Theoretical Study of Changes in π-Electron Delocalization in the Analogues of an *ortho*-Hydroxy Schiff Base When the Proton Is Replaced with Li⁺ or BeH⁺

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Molecular geometries of *ortho*-hydroxy Schiff base in keto-enamine and enol-imine tautomeric forms, its anion, and their derivatives in which H⁺ was replaced with Li⁺ or BeH⁺ were optimized at the B3LYP/6-311+G** level of theory. Isodesmic reactions for estimating delocalization due to H-bonding or cation chelating were calculated. Geometry-based aromaticity index HOMA and magnetism-based NICS(1)$_{zz}$ index were used to estimate π-electron delocalization. Keto-enamine tautomer exhibits low aromaticity in the ring and a relatively high π-electron delocalization in the quasi-ring. The reverse was found for enol-imine tautomer. The Li⁺ and BeH⁺ derivatives showed a relatively high π-electron delocalization in the ring and in the quasi-ring. This may be interpreted by an extension of the electron delocalization path in the π-electron system through low-lying unoccupied p-type orbitals of Li⁺ and BeH⁺ cations.

INTRODUCTION

Molecular systems with intramolecular H-bonding are the subject of numerous studies on the interplay between the nature of H-bonding and the character of the spacer linking the proton donating and proton accepting groups.[1] Very spectacular is the way of description of this kind of interaction in terms of resonance-assisted H-bonding (RAHB),[2] which postulates the existence of interrelation between the π-electron delocalization in the spacer and the nature of H-bonding. The easiest and most convincing scheme for this kind of interactions is presented in Figure 1a, which is equivalent to the description via the two canonical structures (Figure 1b) that is sometimes described as in Figure 1c.

Undoubtedly, there is an interplay between the π-electron delocalization shown in Figure 1 and the strength and the nature of H-bonding as documented by numerous studies.[2−6] The resonance effect depicted by arrows results in a decrease of negative charge at the hydroxylic oxygen atom and an increase of electronic charge at the keto-oxygen atom. This leads to a shift of proton toward the center between the oxygen atoms and is associated with a shortening of the O···O distance, hence with an increase of H-bonding strength.[4] The idea of RAHB leads to the conclusion allowing one to define an indicator of the strength of resonance in the systems such as the one shown in Figure 1. The smaller are the differences between both C−O and C−C pairs of bonds lengths (i.e. $q_1 = d_4 − d_1$ and $q_2 = d_2 − d_3$) the greater is the resonance effect and the greater is π-electron delocalization in the spacer. The quantity $Q = q_1 + q_2$ measures the resonance effect in the spacer. It was shown[2] that the Q-parameter correlates well with the O···O interatomic distance, which sometimes serves[4,7] as a qualitative measure of the H-bonding strength. Another method that takes advantage of the bond lengths equalization in the spacer is

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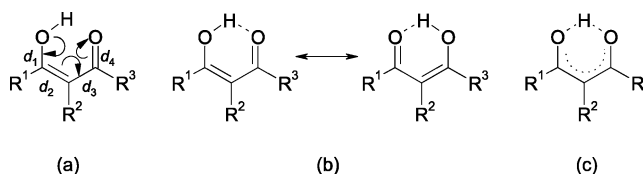
Figure 1. Resonance assisted hydrogen bonding in malonaldehyde.
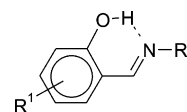
Figure 2. *ortho*-Hydroxy Schiff base.

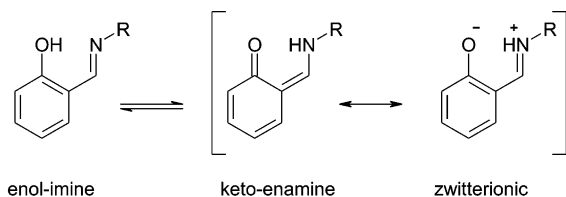the aromaticity index HOMA[8−10] which is defined according to eq 1

