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Routes of π-Electron Delocalization in 4-Substituted-1,2-benzoquinones[†]

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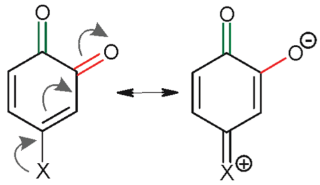

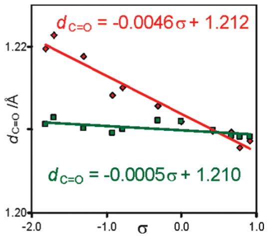

The substituent effect in 4-substituted-1,2-benzoquinone is investigated by means of modeling using B3LYP hybrid functional in conjunction with the 6-311+G(d,p) basis set. The interrelation between different types of substituents, X = NO, NO_2, CN, CHO, H, Me, OMe, OH, NH_2, NHMe and $N(Me)_2$, and both CO groups has been characterized both qualitatively and then quantitatively by means of several measures of π-electron delocalization (HOMA, MCI, DI, FLU) based on structural and electronic properties of 4-substituted-1,2-benzoquinones chosen for analysis. Results of this analysis clearly show that only the meta-placed CO group is affected by substituents, whereas the para-placed CO group is rather insensitive to substitution. These observations may help to explain diversified chemical properties (including reactivity) of CO centers in *o*-benzoquinone derivatives. Among others, they may explain differences in proton-accepting properties of carbonyl O atoms, as it is shown for simple models in which carbonyl groups in *o*-benzoquinone act as proton acceptors in H-bonds of O···H−F type.

Introduction

It has long been known that substituent effect from meta- and para-positions differs in a dramatic way. Quantitatively it was shown in a clear manner already by Hammett himself in his fundamental monograph[1] by introducing two kinds of substituent constants σ_m and σ_p. Taft et al.[2] quantified this difference by assuming that for para-substituent effect the

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[†] Dedicated to the memory of Larry Schaad (1930−2009) and in recognition of his outstanding contribution to theoretical organic chemistry.

(1) Hammett, L. P. *Physical Organic Chemistry*; McGraw Hill: New York, London, 1940; p 188.

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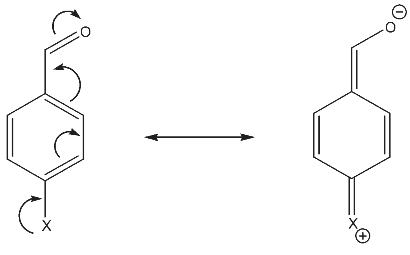
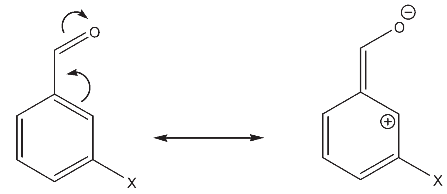
blend of resonance and inductive effect is $\sim$1:1, whereas in meta-substituent effect the contribution of resonance is much lower, only $\sim$33% of that for para one. More precise analysis gave later a similar result.[3] In the last decades of the 20th century, the inductive effect has become frequently identified not necessarily with a through bond but rather through space interactions[4] based mostly on purely electrostatic interactions.[5] An important and interesting problem in the field of research on substituent effects on chemical and physicochemical properties is its transmission in X−R−Y systems, i.e. from the substituent X through the moiety R to the reaction/process site Y. Traditionally the transmission factor of the substituent effect is considered numerically in terms of reaction constants, ρ, the slope of the linear regression of a given physicochemical property on substituent constants. The ρ constants depend on a distance between X and Y, on the environment of the reaction/process (solvent effect, see Reichardt[6]), on kind of the process[7] and on the nature of bonds linking these two groups.[8] In the case of application of the Hammett-like equations to planar molecules,[9] contributions due to the resonance and field effects in the transmission factors may be roughly estimated.

