interesting features of hydrogen bond categories which have essential roles in biochemical reactions and enzyme catalysis as transition state [20-23]. They differ from ordinary types in their stabilization energy. Very strong hydrogen bonds have been widely studied, both experimentally and theoretically [24-36]. This type of H-bonds has been classified into three fundamental types by *Gilli*: negative charged assisted hydrogen bond [(-)CAHB], positive charged assisted hydrogen bond [(+)CAHB] and resonance assisted hydrogen bond [RAHB] where the H-bond donor and acceptor are connected through π -conjugated double bonds [27].

Experimental investigation on this type of H-bond indicates that very strong hydrogen bonds always shows an unusual downfield ^1H NMR chemical shifts ($\delta_{\text{H}}=16-20$) with their proton highly deshielded [25]. On the other hand, it has been shown that the shortening of the $\text{O}\cdots\text{O}$ distance, in $\text{O}-\text{H}\cdots\text{O}$ systems is associated with a decrease of IR $\nu(\text{O}-\text{H})$ stretching frequencies up to 2560 cm^{-1} [24, 25].

Different studies have been carried out to explore the nature of very strong hydrogen bond in literatures [1, 10, 37, 38]. Although, ordinary ones are believed to be electrostatic in nature [10]. *Gilli et al.* have proposed that strong H-bonds have significant covalent characters [27]. The influence of π -electron delocalization on the characteristic of hydrogen bond interactions especially in RAHB has been analyzed and discussed by *Grabowski* [39].

On the other hand, *Alkorta et al.* [40], have investigated some examples of resonance assisted hydrogen bonds by theoretical NMR study. Their computed results show that the stronger intramolecular hydrogen bonds in unsaturated compounds are directly associated with the σ -skeleton of the molecule that allows the two heteroatoms (the HB donor and the HB acceptor) to be in closer proximity than in the saturated ones and the NMR properties of these molecules do not receive significant contributions from resonance.

We have studied the nature of very strong hydrogen bonds including RAHB in our previous work [12]. In the current research, the main purpose is to study the influence of π electron delocalization and hyperconjugation on the strength of H-bond as well as the nature of heteroatom RAHB in two different categories of compounds.

The structural, electronic and bonding properties of these compounds have been computed.

COMPUTATIONAL DETAILS AND THEORIES

The calculation of molecular geometries was done and their electronic wave functions were performed using Gaussian 2003 series of programs [41]. Geometry optimization was carried out at B3LYP/6-311++G** [42, 43] level of theory. Frequency analysis was also performed for the structures to make sure that they were minimum structures. *Bader's* Quantum Theory of Atoms In Molecules (QTAIM) was applied to obtain electronic parameters of our disred systems and more details about the nature of hydrogen bonds [44]. QTAIM is based on the analysis of electronic density topology and identifies chemical bond as a Bond Critical Point (BCP) and the corresponding Bond Paths (BP). AIM 2000 package [45] was used to find different types of Critical Points (CPs).

BCP and Ring Critical Point (RCP) were analyzed in terms of the following characteristics [44]. The electronic density $\rho(\mathbf{r})$ at the CP, its Laplacian, which is related to the bond interaction energy by a local expression of the virial theorem Eq(1) and the total electronic energy density at the CP, $H(\mathbf{r})$ Eq (2). For the latter its components were also considered: the potential electronic energy density (V) must be negative and the electronic kinetic energy density (G) which is always positive [46, 47]:

$$\left(\frac{\hbar^2}{4m}\right)\nabla^2\rho(\mathbf{r}) = 2G(\mathbf{r}) + V(\mathbf{r}) \quad (1)$$

$$H(\mathbf{r}) = G(\mathbf{r}) + V(\mathbf{r}) \quad (2)$$

Delocalization indices and ellipticities were also calculated for the important bonds of the systems.

Hyperconjugation is one of the mechanisms that can make more stable RAHB, which will be explained very briefly here. Orbital models predict that the mechanism of hyperconjugation induces partial double-bond character into what is formally a single bond in the cases a methyl group is linked to an unsaturated system. Hyperconjugation results from the interaction of electrons in a σ -bond (usually $\text{C}-\text{H}$ or $\text{C}-\text{C}$) with an adjacent empty (or partially filled) p-orbital or a π^* -orbital to give an extended molecular orbital that increases stability of the system by extension of the conjugation chain. Hyperconjugation is transfer of electron(s) from

a bonding orbital, ω_{ij} (defining a region, i,j) to an anti-bonding one, ω_{kj}^* (defining another region, k, j) [48, 49].

Two different types of hyperconjugation have been elaborated in literature, $\sigma \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$ donor-acceptor interactions are classified as the primary case and the secondary one is $\sigma \rightarrow \sigma^*$ [50].

Natural Bond Orbital (NBO) program [51], which is implemented in Gaussian 03 package was also used to studying the details of the hyperconjugation mechanism of methyl substituents by mainly focusing on charge transfer between donor and acceptor orbital participating in hyperconjugation. The NBO analysis introduced by Weinhold *et al.* [52-54] transforms the delocalized molecular orbitals into localized ones that are closely related to chemical bond concepts.