$$\text{HOMA} = 1 - \frac{\alpha}{n}\sum(R_{\text{opt}} - R_i)^2 \qquad (1)$$

in which the R_i are the bonds lengths as e.g. d_1 through d_4 in Figure 1, R_{opt} stands for the bond length when there is a full π-electron delocalization in the system, α is a normalization factor to give HOMA = 0 for the systems with fully localized double bonds and HOMA = 1 for the fully delocalized system, and n is the number of bonds taken into consideration.[9] HOMA is useful for various systems and bond types.[11]
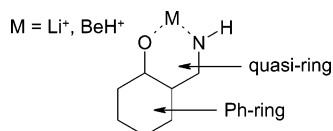
The systems with OH···N H-bonding are more complex, since it is not possible to estimate directly the q_1 parameter of the Gilli approach; however, an approximated way was proposed.[12] The *ortho*-hydroxy Schiff base is presented in Figure 2. Introducing substituents into the phenyl ring or to the nitrogen atom may modify the H-bond properties. These systems are well-known and are of great interest, mostly owing to their chelating properties[13] and intramolecular H-bond.[14]

Due to different electronegativities of the oxygen and nitrogen atoms, Pauling's χ values are 3.44 and 3.04,[15] respectively, an asymmetric H-bond is formed. However, its

Figure 3. Tautomeric and canonical forms of *ortho*-hydroxy Schiff base.

Figure 4. The studied *ortho*-hydroxy Schiff base systems.

Figure 5. Structures of studied Schiff bases optimized at the B3LYP/6-311+G** level of theory: **1a** − enol-imine, **1b** − enol-imine (open conformation), **2** − keto-enamine, **3** − Li-derivative, **4** − BeH-derivative, **5** − anion.

Scheme 1. Isodesmotic Reaction for Calculation of Delocalization Energy

structure depends on the kind of substituent in the phenyl-ring and/or on the functional group attached to the nitrogen atom (Figure 2). It was shown, for instance, that in 5-nitro-N-salicylideneethylamine (NSEA) the $-NO_2$ substituent causes the formation of a through-resonance assisted ionic H-bond.[16] Substitution at the nitrogen atom may lead to similar consequences[17] and again an ionic H-bond is formed.

In general, depending on the position of the proton, two tautomeric forms may be obtained: enol-imine and keto-enamine (Figure 3). The latter may be represented by the canonical form known as a zwitterionic.

It has been shown that when a zwitterionic H-bond is formed, the π-electron delocalization in the ring decreases significantly, from the HOMA[9] value ~0.98 for 4-nitrophenols (for geometry obtained by Coppens et al.[18]) to 0.732 for NSEA. A question arises whether there is any correlation between aromaticity of the ring and π-electron delocalization observed in the spacer built up of OCCCN which, including H-bonding, forms a quasi-ring.[19−21]

The H-bonding interactions are in principle electrostatic in nature,[22] in which ionic character is limited but may appear since the electronegativities of atoms forming an H-bonding region in *ortho*-hydroxy Schiff bases allow for this kind of interaction: Pauling electronegativity values of H, N, and O are 2.20, 3.04, and 3.44, respectively.[15]

What kind of changes in the spacer may be expected when H^+ is replaced with Li^+ or BeH^+? Pauling electronegativity of Li is much lower (0.98[15]), and hence, the interactions are much more ionic[23] in nature than those observed in the case of H-bonding. However, the difference between hydrogen and lithium consists also in electron energetics of their atomic structure. The lowest unoccupied 2p orbital in H is much higher than in Li or Be. Thus the following problem arises: can the low-lying p-type orbitals of Li^+ and BeH^+ participate in π-electron delocalization in the quasi-ring shown in Figure 4.

The aim of this paper is to show how the replacement of H^+ in a simple *ortho*-hydroxy Schiff base with Li^+ or BeH^+ cations (Figure 4) changes π-electron delocalization in the Ph-ring and quasi-ring and also whether there is any dependence between those changes.