The purpose of this paper is a special approach to the transmission phenomenon of substituent effect by showing how the meta- and para-type substitution, with respect to the carbonyl groups (see Schemes 3 and 4), in *o*-benzoquinone derivatives influences the properties of CO group. The other issue is to investigate the communication's routes of these interactions. It may be studied by analyzing the bonds linking the substituent in position 4 with carbonyl groups in position 1 (para position) and in position 2 (meta position). It has to be noted that in classical cases (e.g., X−Ph−Y-type systems) the resonance effect of the substituent X on reaction site Y is mostly acting for para- or para-type[10,11] positions, whereas for meta type positions it is much weaker. This is illustrated by Schemes 1 and 2 for benzaldehyde substituted by electron-donating groups. Finally it will be shown how these interactions affect properties of the ring in substituted *o*-benzoquinone.

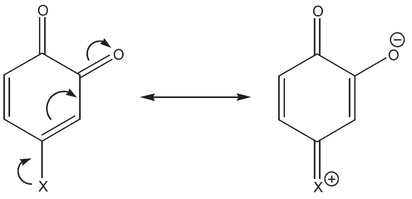
SCHEME 1. Interaction between π-Electron-Donating Substituent and Carbonyl Group for Para-Substituted Benzaldehyde System



SCHEME 2. Interaction between π-Electron-Donating Substituent and Carbonyl Group for Meta-Substituted Benzaldehyde System



SCHEME 3. Interaction between π-Electron-Donating Substituent and Carbonyl Group for Meta-Type Substitution in 4-X-1,2-Benzoquinone



Resonance theory[12] applied to the problem considered in this paper leads to structures presented in Schemes 3 and 4 showing qualitatively a difference in π-electron interactions between substituents X, electron-donating or electron-accepting, to C1O and C2O groups (see Scheme 5 for atom numbering).

If the substituent is π-electron donating, the preferred communication is only with C2O group as shown by resonance effect presented in Scheme 3. In the case of an electron-attracting substituent, it will compete with both carbonyl groups, attracting electrons from the ring, and the formal charge, due to resonance, will be located at C3. Note that in both cases (Schemes 3 and 4) bond b2 (see Scheme 5) is not involved in resonance effects of substituents with the carbonyl groups. As seen from the schemes, neither π-electron-donating nor electron-attracting substituents communicate with C1O.

The purpose of this paper is to illustrate the presented above difference in a more quantitative way, using quantitative measures of π-electron delocalization as: HOMA,[13,14] bond characteristics based on the quantum theory of atoms in molecules (QTAIM),[15] the aromatic fluctuation (FLU) index,[16] and the multicenter index (MCI),[17] both being the

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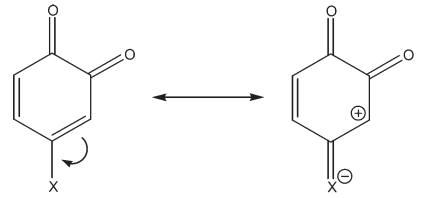
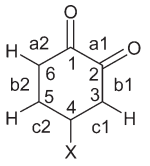
SCHEME 4. **Interaction between π-Electron-Attracting Substituent and Carbonyl Group for Para-Type Substitution in 4-X-1,2-Benzoquinone**



SCHEME 5. **Labeling of Bonds and Atoms in 4-X-Substituted Derivatives of 1,2-Benzoquinone; X = NO, NO_2, CN, CHO, H, Me, OMe, OH, NH_2, NHMe, and $N(Me)_2$**

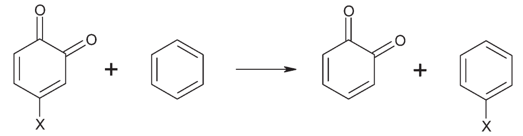


measures of electron density-based delocalization. It is worth noting that MCI has been recently proven to work correctly for different series of aromatic systems,[18] and it can be applied not only to rings but also to the analysis of fragments of the ring, i.e. to the electronic delocalization in a certain part of them.

Methodology

As an object of investigation the set of systems shown in Scheme 5 was chosen. The full geometry optimization was performed using B3LYP hybrid functional[19] in conjunction with 6-311G basis set[20] with polarization and diffuse functions, the latter included for non-hydrogen atoms only, i.e., 6-311+G-(d,p). For two *o*-benzoquinone derivatives (X = H and NMe_2) the formation of H-bonds with an external HF molecule were studied. In this case, two types of H-bonded complexes were analized: (i) assuming linearity $C{=}O\cdots H{-}F$ and (ii) without constraints. For optimized structures the frequency analysis was performed in order to check whether all geometries correspond to true ground-state stationary points. Gaussian 03[21] set of codes was used for this part of calculations.

