

Non-additive effects of two substituents in disubstituted benzenes in terms of indirect interorbital interactions

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Abstract

The paper continues the investigation of the heteroatom influence in substituted benzenes by means of the non-canonical method of molecular orbitals (MOs) started previously [J. Mol. Struct. (Theochem) 507 (2000) 253]. The general expression for the one-electron density matrix [J. Mol. Struct. (Theochem) 343 (1995) 183] is applied now for interpretation of the electron density distribution in disubstituted benzenes containing an electron-donating substituent (D) and an electron-accepting one (A). Terms of the power series for occupation numbers responsible for the non-additive part of the total influence of two substituents (intersubstituent interaction) are derived and analysed. The interaction under study is shown to manifest itself as two effects, viz. (i) as an alteration in the extent of the intramolecular charge transfer between an individual substituent and the phenyl ring owing to the indirect participation of orbitals of the another substituent and (ii) as an additional indirect charge transfer between the substituents D and A by means of orbitals of the phenyl ring playing the role of mediators. Comparative analysis of both effects in *para*-, *ortho*- and *meta*-disubstituted benzenes also is carried out. An explicit relation is established between the extent of intersubstituent interaction and coefficients of MOs of benzene at the sites of substitution. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Numerous facts indicate that the influence of several substituents upon the phenyl ring cannot be expressed as a sum of their individual increments. Such a non-additivity of the total influence is especially evident if two substituents of opposite nature (i.e. an electron-donating substituent (D) and an electron-accepting one (A)) take *para*- and *ortho*-positions in the (D,A)-disubstituted benzenes.

As for instance, the *para*-nitro-aniline molecule

proves to be a significantly weaker base as compared to that predicted on the basis of the Hammett equation [1,2]. Furthermore, abnormally large shifts of absorption maxima towards the longer wave lengths are observed in the UV spectra of various (D,A)-disubstituted benzenes as compared to respective mono-derivatives if the second substituent is introduced into the *para*- or *ortho*-position with respect to the first one [3–7] (cf. the UV spectra of aniline and *para*-nitroaniline [3–6]). Non-additivity of the heteroatom influence in (D,A)-disubstituted benzenes has also been demonstrated on the basis of their IR [8] and ESCA spectra [9].

In this context, the dipole moments of (D,A)-disubstituted benzenes deserve particular attention. Indeed,

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these moments exceed considerably the sum of dipole moments of respective two monosubstituted molecules [1,10]. For example, the dipole moment of aniline (1.53D) when added to that of nitrobenzene (4.00D) yields the value 5.53D, whereas the actual dipole moment of *para*-nitro-aniline equals to 6.20D. These facts not only serve as a direct evidence of an intersubstituent interaction, but also indicate an additional intramolecular charge transfer to be a consequence of such an interaction. This hypothetical effect is referred to as the direct conjugation [1] or through-conjugation [11].

The first theoretical accounting for the intersubstituent interaction in (D,A)-disubstituted benzenes was given on the basis of the valence bond method [12]. To this end, the concept of the so-called chinoidal resonance structures was invoked, and these were assumed to participate considerably in the final electronic structure of *para*- and *ortho*-(D,A)-disubstituted molecules (no chinoidal structures may be drawn for *meta*-derivatives of benzene, and the well-known negligible intersubstituent interaction in *meta*-(D,A)-disubstituted benzenes also proved to be supported).

As opposed to the usual chemical formulas of substituted benzenes, the chinoidal structures contain a positively charged donor (D^+) and a negatively-charged acceptor (A^-). Thus, participation of these hypothetical structures in the actual electronic structure implies a partial through-ring charge transfer to take place between the electron-donating and the electron-accepting substituents. It is also noteworthy here that the bond lengths and valence angles determined experimentally within the phenyl rings of *para*- and *ortho*-(D,A)-disubstituted benzenes (see e.g. [11,13,14]) proved to be in agreement with those predicted on the basis of chinoidal structures.

In the framework of the method of molecular orbitals (MOs), the electronic structures of heteroatom-containing molecules are usually related to peculiarities of certain conjugated hydrocarbon containing the same number of π -electrons (the so-called isoconjugated hydrocarbon) [1,15]. For example, substituted benzenes containing the OR and NR_2 groups ($R = H, CH_3, C_2H_5$, etc.) are considered as 'perturbed' anions $Ar-(CH_2)^-$, where the perturbation coincides with the difference between the electronegativity of the heteroatom (O or N) and that of the carbon atom. Using the PMO method [1] along with the well-known properties of alternant hydrocarbons, it has

been demonstrated that an additional stabilization energy is peculiar to *para*- and *ortho* (D,A)-derivatives of benzene as compared to the sum of stabilization energies of respective mono-substituted molecules. These results also are in line with the concept of direct conjugation [1].

It should be noted, however, that it is the benzene molecule and not the isoconjugated hydrocarbons that is considered as the parent hydrocarbon of substituted benzenes in the chemical sense. In this connection, an interpretation of the intersubstituent effects in terms of interactions between orbitals of the phenyl ring and those of the substituents would be preferable, even more so because such an interpretation was suggested recently [16] for the influence of a single substituent upon the phenyl ring in mono-derivatives. Moreover, interpretation of the above-expected type implies the establishment of an explicit relation between the electronic structure of benzene and the extent of the intersubstituent interaction for various disubstituted benzenes.

In the above-cited contribution, the direct way of obtaining the one-electron density matrix (bond order matrix) [17–19] on the basis of solution of the so-called commutation equation [20] by means of power series has been applied. In as much as the first members of this series have been expressed in terms of matrices describing the direct and indirect interactions of basis orbitals, application of this approach offered a possibility for interpretation of the electron density distribution in mono-substituted benzenes in terms of direct and indirect interactions between MOs of benzene and those of the substituent. An analogous interpretation of the intersubstituent effects also may be anticipated on the basis of the same approach.

In this connection, the main aim of this paper consists in applying the approach developed in Refs. [17–19] for the investigation of the non-additive part of the total influence of two substituents in (D,A)-disubstituted benzenes.

