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H-Bonding-Assisted Substituent Effect[†]

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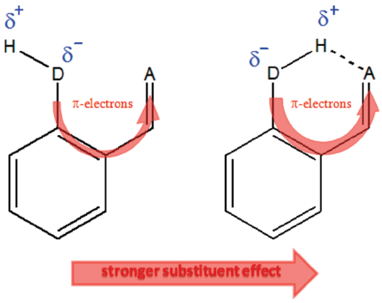

In this paper we investigate the influence of intramolecular noncovalent interaction, i.e., H-bonding and Li-bonding, on the properties of substituents communicating through the resonance (mesomeric) effect in such molecular systems as salicylaldehyde, *o*-hydroxy Schiff base, *o*-nitrosophenol, and their lithium analogues. The investigated systems are usually considered as molecular patterns of intramolecular resonance-assisted hydrogen bonds (or its analogues in the case of Li-bonded systems). We show that the relation between intramolecular noncovalent interactions, $A{-}H\cdots B$ and $A{-}Li\cdots B$, and the π-electron delocalization in the sequence of π-conjugated covalent bonds linking A and B can be considered in terms of the Hammett-like substituent effect in which electron-donating and electron-withdrawing properties of substituents are affected by the noncovalent interaction.

Introduction

Hydrogen bonding is one of the most important interactions since it is responsible for most processes in the bio- and geospheres as well as playing an important role in the development of new materials.[1−8] In the past two decades Gilli et al.[9−17] introduced a concept of resonance-assisted hydrogen bonding (RAHB) in which H-bonding strength is related to the π-electron delocalization in the spacer between the proton-donating -AH group and a proton-accepting -B group in $R^1A\text{-}H\cdots BR^2$. In a particular case, when R^1 and R^2 are linked covalently, the H-bond is the intramolecular one. According to Gilli's concept of RAHB, a mechanism of synergetic interplay is assumed between the resonance of π-electrons in the spacer and the H-bond formation. Undoubtedly, the electronic properties of -AH and -B groups interacting via intramolecular H-bonding change in comparison with their states before interaction.[18] The consequences of

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[†] Dedicated to our friend Profesor Gastone Gilli (University of Ferrara, Italy) in recognition of his remarkable contribution to the field of research on hydrogen bonding.

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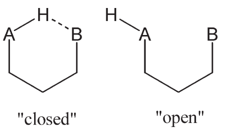
H-bond formation may be observed while comparing the energy of the H-bonded system with its "open" conformation[19] as shown in Scheme 1. It should be stressed, however, that the difference in energy mentioned above consists of at least three contributions: the H-bond formation that stabilizes the system in question, the changes in π-electron delocalization, and finally the deformation energy, which destabilizes it.[20]

It has to be mentioned that the original concept of RAHB was later criticized by some authors. For the criticism of RAHB, see refs 21−24. According to this criticism the stronger H-bonds in RAHB models result from steric effects and not from the π-electron delocalization, as it was proposed by Gilli. It is worth mentioning, however, that in numerous papers the direct relation between the π-electron structure and the parameters of RAHB was reported (see, for example, refs 25−38).

The electronic properties of the interacting groups, which may be called substituents, are often described by use of substituent constants,[39−44] usually labeled by Greek letter σ. In the original version, the substituent acts on a functional group (reaction site) at which the reaction (or physicochemical process) takes place and the substituent effect is observed, which is manifested in a change in chemical/physicochemial behavior of the functional group.[45] In the case of H-bonded systems, AH and B may be considered as a "reaction site" and a substituent, respectively. For both cases the substituent constants may be used for measuring the electron-donating/-accepting property of the group in question. These constants were determined experimentally by direct measurements of the changes in reactivity (rate constants) or equilibria (equilibrium constants) observed at the particular functional group.

SCHEME 1



Since the nature of the interaction between the substituent and the reaction site depends also on the kind of group serving as the reaction site, a variety of substituent constants are in use.[39,46,47] It was also shown that the magnitude of the substituent constants depends not only on the nature of the reaction site[45,48] but also on the environment in which a given process is carried out.[49]

Very recently we have attempted[49] to consider the -AH and -B groups interacting via intramolecular hydrogen bond as substituents whose electronic properties, in the Hammett sense,[39] change as a result of the H-bond formation.[50,51] As a result of H-bonding formation, the A−H bond becomes longer, its electron-donating properties change because of the formation of $A^{\delta-}-H^{\delta+}$ and as a substituent this group becomes more electron-donating. Thus the substituent constant (σ^+) should become more negative. Simultaneously, close spatial arrangement of the proton from the -OH group and the -B leads to the formation of $B\cdots H^{\delta+}$ contact. This results in an increase of the electron attracting power of $B\cdots H^{\delta+}$ at least in comparison with B. In consequence the magnitude of the substituent constant (σ^-) should increase.

