# Relation between π-Electron Localization/Delocalization and H-Bond Strength in Derivatives of *o*-Hydroxy-Schiff Bases[†]

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stronger HB   weaker HB
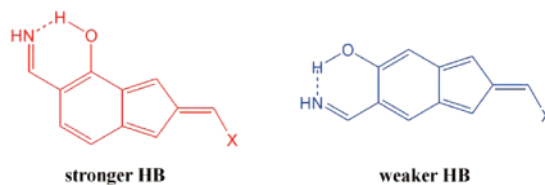
Detailed investigations of electronic effects taking place within the molecular system of *o*-hydroxy Schiff bases have been performed. The analysis of geometry, local and global aromaticity, selected AIM-based parameters, and finally, π-electron currents induced in the systems under consideration have been performed on the basis of quantum chemical calculations at the B3LYP/6-311+G** level of theory. The relation between localization/delocalization of π-electrons within the whole system has been described. It has been shown that the character of the bond which is common to the phenylic ring and the quasi-ring formed as a result of H-bond formation has a crucial impact on the strength of H-bonding. The strongest H-bonds can be observed for the systems in which the sequence of formally single and double bonds within the H-bridged quasi-ring enable a π-electronic coupling. These observations indicate that π-electron effects play a fundamental role in the stabilization of the hydrogen bridge within *o*-hydroxy Schiff bases. Analysis of π-ring currents induced by a magnetic field perpendicular to the molecular plane of selected analyzed systems confirms these conclusions.

Introduction

o-Hydroxy Schiff bases represent an important class of compounds that are of great interest to the investigators mostly because of the intramolecular H-bond.[1,2] Depending on the position of proton in the H-bond, the *o*-hydroxy Schiff bases exhibit two tautomeric forms: enol−imine and keto−enamine (Figure 1). In the latter case, a proton transfer may cause a change in the electron structure: the electronic and protonic states are clearly coupled, and an intramolecular charge transfer may occur. Hence, a zwitterionic structure may appear.[3,4]
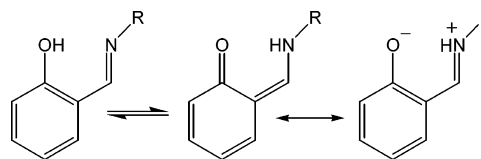

FIGURE 1. Tautomeric forms of a simple *o*-hydroxy Schiff base.

The above-mentioned tautomerism is closely related to photo-, thermo-, and solvatochromic properties observed in Schiff bases,[5−8] and a variety of their applications were revealed in both theoretical and experimental investigations.[9−13] Important aspects of the imine formation mechanism in physiological tempering of human immune system and also antitumor and

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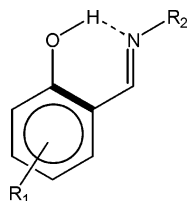
FIGURE 2. Scheme of substituted *o*-hydroxy Schiff base. The CC bond common to the phenylic ring and the chelating chain is represented by a bold line. Within the text this bond has been labeled as B_c. The chelating chain links groups involved in H-bonding, namely the hydroxyl and imine groups (this molecular arrangement is also called a quasi-ring).

antiviral properties of Schiff bases attracted considerable attention.[14-18] As mentioned above, the position of the proton in the $-OH\cdots N-$ region dramatically affects the interactions and plays a very important role in determining the physical, chemical, and biological properties of *o*-hydroxy Schiff bases.

The position of the proton depends on the nature of R_1 and R_2 (Figure 2). If R_1 is a nitro group in the para position with respect to the OH group, then in the crystalline state an ionic structure is realized, as documented by X-ray and solid-state NMR study.[19] This is due to a through-resonance effect of the electron-accepting nitro and electron-donating hydroxy groups leading to a substantial withdrawal of the negative charge from the oxygen atom in OH and, hence, facilitating the proton transfer to the nitrogen atom of the imine group. This kind of H-bond occurs quite rarely—most *o*-hydroxy Schiff bases ($\sim$90%)[20] exist in crystalline state in a neutral enol—imine form. Substantial changes in the H-bond region are also observed for cases where the R_2 group is attached to the nitrogen atom.[21,22]

The CN group as a proton acceptor and OH as a proton donor are linked by a system of covalent bond chain of sp^2 hybridized atoms. Thus, they may form a system of conjugated OCCCN bonds and participate in the resonance effect between electron-donating OH and electron-accepting CN groups. Intramolecular H-bond formation changes the electron-accepting and electron-

donating properties of CN and OH groups, respectively. This leads to changes in π-electron delocalization in the chain. Gilli et al.[3,23,24] introduced the concept of resonance-assisted hydrogen bond (RAHB) assuming that π-electron delocalization in the conjugated system is associated with the H-bond formation. The π-electrons of the OCCCN system interact via the intramolecular H-bond, forming a six-membered ring that has some enhanced π-electron delocalization and is sometimes called a quasi-ring.[25] It is worth mentioning that this kind of interaction can be found in many important chemical species, among others in protonated proton sponges.[26-28]

Since many of the Schiff bases have practical important applications due to their photo- and thermochromism,[12,29] second-harmonic generation, and linear electro-optic modulation,[30-36] systematic studies of mutual dependence of the electron structure in the H-bond bridge on π-electron delocalization in the linking chain (OCCCN) and in the phenyl ring are of great importance.

