

Heteroatom influence in substituted benzenes and pyridine-like heterocycles in terms of direct and indirect intramolecular interactions

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Received 27 October 1999; accepted 3 November 1999

Abstract

The general expression for the one-electron density matrix obtained previously for saturated organic molecules (V. Gineityte, J. Mol. Struct. (Theochem), 343 (1995) 183) is shown to be applicable also to substituted benzenes and pyridine-like heterocycles. On this basis, a new interpretation of the influence of a heteroatom (substituent) upon the remaining fragment of an aromatic molecule is suggested. To this end, the occupation number of a $2p_z$ AO of the aromatic ring has been expressed as a sum of five terms, two of them describing the intramolecular charge transfer and the remaining ones representing the secondary (induced) dipole moments arising within the ring under the influence of heteroatom, viz. the so-called *ipso-ortho* (*para-meta*), *para-ipso* and *ortho-meta* dipole moments. Just the latter two moments proved to play the principal role in the formation of the observed picture of the electron density distribution, viz. of an increase (reduction) of occupation numbers of $2p_z$ AOs in the *ortho* and *para* positions after introducing an electron-donating (accepting) substituent. For pyridine-like heterocycles and substituted benzenes, these dipole moments are determined mostly by the direct and the indirect interactions, respectively, between the highest occupied and the lowest vacant MO of benzene. Orbitals of the heteroatom (substituent) play the role of mediators in the above-mentioned indirect interaction. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Substituted benzenes; Pyridine-like heterocycles; Heteroatom influence; Direct (through-space) interactions of orbitals; Indirect (through-bond) interactions of orbitals; Intramolecular charge transfer

1. Introduction

Numerous experimental investigations of predominant directions of electrophilic substitution in mono-substituted benzenes (Ar-Z) and pyridine-like heterocycles ($\text{C}_5\text{H}_5\text{Z}$) resulted in simple and general rules describing the heteroatom influence in these molecules (see e.g. Refs. [1–4]). Thus, two types of substituents (Z) are distinguished in substituted benzenes that provide for different directions of the

subsequent electrophilic substitution, namely the electron-donating substituents ($\text{Z} = \text{OR}, \text{NR}_2$, where $\text{R} = \text{H}, \text{CH}_3$, etc.) that favour the formation of *ortho* and *para* disubstituted molecules, and the electron-accepting ones ($\text{Z} = \text{COR}, \text{COOR}, \text{NO}_2$, etc.) that provide for *meta* orientation of the electrophilic agent. Turning from the benzene molecule to pyridine-like systems containing an electronegative heteroatom ($\text{Z} = \text{N}, \text{P}$, etc.) is similar to introducing an electron-accepting substituent into the former, and *meta*-disubstituted molecules result from a subsequent electrophilic substitution in this case.

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The above-described trends have been supported many times by quantum-chemical calculations of populations of $2p_z$ AOs of carbon atoms within the phenyl ring [5]. Indeed, populations of the $2p_z$ AOs in the *ortho* and *para* positions increase (reduce) vs. those of benzene after the introduction of an electron-donating (accepting) substituent.

The first theoretical explanation of these rules was given on the basis of the valence bond method [6]. Thus, the resonance structures of substituted benzenes representing the intramolecular charge transfer between the phenyl ring and the substituent Z, indicate that the population acquired (lost) by the phenyl ring becomes located in the *ortho* and *para* positions with respect to the substituent.

In the framework of the method of molecular orbitals (MOs), the electron density distribution of the substituted molecule is usually accounted for by the electronic structure peculiarities of certain conjugated hydrocarbon [7]. Thus, substituted benzenes containing the OR and NR_2 -groups are considered as “perturbed” anions $\text{Ar}-(\text{CH}_2)^-$, where the perturbation coincides with the difference between the electronegativity of the heteroatom (O or N) and that of the carbon atom. As a result, the electron density distribution in the relevant substituted benzene is related to constitution of the non-bonding MO of this anion, the latter being reckoned to odd alternate hydrocarbons. Molecules containing electron-accepting groups also are considered as “perturbed” alternate hydrocarbons, only an even alternate hydrocarbon usually serves as a prototype here (e.g. $\text{Ar}-\text{CH}=\text{CH}_2$ corresponds to $\text{Ar}-\text{COR}$). Finally, the pyridine-like heterocycles are considered as “perturbed” benzenes. In these cases an interpretation of the electron density distribution in the substituted molecule becomes possible owing to the rule of alternating signs of the atom–atomic polarizabilities peculiar to even alternate hydrocarbons [8–11]. It should be noted, however, that the above-enumerated hydrocarbons do not coincide with the parent hydrocarbons of the substituted molecules in the chemical sense except for the case of pyridine-like heterocycles.