The purpose of this paper is to extend the above-mentioned ideas to include the systems with OH···O═N and OH···N(H)═CH interactions in *o*-hydroxybenzaldehyde and *o*-hydroxy Schiff base and present the changes in electronic properties of the AH and B groups in a more quantitative way, i.e. to show how the electron-donating power of A−H and electron-accepting power of B change due to the H-bond formation $A^{\delta-}-H^{\delta+}\cdots B$.

It was recently reported that in Li-bonded *quasi*-rings the effect of π-electron delocalization accompanying the formation of such a ring is much more effective than in the case of H-bonded analogues.[37] Thus, in order to have a better insight into the investigated phenomenon, we additionally analyze Li-bonded systems, being analogues of H-bonded ones.

Methodology. Geometries of all molecular systems shown in Figure 1 and its monosubstituted analogues were optimized using DFT-B3LYP[52−55] hybrid functional in conjunction with 6-311+G(d,p)[56,57] basis set. C_s symmetry was kept in the optimization procedure. The frequency analysis was

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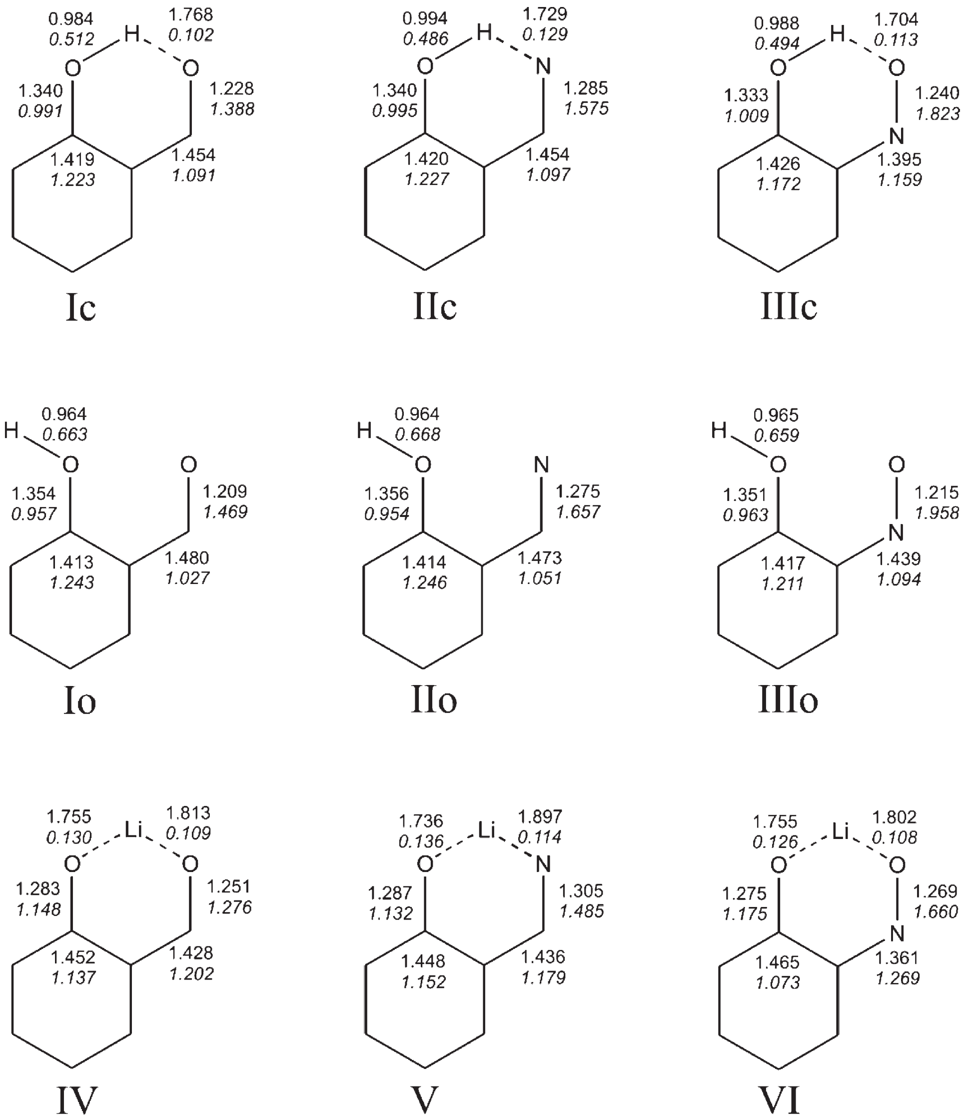