The common CC bond for both the phenyl ring and quasi-rings (bold in Figure 2 and further called B_c) is of particular interest. The aim of our studies was to investigate how the π-electron distribution of the ring, in particular that of the B_c bond, was related to the strength of H-bonding in OH$\cdots$N. It was shown that β-enaminone/iminoenol tautomerism depends substantially on the kind of moiety to which the enaminone is fused.[37] Defining $\Delta E = E(O-H\cdots N) - E(N-H\cdots O)$ as the energy difference between the two H-bond minima, it was shown that for enaminone $\Delta E = 33.49$ kJ/mol, for iminophenol $\Delta E = -14.95$ kJ/mol, and for 1-imino-2-naphthol $\Delta E = 1.88$ kJ/mol. Thus, the absolute value of ΔE and the position of the more stable protonation depends on the flexibility of the π-electron structure which is most fixed in the case of naphthalene derivative, since the C1C2 bond is most likely a double bond. A similar conclusion can be drawn from the experimental structural study and ab initio modeling of 2-hydroxyacetonaphthylimine.[38] Interestingly, metal chelates derived from 3-hydroxy-2-naphthalaldehyde are less stable than its 1,2- or 2,1-isomers,[39,40] indicating a substantial role of the double character of the CC bond involved in chelating metal.

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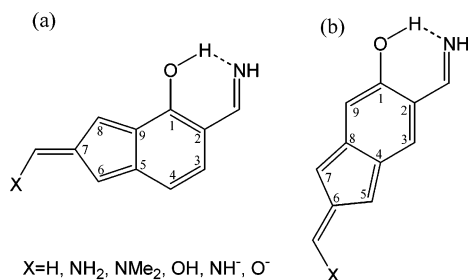
(a)   (b)

X=H, NH₂, NMe₂, OH, NH⁻, O⁻

FIGURE 3. Schematic representation of the systems taken into consideration. For the purposes of discussion, these two systems are labeled (a) and (b).

In this situation, it seemed to be very interesting and important to study how the strength of H-bonding in *o*-hydroxy Schiff bases depends on the nature of the B_c bond. In order to find the relation between B_c bond characteristics and H-bond properties, a few molecular model systems are considered in which the fulvene ring is fused to the phenyl ring of the *o*-hydroxy Schiff base as shown in the scheme in Figure 3.

Depending on the position of fusion, the B_c bond is either short, double type (case a), or long, single type (case b). In order to modify its length in both cases, we investigated the derivatives with various substituents attached at the exocyclic carbon in fulvene, as shown in Figure 3. The electron-donating substituents aromatize the five-membered ring[41] and therefore change the π-electron delocalization in the phenylic ring, in this way increasing π-delocalization within the latter. As a result, the B_c bond becomes longer in case (a) and shorter in case (b).

Methodology

The molecular structures were optimized at the B3LYP/6-311+G** level using Gaussian03.[42] Geometrical parameters of the rings and quasi-rings (C−C, C−N, and C−O bond lengths) were used to calculate the aromaticity index HOMA[43,44] according to the following equation

$$\text{HOMA} = 1 - \frac{1}{n}\sum_{j=1}^{n} \alpha_i (R_{\text{opt},i} - R_j)^2$$

where *n* represents the total number of bonds taken into the summation and α_i is a normalization constant (for CC bonds $\alpha_{C-C} = 257.7$, for CN bonds $\alpha_{C-N} = 93.52$ and for CO bonds $\alpha_{C-O} = 157.38$) fixed to give HOMA = 0 for a model

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nonaromatic system, e.g., Kekulé[45] structure of benzene and HOMA = 1 for the system with all bonds equal to the optimal value $R_{\text{opt},i}$ assumed to be realized for fully aromatic systems ($R_{\text{opt,CC}} = 1.388$ Å, $R_{\text{opt,CN}} = 1.334$ Å, $R_{\text{opt,CO}} = 1.265$ Å).

Estimation of the approximate value of H-bonding, was carried out following the procedure suggested by Grabowski.[46] The difference between the geometry of the closed (H-bonded) and open conformation of the studied system was used as one of the H-bonding strength estimators. According to this procedure, changes in geometry result from H-bond formation as well as from π-electron reorganization in the molecule.