2. The expressions for occupation numbers of basis orbitals of disubstituted benzenes to within the fourth order terms inclusive. Discussion of the second and third order terms

Let us consider a (D,A)-disubstituted benzene of

any constitution. As in Refs. [16,17,21,22], the initial Hückel type model Hamiltonian matrix \mathbf{H} of our molecule is assumed to consist of the zero order matrix $\mathbf{H}_{(0)}$ and of the first order matrix $\mathbf{H}_{(1)}$, the former containing the one-electron energies of basis orbitals and the latter involving the resonance parameters.

As in Ref. [16], the electron-donating substituent D will be characterized by a single initially occupied orbital $\varphi_{(+d)}$, whereas the electron-accepting one will be represented by an initially vacant orbital $\varphi_{(-a)}$. As a result, the total basis set $\{\varphi\}$ will consist of the initially occupied MOs of benzene $\varphi_{(+)i}$, $i = 1, 2, 3$ and of their initially vacant counterparts $\varphi_{(-)j}$, $j = 4, 5, 6$ along with the above-defined two orbitals of substituents $\varphi_{(+d)}$ and $\varphi_{(-a)}$.

To study the populations of basis orbitals, let us turn to the power series for the bond order matrix [17–19]. Terms of this series within the second order inclusive were derived in Ref. [17]. As a result, the occupation numbers of basis orbitals have been expressed as follows:

$$X_{(+k)}^{(2)} = 2[1 - \mathbf{G}_{(1)}\mathbf{G}_{(1)}^+]_{kk} \equiv 2 \left[1 - \sum_r^{\text{IVBOs}} (G_{(1)kr})^2 \right] \quad (1)$$

$$X_{(-l)}^{(2)} = 2(\mathbf{G}_{(1)}^+\mathbf{G}_{(1)})_{ll} \equiv 2 \sum_p^{\text{IOBOs}} (G_{(1)pl})^2 \quad (2)$$

where the subscripts k and p correspond to the initially occupied basis orbitals (IOBOs), whilst l and r refer to the initially vacant basis orbitals (IVBOs). Sums over p and r embrace all the IOBOs and all the IVBOs of the molecule, respectively, and $G_{(1)kl}$ is an element of certain first order matrix $\mathbf{G}_{(1)}$ introduced in Ref. [17]. This element takes the form

$$G_{(1)kl} = - \frac{\langle \varphi_{(+k)} | \hat{H} | \varphi_{(-l)} \rangle}{E_{(+k)} - E_{(-l)}} \quad (3)$$

and describes the direct (through-space) interaction between orbitals $\varphi_{(+k)}$ and $\varphi_{(-l)}$. The numerator of the right-hand side of Eq. (3) contains the Hückel type Hamiltonian matrix element (resonance parameter) between basis orbitals indicated within the bra- and ket-vectors, and the denominator involves the relevant difference in one-electron energies. The

superscript $+$ of Eqs. (1) and (2) designates the Hermitian conjugate matrix $\mathbf{G}_{(1)}$, whereas the superscript (2) indicates the order of the terms included.

Let us dwell now on populations of the electron-donating orbital ($\varphi_{(+d)}$) and of the electron-accepting one ($\varphi_{(-a)}$). Then the elements $G_{(1)dr}$ and $G_{(1)pa}$ contained within Eqs. (1) and (2) describe the direct interactions of pairs of orbitals ($\varphi_{(+d)}$, $\varphi_{(-)r}$) and ($\varphi_{(+p)}$, $\varphi_{(-a)}$), respectively.

The direct interactions between orbitals $\varphi_{(+d)}$ and $\varphi_{(-a)}$ represented by the element $G_{(1)da}$ evidently are of a negligible value for *para*-disubstituted benzenes. On the other hand, just these molecules are known to be characterized by the largest intersubstituent interaction. This implies that the direct interaction $G_{(1)da}$ (probably present in *ortho*-derivatives) hardly plays a decisive role in the formation of the intersubstituent effects. Thus, let us accept the equality

$$G_{(1)da} = 0 \quad (4)$$

As a result, only the initially vacant and the initially occupied MOs of benzene, respectively, remain within the sums of the right-hand sides of Eqs. (1) and (2) for $k = d$ and $l = a$. This, in turn, implies that the populations $X_{(+d)}^{(2)}$ and $X_{(-a)}^{(2)}$ do not depend on the presence of the opposite substituent (A and D, respectively). Hence, the expressions of Eqs. (1) and (2) describe the independent influences of individual substituents upon the phenyl ring. Thus, terms of higher orders should be considered when looking for the intersubstituent interaction.

The third and fourth order members of the power series for the bond order matrix also may be derived as described in Ref. [17]. The third order contributions to occupation numbers of orbitals $\varphi_{(+k)}$ and $\varphi_{(-l)}$ take the form

$$\begin{aligned} \Delta X_{(+k)}^{(3)} &= -2(\mathbf{G}_{(1)}\mathbf{G}_{(2)}^+ + \mathbf{G}_{(2)}\mathbf{G}_{(1)}^+)_{kk} \\ &\equiv -4 \sum_r^{\text{IVBOs}} G_{(1)kr}G_{(2)kr} \end{aligned} \quad (5)$$

$$\begin{aligned} \Delta X_{(-l)}^{(3)} &= 2(\mathbf{G}_{(1)}^+\mathbf{G}_{(2)} + \mathbf{G}_{(2)}^+\mathbf{G}_{(1)})_{ll} \\ &\equiv 4 \sum_p^{\text{IOBOs}} G_{(1)pl}G_{(2)pl} \end{aligned} \quad (6)$$

where $G_{(2)kl}$ is an element of certain second order

matrix $\mathbf{G}_{(2)}$ [17] describing the indirect interactions between the IOBO $\varphi_{(+k)}$ and the IVBO $\varphi_{(-l)}$ by means of a single mediator. This element takes the form

$$G_{(2)kl} = \frac{1}{E_{(+k)} - E_{(-l)}} \times \left\{ \sum_m^{\text{IOBOs}} \frac{S_{km}R_{ml}}{E_{(+m)} - E_{(-l)}} - \sum_n^{\text{IVBOs}} \frac{R_{kn}Q_{nl}}{E_{(+k)} - E_{(-n)}} \right\} \quad (7)$$