The stabilization energy E (2) associated with charge transfer between donor (i) and acceptor (j) can be evaluated by second-order perturbation theory analysis of the Fock matrix.

$$E(2) = \Delta E_{ij} = \Delta E_{CT} = -2 \frac{\langle i | \hat{F} | j \rangle^2}{\epsilon_j - \epsilon_i} \quad (3)$$

Where ϵ_i and ϵ_j are NBO orbital energies, and \hat{F} is the Fock operator. The quantities of transferred charge from a given donor orbital to a given acceptor orbital may be estimated again using the perturbation theory arguments, leading to the following approximate formula:

$$q_{CT} \approx 2 \left(\frac{\langle i | \hat{F} | j \rangle}{\epsilon_j - \epsilon_i} \right)^2 \quad (4)$$

RESULTS AND DISCUSSION

Geometrical properties

We have studied several systems which contain heteroatom RAHBs in both enol and keto forms. Our species are defined in Fig. 1 and can contain oxygen, nitrogen, sulfur and phosphorus. From the primary evidences in Table 1, it is clear that the enol form of O-H...N is the strongest one and its stabilization energy is approximately 17.30 kcal/mol. In fact, it seems that O-H...N RAHB has also the most important species because it plays a vital role in protein folding and DNA pairing. Moreover, this interaction is one of the

Table 1: Different heteroatom RAHB systems, Charge Density at BCP_{HB} , Stabilization Energy of HB and its Bond length.

Molecule	-X	-Y	[-2] ρ_{HB}	ΔE_{HB}^*	r_{HB} (Å°)
enol	-O	-N	5.66	17.30	1.679
	S-	-P	2.17	3.39	2.355
	-S	-N	3.81	8.63	1.882
	-O	-P	2.22	3.98	2.281
	-O	-S	4.26	9.80	2.051
keto					
	-O	-N	2.68	6.32	1.972
	S-	-P	no HB	no HB	no HB
	-S	-N	2.76	5.43	1.540
	-O	-P	no HB	no HB	no HB
	-O	-S	3.04	6.73	1.935

* Stabilization energy of RAHB (kcal/mole)

[-2] means that the reported values should be multiplied by 10^{-2} .

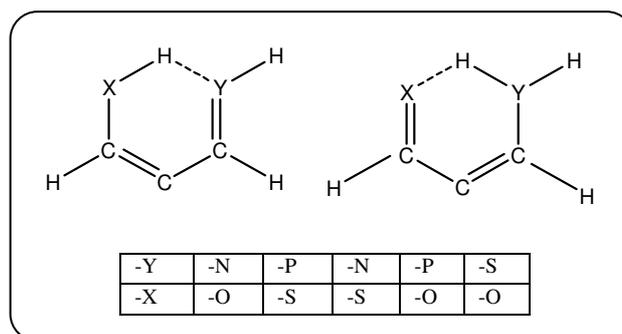


Fig 1: Schematic figures of several systems containing heteronuclear RAHB.

crucial features in crystal engineering [55]. For instance, the studies of O-H...N RAHBs have been conducted for the crystal structures of β -enamiones [29], β -ketoarylhydrazones [56], ketohydrazone-azo-enol [31] systems and many others. Hence, we have restricted our study to two different categories of compounds which contain O-H...N RAHBs. Schematic figures of investigated the systems are summarized in Fig. 2.

The compounds in Fig. 2 have a six member ring closed by H-bond. This ring contains a system, which is consisted of bonds; $H_5 - O_6, O_6 - C_1, C_1 = C_2, C_2 - C_3, C_3 = N_4$ (or $C_1 = N_2, N_2 - C_3$ and $C_3 = N_4$) and $N_4 \cdots H_5$. This ring is denoted by "core system" throughout the text. To examine the influence of electron

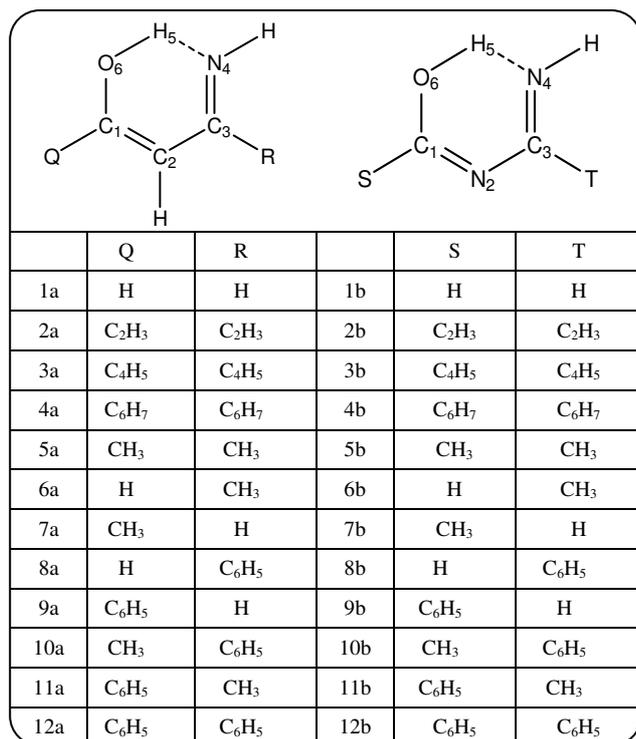


Fig 2: Schematic figures of investigated molecules containing N...H-O RAHB.

delocalization on the strength of H-bond and its stabilization energy, distinguishable types of substituents have been selected. Based on the different effects of substituents on hydrogen bond strength in Q and R (or S and T) position, they have been divided into three kinds: (1) Polyene, which are nearly in the plane of the core system and are expected to participate in conjugation, directly, (2) Methyl group which are responsible for the hyperconjugation mechanism and are considered to stabilize H-bond in this way (3) phenyl group which generally affects conjugation by donating electron to core system. The simultaneous effects of hyperconjugation and phenyl group have also been studied.