Wave functions were calculated on the basis of fully optimized geometries using the same level of accuracy as in the optimization process. Topological analysis of the electron density[47] was performed using AIM2000 program.[48] The number of critical points found for all of the analyzed systems is in agreement with the Poincaré−Hopf rule.[49] The following parameters of the bond critical points were analyzed: the density of the total energy of electrons (*H*) and its two components, the kinetic (*G*) and potential (*V*) electron energy densities (according to the definitions $G > 0$ and $V < 0$ and $H = G + V$). The density of total electron energy may have both positive and negative values, depending on the dominating component. Generally it can be said that the positive value of *H* characterizes the molecular regions in which the electrons move faster, whereas the negative value of *H* characterizes the regions in which the electrons are relatively localized. The analysis of *H* can afford particularly valuable information if electronic parameters of the bond critical point are considered. Here, we use the values of *H* measured at the H-bond critical point as an additional criterion of the strength of the H-bonding under consideration.[50−54]

Results and Discussion

It is well-known that the aromaticity of a fulvene ring increases with an increase of the electron-donating power of the substituent.[41] Thus, the different fusion of fulvene moiety to the phenyl ring should affect the aromatic character of the latter. Indeed, this is the case. Introduction of substituents with an increasing electron-donating property (X = H, OH, NH₂, NMe₂, O⁻, NH⁻ in Figure 3) to the exocyclic carbon atom in

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SCHEME 1
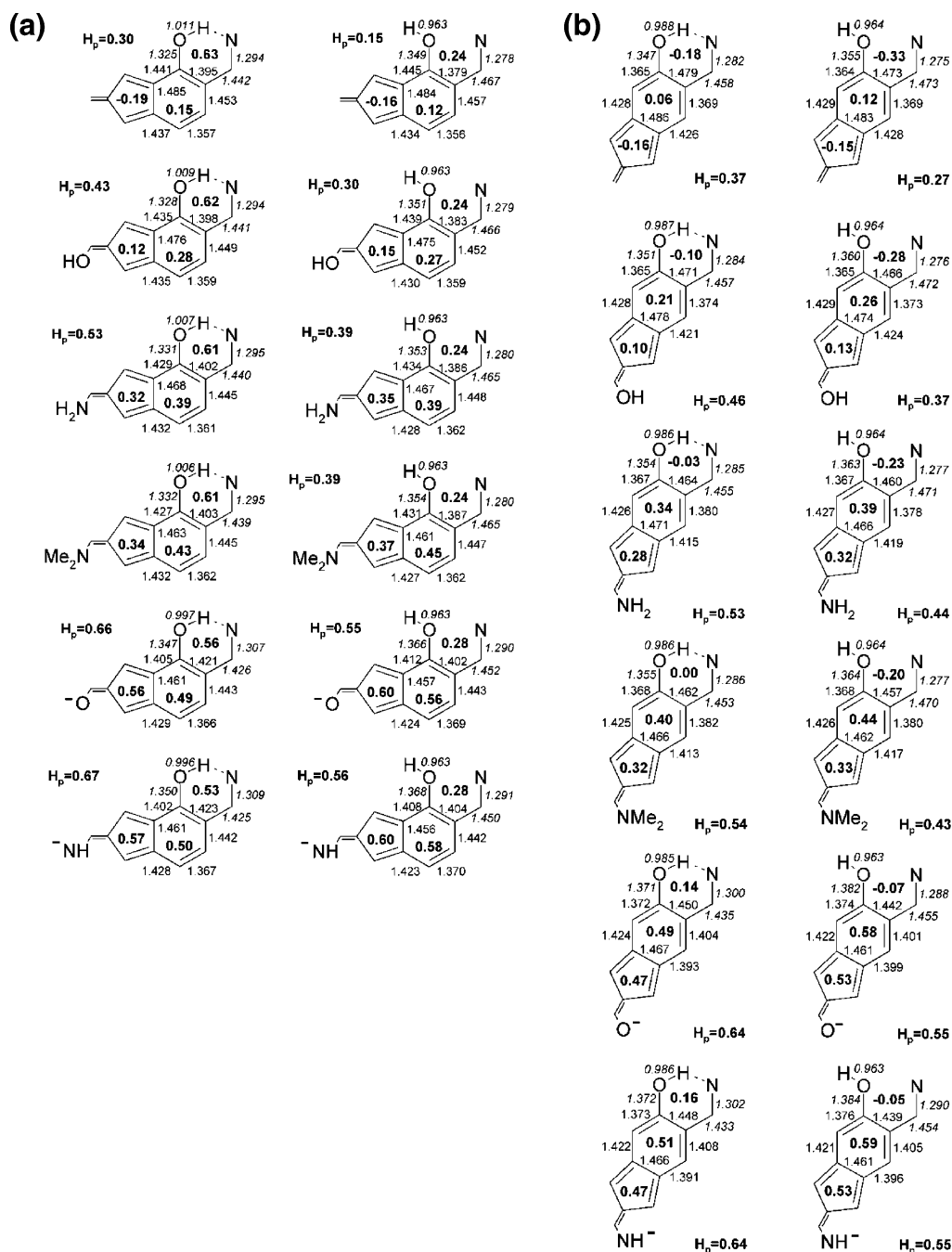
fulvene causes regular changes in the aromaticity of both the five- and six-membered rings. The correlations of HOMA on σ^+ (values taken from refs 55 and 56) are at least good (the lowest absolute value of R is 0.976 and regressions are shown in Figures 1S(a) and 1S(b) in the Supporting Information). Detailed data for both series are given in parts a and b of Scheme 1, which present bond lengths and values of the HOMA index for five- and six-membered rings, quasi-rings (numbers inside the rings), and also for the perimeter which is built up of the sequence of atoms forming the OCC···CCN skeleton excluding CC bond common for fulvene and phenylic rings (H_p values). To show how the H-bonding is related to the changes in geometry of the remainder of the molecule, the data are given for