FIGURE 1. Bond lengths (plane text, in Å) and dicenter electron delocalization index values (*italic*, in au) estimated for selected bonds. The distribution of single- and double-character bonds is omitted for clarity.

used to verify whether the optimized geometries correspond to the ground state stationary points or transition states. No imaginary frequencies were found. All calculations were performed with the use of the Gaussian09 set of codes.[58]

As a geometry-based indicator of local aromaticity, the HOMA index (harmonic oscillator model of aromaticity) was applied. According to its definition[59,60] HOMA can be expressed by the following equation:

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

where n represents the total number of bonds in the molecule and α_i is a normalization constant (for CC bond, $R_{\mathrm{opt,CC}}$ = 1.388 Å, $\alpha_{\mathrm{C-C}}$ = 257.7; for CN bond, $R_{\mathrm{opt,CN}}$ = 1.334 Å, $\alpha_{\mathrm{C-N}}$ = 93.52; for CO bond, $R_{\mathrm{opt,CO}}$ = 1.251 Å, $\alpha_{\mathrm{C-O}}$ = 158.38; for NO bond, $R_{\mathrm{opt,NO}}$ = 1.251 Å, $\alpha_{\mathrm{N-O}}$ = 57.21) fixed to give HOMA = 0 for a model nonaromatic system, e.g., the Kekulé structure of benzene and HOMA = 1 for the system with all bonds equal to the optimal value $R_{\mathrm{opt},i}$, assumed to be realized for fully aromatic systems.[59] The higher is the HOMA value, the more "aromatic" is the ring in question and hence the more delocalized are the π-electrons of the system. HOMA may be estimated for the set of bonds forming the ring but also for any part of that ring or other sequence of bonds for which delocalization can be considered. In the case of *quasi*-rings HOMA was estimated for the sequence of (H)O−C═C−C═A bonds.

As an electron -density-based measure of aromaticity the *para*-delocalization index (PDI)[61] was implemented. PDI is the mean of all delocalization indices (δ(A,B))[62,63] of *para*-related carbon atoms in a given six-membered ring.

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TABLE 1. Selected Data Discussed in This Paper

	$HOMA_{quasi}$	PDI_{quasi}	$\%Del_{quasi}$	$HOMA_{ben}$	PDI_{ben}	σ_p^+ (OH)	σ_p^- (acc)	$\Delta\sigma_p^a$
Ic	0.38	0.023	49	0.926	0.081	−1.11	1.06	2.17
Io	−0.02		27	0.957	0.086	−0.89	0.57	1.46
IIc	0.38	0.024	50	0.926	0.083	−1.11	0.53	1.64
IIo	0.08		35	0.954	0.087	−0.86	−0.07	0.79
IIIc	0.64	0.03	78	0.888	0.074	−1.22	1.6	2.82
IIIo	0.41		56	0.946	0.082	−0.94	0.94	1.88
IV	0.61	0.029	96	0.649	0.069	−1.99	1.65	3.64
V	0.6	0.028	88	0.701	0.071	−1.93	1.74	3.67
VI	0.59	0.04	76	0.498	0.061	−2.12	2.37	4.49

[a] Defined as $\Delta\sigma_p = |\sigma_p^+(OH) - \sigma_p^-(acc)|$.

For monodeterminant closed-shell wave function the delocalization index value between atoms A and B, $\delta_{A,B}$, was obtained by summations over all of the $N/2$ occupied molecular orbitals;

$$\delta(A, B) = 4\sum_{i,j}^{n/2} S_{ij}(A)S_{ij}(B)$$

where $S_{ij}(A)$ is the overlap between molecular orbitals i and j within the basin of atom A.