In present study, we are interested in analyzing the degree of conjugation in the core system involving C₁, C₂(N₂) and C₃ in two selected categories. The degree of conjugation has been measured by a generalized conjugation index ζ defined by the difference in bond length between the longest and shortest carbon-carbon (carbon-nitrogen) bonds, namely C₂-C₃ (N₂-C₃) and C₁=C₂ (C₁=N₂). These are discussed below in three different sections.

Polyene effects

From the geometrical properties of the core systems in Table 2, it is clear that by increasing the number of C=C in substituents, the N₄...H₅ distance will be declined from 2a(b) to 4a(b) in comparison with the reference molecule, 1a(b). It is also obvious that O₆-H₅ distance becomes longer than 1a (b) to 4a (b). By comparing C₁=C₂ (C₁=N₂) and C₂-C₃ (N₂-C₃) distances in these series, which are getting longer, the values of ζ have a decreasing order. So, these polyenes control H-bond strength by delocalization of electron through the core systems.

Methyl effects

From the results 5a(b) to 7a(b) in Table 2, it is clear that the methyl group affects N₄...H₅ distances which become shorter than the reference system 1a(b). The C₂-C₃ (N₂-C₃) distances are getting longer, except for 7a(b). We will see in NBO (Section 3.3) that methyl has hyperconjugation effect.

Phenyl effects

The investigated systems with phenyl substituents, are 8a (b), 9a (b) and 12 a(b). In all cases, the N₄...H₅ distance has decreasing order in comparison with the reference 1a(b). Phenyl affects C₂-C₃ (N₂-C₃) by making it longer when it is located in Q(S), while in R(T) position, this bond becomes shorter than the reference system 1a(b). Besides, when the phenyl ring is in Q and S positions it induces more stability than in R and T positions, because the phenyl ring is in same the plane as the core system, and π electrons will be delocalized better, but in R and T positions, due to steric hindrance of H outside of the core system, phenyl ring cannot stay in the same plane as the core system.

To study the effect of hyperconjugation together with the phenyl group effects, we have two other systems, that is, 10a (b) and 11a (b). When the phenyl group is in Q(S) and the methyl is located in R(T) position in 11a(b), there is a slightly more decrease in N₄...H₅ distance in comparison with 10a(b), and consequently more stable than 10a(b).

Table 2: Geometry parameters of the core system in categories a and b (all bond lengths are in Angstrom).

Species	O ₆ ... N ₄	N ₄ ... H ₅	O ₆ - H ₅	C ₁ = C ₂	C ₂ - C ₃	ξ ^a
1a	2.580	1.679	1.009	1.362	1.439	0.077
2a	2.544	1.622	1.016	1.375	1.444	0.069
3a	2.537	1.610	1.018	1.378	1.443	0.065
4a	2.534	1.605	1.019	1.379	1.443	0.064
5a	2.546	1.626	1.017	1.369	1.445	0.076
6a	2.563	1.656	1.029	1.360	1.450	0.090
7a	2.546	1.649	1.021	1.370	1.436	0.066
8a	2.554	1.643	1.015	1.362	1.449	0.087
9a	2.544	1.620	1.016	1.376	1.433	0.057
10a	2.537	1.613	1.018	1.369	1.446	0.077
11a	2.528	1.597	1.021	1.373	1.443	0.069
12a	2.520	1.585	1.023	1.375	1.442	0.067
Species	O ₆ ... N ₄	N ₄ ... H ₅	O ₆ - H ₅	C ₁ = N ₂	N ₂ - C ₃	ξ ^a
1b	2.526	1.634	1.016	1.296	1.381	0.085
2b	2.487	1.567	1.027	1.310	1.385	0.075
3b	2.483	1.557	1.029	1.313	1.384	0.071
4b	2.481	1.555	1.029	1.314	1.384	0.070
5b	2.490	1.573	1.025	1.304	1.387	0.083
6b	2.501	1.593	1.024	1.296	1.392	0.096
7b	2.516	1.590	1.024	1.306	1.377	0.071
8b	2.494	1.582	1.026	1.295	1.391	0.096
9b	2.502	1.589	1.021	1.310	1.370	0.059
10b	2.488	1.562	1.028	1.304	1.387	0.083
11b	2.477	1.548	1.032	1.309	1.381	0.072
12b	2.470	1.536	1.034	1.309	1.380	0.071

a. Generalized conjugated index (Angstrom) equal to longer and shorter CC bonds difference.

Quantum Theory of Atoms-In-Molecules Analysis

In the following sections, we will present the QTAIM parameters to see if they can support the correlation between stability (strength) of hydrogen bond and QTAIM parameters values for the substituted species in comparison with the unsubstituted compounds.

Intramolecular hydrogen bond energy

The stabilization energy related to intramolecular H-bonds has been estimated by using the local potential energy density proposed by *Espinosa* [58, 59]. In this

method, the stabilization energy of the hydrogen bond, E_{HB} , is equal to one-half of the local potential energy density at the hydrogen bond critical point multiplied by the atomic volume element a_0^3 .

$$E_{HB} = -\frac{a_0^3}{2} V_{CP} \approx -\frac{V_{CP}}{2} \quad (5)$$

All the estimated intramolecular RAHB stabilization energies in accordance with Eq. (5) are shown in Table 3, where there are significant differences between the strength of H-bond in unsubstituted molecules and their

Table 3: QTAIM parameters at the BCP of the $N_4...H_5$ bond and RCP (in atomic unit)