SCHEME 6. **Scheme of Homodesmotic Reaction Used for Calculation of SESE**



The geometry-based index of aromaticity HOMA[14] may serve as a convenient, reliable,[22] and easily accessible quantitative measure of π-electron delocalization[23] of the system (in the ring). The formula for HOMA reads:

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

where n is the number of bonds taken into the summation; α_i is a normalization constant (for CC and CO bonds $\alpha_{CC} = 257.7$ and $\alpha_{CO} = 157.38$) fixed to give HOMA = 0 for a model nonaromatic system and HOMA = 1 for the system with all bonds equal to the optimal value $R_{\mathrm{opt},i}$ assumed to be realized for full aromatic systems (for CC and CO bonds $R_{\mathrm{opt,CC}}$ is equal to 1.388 and $R_{\mathrm{opt,CO}} = 1.265$ Å); R_j denotes bond lengths taken into calculation.

In order to estimate the energy parameter corresponding to the interaction between the given substituent and the carbonyl groups the substituent effect stabilization energy (SESE) approach was applied. The homodesmotic reaction chosen for estimation of SESE values can be found in Scheme 6. All SESE numerical data are collected in the Supporting Information (SI).

For the optimized geometries a detailed analysis of the electron distribution function was performed according to the QTAIM proposed by R. F. W. Bader,[15] using AIM2000[24] program. The following parameters are discussed: electron density measured at the bond critical point (BCP), ρ_{BCP}, and the values of the delocalization indices (DIs) and MCI. For monodeterminantal wave functions the DI is given by:

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

The summations in eq 2 run over all the spin-occupied molecular orbitals. $S_{ij}(A)$ is the overlap between molecular orbitals i and j within the basin of atom A as defined by the QTAIM partition (although other partitions can be used[25]). $\delta(A,B)$ provides a quantitative idea of the number of electron pairs delocalized or shared between atoms A and B. On the other hand, the MCI is a particular extension of the I_{ring} index:[26]

$$I_{\mathrm{ring}}(\mathcal{A}) = \sum_{i_1, i_2, \ldots, i_N} n_{i_1} \cdots n_{i_N} S_{i_1 i_2}(A_1) S_{i_2 i_3}(A_2) \cdots S_{i_N i_1}(A_N) \qquad (3)$$

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n_i being the occupancy of molecular orbital (MO) i and $\mathcal{A} = \{A_1, A_2, ..., A_N\}$ a string containing the set of N atoms forming the ring structure. This expression is used both for closed-shell and open-shell species.[27] Summing up all the I_{ring} values, resulting from the permutations of indices $A_1, A_2, ..., A_N$, the MCI index[17] is defined as:

$$\text{MCI}(\mathcal{A}) = \frac{1}{2N} \sum_{P(\mathcal{A})} I_{\text{ring}}(\mathcal{A}) \tag{4}$$

where $P(\mathcal{A})$ stands for a permutation operator which interchanges the atomic labels $A_1, A_2, ..., A_N$ to generate up to the $N!$ permutations of the elements in the string $\mathcal{A}$.[17,28] The I_{ring} and MCI give a measure of the electronic delocalization among the centers $A_1, A_2, ..., A_N$. When computed in an aromatic ring, the more positive the MCI, the more aromatic the ring. The analysis of the delocalization in the ring by MCI has been complemented with the calculation of the fluctuation index of aromaticity (FLU),[16] which measures the amount of electron sharing between contiguous atoms. It is defined as:

$$\text{FLU}(\mathcal{A}) = \frac{1}{N} \sum_{i=1}^{N} \left[\left(\frac{V(A_i)}{V(A_{i-1})} \right)^{\alpha} \left(\frac{\delta(A_i, A_{i-1}) - \delta_{\text{ref}}(A_i, A_{i-1})}{\delta_{\text{ref}}(A_i, A_{i-1})} \right) \right]^2 \tag{5}$$

where $A_0 \equiv A_N$ and $V(A)$ is the atomic valence given by:

$$V(A_i) = \sum_{A_j \neq A_i} \delta(A_i, A_j) \tag{6}$$

and α is a simple function to make sure that the first term in eq 5 is always greater or equal to 1, so it takes the values:

$$\alpha = \begin{cases} 1 & V(A_i) > V(A_{i-1}) \\ -1 & V(A_i) \leq V(A_{i-1}) \end{cases} \tag{7}$$