closed (H-bonded) and open conformations. It should be also pointed out that for the clarity of Scheme 1 only those H atoms involved in H-bonds or belonging to substituents are shown.

Despite substantial similarity in aromaticity change of five- and six-membered rings in both cases (a) and (b), it can be noted that there is a dramatic difference in the length of the B_c bond (bold in Figure 2 and denoted as d(CC)). For unsubstituted species, the lengths are 1.395 and 1.479 Å for (a) and (b), respectively, which results from the localizing power of fulvene moiety (double bond fixation[57]). Introduction of electron-donating substituents at fulvene makes the B_c bond longer by 0.028 Å in the case (a) and shorter by 0.031 in the case (b).

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For both cases, the substituent effect (going from the unsubstituted species to that with the NH^- substituent) on d(CC) is numerically comparable, but working in opposite directions. However, the electron-donating substituents in the exocyclic position in fulvene decrease this power substantially in both cases (a and b), and hence, the observed changes occur. The effect of different behavior in (a) and (b) cases may be interpreted in terms of the so-called bond number conservation rule[58−60] applied to C−C bonds in π-electron hydrocarbons. Qualitatively, $2p_z$ orbitals at each of the fusion carbon atoms in both the benzene ring and the imine group overlap with three $2p_z$ orbitals belonging to the neighboring carbon atoms. This leads to a possibility of π-electron conjugation in all three directions. Such a situation occurs almost uniformly in the case of carbon atoms of the central C4a−C8a bond of naphthalene. The length of the bonds between C4a and C8a atoms and the adjacent carbon atoms, estimated via optimization at the B3LYP/6-311+G** level,[61] is similar (1.420, 1.420, and 1.432 Å), and at the same time, it is comparable with the CC bond lengths in graphite 1.422(1) Å.[62] In the molecules studied, the situation is different. In case (a), the B_c bond is relatively short (1.395 Å) for X = H, and it becomes longer with an increase of the electron-donating power of X. For X = NH^-, the length is 1.423 Å, and CC bonds adjacent to B_c are 1.425 and 1.442 Å; thus, the situation is similar to that observed in the central CC bonds of naphthalene or in graphite. The situation for case (b) is completely different. Due to a localizing effect of the double bond in the fulvene ring, the two short CC bonds linking the B_c bond are rather short; for X = H they are equal to 1.365 and 1.369 Å. An increase of the electron-donating power of X leads to a lengthening of both of them to 1.373 and 1.408 Å, respectively, and according to the bond number conservation rule, it shortens the B_c bond. A very long B_c bond in the "aromatic" ring for cases (b) may be the cause of a different (in comparison with case (a)) mode of interactions between the OH⋯N and the remainder of the molecule.

The aim of the present paper was to investigate the dependence of H-bond strength of the OH⋯N bridge on the length of the B_c bond and on the aromaticity of the phenylic and quasi-rings. For this purpose, we used two well-accepted quantitative descriptors of H-bond strength: the OH bond length, d(OH),[23,24] and the electron energy density in BCP of the N⋯H bond, H(N⋯H).[50,63] Both of these parameters are well correlated to each other ($R = -0.997$), as shown in Figure 2S (Supporting Information). Due to a substantial difference in behavior of the B_c bond between case (a) and case (b), and also because of a different mechanism that caused that behavior, in the next sections those two cases will be discussed separately.