The meanings of designations of Eq. (7) coincide with those of Eq. (3), and

$$S_{km} = \langle \varphi_{(+k)} | \hat{H} | \varphi_{(+m)} \rangle, \quad R_{ml} = \langle \varphi_{(+m)} | \hat{H} | \varphi_{(-l)} \rangle, \\ Q_{nl} = \langle \varphi_{(-n)} | \hat{H} | \varphi_{(-l)} \rangle \quad (8)$$

It is seen that both IOBOs and IVBOs of the molecule play the role of mediators in the indirect interaction between orbitals $\varphi_{(+k)}$ and $\varphi_{(-l)}$. To be an efficient mediator, however, the orbital under consideration ($\varphi_{(+m)}$ or $\varphi_{(-n)}$) should overlap with both $\varphi_{(+k)}$ and $\varphi_{(-l)}$. Hence, orbitals situated in between the indirectly interacting orbitals meet this condition best of all.

Let us revert now to Eqs. (5) and (6) and take the population alterations of orbitals $\varphi_{(+d)}$ and $\varphi_{(-a)}$ ($k = (+d)$, $l = (-a)$). Two types of contributions may be distinguished within the right-hand sides of expressions for $\Delta X_{(+d)}^{(3)}$ and $\Delta X_{(-a)}^{(3)}$, namely contributions of the opposite substituent ($r = (-a)$ and $p = (+d)$, respectively) and those of phenyl ring ($r = (-)4, (-)5, (-)6$ and $p = (+)1, (+)2, (+)3$). Increments of the first type vanish owing to the assumption of Eq. (4) whatever the indirect interaction $G_{(2)da}$, whereas contributions of the second type should be considered separately.

Let us start with the notation that elements S_{km} , R_{ml} and Q_{nl} between pairs of MOs of benzene are equal to zero [16]. Indeed, a diagonal Hamiltonian matrix block corresponds to the subset of MOs of phenyl ring (benzene), and the diagonal elements of this block may be entirely included into the zero order term $\mathbf{H}_{(0)}$ without any restriction. This also implies the equality $G_{(1)ij} = 0$ for $i = (+)1, (+)2, (+)3$ and $j = (-)4, (-)5, (-)6$.

Let us consider now the elements $G_{(2)dj}$ and $G_{(2)ia}$ corresponding to $r = j = (-)4, (-)5, (-)6$ and $p = i = (+)1, (+)2, (+)3$ and determining the contributions of the phenyl ring to population alterations $\Delta X_{(+d)}^{(3)}$ and $\Delta X_{(-a)}^{(3)}$. From Eq. (7) and the above-discussed zero values of resonance parameters inside the subset of orbitals of benzene it follows that $G_{(2)dj} \neq 0$ and $G_{(2)ia} \neq 0$ only if $R_{da} \neq 0$. The latter requirement is not consistent with Eq. (4) as Eq. (3) indicates. Thus, the equalities $G_{(2)dj} = 0$ and $G_{(2)ia} = 0$ should be accepted. As a result, the third order increments to the intersubstituent interaction also may be ignored.

The fourth order contributions to the same populations are

$$\Delta X_{(+k)}^{(4)} = -2(\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+ + \mathbf{G}_{(1)}\mathbf{G}_{(3)}^+ + \mathbf{G}_{(3)}\mathbf{G}_{(1)}^+ + \mathbf{G}_{(2)}\mathbf{G}_{(2)}^+)_{kk} \quad (9)$$

$$\Delta X_{(-l)}^{(4)} = 2(\mathbf{G}_{(1)}^+\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+\mathbf{G}_{(1)} + \mathbf{G}_{(1)}^+\mathbf{G}_{(3)} + \mathbf{G}_{(3)}^+\mathbf{G}_{(1)} + \mathbf{G}_{(2)}^+\mathbf{G}_{(2)})_{ll} \quad (10)$$

For further convenience, let us introduce the following notations for separate increments of Eqs. (9) and (10)

$$\Delta X_{(+k)}^{(4)1} = -2(\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+)_{kk} \\ \equiv -2 \sum_{p,l,m} G_{(1)kp} G_{(1)pl}^+ G_{(1)lm} G_{(1)mk}^+ \quad (11)$$

$$\Delta X_{(-l)}^{(4)1} = 2(\mathbf{G}_{(1)}^+\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+\mathbf{G}_{(1)})_{ll} \\ \equiv 2 \sum_{r,s,t} G_{(1)lr}^+ G_{(1)rs} G_{(1)st}^+ G_{(1)tl} \quad (12)$$

$$\Delta X_{(+k)}^{(4)2} = -2(\mathbf{G}_{(1)}\mathbf{G}_{(3)}^+ + \mathbf{G}_{(3)}\mathbf{G}_{(1)}^+)_{kk} \\ \equiv -4 \sum_r G_{(1)kr} G_{(3)kr} \quad (13)$$

$$\Delta X_{(-l)}^{(4)2} = 2(\mathbf{G}_{(1)}^+\mathbf{G}_{(3)} + \mathbf{G}_{(3)}^+\mathbf{G}_{(1)})_{ll} \equiv 4 \sum_p G_{(1)pl} G_{(3)pl} \quad (14)$$

$$\Delta X_{(+k)}^{(4)3} = -2(\mathbf{G}_{(2)}\mathbf{G}_{(2)}^+)_{kk} \equiv -2 \sum_r (G_{(2)kr})^2 \quad (15)$$

$$\Delta X_{(-l)}^{(4)3} = 2(\mathbf{G}_{(2)}^+\mathbf{G}_{(2)})_{ll} \equiv 2 \sum_p (G_{(2)pl})^2 \quad (16)$$