Thus the problem of interrelations between π-electron delocalization in the Ph-ring and the quasi-ring with the varying cation is the subject of the present study. It is intended to show that the nature of π-electron delocalization in the case of H^+ derivative is substantially different from
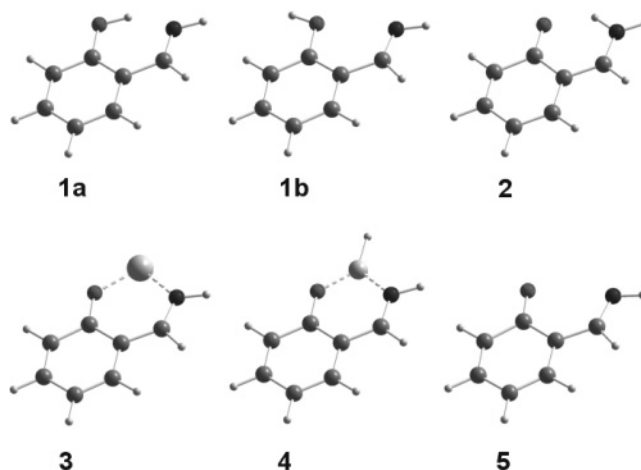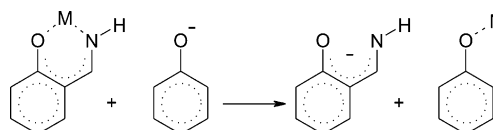
that observed for Li^+ or BeH^+ derivatives. It should be mentioned here that even old literature data suggest unusual properties of metal chelated π-electron systems such as metal chelates of 1,3-diketones.[24−27] Perrin et al.[28] found that metal chelates of 1,3-diketones have the metal centered between two donor oxygen atoms, whereas the parent enol form has the proton closer to one oxygen atom than to the other.

METHODOLOGY

Ab initio modeling at the B3LYP/6-311+G** and MP2/aug-cc-pVDZ levels of theory was applied to the *ortho*-hydroxy Schiff base in keto-enamine and enol-imine tautomeric forms, its anion and derivatives in which H^+ was replaced with Li^+ and BeH^+ cations. All calculations were performed using the Gaussian03 series of programs.[29] The optimized structures of the studied systems are presented in Figure 5.

For all molecules the values of the HOMA[9] index for the Ph-ring and the quasi-ring (OCCCN moiety) were calculated. Moreover, for the Ph-ring NICS,[30,31] NICS(1)[32] and NICS(1)$_{zz}$[33] values were estimated using the GIAO method at the HF/6-31+G* level of theory (Gaussian03[29]).

For molecules **1**, **3**, and **4** delocalization energy, E_{del}, was estimated according to the isodesmotic reaction presented in Scheme 1.

Delocalization energy, E_{del}, due to the interaction of the anion of the *ortho*-hydroxy Schiff base with cations is calculated as the difference between the energy of the right-hand side of Scheme 1 and the left-side one. This quantity may be interpreted as the energetic measure of π-electron delocalization in the whole molecule due to interaction with **M**.

Table 1. Calculated HOMA and NICS(1)$_{zz}$ Values, Total Energies for MP2 Calculations, E_{MP2} (hartree) for All Systems and Delocalization Energies, and E_{del} (kcal·mol^{-1}), for **1a**, **1b**, **3**, and **4**

| | | B3LYP/6-311+G** | | | | MP2/aug-cc-pVDZ | | | | |
| | | HOMA | | NICS(1)$_{zz}$ | | HOMA | | NICS(1)$_{zz}$ | | |
	system	Ph-ring	quasi-ring	Ph-ring	E_{del}	Ph-ring	quasi-ring	Ph-ring	E_{del}	E_{MP2}
1a	H$^+$ enol-imine	0.93	0.38	−27.15	8.00	0.85	0.19	−27.13	7.80	−399.702
1b	H$^+$ enol-imine (open)	0.95	0.09	−28.36	−6.20	0.87	−0.06	−28.18	−5.10	−399.682
2	H$^+$ keto-enamine	0.39	0.57	−12.94		0.43	0.58	−15.52		−399.690
3	Li$^+$	0.70	0.58	−21.38	27.60	0.64	0.45	−21.99	25.50	−406.657
4	BeH$^+$	0.82	0.70	−24.07	32.30	0.76	0.56	−24.49	33.30	−414.462
5	Schiff anion	0.42	0.25	−17.02		0.36	0.20	−17.80		−399.143