The Case with a Short Common CC Bond (Case a). Let us now investigate how both quantifiers of H-bond strength mentioned above depend on the B_c bond length, d(CC). Parts a and b of Figure 4 display the plots of d(OH) and H(H⋯N)
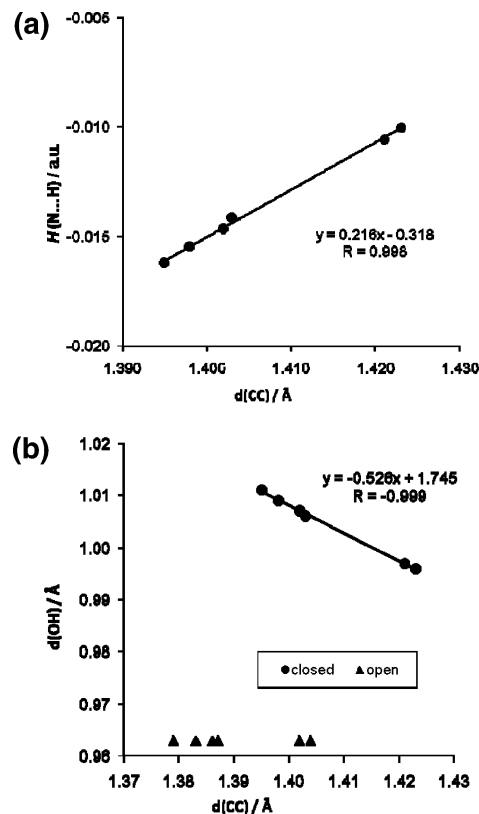

FIGURE 4. Dependence between the total electron energy density estimated in BCP of N⋯H (a) and O−H bond length (b) versus the length of the B_c bond (estimated for the case (a)).

versus d(CC). In both cases, the correlation is excellent and supports the reliable opinion that a lengthening of the CC bond leads to a decrease of H-bond strength. In both cases, it is apparent that there is a regular relationship between the "strength" of H-bonding approximated by H(H⋯N) and d(OH) values and the length of the B_c bond: the shorter B_c is, the stronger the H-bond becomes; i.e., the longer d(OH) is, the more negative H(H⋯N) becomes. In Figure 4b, the d(OH) values for the open conformer, i.e., without H-bonding, are also given. In the case of Figure 4b, there is no dependence of d(OH) on d(CC) for the open conformations, even for a very short B_c bond. Thus, the elongation of the OH bond is directly connected with the effect of H-bonding and can be observed only in the case when a quasi-ring is formed.

Even a substantial change in CO bond length for the open conformer does not affect the OH bond length. According to the above findings, it can be expected that the changes due to H-bond formation in the quasi-ring go together with partial reorganization of the bonds (mainly π-bonds, with the exception for the OH bond). This phenomenon is characteristic for resonance-assisted hydrogen bonds (RAHB) as proposed by Gilli and his co-workers.[3,24,55] According to that concept, the formation of RAHB is associated with an increase of π-electron delocalization in the π-electron OCCCN chain linking covalently OH and NC groups interacting via H-bonding. In fact, the overall degree of the π-electron delocalization measured by HOMA for the quasi-ring increases significantly with an increase of H-bond strength, as shown in Figure 5.

The correlation is good ($R = -0.98$). Note that the dependence on HOMA for perimeter is worse ($R = 0.93$), and its slope, in absolute value, is almost four times smaller than that

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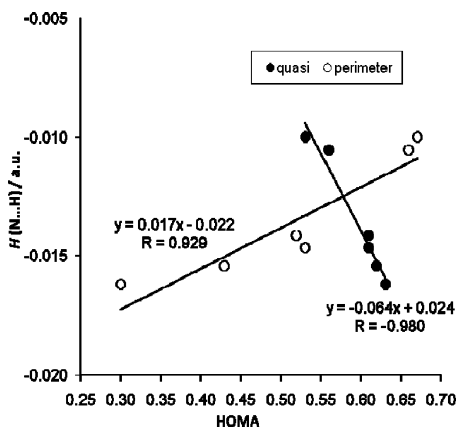(63) Grabowski, S. J.; Sokalski, W. A.; Dyguda, E.; Leszczynski, J. *J. Phys. Chem.* **2006**, *110*, 6444.

FIGURE 5. Dependence of the total electron energy density in BCP of N···H on HOMA values in the quasi-ring (filled circles) and in the perimeter (empty circles), estimated for case (a).

for the quasi-ring. This may suggest that the π-electron interaction between OH and CN involved in the H-bonding takes place through the π-electron structure of the quasi-ring and may be due to an increased substituent effect of OH···N and H···N=C on the OCCCN chelating chain. Due to H-bonding, both of these substituents increase their electron-donating and -accepting power, respectively, leading to an increase of π-electron delocalization in the quasi-ring.