The element $G_{(3)kl}$ of the third order matrix $\mathbf{G}_{(3)}$ involved in Eqs. (13) and (14) describes the indirect interaction between a pair of orbitals $\varphi_{(+k)}$ and $\varphi_{(-l)}$ by means of two mediators. The expression for this element takes the form

$$\begin{aligned} G_{(3)kl} = & \frac{-1}{E_{(+k)} - E_{(-l)}} \\ & \times \left\{ \sum_j^{\text{IOBOs}} \sum_m^{\text{IOBOs}} \frac{S_{kj}S_{jm}R_{ml}}{(E_{(+j)} - E_{(-l)})(E_{(+m)} - E_{(-l)})} \right. \\ & - \sum_j^{\text{IOBOs}} \sum_r^{\text{IVBOs}} \left[\frac{S_{kj}R_{jr}Q_{rl}}{(E_{(+j)} - E_{(-l)})(E_{(+j)} - E_{(-r)})} \right. \\ & + \frac{S_{kj}R_{jr}Q_{rl}}{(E_{(+k)} - E_{(-r)})(E_{(+j)} - E_{(-r)})} \\ & + \frac{R_{kr}R_{rj}^+R_{jl}}{(E_{(+j)} - E_{(-r)})(E_{(+j)} - E_{(-l)})} \\ & \left. \left. + \frac{R_{kr}R_{rj}^+R_{jl}}{(E_{(+k)} - E_{(-r)})(E_{(+j)} - E_{(-r)})} \right] \right\} \\ & + \left. \sum_p^{\text{IVBOs}} \sum_r^{\text{IVBOs}} \frac{R_{kr}Q_{rp}Q_{pl}}{(E_{(+k)} - E_{(-p)})(E_{(+k)} - E_{(-r)})} \right\} \quad (17) \end{aligned}$$

Pairs of mutually overlapping orbitals situated in between the orbitals $\varphi_{(+k)}$ and $\varphi_{(-l)}$ are the most efficient mediators of this indirect interaction. Terms defined by Eqs. (11)–(16) will be studied separately in Section 3.

3. Studies of separate fourth order increments to the intersubstituent interaction

Terms defined by Eqs. (11) and (12) yield the following contributions to occupation numbers of

basis orbitals $\varphi_{(+d)}$ and $\varphi_{(-a)}$

$$\Delta X_{(+d)}^{(4)1} = -2 \sum_p^{\text{IVBOs}} \sum_l^{\text{IOBOs}} \sum_m^{\text{IVBOs}} G_{(1)dp}G_{(1)pl}^+G_{(1)lm}G_{(1)md}^+ \quad (18)$$

$$\Delta X_{(-a)}^{(4)1} = 2 \sum_r^{\text{IOBOs}} \sum_s^{\text{IVBOs}} \sum_t^{\text{IOBOs}} G_{(1)ar}^+G_{(1)rs}G_{(1)st}^+G_{(1)ta} \quad (19)$$

These contributions prove to be irrelevant to the intersubstituent interaction.

To show this, let us dwell on the correction $\Delta X_{(+d)}^{(4)1}$. Eq. (4) indicates that $p = (-)4, (-)5, (-)6$ in the right hand side of Eq. (18). Similarly, $m = (-)4, (-)5, (-)6$, if the equality $G_{(1)md}^+ = G_{(1)dm}$ is taken into consideration. We then obtain that $l = (+)d$ yields the only non-zero contribution and the increment under study takes the form

$$\Delta X_{(+d)}^{(4)1} = -2 \sum_p^{\text{IVBOs}} \sum_m^{\text{IVBOs}} (G_{(1)dp})^2(G_{(1)dm})^2 \quad (20)$$

It is seen that this contribution does not depend on the position of the electron-accepting substituent. Similarly, $\Delta X_{(-a)}^{(4)1}$ may be shown to be independent of the position of the substituent D.

Let us now turn to contributions defined by Eqs. (13) and (14). These are

$$\Delta X_{(+d)}^{(4)2} = -4 \sum_r^{\text{IVBOs}} G_{(1)dr}G_{(3)dr}, \quad (21)$$

$$\Delta X_{(-a)}^{(4)2} = 4 \sum_p^{\text{IOBOs}} G_{(1)pa}G_{(3)pa}$$

where $r = (-)4, (-)5, (-)6$ and $p = (+)1, (+)2, (+)3$ if Eq. (4) is taken into consideration. It is seen that the population alteration $\Delta X_{(+d)}^{(4)2}$ is determined by products of the direct and the indirect interactions by means of two mediators between the electron-donating orbital $\varphi_{(+d)}$ and an initially vacant MO of benzene $\varphi_{(-)r}$. Similarly, products of the direct and of the indirect interactions between orbitals $\varphi_{(-)a}$ and $\varphi_{(+p)}$ arise within the expression for $\Delta X_{(-a)}^{(4)2}$, where $\varphi_{(+p)}$ coincides with an initially occupied MO of benzene. If we are interested in terms describing the intersubstituent interaction, the orbitals of the opposite substituent (i.e. $\varphi_{(-)a}$ and $\varphi_{(+d)}$,

respectively) should be considered as mediators for the indirect interaction $G_{(3)dr}$ and $G_{(3)pa}$. An MO of benzene evidently plays the role of the second mediator in both cases.