The $\delta_{\text{ref}}(\text{C,C}) = 1.389$ e, calculated from benzene at the B3LYP/6-311++G(d,p) level, was used in the calculations. FLU is close to 0 in aromatic species, and differs from it in nonaromatic ones.

All calculations of the MCI and FLU indices have been performed with the Gaussian 03[21] and AIMPAC[24a] packages of programs, at the B3LYP/6-311+G(d,p) level of theory. Calculation of atomic overlap matrices (AOM) and computation of DIs and MCIs has been performed with the AIMPAC and ESI-3D[29] collection of programs. Calculation of DIs with the density functional theory (DFT) cannot be performed exactly because the electron-pair density is not available at this level of theory.[30] As an approximation, we have used the Kohn–Sham orbitals obtained from a DFT calculation to compute Hartree–Fock-like DIs. The MCI values have also been obtained from the Kohn–Sham orbitals using eqs 3 and 4.

Results and Discussion

There are two aspects of substituent effects affecting 4-substituted *o*-benzoquinone derivatives: (i) a problem of communication between substituent X and both carbonyl groups, and of indication of the route of communication, and (ii) how the substituents affect the π-electron delocalization in the ring of benzoquinone. They present different general phenomena and are considered in separate ways.

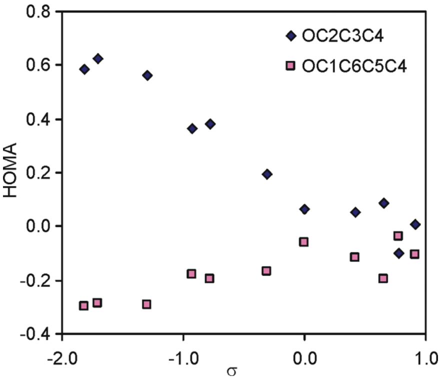

FIGURE 1. Dependence of HOMA for transmission paths OC2C3C4 (meta-type way) and OC1C6C5C4 (para-type way) on substituent constants σ (σ_p^+ for electron-donating substituents and for others σ_p).

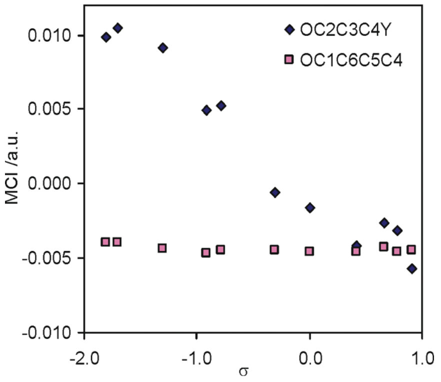

FIGURE 2. Dependence of MCI for transmission paths OC2C3C4Y and OC1C6C5C4 on substituent constants σ (σ_p^+ for electron-donating substituents and for others σ_p).

Communication between Substituent and the Carbonyl Groups. Consider first the way in which π-electron delocalization indices as HOMA,[14] MCI[17] and FLU[16] describe communication paths between substituent X and both carbonyl groups: OC2C3C4 (meta-type way) and OC1C6C5C4 (para-type way), for labeling see Scheme 5. We assume that for electron-donating substituents the appropriate substituent constants are σ_p^+ and for others σ_p, all taken from Taft et al. review.[31] Figures 1 and 2 present the scatter plots for these relationships. Moreover, if the HOMA values are plotted against the SESE (see Scheme 6), the latter correlate nicely with σ_p^+ for electron-donating substituents and for others σ_p by equation SESE $= -5.44\,\sigma - 0.023$ with $cc = -0.975$ (Figure S1, SI), then HOMA vs SESE relationship is very similar to that in Figure 1, see Figure S2 (SI).