H-Bond Interaction OH···NC in Terms of Varying Substituent Effects. It should be emphasized that the shortening of the B_c bond in the quasi-ring is governed by a strong double-bond localizing force of fulvene moiety fused to the benzene ring at which the OH and CN groups are in the ortho position separated just by the above-mentioned B_c bond. Its length is elongated by electron-donating substituents at the exocyclic carbon atom of the fulvene moiety. On the other hand, the OH···NC interactions may be considered from the point of view of the chelating chain as a push–pull interaction between them, and the strength of these mesomeric interactions has to depend on the position of proton. The substituent constants σ^+ for OH and σ^- for PhCH=NH are −0.92 and 0.54, respectively.[55] As a result of H-bond formation, the proton moves away from oxygen (OH → O$^-$···H$^+$) approaching the nitrogen atom in the imine group (CN → CN···H$^+$). In both cases, the power of their substituent effect increases, and the absolute values of the respective constants increase: σ^+ for O$^-$···H$^+$ becomes more negative and σ^- for CN···H$^+$ becomes more positive. It is well-known that the intramolecular charge transfer increases with an increase of the sum of absolute values of substituent constants of both interacting substituents. In the case of a lack of H-bond as it is for the open conformations, HOMA may be treated as a measure of π-electron delocalization in the OCCCN chain due to, almost exclusively, the substituent effect of hydroxyl and imine groups. The HOMA values of open conformations for case (a) are almost constant; the range of changes is between 0.28 for (X = NH$^-$) and 0.24 for (X = H), with a mean value HOMA = 0.25. For H-bonded systems, the range is from 0.63 to 0.53, with a mean value equal to 0.61. Thus, the difference between the mean values, ∼0.36 unit of HOMA, may be considered as a measure of the increase of π-electron delocalization due to the H-bond formation. In other words, as a result of the H-bond formation the overall substituent effect influencing the chelating chain dramatically increases. This is associated
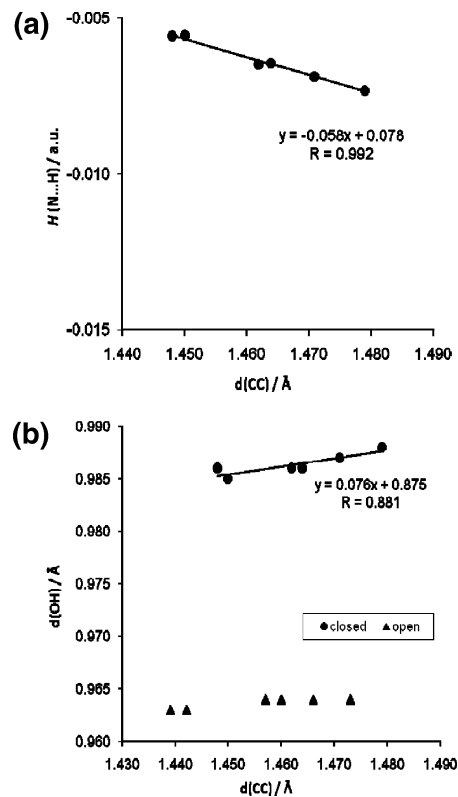

FIGURE 6. Dependence between the total electron energy density estimated in BCP of N···H (a) and O−H distance (b) versus the length of the B_c bond (estimated for the case (b)).

with an increase of H-bond strength, according to the Gilli concept of RAHB.[3,23,64]

The Case with a Long Common CC Bond (Case b). Electron-donating substituents at the exocyclic carbon atom in fulvene fragment of molecules (b) cause the change in the B_c bond length in the range from 1.448 to 1.479 Å, going from NH$^-$ to H. This kind of changes is contrary to that observed for case (a). Since this bond is a part of both the quasi-ring and the aromatic one, its increase in length results in a substantial decrease of HOMA value from 0.16 to −0.18 for the quasi-ring and from 0.51 to 0.06 for the phenylic ring. Thus, the resonance-assisting OH···N interaction via the link in the quasi-ring seems to be much less probable in this case than in the former one, and it becomes even less probable when the electron-donating power of the substituent increases. Figure 6 presents the dependence of H-bond strength quantified by the H(N···H) value estimated in BCP of N···H on d(CC).

The dependence of the total electron energy density in BCP$_{H···N}$ on d(CC) for case (b) differs dramatically from the analogical relation for case (a). First, the slope is negative (−0.058), whereas for case (a) it was positive (0.216), for regression of almost the same high precision (R values for both cases ∼0.99). Thus, in case (b), the lengthening of the B_c bond is associated with an increase of the H-bonding strength! This might support the hypothesis that the transmission of the substituent effect due to H-bonding does not pass through the B_c bond but follows a different path. Moreover, the slope for case (b), in absolute value, is 3.7 times smaller than for case (a). Obviously, this means that in case (b) the H-bonding affects

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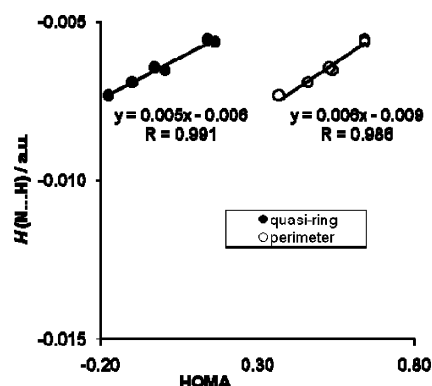
much less the π-electron delocalization in the quasi-ring as compared with case (a). A similar relationship was observed for $d(OH)$ vs $d(CC)$ as shown in Figure 4b: in case (a), a lengthening of $d(CC)$ leads to a weakening of H-bonding, whereas in case (b) a reverse dependence occurs.