Species	QTAIM parameters at the BCP of the $N_4...H_5$ bond and RCP							
	ΔE_{HB}^*	ρ_{BCP} [-2]	$\nabla^2\rho_{BCP}$ [-1]	$\nabla^2\rho_{BCP}$ [-2]	$V_{BCP}(r)$ [-2]	$H_{BCP}(r)$ [-2]	ρ_{RCP} [-2]	$\nabla^2\rho_{RCP}$ [-1]
$\dagger R^2$ value	-	0.99	0.82	0.96	0.99	0.99	0.96	0.96
1a	17.30	5.66	1.11	4.11	-5.46	-1.35	1.90	1.25
2a	20.61	6.51	1.10	4.67	-6.58	-1.91	1.99	1.31
3a	21.39	6.70	1.09	4.77	-6.82	-2.04	2.00	1.32
4a	21.71	6.78	1.08	4.82	-6.93	-2.10	2.02	1.32
5a	20.40	6.46	1.09	4.62	-6.50	-1.88	1.98	1.31
6a	18.58	6.02	1.10	4.34	-5.92	-1.58	1.94	1.28
7a	18.83	6.06	1.11	4.39	-6.00	-1.60	1.92	1.29
8a	19.42	6.23	1.10	4.45	-6.19	-1.71	1.96	1.29
9a	20.69	6.51	1.10	4.47	-6.60	-1.91	2.01	1.32
10a	21.24	6.67	1.09	4.75	-6.77	-2.02	2.01	1.32
11a	22.31	6.91	1.08	4.91	-7.11	-2.20	2.04	1.34
12a	23.12	7.11	1.07	5.03	-7.37	-2.34	2.06	1.36
	ΔE_{HB}^*	ρ_{BCP} [-2]	$\nabla^2\rho_{BCP}$ [-1]	$\nabla^2\rho_{BCP}$ [-2]	$V_{BCP}(r)$ [-2]	$H_{BCP}(r)$ [-2]	ρ_{RCP} [-2]	$\nabla^2\rho_{RCP}$ [-1]
R^2 value	-	0.99	0.93	0.98	0.99	0.99	0.94	0.96
1b	20.01	6.32	1.12	4.60	-6.39	-1.79	2.19	1.43
2b	24.66	7.44	1.07	5.27	-7.87	-2.59	2.29	1.50
3b	25.38	7.62	1.05	5.36	-8.10	-2.73	2.30	1.51
4b	25.60	7.67	1.05	5.39	-8.15	-2.76	2.31	1.51
5b	24.30	7.34	1.07	5.21	-7.73	-2.51	2.28	1.50
6b	22.84	7.01	1.08	4.98	-7.26	-2.28	2.25	1.48
7b	22.93	7.02	1.10	5.01	-7.31	-2.30	2.26	1.48
8b	23.62	7.21	1.07	5.11	-7.53	-2.43	2.29	1.50
9b	22.90	7.00	1.10	5.03	-7.30	-2.27	2.28	1.48
10b	25.11	7.55	1.06	5.33	-8.00	-2.67	2.30	1.52
11b	26.10	7.80	1.03	5.44	-8.32	-2.88	2.33	1.54
12b	27.90	8.04	1.01	5.58	-8.64	-3.06	2.36	1.56

* Stabilization energy of RAHB (kcal/mole), $\dagger R^2$ value of correlation between QTAIM parameter and ΔE_{HB}^* , [-x] means that the reported value should be multiplied by 10^{-x} .

substituted ones. The increasing order of H-bond strength in substituted molecules in three groups of substituents are the same as the decreasing order of $N_4 \cdots H_5$ distance in both categories a and b. The maximum values for H-bond strength belong to 12a and 12b and are 23.12 and 27.90 kcal/mol respectively.

QTAIM parameters at BCP of $N_4 \cdots H_5$ and RCP

It is shown by QTAIM parameters at BCP of $N_4 \cdots H_5$ and RCP of the ring which is closer to H-bond that the growth of H-bond stabilities are accompanied with increase in electron density at the BCP. Moreover, there are good correlations between stability of our species with QTAIM parameters such as G, V and H as presented in Table 3. Correlation R^2 values for G, V and H for category a are 0.96, 0.99 and 0.99, and for b are 0.98, 0.99 and 0.99, respectively. There are also good correlations between $\rho_{RCP}(r)$, $\rho_{BCP}(r)$ and also $\nabla^2\rho_{RCP}(r)$ with stabilization energy of $N_4 \cdots H_5$. Their R^2 values for category a are 0.96, 0.99 and 0.96, respectively, and the corresponding values for b are 0.94, 0.99 and 0.96, respectively.

The chemical nature of RAHB

To describe the nature of the bond in RAHB, we are in position to use some QTAIM parameters in its BCP, Laplacian of $\rho(r)$, $\nabla^2\rho_{BCP}$, in Eq. (1). A negative $\nabla^2\rho_{BCP}$, shows the excess potential energy at BCP. This means that electronic charge is concentrated in the inter-nuclear region, and it has shared (or covalent) interactions. A positive $\nabla^2\rho_{BCP}$ reveals that the kinetic energy contribution is greater than the potential energy, and shows depletion of electronic charge along the bond path. This is a closed shell (or electrostatic) interactions. The electronic energy density $H(r)$ at BCP is given by Eq. (2). There is sometimes a bond with covalent character at BCP with negative $H(r)$ from Eq. (2), namely $|V(r)| > |G(r)|$, and simultaneously, the condition from Eq. (1) is $|V(r)| < 2G(r)$ which gives a positive Laplacian ∇^2 (closed-shell interaction). Consequently, they must be termed as bonds with partially covalent and partially electrostatic [60]. Therefore, we would say that the nature of this hydrogen bond $N_4 \cdots H_5$ for all compounds, namely, 1a-12a and 1b-12b, are partially covalent and partially electrostatic. As the value for H becomes more

negative, the percentage of covalent character will increase, and the hydrogen bond will get stronger. The ascending order shows that the covalent attribution in $N_4 \cdots H_5$ is enhanced by increasing π -delocalization. For comparison, we have to remember that normal hydrogen bonds such as that in H_2O are characterized as electrostatic (closed-shell) interaction; a $\rho(r)$ value at the BCP which lies within the range 0.002, 0.04 a.u. and positive values for both $\nabla^2\rho_{BCP}$ and $H(r)$ at the BCP [61].