RESULTS AND DISCUSSION

Geometry-Based Measures of π-Electron Delocalization: Comparison of Gilli's Q and HOMA. In this report we will discuss the problem of π-electron delocalization in the spacer and in the phenyl ring. It should be stressed here that the Gilli Q parameter[2] is widely accepted as a measure of resonance effect in the spacer,[1b] thus of π-electron delocalization. The latter is also reliably described by the aromaticity index HOMA.[9,34] Both above-mentioned parameters are defined by the use of bond lengths in the spacer, and hence they should be at least qualitatively equivalent. Figure 6 illustrates the interrelation between the Gilli Q parameter and HOMA index for 25 experimental data set of systems with O−H···O intramolecular H-bonding determined by Gilli et al.[2]

The interrelation between HOMA and Q is quadratic, since HOMA is a quadratic function of the differences of bond lengths whereas Q is a linear function. Nevertheless, on the basis of this dependence it may be stated that there exists a good agreement between the Gilli concept of π-electron delocalization measured by Q-values and HOMA, which was defined as a geometry-based aromaticity index. It is important to mention that the HOMA index, which is in the presented case equivalent to Gilli's Q parameter, has much wider applications as a measure of π-electron delocalization.[10]

There are two advantages of this comparison: (i) the scatter plot illustrates a qualitative equivalence of these two approaches, and (ii) it allows one to place the Gilli Q parameter of π-electron delocalization in the spacer on the scale known for aromatic systems. The classical way is to accept the thesis that in the case of benzene there is a full π-electron delocalization, whereas for its Kekulé structure there are localized single and double bonds.[35] For these two cases HOMA equals 1.0 and 0.0, respectively. Thus for the set of enol form of the β-diketone fragment with O−H···O
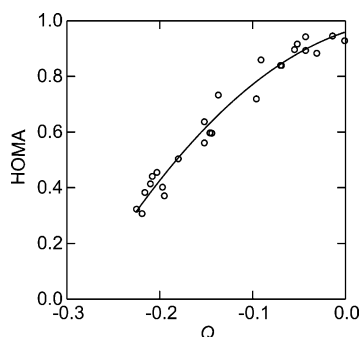
Figure 6. Dependence of HOMA values vs Gilli's Q parameter for π-electron delocalization in the OCCCO moiety. Correlation coefficient for the quadratic approximation is equal to 0.984 for 25 data set.

intramolecular H-bonding studied by Gilli[2] the variation of π-electron delocalization reaches more than half of the scale for the difference between benzene and its Kekulé structure!

The above results allow us to conclude that H-bonding affects bond lengths in the spacer in a regular way and the Gilli Q and HOMA indices values are good measures of these changes. It should be noted here that following the Hellmann−Feynman theorem[36] the distribution of electronic density in the molecule (or any chemical entity) determines the forces acting on the nuclei, which in turn define geometry of the molecule in question. Thus geometry may be a reliable description of the electron distribution and, applying appropriate references, may be used for the description of π-electron delocalization.

Analysis of π-Electron Delocalization for H-, Li-, and BeH-Bonded π-Electron Systems. Here we study the influence of the chelated cations: proton, Li$^+$, or BeH$^+$ on the geometry and π-electron delocalization in the title compounds. NICS(1)$_{zz}$, HOMA, and delocalization energies (E_{del}) due to the chelating were estimated and are discussed.

Table 1 presents all the above-mentioned computed data. Computations were carried out using two theory levels: B3LYP/6-311+G** and MP2/aug-cc-pVDZ. The first method of optimization is recommended by Wiberg[37] as one leading to satisfactory structures. It may be supported by C−C bond lengths for benzene: the calculated value is 1.3943 Å and is close to 1.3972(5) Å[38] obtained from the most reliable experimental measurements (single-crystal neutron diffraction at 15 K). The second method gives 1.4078 Å. In consequence, HOMA estimated for benzene from B3LYP/6-311+G** geometry is 0.99 (note that HOMA is based on empirically estimated R_{opt}[9]), whereas for MP2/aug-cc-pVDZ is 0.90. This difference is remarkable, and therefore for further discussion we used the HOMA and NICS(1)$_{zz}$ values based on the B3LYP/6-311+G** geometry. However, it is worth mentioning here that although the values of HOMA and NICS(1)$_{zz}$ obtained at those two levels of theory differ in absolute values, they show the same tendencies. Of three NICSs[31−33] the NICS(1)$_{zz}$ will be used in further discussions since this version seems to be the most reliable measure of π-electron delocalization.[33,39−41]