The observed differences in dependencies of H-bonding strength on the length of the B_c bond between cases (a) and (b) raise the question "Why?" The answer may be suggested when we look at Figures 5 and 7, where the density of the total electron energy in $BCP_{H...N}$ is plotted against the HOMA values for the perimeter of the whole molecule except the H-bond itself and for the quasi-ring.

In the case (a) (Figure 5), the strength of the H-bond increases in line with an increase of HOMA values in the quasi-ring, i.e., with an increase of the quasi-aromatic π-electron delocalization. The dependence of H on HOMA for perimeter has an opposite slope, indicating that an increase of H-bonding strength follows a decrease of π-electron delocalization in the perimeter. A substantial difference also occurs between case (a) and case (b) for the values of $H(N\cdots H)$. The H-values for case (a) are twice as large as for case (b). In case (b) (Figure 7), the regression lines $H(N\cdots H)$ vs HOMA for the quasi-ring and for the perimeter are parallel, both with a positive slope indicating a decrease of H-bonding strength as a result of an increase of π-electron delocalization in both the perimeter and the quasi-ring. This means that in the latter case, the cooperative effect between the H-bond formation and its strength on the one hand and π-electron delocalization on the other is equally shared between the interactions via the quasi-ring and the perimeter.

Analysis of π-Electron Current Densities. The plots of π-ring currents induced by a magnetic field perpendicular to the molecular plane of selected analyzed systems are shown in Figure 8.[65] Quite remarkably, in both cases (a)-H (Figure 8a) and (b)-H (Figure 8d) (those with X = H, see also Figure 3), the five-membered fulvene ring sustains an internal paratropic ring current (i.e., a paramagnetic vortex), whereas diatropic flow, extending to the exocyclic C−C double bond, is observed beyond the molecular periphery. Moreover, in these cases, there are local currents in the region of formally double bonds of phenyl rings. This clearly indicates the ability of fulvene moiety to localize the π-electrons in the attached phenyl ring.

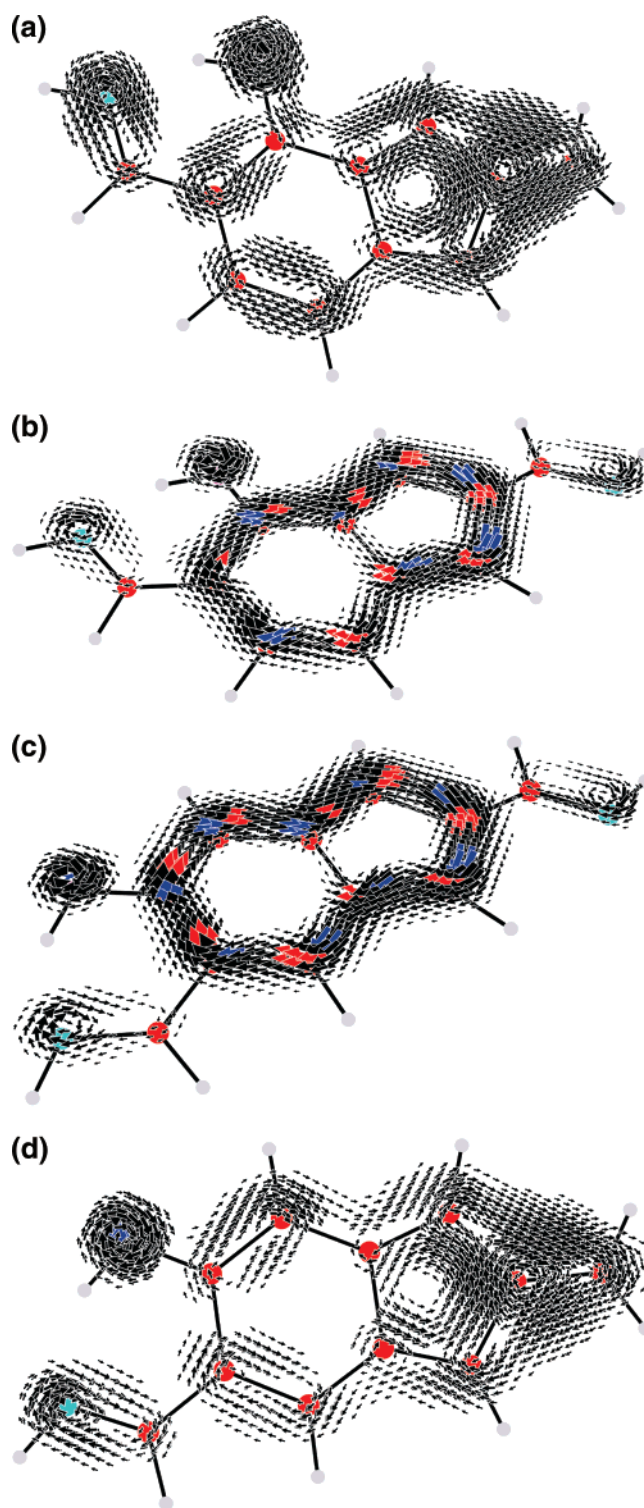(65) The LINUX and WINDOWS version of the graphic code used to obtain the 3D representation s available free of charge at https://theochem.chimfar.unimo.it/VEDO3/quasi-ring.