$\delta_{A,B}$ provides a quantitative idea of the number of electrons delocalized or shared between atoms A and B. In the case of two atoms formally interacting in the chemical bond the value of $\delta_{A,B}$ may be considered as the AIM-based bond order.[64−67]

The electron-donating and electron-withdrawing power of substituents interacting through the H- or Li-bonding was quantified by means of Hammett's substituent constants σ^+ and σ^-.[20,39−41,43,45] These quantities may be obtained from the empirical relationship between the parameters of the π-electron delocalization in the fulvene/heptafulvene rings presented by geometry-based aromaticity index HOMA and the substituent constant of the group attached at the exocyclic carbon atom. For details regarding the procedure of the σ^- and σ^+ constants estimation see refs 51, 68 and the Supporting Information associated with this paper. For the definition of % Del parameters see ref 69 and the Supporting Information associated with this paper. It is worth mentioning that the large positive value of a given σ constant implies high electron-withdrawing power by inductive and/or resonance effect, relative to the hydrogen atom, whereas the large negative value of a given constant implies high electron-releasing power relative to the hydrogen atom.

It is also worth mentioning that we analyzed the energetic aspects of phenomena acting in discussed systems, using for this purpose the energy parameters of homodesmotic reactions. However, no decisive conclusion has been reached in this way. The lack of clear conclusion in that case results from the fact that in systems under discussion there are several π-electron effects acting simultaneously. For instance, the π-electron stabilization in *quasi*-ring, which should be reflected in relatively lower total energy of the closed conformer, acts against the π-electron stabilization within the aromatic ring, which in turn leads to partial increase of total energy of the system under consideration (see ref 29 for more details). For this reason the energy parameters, obtained on the basis of homodesmotic reactions, do not lead to any decisive conclusion. Thus, we omit these results in the discussion, attaching numerical values to the Supporting Information, page S6, Figure S1.

Results and Discussion

The molecular systems shown in Figure 1 were taken into account in the present studies. All the optimized geometries are collected in Supporting Information file associated with this paper. Selected numerical data can be found in Table 1. Additionally, the values of bond lengths and delocalization indices corresponding to those bonds are presented in Figure 1.

As it can be seen from the values estimated for the *quasi*-rings ($HOMA_{quasi}$, PDI_{quasi}, and % Del_{quasi} in Table 1), in the case of all H-bonded systems there is a clear increase of delocalization due to formation of the H-bonding. This is reflected by an increase of HOMA, PDI, and % Del values. Since in the investigated systems the H-bonds under discussion can be classified as RAHBs, the increase of delocalization in *quasi*-ring due to H-bond formation may be explained according to the concept proposed by Gilli and co-workers.[9−17] Nevertheless, another explanation can be given. Two substituents, namely, the -OH group and the substituent being in position *ortho* with respect to this group, interact through the mesomeric (resonance) effect. It should be emphasized that this effect proceeds no matter whether there is a noncovalent interaction between both substituents (e.g., the H-bond). This is directly connected with the fact that the hydroxyl group is generally known as a π-electron-donating species, whereas -CO, -CN, and -NO groups reflect π-electron accepting properties. The obvious differences in the degree of electron delocalization can be noticed when comparing *closed* and *open* conformers from Figure 1, systems **I**, **II**, and **III**. The *closed* systems are more delocalized, which is clearly due to the fact that in these cases both substituents interact through the H-bond. It can be expected that the proximity of the partially positively charged hydrogen in H-bridge will affect the proton-accepting groups, -CO, -CN, or -NO, increasing their electron-withdrawing properties. As a result of the same mechanism the electron-donating properties of the hydroxyl group will increase for the *closed* conformers. It is well-known that the substituent effect in disubstituted π-electron systems increases with an increase of the difference between electron-accepting and -donating power of the

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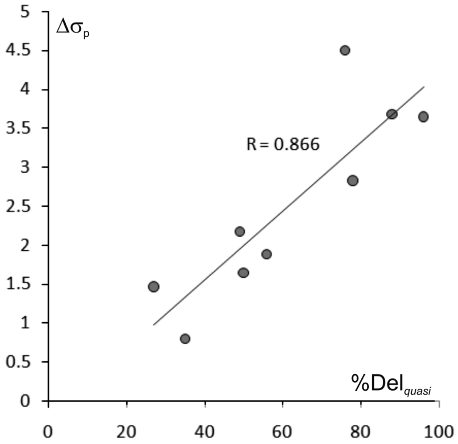

FIGURE 2. Interrelation between the degree of delocalization within the *quasi*-ring (reflected by % Del parameter) and the values of $\Delta\sigma_p$ parameter.