Additivity of the population alteration $\Delta X_{(+d)}^{(4)2}$ (and $\Delta X_{(-a)}^{(4)2}$) with respect to contributions of the initially vacant (occupied) MOs of benzene is evident from Eq. (21). The increments of the IVBO $\varphi_{(-)n}$ and of the IOBO $\varphi_{(+m)}$ to the population alterations $\Delta X_{(+d)}^{(4)2}$ and $\Delta X_{(-a)}^{(4)2}$ are

$$\Delta X_{(+d,(-)n)}^{(4)2} = -4G_{(1)dn}G_{(3)dn}, \quad (22)$$

$$\Delta X_{(-a,(+)m)}^{(4)2} = 4G_{(1)ma}G_{(3)ma}$$

Let us revert now to Eqs. (13) and (14) and take $k = (+)m$ and $l = (-)n$, respectively. In as much as the direct interactions $G_{(1)ij}$ take zero values for MOs of benzene, we obtain that only $r = (-)a$ and $p = (+)d$ yield non-zero contributions to $\Delta X_{(+m)}^{(4)2}$ and $\Delta X_{(-n)}^{(4)2}$, respectively, i.e.

$$\Delta X_{(+m)}^{(4)2} = -4G_{(1)ma}G_{(3)ma}, \quad (23)$$

$$\Delta X_{(-n)}^{(4)2} = 4G_{(1)dn}G_{(3)dn}$$

Comparison of Eqs. (22) and (23) shows that an additional population equal to $4G_{(1)ma}G_{(3)ma}$ is transferred between the IOBO of benzene $\varphi_{(+m)}$ and the electron-acceptor A owing to the presence of the electron-donating substituent D. Similarly, the population equal to $4G_{(1)dn}G_{(3)dn}$ is additionally transferred between the electron-donating orbital $\varphi_{(+d)}$ and an IVBO of benzene $\varphi_{(-)n}$ if the electron-acceptor A is introduced. Orbitals of the opposite substituent (D and A, respectively) participate indirectly in this charge transfer as mediators of the indirect interactions between orbitals of the substituent under consideration and those of the phenyl ring described by the elements $G_{(3)ma}$ and $G_{(3)dn}$.

Therefore, alteration in the electron-donating effect of the substituent D upon the phenyl ring may be expected after introducing a substituent of the electron-accepting nature (A) and, vice versa, the electron-accepting effect of the latter seems to change if an electron-donating substituent is additionally introduced (estimations of signs and of absolute values of this effect will be carried out in Section 4).

Let us consider now the last increments defined by

Eqs. (15) and (16). For $k = (+)d$ and $l = (-)a$ we obtain

$$\Delta X_{(+d)}^{(4)3} = -2 \sum_r^{IVBOs} (G_{(2)dr})^2, \quad (24)$$

$$\Delta X_{(-a)}^{(4)3} = 2 \sum_p^{IOBOs} (G_{(2)pa})^2$$

As it was discussed in Section 2, the elements $G_{(2)dj}$ and $G_{(2)ia}$ take small values for $i = (+)1, (+)2, (+)3$ and $j = (-)4, (-)5, (-)6$ coinciding with MOs of benzene. Hence, the increments $r = (-)a$ and $p = (+)d$ are the most significant ones within the right-hand sides of Eq. (24). We then obtain

$$\Delta X_{(+d)}^{(4)3} \approx -2(G_{(2)da})^2, \quad \Delta X_{(-a)}^{(4)3} \approx 2(G_{(2)da})^2 \quad (25)$$

where $G_{(2)da}$ is defined by Eq. (7), and both IOBOs and IVBOs of benzene play the role of mediators here.

It is seen that a population proportional to the square of the indirect interaction between orbitals $\varphi_{(+d)}$ and $\varphi_{(-)a}$ by means of orbitals of the phenyl ring is transferred from the electron-donating substituent (D) to the electron-accepting one (A). This implies an indirect charge transfer to take place between substituents of different nature in (D,A)-disubstituted benzenes, where the phenyl ring plays the role of mediator.

4. Comparison of *para*-, *ortho*- and *meta*-(D,A)-disubstituted benzenes

In this section we are about to compare the relative values of separate increments to the intersubstituent interaction for different positions of the two substituents. To this end, let us turn to Eqs. (21) and (25).

Let β_0 be the standard resonance parameter for the neighboring pairs of $2p_z$ AOs of benzene, whereas α_0 will stand for the Coulomb parameter referring to these AOs. Let us accept the equalities $\alpha_0 = 0$ and $\beta_0 = 1$ for further convenience. Then the one-electron energies of MOs of benzene are equal to 2, 1, 1, -1, -1, -2 [15] (Fig. 1), whereas those of substituents take certain values $\epsilon_{(+d)}$ and $-\epsilon_{(-a)}$, where $\epsilon_{(+d)} > 0$ and $\epsilon_{(-a)} > 0$. Accordingly, the D-C_{Ar} and A-C_{Ar} bonds will be represented by positive resonance

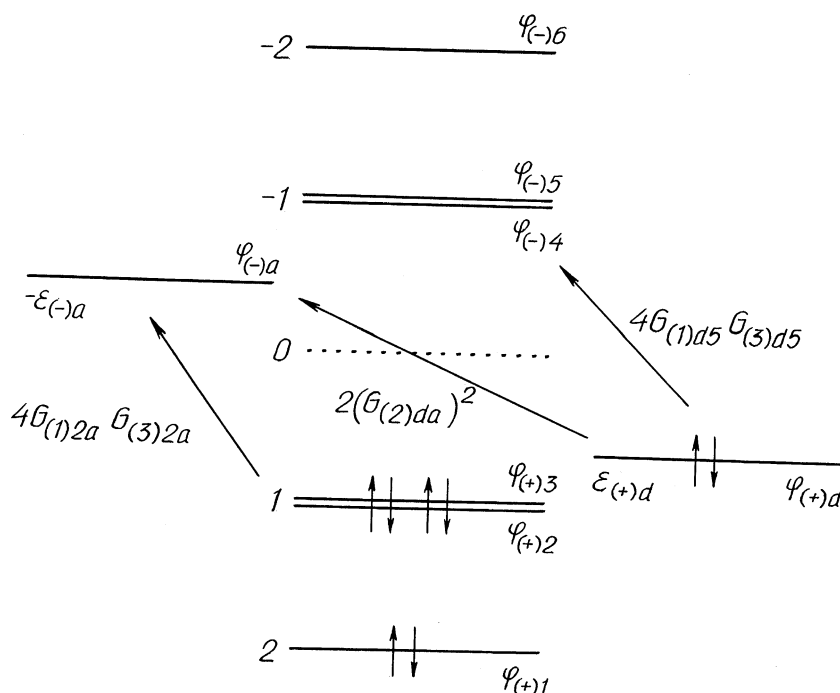


Fig. 1. Relative positions of one-electron energies corresponding to basis orbitals of (D,A)-disubstituted benzenes. The MOs of benzene are shown in the central part of the diagram, whereas the orbitals of an electron-donating and electron-accepting substituents are shown in the right and left part, respectively. Arrows indicate the additional charge transfer which takes place owing to the intersubstituent interaction defined by Eqs. (22), (23) and (25).

parameters $\sigma_{(+d)}$ and $\sigma_{(-a)}$, the absolute values of which are close to 1.