delocalization effects in strength of RAHBs

To examine the effects of π -delocalization in more details, we need some parameters which would demonstrate the effects more precisely. The results of electron delocalization index (EDI) of bonds in the core system are reported in Table 4. Sum1 in Table 4 is summation of EDI of all bonds in the core system (six bonds), Sum2 is summation EDI of five bonds (except $N_4 \cdots H_5$ bonds). Hydrogen bond is actually a donor and acceptor bond. It depends on the attached group to the hydrogen bond. If a group is electron donating one, the hydrogen bond will be getting stronger and will have more EDI; otherwise, vice versa. RAHB is a strong hydrogen bond, because it is in six-member ring containing conjugated double bond. As shown by results in Table 4, all substituents give electron to the core system, and the core system can transfer electrons to $N_4 \cdots H_5$ through conjugated double bond. Sum1 and Sum2 show the provided electrons by substituents do not stay in conjugated system of the core systems, but go to the hydrogen bond $N_4 \cdots H_5$, whose its EDI increases.

In addition to analyzing delocalization of important bonds, it is useful to introduce another QTAIM parameter which would measure the extent of conjugation. Any quantity derived from the Hessian's eigenvalues, such as Laplacian, is invariant under the choice of coordinate system used. It has been proposed to use eigenvalues λ_1 , λ_2 and λ_3 of the Hessian of ρ . The ratio of $|\lambda_1|$ and $|\lambda_2|$ measure the disparity between two orthogonal curvatures and leads to the so-called ellipticity ε . This quantity is defined as $(\lambda_1/\lambda_2) - 1$ and ranges between zero and infinity. The first term is always positive and is manifestly larger than or equal to 1, because of $|\lambda_1| \geq |\lambda_2|$. The ellipticity

Table 4: Electron delocalization index (EDI) of bonds in the core system in categories a and b.

Species	$N_4 \cdots H_5$	O-H	C-O	$C_1 = C_2$	$C_2 - C_3$	$C_3 = N_4$	Sum2 [*]	Sum1 [*]
1a	0.147	0.467	1.049	1.520	1.163	1.541	5.740	5.887
2a	0.162	0.452	1.021	1.431	1.145	1.454	5.503	5.665
3a	0.165	0.448	1.017	1.408	1.129	1.415	5.417	5.582
4a	0.167	0.447	1.012	1.375	1.123	1.409	5.366	5.533
5a	0.162	0.454	1.027	1.479	1.141	1.482	5.583	5.745
6a	0.155	0.463	1.053	1.529	1.130	1.496	5.671	5.826
7a	0.155	0.461	1.028	1.475	1.130	1.523	5.617	5.773
8a	0.158	0.455	1.058	1.483	1.123	1.462	5.581	5.739
9a	0.162	0.448	1.021	1.426	1.158	1.509	5.562	5.724
10a	0.165	0.450	1.029	1.434	1.123	1.451	5.487	5.652
11a	0.169	0.443	1.021	1.431	1.121	1.466	5.482	5.651
12a	0.173	0.438	1.021	1.398	1.127	1.436	5.420	5.593
Species	$N_4 \cdots H_5$	O-H	C-O	$C_1 = N_2$	$N_2 - C_3$	$C_3 = N_4$	Sum2 [*]	Sum1 [*]
1b	0.157	0.456	1.027	1.383	1.087	1.509	5.462	5.619
2b	0.176	0.435	0.998	1.297	1.064	1.422	5.216	5.392
3b	0.179	0.429	0.993	1.276	1.058	1.390	5.146	5.325
4b	0.180	0.426	0.989	1.265	1.050	1.374	5.104	5.284
5b	0.175	0.439	1.005	1.336	1.066	1.449	5.295	5.470
6b	0.170	0.443	1.031	1.384	1.053	1.459	5.370	5.540
7b	0.169	0.440	1.001	1.330	1.092	1.470	5.333	5.502
8b	0.173	0.437	1.033	1.359	1.073	1.426	5.328	5.501
9b	0.168	0.437	0.993	1.287	1.082	1.470	5.269	5.437
10b	0.177	0.432	1.004	1.308	1.046	1.415	5.205	5.382
11b	0.183	0.429	0.999	1.286	1.050	1.424	5.188	5.371
12b	0.186	0.423	0.995	1.268	1.047	1.393	5.126	5.312

• Sum1 is summation of EDI of all bonds in core system (six bonds), Sum2 is summation of EDI of five bonds (except N-H bond).

at BCP measures the extent to which ρ is elongated in one direction compared to another, and both are perpendicular to the Atomic Interaction Line (AIL). In the case of multiple bonds, the ellipticity can acquire an interpretation as a quantitative index of the π -character of the double bonds. It has been shown that ellipticity can interpret conjugation effects as well as hyperconjugation [61].