Indeed, both substituted benzenes and pyridine-like heterocycles are usually considered as derivatives of benzene. In this connection, an interpretation of the heteroatom influence in substituted benzenes in terms of interactions between orbitals of the phenyl ring and

those of the substituent Z would be preferable. Such an interpretation also implies the establishment of an explicit relation between the electronic structure of benzene and the electron density distribution in substituted molecules.

To achieve this end, the direct way of obtaining the one-electron density matrix (bond order matrix) [12–14] on the basis of solution of the so-called commutation equation [15] by means of power series seems to be appropriate. This expectation is based on the success of this approach when studying the heteroatom influence in substituted alkanes [14].

Two points form the basis of the above-mentioned efficiency of the direct way of deriving the expressions for occupation numbers of basis orbitals. The first one consists in the particular constitution of the power series for the one-electron density matrix (DM) obtained in Ref. [12]. Thus, the first three members of this series have been expressed in terms of principal matrices $G_{(1)}$ and $G_{(2)}$ describing the direct and indirect interactions of basis orbitals $\{\varphi\}$ underlying the initial Hamiltonian matrix. As a result, the occupation numbers of these orbitals also proved to be interpretable in terms of these interactions. In the case of substituted alkanes the basis set $\{\varphi\}$ coincided with bonding and antibonding bond orbitals (BOs). These orbitals, in turn, may be interpreted as fragmental orbitals of the above-mentioned compounds (individual bonds play the role of the principal fragments of saturated molecules [16]).

The second point determining the efficiency of the approach lies in the fact that several meaningful additive components of the heteroatom influence reveal themselves after transforming the obtained DM represented on the basis of fragmental orbitals $\{\varphi\}$ into the basis of AOs $\{\chi\}$, and each of these components proves to be expressed in terms of direct and indirect interactions of fragmental orbitals [14]. Thus, polarization and depolarization of bonds and the intramolecular charge transfer played the role of the additive components of heteroatom influence in substituted alkanes, and served to account for the observed picture of the electron density distribution in these molecules.

An important feature of the power series for the DM derived in Ref. [12] consists in the fact that no explicit definition of the basis set $\{\varphi\}$ is required. The only condition imposed on this basis was the possibility of

revealing two subsets of basis functions within the set $\{\varphi\}$ so that the energy differences between orbitals of different subsets exceed considerably the intersubset resonance parameters, and one of these subsets is initially occupied in addition. In the basis of BOs this requirement was met owing to the large energy gap between the initially occupied bonding BOs and the initially vacant antibonding BOs as compared to the interbond resonance parameters.

The initially occupied and the initially vacant MOs of benzene along with orbitals of the substituent play the role of fragmental orbitals in our case. Moreover, these orbitals also are likely to meet the above-described condition. Given that this is the case, the expressions for the DM obtained in Ref. [12] may be directly applied to substituted benzenes and pyridine-like heterocycles in the basis of the above-mentioned orbitals (the MOs of benzene will be sufficient to study the pyridine-like systems). In this paper, we are about to carry out such an application at first (Section 2) and then we will verify the validity of the above-discussed condition (Section 3).

To obtain the occupation numbers of $2p_z$ AOs of carbon atoms of the aromatic ring determining the electron density distribution in substituted benzenes, a six-dimensional transformation matrix C containing the coefficients of MOs of benzene in terms of $2p_z$ AOs should be used, and additive components of the heteroatom influence may be expected to reveal themselves after this transformation.

Therefore, the main aim of this paper consists in establishing the additive components of the heteroatom influence in substituted benzenes and pyridine-like heterocycles and in expressing them in terms of direct and indirect interactions of fragmental orbitals of these molecules. Thereupon, these components will be used for interpretation of the observed pictures of the electron density distribution. Similarity and differences between substituted benzenes and pyridine-like heterocycles also will be discussed.