The above-described one-electron energies of basis orbitals allow us to conclude that the direct interactions $G_{(1)d6}$ and $G_{(1)1a}$ are of sufficiently small values owing to large energy denominators of their definition (see Eq. (3)). For the same reason, the orbitals $\varphi_{(+1)}$ and $\varphi_{(-6)}$ are not efficient mediators for the indirect interactions of orbitals $\varphi_{(+d)}$ and $\varphi_{(-a)}$. Hence, we may confine ourselves to four orbitals of benzene $\varphi_{(+2)}$, $\varphi_{(+3)}$, $\varphi_{(-4)}$, $\varphi_{(-5)}$.

Let us start with the analysis of the population alteration $\Delta X_{(+d)}^{(4)2}$.

4.1. Alteration in the electron-donating effect of the substituent D upon the phenyl ring

Let us ascribe the first number to the position of the phenyl ring the electron-donating substituent is attached to. The position of the electron-accepting substituent will vary in accordance with the isomer

under consideration. Then the above-mentioned four MOs of the phenyl ring may be defined as follows [15]:

$$\varphi_{(+2)} = b(\chi_1 - \chi_4) + c(\chi_2 - \chi_3 - \chi_5 + \chi_6) \quad (26)$$

$$\varphi_{(+3)} = d(\chi_2 + \chi_3 - \chi_5 - \chi_6)$$

$$\varphi_{(-4)} = d(-\chi_2 + \chi_3 - \chi_5 + \chi_6)$$

$$\varphi_{(-5)} = b(\chi_1 + \chi_4) - c(\chi_2 + \chi_3 + \chi_5 + \chi_6)$$

where

$$b = 2c = 0.577, \quad d = 0.5 \quad (27)$$

It is seen that the resonance parameters $S_{d3} = \langle \varphi_{(+d)} | \hat{H} | \varphi_{(+3)} \rangle$ and $R_{d4} = \langle \varphi_{(+d)} | \hat{H} | \varphi_{(-4)} \rangle$ take zero values owing to zero increments of the AO χ_1 within the orbitals $\varphi_{(+3)}$ and $\varphi_{(-4)}$. The equality $R_{d4} = 0$ implies that $G_{(1)d4} = 0$ and thereby $\Delta X_{(+d,(-4))}^{(4)2} = 0$.

We then obtain

$$\Delta X_{(+d)}^{(4)2} \approx -4\Delta X_{(+d,(-)5}^{(4)2} = -4G_{(1)d5}G_{(3)d5} \quad (28)$$

where

$$G_{(1)d5} = -\frac{R_{d5}}{1 + \epsilon_{(+d)}} \quad (29)$$

and the element $G_{(3)d5}$ is defined by Eq. (17), where $k = (+)d$, $l = (-)5$. It is seen that the orbitals $\varphi_{(+2)}$ and $\varphi_{(-a)}$ should be considered as mediators of the indirect interaction $G_{(3)d5}$. Then only the second sum of Eq. (17) is required, where $j = (+)2$ and $r = (-)a$. Moreover, the third and fourth terms within the square bracket of Eq. (17) vanish owing to the equality $R_{kr} = R_{da} = 0$. As a result, the following expression for $G_{(3)d5}$ may be obtained

$$G_{(3)d5} = \frac{S_{d2}R_{2a}Q_{a5}}{(1 + \epsilon_{(+d)})(1 + \epsilon_{(-a)})} \times \left[\frac{1}{2} + \frac{1}{(\epsilon_{(+d)} + \epsilon_{(-a)})} \right] \quad (30)$$

Substituting Eqs. (29) and (30) into Eq. (28) yields

$$\Delta X_{(+d)}^{(4)2} \approx \frac{4R_{d5}S_{d2}R_{2a}Q_{a5}}{(1 + \epsilon_{(+d)})^2(1 + \epsilon_{(-a)})} \times \left[\frac{1}{2} + \frac{1}{(\epsilon_{(+d)} + \epsilon_{(-a)})} \right]. \quad (31)$$

It is seen that the sign of this increment depends on the sign of product of four resonance parameters.

The equality $S_{d2} = R_{d5} = b\sigma_{(+d)} > 0$ follows from Eq. (26) and it is valid for any isomer, whereas the remaining two resonance parameters R_{2a} and Q_{a5} depend on the relative position of the electron-accepting substituent.

Let us start with the *para*-(D,A)-disubstituted molecules. The equalities $R_{2a}^{para} = -b\sigma_{(-a)}$ and $Q_{a5}^{para} = b\sigma_{(-a)}$ follow from Eq. (26) in this case and the increment $\Delta X_{(+d)}^{(4)2,para}$ takes the form

$$\Delta X_{(+d)}^{(4)2,para} \approx \frac{-4b^4\sigma_{(+d)}^2\sigma_{(-a)}^2}{(1 + \epsilon_{(+d)})^2(1 + \epsilon_{(-a)})} \times \left[\frac{1}{2} + \frac{1}{(\epsilon_{(+d)} + \epsilon_{(-a)})} \right] < 0 \quad (32)$$

and proves to be negative. This implies that the electron-donating substituent loses more population if the electron-accepting substituent is introduced into the *para* position, and this additional population is acquired by the initially vacant orbital of benzene $\varphi_{(-)5}$. Hence, the electron-donating effect of the former upon the phenyl ring is strengthened owing to the indirect participation of the second substituent.