The ellipticities of two bonds which are anticipated to contribute to the conjugation of the core system are shown in Table 5. Ellipticities for $C_1 = C_2$ ($C_1 = N_2$) and

$C_2 - C_3$ ($N_2 - C_3$) show that there is no regular order in ϵ changes. In spite of the reduction in ϵ_1 values and an increase ϵ_2 in most cases, these changes do not have the same order as H-bond strength or BCP electron density.

The most important feature of this type of RAHB is the distance between two heteroatoms $O_6 \cdots N_4$. All substituents cause to decrease the distance between two heteroatoms $O_6 \cdots N_4$. The correlation between H-bond strength and $O_6 \cdots N_4$ distance are rather good and R^2

Table 5: Bond ellipticities of core system in a and b categories.

Species	λ_{1C1-C2}	λ_{2C1-C2}	ϵ_1	λ_{1C2-C3}	λ_{2C2-C3}	ϵ_2	$\epsilon_1-\epsilon_2$
1a	-0.708	-0.532	0.330	-0.592	-0.511	0.159	0.171
2a	-0.692	-0.529	0.308	-0.589	-0.506	0.165	0.144
3a	-0.687	-0.528	0.302	-0.590	-0.506	0.167	0.135
4a	-0.686	-0.528	0.298	-0.591	-0.506	0.168	0.131
5a	-0.698	-0.523	0.335	-0.583	-0.500	0.165	0.170
6a	-0.710	-0.529	0.342	-0.579	-0.501	0.156	0.186
7a	-0.695	-0.522	0.331	-0.596	-0.510	0.169	0.162
8a	-0.784	-0.530	0.336	-0.577	-0.489	0.158	0.178
9a	-0.685	-0.522	0.311	-0.599	-0.510	0.174	0.137
10a	-0.695	-0.520	0.338	-0.581	-0.497	0.169	0.169
11a	-0.687	-0.520	0.322	-0.586	-0.501	0.169	0.153
12a	-0.685	-0.521	0.315	-0.584	-0.498	0.173	0.142
Species	λ_{1C1-N2}	λ_{2C1-N2}	ϵ_1	λ_{1N2-C3}	λ_{2N2-C3}	ϵ_2	$\epsilon_1-\epsilon_2$
1b	-0.866	-0.738	0.173	-0.679	-0.649	0.047	0.126
2b	-0.836	-0.717	0.166	-0.678	-0.639	0.060	0.106
3b	-0.832	-0.713	0.166	-0.679	-0.638	0.064	0.102
4b	-0.830	-0.711	0.166	-0.679	-0.637	0.065	0.101
5b	-0.847	-0.722	0.172	-0.672	-0.640	0.050	0.122
6b	-0.865	-0.736	0.175	-0.664	-0.635	0.046	0.129
7b	-0.847	-0.724	0.170	-0.685	-0.651	0.052	0.118
8b	-0.862	-0.734	0.176	-0.664	-0.633	0.048	0.127
9b	-0.834	-0.720	0.160	-0.692	-0.654	0.058	0.101
10b	-0.845	-0.721	0.172	-0.672	-0.638	0.053	0.119
11b	-0.835	-0.719	0.162	-0.678	-0.642	0.056	0.106
12b	-0.832	-0.717	0.161	-0.679	-0.640	0.060	0.101

values are 0.998 and 0.995 for series a and b respectively. It seems that these substituents influence on the core skeleton by structural factors and make it more suitable for H-bonding interactions in comparison with the unsubstituted molecules. These results show that as hydrogen bond strength increases, the attracting force between the two unconnected heteroatoms increases too.

NBO results and hyperconjugation

The effect of hyperconjugation is discussed here for species with CH₃ substituents in 5a, 6a, 7a, 10a and 11a

(or 5b, 6b, 7b, 10b and 11b) in both Q and R (or S and T) positions. The optimized structures of these molecules is shown in Fig 3. As the results in Table 6 show, both cases of hyperconjugation can be detected in the above-mentioned molecules, though the primary hyperconjugation has noticeable role in comparison with the secondary case, so that the $\sigma \rightarrow \pi^*$ donor-acceptor interaction takes up more than 67% portion of q_{CT} . The results of hyperconjugative charge transfer are presented in Tables 6. These charge transfers can be divided into two categories. The first category is the