FIGURE 8. Plots of π-electron currents evaluated in the plane 1 bohr above the molecular plane of the selected systems: (a) a-(X=H), (b) a-(X=NH−), (c) b-(X=NH−), (d) b-(X=H). The magnetic field is perpendicular to the molecular plane. Diamagnetic flow is clockwise. The size of arrows is proportional to the local modulus of current density. Red (blue) denote ascending (descending) currents.

Therefore, a marked difference is observed in the character of the B_c bond on the basis of diamagnetic π-currents. For the (a)-H system, a significant local circulation along the B_c bond is observed, as could be expected from the proposed modeling.

This is directly connected with the relatively higher amount of π-electrons located on this bond. These electrons can be partially involved in π-electron delocalization in the quasi-ring, which results in relatively stronger H-bonding. In the case of the b-H system the situation is dramatically different. There is no evidence of diamagnetic circulation sustained by the electron distribution of the B_c bond, which can definitely be described as a formally single CC bond. Diamagnetic vortices are instead observed over the adjacent CC bonds. These findings may suggest that the local coupling of the π-electrons within the quasi-ring along this bond is significantly reduced. This obviously results in a weakening of the H-bonding. However, there is no evidence of diatropic ring currents over the quasi-ring in either (a)-H or (b)-H molecular systems. Only the localized circulations over double bonds and selected atoms can be observed.

A remarkably different situation is observed in the case of NH$^-$ substitution; (a)-NH$^-$ (Figure 8b) and (b)-NH$^-$ (Figure 8c). In both systems, strong diamagnetic ring currents are observed along the perimeter of the fused ring system, i.e., fulvene and phenyl rings. Interestingly, the intensity of the currents is higher over the fulvene ring. The C−C bond shared by the 6- and 5-membered rings is not involved in the diatropic ring current to any relevant extent. This is close to the situation found for naphthalene.[66] In the case of the B_c bond common, it seems that in both NH$^-$ derivatives those bonds have a similar character and are involved in significant π-electron delocalization along the perimeter. This results in changes of the strength of H-bonding in the quasi-ring; i.e., the π-electrons involved in the delocalization along the perimeter are probably less involved in the delocalization within the quasi-ring. The clear weakening of H-bonding is observed for the (a)-NH$^-$ case in comparison with its unsubstituted derivative, (a)-H. However, the H-bond strength in the (b)-NH$^-$ case does not differ significantly from that in (b)-H. In general, it is possible to consider (a)-NH$^-$ and (b)-NH$^-$ systems as topological situations being intermediated between both situations: (a)-H and (b)-H. Summarizing, it can be concluded that the strongest H-bonding can be observed for this specific case in which the sequence of formally single and double bonds enable a π-electron coupling.

Otherwise, the H-bond is relatively weaker. The above observations are in excellent agreement with the analysis of local and global aromaticity measured by means of HOMA index.

Conclusions

In summary, there is a clear interrelation between the π-electron localization/ delocalization within the whole Schiff base molecular system and the strength of the hydrogen bonding forming an additional quasi-aromatic ring. Depending on the position of fulvene ring, the B_c bond can be considered as formally single- or double-like. The case of anions substituted with O$^-$ and NH$^-$ groups, in which significant π-electron delocalization over the perimeter occurs, and for which this bond is delocalized rather than typically single or double, can be treated as an exception. If the character of this bond is closer to formally double, then π-electronic coupling within the quasi-ring additionally stabilizes the H-bond. If however, this bond has the characteristics similar to those of a single bond, or the π-electrons are involved in other π-electronic effects, e.g., delocalization over the perimeter built up of fulvene and phenylic rings, then the effect of additional H-bonding stabilization is clearly less effective. Although there is no evidence of ring currents over the quasi-ring, clearly the possibility of π-electronic coupling within this ring motif seems to play an important role in additional stabilization of the H-bond. This phenomenon may be connected to some extent with the π-electronic communication between the OH and C(H)NH substituents.

Supporting Information Available: Figures 1S and 2S and geometries and total energies of molecular systems analyzed in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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(66) See, e.g.: Lazzeretti, P. *Progr. NMR Spectr.* **2000**, *36*, 1, Figure 17.