2. General expressions for occupation numbers of $2p_z$ AOs of the phenyl ring in substituted benzenes

Let us consider a substituted benzene (Ar-Z) containing a substituent (heteroatom) Z of any type. As in Refs. [12,16,17], the initial model Hamiltonian

matrix H of our molecule is assumed to consist of the zero order matrix $H_{(0)}$ containing the one-electron energies of basis orbitals, and of the first order matrix $H_{(1)}$ involving the resonance parameters.

As it was mentioned already, the basis set $\{\varphi\}$ consists of the initially occupied MOs $\{\varphi_{(+i)}\}$, $i = 1, 2, 3$ and of the initially vacant MOs $\{\varphi_{(-j)}\}$, $j = 4, 5, 6$ of the benzene molecule along with the orbitals of the substituent. The transformation matrix C to be used to obtain the populations of $2p_z$ AOs of the phenyl ring, is made up of coefficients of linear combinations of the MOs of benzene in terms of $2p_z$ AOs $\{\chi_k\}$, $k = 1, 2, \dots, 6$. This matrix takes the form [7]

$$C = \begin{pmatrix} a & b & 0 & 0 & b & a \\ a & c & d & -d & -c & -a \\ a & -c & d & d & -c & a \\ a & -b & 0 & 0 & b & -a \\ a & -c & -d & -d & -c & a \\ a & c & -d & d & -c & -a \end{pmatrix} \quad (1)$$

where the coefficients a , b , c and d are

$$\begin{aligned} a &= 0.408; & c &= 0.289; & b &= 2c = 0.577; \\ d &= 0.5 \end{aligned} \quad (2)$$

The occupation numbers of $2p_z$ AOs being sought follow from the expression:

$$\tilde{P}_{(\text{Ph})} = CP_{(\text{Ph})}C^+ \quad (3)$$

where $P_{(\text{Ph})}$ is the six-dimensional block (submatrix) of the total DM of the substituted benzene corresponding to the phenyl ring and represented in the basis $\{\varphi\}$, and $\tilde{P}_{(\text{Ph})}$ is the relevant submatrix in the basis of $2p_z$ AOs $\{\chi_k\}$. Elements of the block $P_{(\text{Ph})}$ may be derived using the expression of Ref. [12] as discussed below:

1. Diagonal elements of the submatrix $P_{(\text{Ph})}$ representing the occupation numbers of basis orbitals $\varphi_{(+i)}$ and $\varphi_{(-j)}$, respectively, take the form

$$P_{(\text{Ph})ii} = 2 + (ii) = 2 - 2 \sum_r^{\text{VBOs}} (G_{(1)ir})^2 \quad (4a)$$

$$P_{(\text{Ph})jj} = (jj) = 2 \sum_p^{\text{OBOs}} (G_{(1)pj})^2 \quad (4b)$$

where the simplified notations (*ii*) and (*jj*) are introduced for convenience and these describe alterations in occupation numbers vs. their initial values. The sum over *r* formally embraces all the initially vacant basis orbitals (denoted by VBOs), whilst the sum over *p* includes the initially occupied basis orbitals (OBOs).

Furthermore, the element $G_{(1)ir}$ of the first order matrix $G_{(1)}$ [12] describes the direct (through-space) interaction between the OBO $\varphi_{(+)i}$ and the VBO $\varphi_{(-)r}$ and takes the form

$$G_{(1)ir} = -\frac{\langle \varphi_{(+)i} | \hat{H} | \varphi_{(-)r} \rangle}{E_{(+)i} - E_{(-)r}} \quad (5)$$

The numerator of this expression contains the Hückel type Hamiltonian matrix element (resonance parameter) between the basis orbitals indicated within the bra- and ket- vectors, and the denominator involves the relevant difference in one-electron energies. It is also seen from Eqs. (4a) and (4b) that the alteration (*ii*) in the occupation number of the initially occupied basis orbital $\varphi_{(+)i}$ and the population (*jj*) of the initially vacant basis orbital $\varphi_{(-)j}$ are determined by squares of the direct interactions between orbitals $\varphi_{(+)i}$ and $\varphi_{(-)j}$ and remaining orbitals of the molecule.