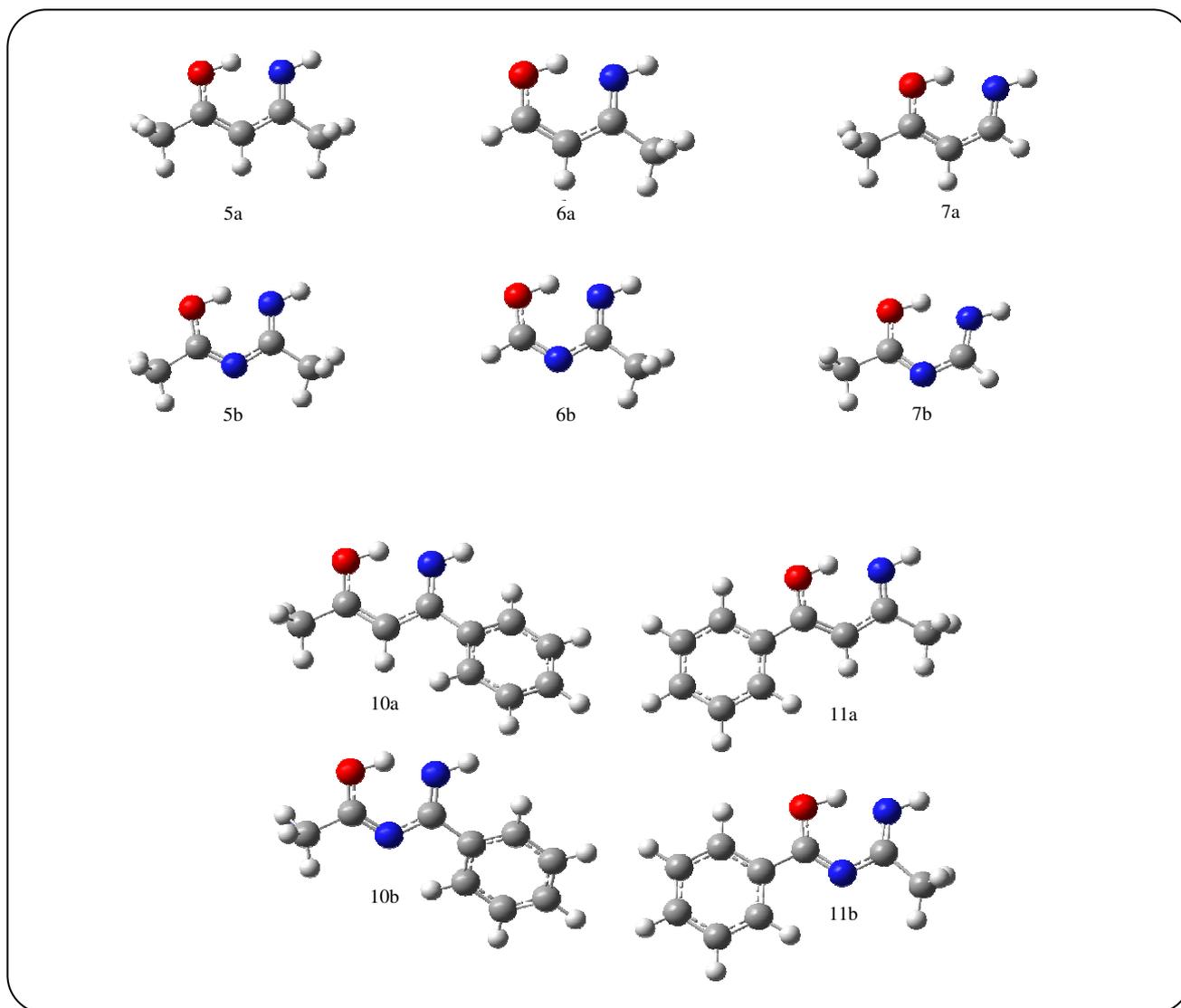


Fig. 3: Optimized structures of molecules contain Methyl Group.

charge transfer including $\sigma_{\text{C-H}} \rightarrow \sigma_{\text{C}_1-\text{C}_2}^*$, $\sigma_{\text{C-H}} \rightarrow \pi_{\text{C}_1-\text{C}_2}^*$ and $\sigma_{\text{C-H}} \rightarrow \sigma_{\text{C}_1-\text{O}_6}^*$ (or $\sigma_{\text{C-H}} \rightarrow \sigma_{\text{C}_1-\text{N}_2}^*$, $\sigma_{\text{C-H}} \rightarrow \pi_{\text{C}_1-\text{N}_2}^*$ and $\sigma_{\text{C-H}} \rightarrow \sigma_{\text{C}_1-\text{O}_6}^*$) from C-H belonging to methyl connected to the core system in Q (or S) position. This type of charge transfers clearly causes an increase in electron density in the core system, which makes stronger hydrogen bond.

The second category of hyperconjugative charge transfers are $\sigma_{\text{C-H}} \rightarrow \sigma_{\text{C}_3-\text{N}_4}^*$, $\sigma_{\text{C-H}} \rightarrow \pi_{\text{C}_3-\text{N}_4}^*$ and $\sigma_{\text{C-H}} \rightarrow \sigma_{\text{C}_3-\text{C}_2}^*$ (or $\sigma_{\text{C-H}} \rightarrow \sigma_{\text{C}_3-\text{N}_2}^*$) from C-H belonging to methyl connected to the core system in R or T.

This type of charge transfer increases the charge of N_4 , making it a better H^+ acceptor which finally it creates stronger hydrogen bond. Hence, hyperconjugative charge transfer can help to make stronger hydrogen bond in the species including methyl groups.

CONCLUSIONS

The purpose of this research was to use the computed results to study the nature and mechanism of hydrogen bonding in different series of heteroatom RAHB systems which would allow a better understanding of experimental evidences. In accordance with our calculated results at B3LYP/6-311++G** level of theory,

Table 6: Donor-acceptor interaction in Hyperconjugation and results of Second-order perturbation theory analysis of the Fock matrix within the NBO Basis (In category a & b).