The same conclusion refers also to the *ortho*-disubstituted molecules, where $R_{2a}^{ortho} = c\sigma_{(-a)}$ and $Q_{a5}^{ortho} = -c\sigma_{(-a)}$ and

$$\Delta X_{(+d)}^{(4)2,ortho} \approx \frac{-4b^2c^2\sigma_{(+d)}^2\sigma_{(-a)}^2}{(1 + \epsilon_{(+d)})^2(1 + \epsilon_{(-a)})} \times \left[\frac{1}{2} + \frac{1}{(\epsilon_{(+d)} + \epsilon_{(-a)})} \right] < 0 \quad (33)$$

In as much as $b = 2c$ [15], the effect is weaker in this case as compared to that in *para* isomers.

For a *meta*-disubstituted molecule, we obtain that $R_{2a}^{meta} = -c\sigma_{(-a)}$ and $Q_{a5}^{meta} = -c\sigma_{(-a)}$, and

$$\Delta X_{(+d)}^{(4)2,meta} \approx \frac{4b^2c^2\sigma_{(+d)}^2\sigma_{(-a)}^2}{(1 + \epsilon_{(+d)})^2(1 + \epsilon_{(-a)})} \times \left[\frac{1}{2} + \frac{1}{(\epsilon_{(+d)} + \epsilon_{(-a)})} \right] > 0 \quad (34)$$

Hence, a suppressing indirect influence of the electron-accepting substituent upon the electron-donating effect of the substituent D follows in this case.

The above analysis also shows that the sign of the correction $\Delta X_{(+d)}^{(4)2}$ is actually determined by the sign of the product $R_{2a}Q_{a5}$ and thereby of the product $C_{(+2,i}C_{(-)5,i}$, the latter consisting of coefficients of MOs of benzene $\varphi_{(+2)}$ and $\varphi_{(-)5}$ for the respective positions of the acceptor (i) with respect to that of the donor ($i = 1$). This implies that the sign of the correction $\Delta X_{(+d)}^{(4)2}$ is directly conditioned by the structure of MOs of benzene.

4.2. Alteration in the electron-accepting effect of the substituent A upon the phenyl ring

Now, it is convenient to ascribe the first number to

the position of the electron-accepting substituent within the phenyl ring. Then the equalities $R_{3a} = 0$ and $Q_{4a} = 0$ follow from Eq. (26). As a result, the contribution of the MO $\varphi_{(+2)}$ (viz. $\Delta X_{(-)a,(+)2}^{(4)2}$) is the most significant one within the expression for the increment $\Delta X_{(-)a}^{(4)2}$, and orbitals $\varphi_{(+d)}$ and $\varphi_{(-5)}$ play the role of two mediators in the indirect interaction described by the element $G_{(3)2a}$. The latter follows from the second sum of Eq. (17), where $k = (+)2$, $l = (-)a$, $j = (+)d$ and $r = (-)5$, and it takes the form

$$G_{(3)2a} = \frac{S_{2d}R_{d5}Q_{5a}}{(1 + \epsilon_{(+d)})(1 + \epsilon_{(-a)})} \times \left[\frac{1}{2} + \frac{1}{(\epsilon_{(+d)} + \epsilon_{(-a)})} \right] \quad (35)$$

where the equality $R_{da} = 0$ is also taken into consideration. Substituting Eq. (35) along with the expression for $G_{(1)2a}$, i.e.

$$G_{(1)2a} = -\frac{R_{2a}}{1 + \epsilon_{(-a)}} \quad (36)$$

into Eq. (22) for $m = (+)2$, we obtain

$$\Delta X_{(-)a}^{(4)2} \approx \Delta X_{(-)a,(+)2}^{(4)2} = -\frac{4R_{2a}S_{2d}R_{d5}Q_{5a}}{(1 + \epsilon_{(+d)})(1 + \epsilon_{(-a)})^2} \times \left[\frac{1}{2} + \frac{1}{(\epsilon_{(+d)} + \epsilon_{(-a)})} \right] \quad (37)$$

In as much as $S_{2d} = S_{d2}$ and $Q_{5a} = Q_{a5}$ as Eq. (8) indicates, the products of four resonance parameters contained within Eqs. (31) and (37) coincide with one another. It is no surprise, therefore, that a similar dependence of the final sign of the correction $\Delta X_{(-)a}^{(4)2}$ on signs of the products of coefficients of MOs of benzene ($C_{(+2,i)}C_{(-5,i)}$) follows in this case. Thus, the resonance parameters $R_{2a} = Q_{5a} = b\sigma_{(-)a}$ do not depend on the position of the electron-donating substituent, whereas S_{2d} and R_{d5} depend on a particular derivative.

For the *para*-disubstituted molecule, $S_{2d}^{para} = -b\sigma_{(+d)}$ and $R_{d5}^{para} = b\sigma_{(+d)}$ and a positive sign of $\Delta X_{(-)a}^{(4)2,para}$ follows. This implies that the electron-accepting substituent acquires more population from the phenyl ring in this case. Similarly, $S_{2d}^{ortho} = c\sigma_{(+d)}$

and $R_{d5}^{ortho} = -c\sigma_{(+d)}$ and a strengthened electron-accepting effect also results for the *ortho*-derivative. For the *meta*-(D,A)-disubstituted system, however, we obtain that $S_{2d}^{meta} = -c\sigma_{(+d)}$ and $R_{d5}^{meta} = -c\sigma_{(+d)}$ and $\Delta X_{(-)a}^{(4)2,meta} < 0$. It is seen that a suppressing mutual influence follows for this molecule.

Therefore, the electron-donating and the electron-accepting effects upon the phenyl ring both are strengthened if the two substituents take *ortho*- and *para*-positions with respect to one another, and the effects are suppressed for *meta* positions of substituents.