Inasmuch as MOs of benzene meet the diagonality requirement for respective submatrix (block) $H_{(\text{Ph})}$ of the Hamiltonian matrix H , the resonance parameters $\langle \varphi_{(+)i} | \hat{H} | \varphi_{(-)j} \rangle$ between pairs of MOs of benzene and thereby the relevant elements of the matrix $G_{(1)}$ actually take zero values. As a result, the sums of Eqs. (4a) and (4b) contain only the basis orbitals of the substituent Z. Hence, squares of the direct interactions between orbitals of the phenyl ring and those of the substituent prove to determine the occupation numbers (*ii*) and (*jj*).

2. The off-diagonal elements of the submatrix $P_{(\text{Ph})}$ representing the bond orders between two initially occupied MOs $\varphi_{(+)i}$ and $\varphi_{(+)i'}$, and those between two initially vacant MOs $\varphi_{(-)j}$ and $\varphi_{(-)j'}$, i.e. the so-called intrasubset bond orders, may be expressed as follows:

$$\begin{aligned} P_{(\text{Ph})i'i'} &= (i'i') = -2 \sum_r^{\text{VBOs}} G_{(1)ir} G_{(1)ri'}^+ \\ &\equiv -2 \sum_r^{\text{VBOs}} G_{(1)ir} G_{(1)i'r} \end{aligned} \quad (6a)$$

$$\begin{aligned} P_{(\text{Ph})j'j'} &= (j'j') = -2 \sum_p^{\text{OBOs}} G_{(1)jp}^+ G_{(1)pj'} \\ &\equiv \sum_p^{\text{OBOs}} G_{(1)pj} G_{(1)pj'} \end{aligned} \quad (6b)$$

where the respective elements of the matrix $G_{(1)}$ are defined by Eq. (5). The superscript + corresponds here to the transposed matrix $G_{(1)}$. The products $G_{(1)ir} G_{(1)ri'}^+$ and $G_{(1)jp}^+ G_{(1)pj'}$ may be interpreted as indirect interactions between basis orbitals $\varphi_{(+)i}$ and $\varphi_{(+)i'}$ (and between $\varphi_{(-)j}$ and $\varphi_{(-)j'}$) by means of orbitals $\varphi_{(-)r}$ and $\varphi_{(+)p}$, respectively. As with Eqs. (4a) and (4b), the sums of Eqs. (6a) and (6b) actually embrace only the orbitals of the substituent.

3. The off-diagonal elements of the submatrix $P_{(\text{Ph})}$ describing the bond order (*ij*) of the intersubset type between an OBO $\varphi_{(+)i}$ and a VBO $\varphi_{(-)j}$ may be expressed as follows [12]:

$$P_{(\text{Ph})ij} = (ij) = -2(G_{(1)ij} + G_{(2)ij}) \quad (7)$$

where $G_{(1)ij}$ takes a zero value in our case, and $G_{(2)ij}$ is an element of certain second-order matrix $G_{(2)}$ representing the indirect interaction between the basis functions $\varphi_{(+)i}$ and $\varphi_{(-)j}$. This element takes the form

$$\begin{aligned} G_{(2)ij} &= \frac{1}{E_{(+)i} - E_{(-)j}} \\ &\times \left\{ \sum_k^{\text{OBOs}} \frac{\langle \varphi_{(+)i} | \hat{H} | \varphi_{(+)k} \rangle \langle \varphi_{(+)k} | \hat{H} | \varphi_{(-)j} \rangle}{E_{(+)k} - E_{(-)j}} \right. \\ &\left. - \sum_r^{\text{VBOs}} \frac{\langle \varphi_{(+)i} | \hat{H} | \varphi_{(-)r} \rangle \langle \varphi_{(-)r} | \hat{H} | \varphi_{(-)j} \rangle}{E_{(+)i} - E_{(-)r}} \right\} \end{aligned} \quad (8)$$

where the meanings of all designations coincide with those of Eq. (5). It is seen that both the initially occupied and the initially vacant basis orbitals (OBOs and VBOs) of the substituent may play the role of mediators in the indirect intersubset interaction.

Therefore, to obtain the populations of $2p_z$ AOs of the phenyl ring, Eqs. (1), (4)–(8) should be substituted into Eq. (3).