Molecule	Position: Charge transfer	ΔE_{CT}^*	$\Delta q_{CT} \uparrow [10^{-3}]$	$\sigma \rightarrow \pi^* \%$
5a	R: $\sigma_{C-H} \rightarrow \sigma_{C_3-N_4}^*$	5.15	7.62	$\Delta q_{CT} : 67.7\%$ $\Delta E_{CT} : 49.1\%$
	$\sigma_{C-H} \rightarrow \pi_{C_3-N_4}^*$	9.04	30.13	
	$\sigma_{C-H} \rightarrow \sigma_{C_3-C_2}^*$	3.91	6.25	
	Q: $\sigma_{C-H} \rightarrow \sigma_{C_1-C_2}^*$	4.20	6.00	
	$\sigma_{C-H} \rightarrow \pi_{C_1-C_2}^*$	8.63	29.03	
	$\sigma_{C-H} \rightarrow \sigma_{C_1-O_6}^*$	5.07	8.60	
		36.00	87.63	
6a	R: $\sigma_{C-H} \rightarrow \sigma_{C_3-N_4}^*$	5.22	7.61	$\Delta q_{CT} : 68.5\%$ $\Delta E_{CT} : 49.0\%$
	$\sigma_{C-H} \rightarrow \pi_{C_3-N_4}^*$	9.14	30.13	
	$\sigma_{C-H} \rightarrow \sigma_{C_3-C_2}^*$	3.97	6.24	
		18.33	43.98	
7a	Q: $\sigma_{C-H} \rightarrow \sigma_{C_1-C_2}^*$	4.19	5.89	$\Delta q_{CT} : 66.0\%$ $\Delta E_{CT} : 48.2\%$
	$\sigma_{C-H} \rightarrow \pi_{C_1-C_2}^*$	8.65	29.03	
	$\sigma_{C-H} \rightarrow \sigma_{C_1-O_6}^*$	5.11	9.08	
		17.95	44.00	
10a	Q: $\sigma_{C-H} \rightarrow \sigma_{C_1-C_2}^*$	4.20	6.02	$\Delta q_{CT} : 66.6\%$ $\Delta E_{CT} : 48.3\%$
	$\sigma_{C-H} \rightarrow \pi_{C_1-C_2}^*$	8.63	28.04	
	$\sigma_{C-H} \rightarrow \sigma_{C_1-O_6}^*$	5.05	8.60	
		17.88	42.66	
11a	R: $\sigma_{C-H} \rightarrow \sigma_{C_3-N_4}^*$	5.10	7.47	$\Delta q_{CT} : 68.9\%$ $\Delta E_{CT} : 49.9\%$
	$\sigma_{C-H} \rightarrow \pi_{C_3-N_4}^*$	9.00	30.15	
	$\sigma_{C-H} \rightarrow \sigma_{C_3-C_2}^*$	3.93	6.12	
		18.03	43.74	
5b	T: $\sigma_{C-H} \rightarrow \sigma_{C_3-N_4}^*$	5.40	8.08	$\Delta q_{CT} : 68.2\%$ $\Delta E_{CT} : 49.0\%$
	$\sigma_{C-H} \rightarrow \pi_{C_3-N_4}^*$	9.74	32.68	
	$\sigma_{C-H} \rightarrow \sigma_{C_3-N_2}^*$	4.38	7.25	
	S: $\sigma_{C-H} \rightarrow \sigma_{C_1-N_2}^*$	4.22	6.34	
	$\sigma_{C-H} \rightarrow \pi_{C_1-N_2}^*$	9.46	32.68	
	$\sigma_{C-H} \rightarrow \sigma_{C_1-O_6}^*$	4.95	8.79	
		39.15	95.82	
6b	T: $\sigma_{C-H} \rightarrow \sigma_{C_3-N_4}^*$	5.46	8.08	$\Delta q_{CT} : 67.6\%$ $\Delta E_{CT} : 50.1\%$
	$\sigma_{C-H} \rightarrow \pi_{C_3-N_4}^*$	9.92	32.67	
	$\sigma_{C-H} \rightarrow \sigma_{C_3-N_2}^*$	4.42	7.55	
		19.80	48.30	

Table 6: Continued

7b	S: $\sigma_{C-H} \rightarrow \sigma_{C_1-N_2}^*$	4.14	6.04	Δq_{CT} : 69.3 % ΔE_{CT} : 51.2 %
	$\sigma_{C-H} \rightarrow \pi_{C_1-N_2}^*$	9.60	33.98	
	$\sigma_{C-H} \rightarrow \sigma_{C_1-O_6}^*$	5.02 18.76	8.99 49.01	
10b	S: $\sigma_{C-H} \rightarrow \sigma_{C_1-N_2}^*$	4.22	6.28	Δq_{CT} : 68.4 % ΔE_{CT} : 49.8 %
	$\sigma_{C-H} \rightarrow \pi_{C_1-N_2}^*$	9.43	32.68	
	$\sigma_{C-H} \rightarrow \sigma_{C_1-O_6}^*$	5.02 18.67	8.79 47.75	
11b	T: $\sigma_{C-H} \rightarrow \sigma_{C_3-N_4}^*$	5.36	7.76	Δq_{CT} : 68.7 % ΔE_{CT} : 49.9 %
	$\sigma_{C-H} \rightarrow \pi_{C_3-N_4}^*$	9.67	32.68	
	$\sigma_{C-H} \rightarrow \sigma_{C_3-N_4}^*$	4.36 19.39	7.01 47.54	

*Charge transfer Stabilization energy (kcal/mol), [†] Quantity of transferred charge (a.u.), the reported value should be multiplied by 10^{-3} .

these hydrogen bonds have partially covalent and partially electrostatic character.

Three different groups of substituents have affected the HB-strength and increased it. However, neither geometrical properties nor QAIM analysis showed any participation of conjugation with HB-strength amplification increases and all the calculated parameters, which could reveal the degree of π -delocalized electron in the core system, did not have any good correlation with HB-strength.

It is evident from the results that the increase of HB-strength in this special category of compounds is more affected by structural factors rather than by the resonance assisted procedure. There are in fact fine correlations between $O_6 \dots N_4$ distances and HB-strength in both series. R^2 value are 0.92 and 0.92 in series a and b respectively. These results suggest that substituents allow the HB donor and acceptor to be in closer vicinity which, in turn, induces stronger HB.

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