As we see (Figures 1 and 2), both delocalization indices, HOMA and MCI, applied to the path of meta-substitution follow linear dependences with correlation coefficients $cc = -0.970$ and -0.978, respectively. This shows a strong increase of π-electron delocalization with an increase of the

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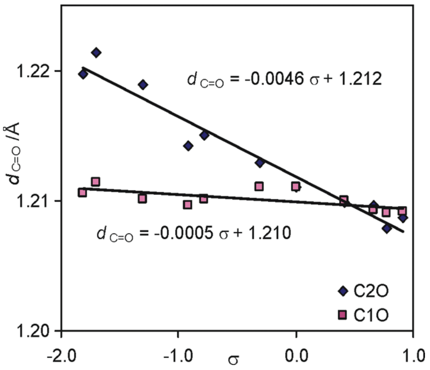

FIGURE 3. Dependence of CO bond lengths, $d_{C=O}$, on substituent constants σ (σ_p^+ for electron-donating substituents and for others σ_p).

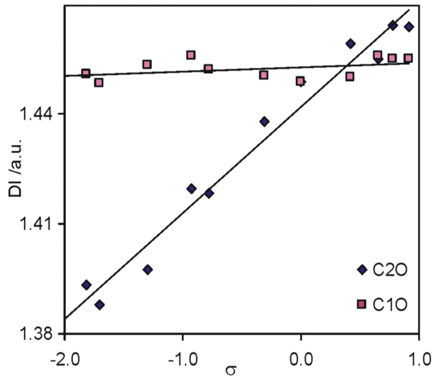

FIGURE 4. Correlation between the bonding DIs of C1O and C2O with substituent constants σ (σ_p^+ for electron-donating substituents and for others σ_p); for C2O bond cc = 0.985.

electron-donating power of the substituent. The interaction between the substituent and another carbonyl group −C1O is totally different. For this case we observe for HOMA a weak and opposite dependence (cc = 0.836) and almost constant values of MCI.

With respect to the tendencies given by MCI, it is worth noting the change of sign of the MCI(OC2C3C4Y) values with the increase of electron-donating power, which clearly reinforces the idea of an important increase in the communication path between the O2 and the substituent with the π-donor character of the substituents. On the other hand, the fact that MCI(OC1C6C5C4) remains constant, and with negative values, proves the disconnection (lack of communication) between O1 and the substituent. It has to be noted that for the OC2C3C4 we have included the first atom (Y) of the X substituent in the calculation of MCI in order to make the two MCI values comparable (both OC2C3C4Y and OC1C6C5C4 refer to a 5-center delocalization index).

When we plot the CO bond lengths against substituent constants σ_p^+ and σ_p, we end up with a picture as in Figure 3. As we see, in both cases (C1O and C2O) the substituent "works" in the same direction, but the bond length of C1O is almost independent of the substituent effect ($cc = -0.641$) with slope = −0.0005, whereas for C2O bond lengths the slope of linear regression is ~10 times greater (−0.0046), with $cc = -0.975$.

The electronic-based DI index has also been applied to analyze the electronic delocalization for the two different CO bonds as shown in Figure 4. As we see, the dependence of the DIs on substituent constants σ_p/σ_p^+ is similar to that presented in Figure 3 for bond lengths, but with slopes of opposite sign.

It is well-known that bond lengths correlate with the value of electron density measured at the bond critical point (BCP) of the given bond, ρ_{BCP}.[10,32] This relation is fulfilled in the present case. The proper graphical representations can be found in Figure S3 (SI), that presents the relation between bond length and ρ_{BCP} estimated for both CO bonds. The same trend in variability is observed, but the range of changes for C1O is much narrower than for C2O. The latter proves our earlier observations that the C1O bond is mostly unchanged due to the presence of X, whereas the C2O one is involved in the interaction with substituents X. A similar observation comes from variability of charges on the oxygen atoms O(C1) and O(C2), presented in Figure S5 (SI). The stretching vibration of the carbonyl group shows also a substantial difference for C1═O and C2═O ones, see Figure S6 (SI). The interaction between X and a given CO group occurs mostly due to the transfer of charge along the sequence of covalent bonds linking X with CO. This is direct consequence of π-conjugation between substituent and reaction center in the ring. Thus, it is worth taking a look at electron density at BCPs of bonds a1, b1, and c1 (see Scheme 5). The relation between ρ_{BCP} and bond lengths of these bonds can be found in Figure S4 (SI). It can be seen that for bonds b1 and c1 the range of diversity is relatively similar, but slightly larger for c1, that is, for formally double bonds with π-electrons which can be involved into direct interaction with X. Clearly, the a1 bond is much less affected by the interaction with X, which in turn proves that no direct π-electron communication between both CO groups or between C1O and X can be noticed. This may be explained with the lack of π-conjugation between C1O and X, but also with the fact that both CO groups are electron-withdrawing centers with strongly polarized C═O bonds, in which the carbon atoms possess partially positive atomic charges. This explains also the relatively longer distances and lower values of ρ_{BCP} found for a1 bond (see Figure S4, SI).