It is noteworthy here that some elements of the initial submatrix $P_{(\text{Ph})}$ take zero values owing to symmetry of the phenyl ring in substituted benzenes. Thus, let the substituent Z take the first position within the phenyl ring (Fig. 1). Then the symmetry plane of

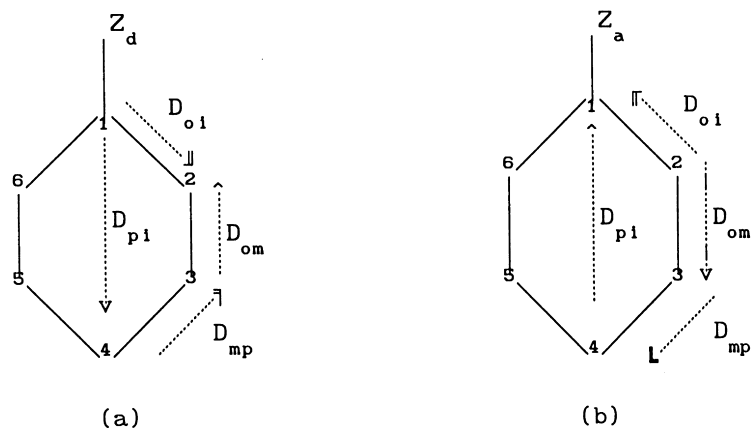


Fig. 1. Diagram representing the induced dipole moments within the aromatic rings of substituted benzenes containing an electron-donating substituent (Z_d) and an electron-accepting one (Z_a). Arrows indicate the direction of an increased population.

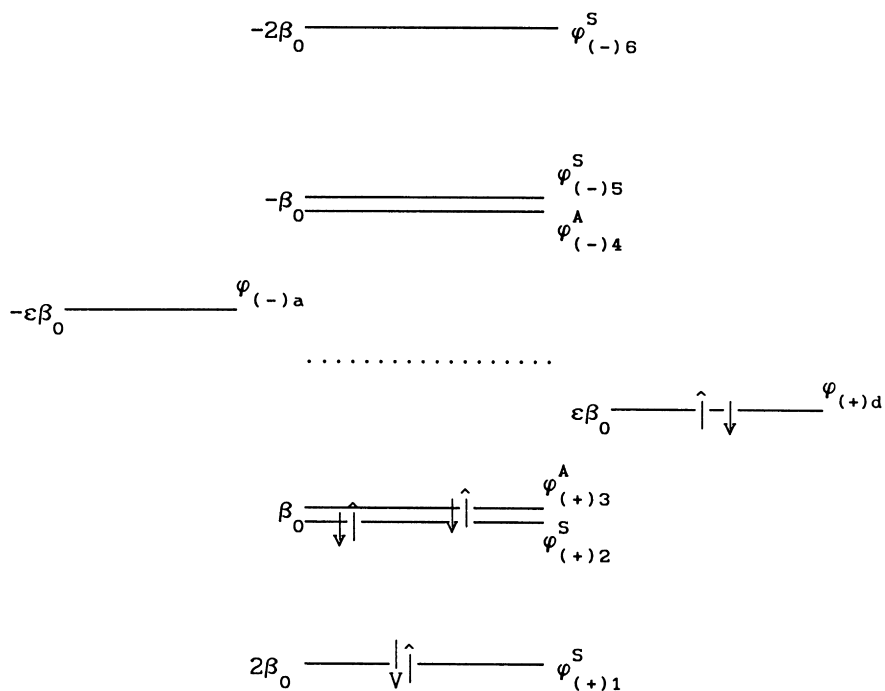


Fig. 2. Relative positions of one-electron energies corresponding to fragmental orbitals of substituted benzenes. The MOs of benzene are shown in the central part of the diagram, whereas the orbitals of an electron-donating and electron-accepting substituents are shown in the right and left part, respectively.

the substituted benzene goes through AOs χ_1 and χ_4 . As a result, the MOs $\varphi_{(+1)}^s$, $\varphi_{(+2)}^s$, $\varphi_{(-5)}^s$ and $\varphi_{(-6)}^s$ are symmetric with respect to this plane as denoted by the superscript *s*, whilst the MOs $\varphi_{(+3)}^a$ and $\varphi_{(-4)}^a$ are antisymmetric with respect to the same plane (Fig. 2). Consequently, the bond orders between orbitals of different symmetry take zero values, viz.

$$(13) = (46) = (24) = (53) = (14) = (63) = (23) \\ = (54) = 0 \quad (9a)$$

and the occupation numbers of the antisymmetric orbitals along with the bond order (34) are not influenced by the substituent, i.e.