interacting substituents (see, for example, ref 70). Let us consider the difference between substituents constants characteristic of the substituents present in the systems under consideration. Since the direct relations between geometry parameters and σ values have been established (see Supporting Information), it is possible to estimate the values of σ^- and σ^+ for each given isomer shown in Figure 1. As it can be seen in Table 1, the larger values of $\Delta\sigma_p$ are for *closed* conformations. Thus, the presence of H-bonding increases the difference between electron-accepting and -donating power of the interacting substituents, as reflected by $\Delta\sigma_p$. In consequence, the more effective π-electron communication can be observed for *closed* structures. This more effective communication between substituents is exhibited by the more delocalized character of the *quasi*-ring. It should be mentioned that the hypothetical system with no π-electron communication between both substituents and between substituents and the benzene ring should be fully localized (with the exception of the benzene ring itself, which by contrast should be fully delocalized). As a result, the degree of delocalization should grow with the increasing difference between electron-accepting and electron-donating power of the interacting substituents, thus with the growing value of the $\Delta\sigma_p$ parameter. Figure 2 illustrates this situation for the systems under discussion. Clearly, with higher values of $\Delta\sigma_p$ the values of % Del are also growing. Similar trends in changes can be observed for both aromaticity indices, HOMA$_{quasi}$ and PDI$_{quasi}$. The changes in bond lengths and delocalization indices related to bond orders also support such an observation.

On the other hand, it is well-known that the communication between substituents through the mesomeric effect leads to partial π-electron localization within the benzene ring. (For basic text, see ref 71. See also refs 29, 72−74.) This can be easily explained by the contribution of charge-separated resonance structures.[75] Therefore, we should also observe a direct relation between $\Delta\sigma_p$ values and the measures of aromatic character of the benzene ring. In fact, such a relation can be found, as shown in Figure 3.

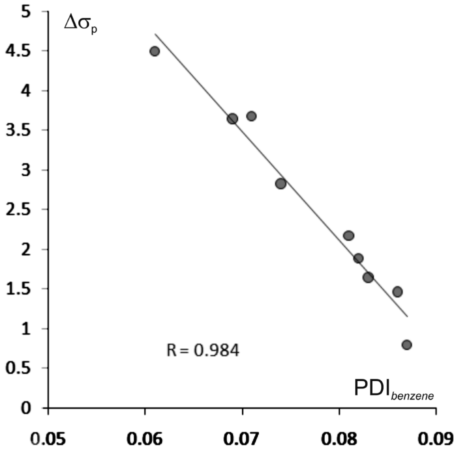

FIGURE 3. Interrelation between $\Delta\sigma_p$ parameter and PDI values estimated for the benzene ring. Clearly, the increasing electron-donating and electron-withdrawing power of substituents, being partially dependent on the presence and strength of H-bond, affects in a systematic way the aromatic character of the benzene ring.

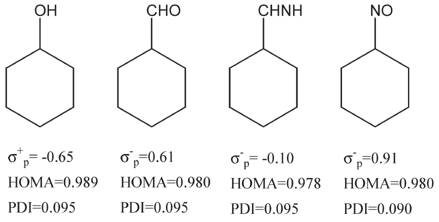

FIGURE 4. Selected data estimated for monosubstituted analogues of **I**, **II**, and **III**.

With the growing value of the $\Delta\sigma_p$ parameter the aromatic character of benzene ring clearly disappears. It should be pointed out that the values of $\Delta\sigma_p$ depend among other things on the presence of H-bonding, since as it was mentioned above, the σ^- and σ^+ parameters change their values due to hydrogen bond formation.

It is worth taking closer look at monosubstituted analogues of **I**, **II**, and **III**. Selected parameters of these systems can be found in Figure 4.

As can be seen, the indicators of aromaticity show relatively more delocalized character of the benzene ring in these systems if comparing with **I**, **II**, and **III**. This is obviously because in this case only one substituent interacts with the π-electron structure of benzene ring. Interestingly, in monosubstituted systems the σ^- values estimated for π-electron-withdrawing groups (i.e., -CHO, -CHNH, and -NO) adopts values very close but systematically larger if comparing with those found for open forms of **I**, **II**, and **III**. This may be explained by the presence of interaction between the lone pairs located on the O or N atom and the lone pairs on hydroxyl O atom. This is the effect that appears in **Io**, **IIo**, and **IIIo**, being exactly opposite to that observed for closed forms of **I**, **II**, and **III** discussed earlier. The negative charge surplus derived from lone pairs on the hydroxyl O atom (see Figure 5) leads to destabilization of the canonic structure with formal charge on the O and N atoms of π-electron-withdrawing groups.