Let us discuss the dramatic difference in π-electron delocalization observed for keto-enamine form **2** of the *ortho*-hydroxy Schiff base and its tautomeric form—the enol-imine **1a**. The latter is energetically privileged (by 7.53 kcal·mol^{-1}), and the aromatic Ph-ring has a very high value of HOMA (0.93) and a strongly negative value of NICS(1)$_{zz}$ (−27.15) indicating strong π-electron delocalization. Contrary to this, the quasi-ring exhibits a rather low value of HOMA (0.38). The rotamer **1b**, for which H-bonding is excluded, has a very

similar HOMA for the Ph-ring but definitely a lower one for the OCCCN fragment, 0.09. This may be caused by a weaker intramolecular charge transfer in **1b** than in the quasi-ring (**1a**), where the −OH group is involved in H-bonding. As a result of H-bonding, the −OH group becomes a stronger π-electron donor, and in consequence a stronger through resonance with the electron accepting imine group appears. The tautomer **2**, of a slightly lower stability, has a much lower HOMA value for the Ph-ring, 0.39, and less negative NICS(1)$_{zz}$ (−12.94), whereas the quasi-ring exhibits reasonably high delocalization, HOMA is equal to 0.57. This picture is in line with many other observations concluding that the group(s) linked by a double bond to the aromatic ring may decrease dramatically its aromatic character. For instance, the pyrrole rings in porphyrins are much less aromatic (HOMA ∼0.5) than in derivatives substituted by common substituents (HOMA ∼0.9).[42] This is due to the fact that the CC(H)C bonds between pyrrole moieties in the macrocycle are about 1.40 Å; hence a high aromaticity of the macrocycle and a low one in the pyrrole rings are observed. This effect is often called as quinonoid destabilization.

When proton is replaced with Li$^+$ or BeH$^+$ the situation changes substantially—these cases do not resemble either case **1** or **2**. The π-electron delocalization in the Ph-ring is between that for **1** and **2**, whereas π-electron delocalization in the quasi-ring is higher than in any of **1** or **2**. Moreover, delocalization energy estimated according to the reaction in Scheme 1 increases significantly. The situation resembles numerically the case of naphthalene, particularly for the system **4**. HOMA for the naphthalene rings optimized at the same level of theory is 0.78, whereas for the Ph-ring and the quasi-ring in molecule **4** HOMA is equal to 0.82 and 0.70, respectively. A substantial π-electron delocalization in molecules **3** and **4** may be explained by a possibility of participation of a low-lying unoccupied p-type orbital of Li$^+$ and BeH$^+$ in delocalization of π-electrons in the quasi-ring therefore including these cations into the delocalization path. This suggestion is well supported by energies of 2p atomic hydrogen and lithium orbitals and molecular p-type orbital of BeH molecule that can roughly approximate p-type orbital levels in the studied systems. The values computed using the UHF/cc-pVQZ level of theory are 14.48, 0.53, and 1.06 eV, respectively. Undoubtedly, within the approximation applied the p-type orbitals for Li and BeH involved in bonding in the quasi-ring have dramatically lower energy than H. Thus in the cases of M = Li$^+$ or BeH$^+$ (Figure 4) they may play a similar role for π-electron delocalization as those at the sp^2 hybridized carbon atom.

Comparison of HOMA values for the ring and quasi-ring for Li-derivative (0.70 and 0.58) and BeH-derivative (0.82 and 0.70) seems to suggest a stronger delocalization in the latter. This may be associated with a less ionic interaction between BeH and nitrogen and oxygen atoms than it is realized in the case of the Li derivative. This difference may be interpreted as being due to the higher electronegativity of Be than Li.

ACKNOWLEDGMENT

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