$$(33) = (44) = (34) = 0 \quad (9b)$$

Taking into account these relations and the equalities

$$2(a^2 + b^2) = 1; \quad 2(a^2 + c^2 + d^2) = 1 \quad (10)$$

(the latter resulting from the unitarity condition for the matrix *C*), the occupation numbers of $2p_z$ AOs χ_1 , χ_2 , χ_3 and χ_4 may be expressed as follows

$$X_{1(4)} = 1 + Q - 2T \mp M; \quad X_{2(3)} = 1 + R + T \pm N \quad (11)$$

where the upper signs correspond to AOs χ_1 and χ_2 , whereas the lower signs refer to AOs χ_4 and χ_3 , respectively. The increments *Q*, *R*, *T*, *M* and *N* are

$$Q = a^2[(11) + (66)] + b^2[(22) + (55)]; \quad (12)$$

$$R = a^2[(11) + (66)] + c^2[(22) + (55)]$$

and

$$T = -2ac[(15) + (26)] = -ab[(15) + (26)];$$

$$M = -2a^2(16) - 2b^2(25) - 2ab[(12) + (56)]; \quad (13)$$

$$N = -2a^2(16) - 2c^2(25) + 2ac[(12) + (56)]$$

and these may be considered as additive components of the occupation numbers.

The first terms of Eq. (11) denoted by *Q* and *R*, are related to alterations in occupation numbers of MOs of the phenyl ring and describe the intramolecular charge transfer between this ring and the substituent *Z*. It may be easily shown that the total population of

the ring is

$$X_{(\text{Ph})} = \sum_{i=1}^6 X_i = 6 + 2(Q + 2R) = 6 + \sum_{m=1}^6 (mm) \\ = 6 + (11) + (22) \dots + (66) \quad (14)$$

and coincides with the total sum of occupation numbers of MOs.

The remaining terms of Eq. (11) (*T*, *M* and *N*) describe the dipole-like contributions to occupation numbers of $2p_z$ AOs. Indeed, the *para-ipso* dipole moment (D_{pi}), the *ortho-meta* dipole moment (D_{om}) and the *ortho-ipso (meta-para)* dipole moment ($D_{\text{oi}} = D_{\text{mp}}$) may be defined as follows (Fig. 1):

$$D_{\text{pi}} = \pm M; \quad D_{\text{om}} = \pm N; \quad D_{\text{oi}} = D_{\text{mp}} = \pm 2T \quad (15)$$

and the total dipole of the phenyl ring becomes

$$D_{(\text{Ph})} = \pm(M - N) \quad (16)$$

From Eq. (13) it is also seen that the dipole moments defined by Eqs. (15) and (16) are related to bond orders between orbitals of the phenyl ring (benzene) arising after substitution. As it follows from Eqs. (6) and (7), these bond orders and thereby the dipole moments D_{pi} , D_{om} , and $D_{\text{oi}} = D_{\text{mp}}$ are determined by indirect interactions between pairs of MOs of the phenyl ring by means of orbitals of the substituent.

Moreover, the above-outlined derivation of Eq. (11) shows that the general constitution of the electron density distribution reflected there does not depend on the nature of the substituent and it is determined by the structure of MOs of benzene involved within the matrix *C*.

3. Studies of the electron-donating and electron-accepting substituents

Let us start with an electron-donating substituent Z_{d} . Let us assume for simplicity that this substituent may be characterized by a single initially occupied orbital $\varphi_{(+)\text{d}}$. The one-electron energy $\epsilon\beta_0$ will correspond to this orbital, where β_0 is the standard resonance parameter for the neighbouring $2p_z$ AOs of benzene. The resonance parameter of the $Z_{\text{d}}-C_1$ bond is assumed to be equal to $\sigma\beta_0$, where the

parameter σ is close to 1. Let us accept the equality $\beta_0 = 1$ for further convenience. Accordingly, the Coulomb parameter α_0 referring to $2p_z$ AOs of the phenyl ring will be taken equal to zero. The resulting relative positions of the energy levels are shown in Fig. 2.