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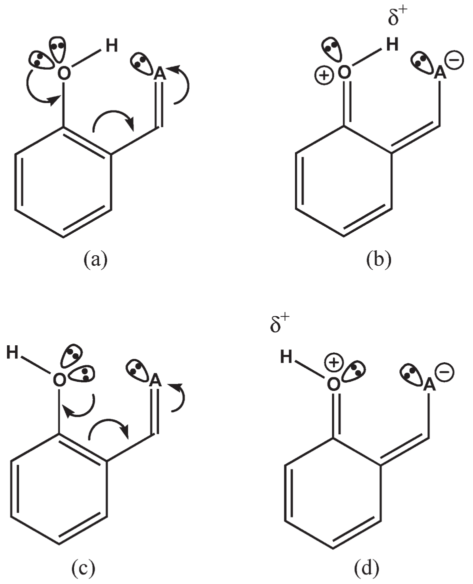

FIGURE 5. Substituent effect in H-bonded (a, b) and "open" (c, d) forms of systems under discussion.

This results in relatively lower electron-withdrawing properties of -CHO, -CHNH, and -NO groups in **Io**, **IIo**, and **IIIo** (reduced contribution from structure d in Figure 5) with respect to its monosubstituted analogues shown in Figure 4. In the case of a hydroxyl group being the electron-donating substituent, the situation differs from that of electron-withdrawing groups. In structure c in Figure 5 there is a surplus of the negative charge in between O and A atoms. Thus, the contribution of the structure with formal positive charge on hydroxyl O atom will be preferred. This results in relatively greater electron-donating properties of the -OH group in **Io**, **IIo**, and **IIIo** with respect to monosubstituted analogues, that is, the phenol molecule (Figure 4). All above-discussed effects are confirmed with substituent constants estimated for **I**, **II** and **III** systems in open and closed forms (Table 1), as well as for their monosubstituted analogues (Figure 4).

It is also worth taking a closer look at Li-bonded systems. Systems **IV**, **V**, and **VI** can be considered as specific metal–ligand complexes in which bidentant ligands formally exist in ionic form coordinating the Li^+ center. Recently it was reported, on the basis of analysis of ring currents induced in related Li-bonded systems, that in fact there is no cyclic diatropic ring current in the *quasi*-ring formed due to Li-bonding.[76] Thus, it may be expected that the Li-bonding mainly leads to the formation of partially ionic structure with negative charge surplus formally located within benzenoid ligand. Such a negative charge surplus would formally be associated with the deprotonated hydroxyl group. As a result, the delocalization of negative charge should proceed along the sequence of bonds linking substituents being in *ortho*-position with respect to each other. In other words, in Li-bonded systems the ionic character of interaction between benzenoid ligand and Li-center should very strongly affect the electron-donating power of the $-O^-$ group. On the other hand, the proximity of Li-cation should increase the electron-withdrawing properties of the -CO, -CN, or -NO groups. In fact, the values of σ^- and σ^+ parameters estimated for systems **IV**, **V**, and **VI** clearly show the efficient increase of the difference between electron-accepting and -donating power of the interacting substituents, when compared with H-bonded analogues. What is interesting, general trends in the H-bonded and Li-bonded systems are the same, as can be seen in Figures 2 and 3. That is why in both kinds of species the changes in the π-electronic structure seems to result from the same effect, namely, π-electron communication between substituents, no matter what kind of interaction affects the properties of substituents communicating through the resonance (mesomeric) effect.

Conclusions

On the basis of our results it can be concluded that in the investigated systems there is a π-electron communication between two substituents, i.e., the proton-donating and proton-accepting group, a kind of communication that is thoroughly considered in terms of the substituent effect. This communication between substituents is exhibited by both geometry and electron distribution-based parameters, including indices of aromaticity. What is particularly important, the formation of a hydrogen bond leads to changes in electron-donating and electron-withdrawing power of substituents, thus affecting the efficiency of π-electron communication between them, leading to clear changes in π-electron structure along the sequence of conjugated covalent bonds. Therefore, it might be postulated that the H-bonding is the assisting effect that amplifies the substituent effect in *ortho*-substituted systems investigated in this paper.

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Supporting Information Available: Details regarding substituent constants estimation, Cartesian coordinates and energies of all structures optimized in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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