Comparison of Eqs. (31) and (37) also shows that the absolute values of corrections $\Delta X_{(+d)}^{(4)2}$ and $\Delta X_{(-)a}^{(4)2}$ coincide with one another if $\epsilon_{(+d)} = \epsilon_{(-)a}$. This particular case corresponds to the coinciding energy intervals of orbitals $\varphi_{(+d)}$ and $\varphi_{(-)a}$ with respect to the energy of a $2p_z$ AO of carbon atom. The occupation numbers of MOs of the phenyl ring do not change in this case.

4.3. Analysis of the indirect charge transfer between substituents by means of the phenyl ring

Let us now compare the indirect charge transfer between substituents for various isomers. To this end, let us turn to Eqs. (7) and (25) for $k = (+)d$ and $l = (-)a$.

Let the first position within the benzene ring be again ascribed to the site the electron-donating substituent is attached to. Then the MOs $\varphi_{(+3)}$ and $\varphi_{(-4)}$ do not contribute to the indirect interaction $G_{(2)da}$ as Eq. (26) indicates. As a result, only the MOs $\varphi_{(+2)}$ and $\varphi_{(-5)}$ may be considered as mediators in this interaction. In this connection, the element $G_{(2)da}$ may be expressed as follows:

$$G_{(2)da} = \frac{1}{(\epsilon_{(+d)} + \epsilon_{(-a)})} \left\{ \frac{S_{d2}R_{2a}}{1 + \epsilon_{(-a)}} - \frac{R_{d5}Q_{5a}}{1 + \epsilon_{(+d)}} \right\} \quad (38)$$

Using the above-discussed expressions for resonance parameters S_{d2} , R_{2a} , R_{d5} and Q_{5a} we then obtain

$$G_{(2)da}^{para} = -\frac{b^2\sigma_{(+d)}\sigma_{(-a)}}{(\epsilon_{(+d)} + \epsilon_{(-a)})} \left\{ \frac{1}{1 + \epsilon_{(-a)}} + \frac{1}{1 + \epsilon_{(+d)}} \right\} \quad (39)$$

$$G_{(2)da}^{ortho} = \frac{bc\sigma_{(+d)\sigma_{(-a)}}}{(\epsilon_{(+d)} + \epsilon_{(-a)})} \left\{ \frac{1}{1 + \epsilon_{(-a)}} + \frac{1}{1 + \epsilon_{(+d)}} \right\} \quad (40)$$

$$G_{(2)da}^{meta} = -\frac{bc\sigma_{(+d)\sigma_{(-a)}}}{(\epsilon_{(+d)} + \epsilon_{(-a)})} \left\{ \frac{1}{1 + \epsilon_{(-a)}} - \frac{1}{1 + \epsilon_{(+d)}} \right\} \quad (41)$$

Comparison of Eqs. (39)–(41) shows that the expression for $G_{(2)da}^{meta}$ differs from those of $G_{(2)da}^{ortho}$ and $G_{(2)da}^{para}$ in signs of terms within the braces. Indeed, different signs of these two terms are present in Eq. (41) in contrast to Eqs. (39) and (40). This result may be traced back to different signs of products $S_{d2}R_{2a}$ and $R_{d5}Q_{5a}$ for different isomers and thereby to the constitution of MOs of benzene.

The above-analysed structure of Eqs. (39)–(41) implies that the smallest (or even zero) value of the indirect interaction and thereby of the indirect charge transfer between substituents D and A is peculiar to *meta*-(D,A)-disubstituted benzenes. So far as *ortho* and *para* derivatives are concerned, the relation

$$(G_{(2)da}^{para})^2 > (G_{(2)da}^{ortho})^2 \quad (42)$$

follows from the equality $b = 2c$ [15].

Therefore, the largest indirect charge transfer may be expected to take place between substituents in the *para*- and *ortho*-positions with respect to one another, and the smallest one is likely to be peculiar to *meta*-derivatives of benzene.

5. Concluding remarks

Application of the power series for the one-electron density matrix [17–19] to investigation of electronic structures of (D,A)-disubstituted benzenes yields the following principal results:

1. It is shown that there are two fourth order intersubstituent effects in the molecules under study. First, it is an alteration in the extent of electron-donating (accepting) effect of each individual substituent upon the phenyl ring which arises owing to the indirect participation of orbitals of the opposite substituent and, second, it is the indirect charge transfer between substituents by means of the phenyl ring, the latter playing the role of mediator.

Hence, the approach applied gives us a real insight into the nature of the intersubstituent interaction in (D,A)-disubstituted benzenes.

2. The above-mentioned two components of the intersubstituent interaction, in turn, have been explicitly expressed in terms of direct and indirect interactions between orbitals of substituents and the MOs of benzene. As a result, the different extent of the intersubstituent interaction for *para*, *ortho*, and *meta* isomers following from experimental facts becomes directly related to the particular constitution of the highest occupied and lowest vacant MOs of benzene. An analogous interrelation has been established previously for the electron density distribution in mono-substituted benzenes [16]. These results support the implicit assumption of the classical chemistry about the properties of derivatives being directly related to those of the parent hydrocarbon.

Furthermore, there are good prospects for other applications of the obtained results:

1. Modelling of the electrophilic substitution reaction in mono-substituted benzenes containing an electron-donating substituent (D = OR, NR₂, where R = H, CH₃, etc.) seems to be feasible on the basis of the obtained expressions for the electron density distribution. The approaching electrophilic agent will play the role of the electron-accepting substituent (A) in such a model. Then the well-known fact that the electron-donating substituents favour the formation of *ortho*- and *para*-disubstituted molecules [10,23–25] may be traced back to the above-established strong intersubstituent interactions just in these positions.
2. The expressions of Eqs. (18)–(25) may be directly applied also to other types of (D,A)-disubstituted hydrocarbons provided that the direct interaction between orbitals of substituents may be ignored. This possibility is based on the fact that derivation of the general expressions for the intersubstituent interaction was carried out in Section 3 without specifying the actual structure of the hydrocarbon fragment.

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