One more argument comes from statistical analysis of bond lengths in the system in question. Table S1 (SI) presents the relevant data. When we look at the estimated standard deviation (esd) values we see clearly that bonds involved in resonance type of communication path between substituent and CO group are characterized by much higher esd values, for b1, c1, and C2O they are 0.015, 0.011, and 0.005, respectively, which may be compared with data for b2, c2, and C1O: 0.002, 0.006, and 0.001. Delocalization due to resonance substituent effect affects strongly bond lengths and this is registered by their greater changeability described by esd-values.

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TABLE 1. Geometrical (in Å) and Energetic (in kcal/mol) Parameters of the O···H−F Hydrogen Bond in 4-X-*o*-Benzoquinone, where X = H, and NMe$_2$ Linearity C═O···H−F Is Assumed

4-X-		C1═O	O1···H	H−F	C2═O	O···H	H−F	ΔE_{HB}
4-H-		1.211			1.211			
	O···HF	1.214	1.796	0.932	1.210			−7.21
4-NMe$_2$-		1.211			1.221			
	O1···HF	1.215	1.775	0.934	1.221			−8.17
	O2···HF	1.210			1.227	1.714	0.938	−10.17

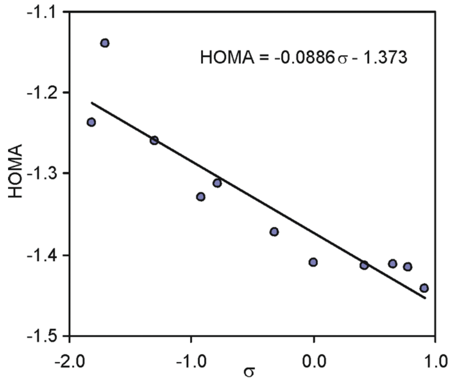

FIGURE 5. Dependence of aromaticity index HOMA of the ring on substituent constants σ (σ_p^+ for electron-donating substituents and for others σ_p), cc = −0.930.

In order to present chemical consequences of substituent effect on both carbonyl groups, their ability to form H-bonding is considered. For that purpose, a method of approaching HF molecule along line of CO bonds is carried out[33] to find an equilibrium complex. The computation was repeated for all fully relaxed geometrical parameters. In this case two type of H-bonded systems were found: with O···H−F turned toward the nearest hydrogen atom (Table S2a, SI) and with O···H−F turned toward the nearest oxygen atom (Table S2b, SI). It should be noted that the former is stronger than the latter. These studies are done for two cases: for a substituent strongly electron-donating (X = NMe$_2$) and for an unsubstituted molecule (X = H).

The results presented in Tables 1 and S2 (SI) show that the strength of interactions depend on the type of carbonyl group. In line with expectation, the weakest H-bond was found for the unsubstituted complex. The electron-donating power of the substituent (X = NMe$_2$) increases strength of intermolecular interactions. Moreover, the strongest H-bonding is found for C2O in which Scheme 3 predicts negative charge at oxygen atom.

Substituent Effect on the π-Electron Delocalization in the Ring of Benzoquinone. When π-electron delocalization is concerned for the whole ring, then we find again an acceptable linear dependence of delocalization indices HOMA, MCI, and FLU on substituent constants, as shown in Figures 5−7 and numerically presented in Table S3 (SI).

As we see, all three indices, geometry-based HOMA and electronic-based MCI and FLU applied to evaluate the π-electron delocalization (aromaticity) in the whole ring plotted against substituent constants, present a like picture. That is, the higher the electron-donating power of the substituent, the higher the electronic delocalization in the ring. In general, however, all indices indicate that the six-membered ring in *o*-benzoquinones is nonaromatic.

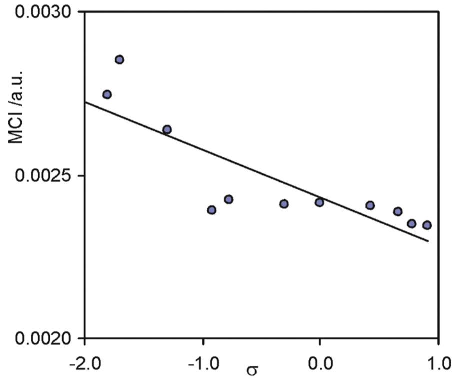

FIGURE 6. Correlation between electron-based aromaticity index MCI of the ring and substituent constants σ (σ_p^+ for electron-donating substituents and for others σ_p), cc = −0.843.

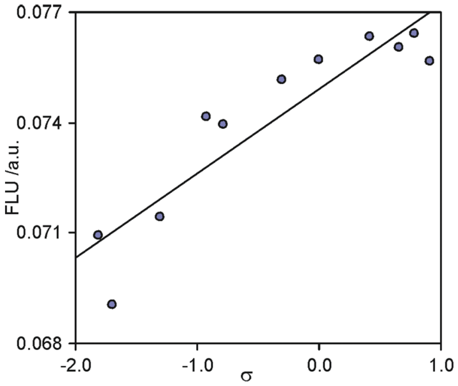

FIGURE 7. Correlation between electron-based aromaticity index FLU of the ring and substituent constants σ (σ_p^+ for electron-donating substituents and for others σ_p), cc = 0.913.

Conclusions

1. Substituent effects in 4-substituted-1,2-benzoquinone derivatives, described by simple resonance structures, are documented quantitatively by the use of the delocalization indices HOMA and MCI. Our results indicate a clear increase of π-electron delocalization via the C4C3C2O path with the increase in the π-donor character of the substituent. This effect is not seen for the C4C5C6C1O path.
2. Comparison of meta- and para-substituted benzaldehyde (Schemes 1 and 2) and the title compounds (Schemes 3 and 4) leads to a simple rule that, if the number of bonds between an electron-accepting atom and an electron-donating one is even (4 or 6), then the intramolecular charge transfer is possible; i.e., the resonance effect works. If the number of bonds is odd, then the resonance route of communication is expressed very weakly.
3. A negative charge predicted by the resonance structure for C2O is in line with a stronger H-bond formed with C2O than with C1O.
4. Carbonyl groups C1O and C2O behave also in a dramatically different way. The bond length and DI

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[33] Krygowski, T. M.; Zachara, J. E.; Szatyłowicz, H. *J. Phys. Org. Chem.* **2005**, *18*, 110–114.

of C2O depend strongly on substituent constants, whereas those of C1O show almost no dependence on these constants.

(5) Aromaticity indices of the ring depend strongly on substituent constants (σ_p^+ for electron-donating substituents and for others σ_p) and SESE values—the more electron-donating the substituent, the more aromatic the ring.

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Supporting Information Available: Figures: SESE vs substituent constant, HOMA (of the ring and for transmission paths: OC2C3C4 and OC1C6C5C4) vs SESE, electron density at BCP for CO and CC bonds vs their bond lengths, and Mulliken charges on the oxygen atoms and the frequency stretching vibrations for both carbonyl groups vs substituent constants. The tables contain: (S1) bond lengths, their mean values, and estimated standard deviations for 4-X-*o*-benzoquinone; (S2) for the H-bonded complexes of the derivatives: X = H and NMe_2, geometrical and energetic parameters of the O···H−F hydrogen bond (results of the optimization without constraints); and (S3) numerical characteristic of π-electron delocalization for 4-X-*o*-benzoquinones. Cartesian coordinates and computed total energies of optimized molecules and H-bonded complexes. This material is available free of charge via the Internet at http://pubs.acs.org.