From Eqs. (4a) and (6a) along with Fig. 2, it follows that there are no mediators for indirect interactions between the MOs $\varphi_{(+1)}$ and $\varphi_{(+2)}$ of the phenyl ring in this case. As a result, we obtain that

$$(11) = (22) = (12) = 0 \quad (17)$$

Furthermore, ϵ -dependent functions $Q_d(\epsilon)$ and $R_d(\epsilon)$ may be introduced to describe the dependence of terms Q and R , respectively, on the electronegativity of the substituent, the latter being proportional to parameter ϵ . These functions take the form

$$Q_d(\epsilon) = a^2(66) + b^2(55) = 2\sigma^2\kappa(\epsilon) \quad (12)$$

$$R_d(\epsilon) = a^2(66) + c^2(55) = 2\sigma^2\rho(\epsilon)$$

where

$$\kappa(\epsilon) = \frac{a^4}{(\epsilon + 2)^2} + \frac{b^4}{(\epsilon + 1)^2} > 0; \quad (19)$$

$$\rho(\epsilon) = \frac{a^4}{(\epsilon + 2)^2} + \frac{b^2c^2}{(\epsilon + 1)^2} > 0$$

Eq. (4b) is used here when obtaining the populations (55) and (66) of the initially vacant MOs of benzene $\varphi_{(-)5}$ and $\varphi_{(-)6}$.

It is seen that both $Q_d(\epsilon)$ and $R_d(\epsilon)$ are positive. Hence, charge is being transferred from the orbital $\varphi_{(+d)}$ to orbitals of the phenyl ring and this trend is in accordance with the electron-donating nature of the substituent.

It is also seen that $\kappa(\epsilon) > \rho(\epsilon)$ for any ϵ and thereby $Q_d(\epsilon) > R_d(\epsilon)$. Hence, the *ipso* and *para* positions of the phenyl ring acquire more population as compared to *ortho* and *meta* positions. This result may be easily accounted for by the fact that the acquired population becomes located mostly on the lowest-vacant MO $\varphi_{(-)5}$ containing larger coefficients at the $2p_z$ AOs χ_1 and χ_4 .

Furthermore, the corrections $2\sigma^2\kappa(\epsilon)$ and $2\sigma^2\rho(\epsilon)$ are small even for $\epsilon \approx 0$ to say nothing about larger values of this parameter (ϵ is assumed to be positive

for electron-donating substituents). This fact speaks in favour of applicability of the approach in general to substituted benzenes.

Let us turn now to the dipole-like terms T , M and N , described by Eq. (13).

Contributions to these terms of the intersubset type determined by the indirect interactions between an OBO $\varphi_{(+i)}$ and a VBO $\varphi_{(-j)}$ as shown in Eqs. (7) and (8) take the form:

$$P_{(\text{Ph})ij} = (ij) = -2G_{(2)ij} \\ = -\frac{2\langle\varphi_{(+i)}|\hat{H}|\varphi_{(+d)}\rangle\langle\varphi_{(+d)}|\hat{H}|\varphi_{(-j)}\rangle}{(E_{(+i)} - E_{(-j)})(E_{(+d)} - E_{(-j)})} \quad (20)$$

where $\varphi_{(+d)}$ is the only mediator of the indirect interaction between the MOs $\varphi_{(+i)}$ and $\varphi_{(-j)}$.

Inasmuch as all MOs of benzene are described by a positive coefficient at the AO χ_1 as shown in Eq. (1), the resonance parameters involved within the numerator of Eq. (20) are positive (in β_0 units). Hence, all the bond orders (ij) of the intersubset type are negative, viz.

$$(15) = -2\frac{ab\sigma^2}{3(\epsilon + 1)} < 0;$$

$$(26) = -2\frac{ab\sigma^2}{3(\epsilon + 2)} < 0; \quad (21)$$

$$(16) = -2\frac{a^2\sigma^2}{4(\epsilon + 2)} < 0;$$

$$(25) = -2\frac{b^2\sigma^2}{2(\epsilon + 1)} < 0.$$

On the other hand, the only bond order (56) of the intrasubset type defined by Eq. (6b) is positive, viz.

$$(56) = 2\frac{ab\sigma^2}{(\epsilon + 1)(\epsilon + 2)} > 0 \quad (22)$$

Let us introduce now the functions $T_d(\epsilon)$, $M_d(\epsilon)$ and $N_d(\epsilon)$, like those of Eq. (18). We then obtain

$$T_d(\epsilon) = 2\sigma^2\tau(\epsilon); \quad M_d(\epsilon) = 2\sigma^2\mu(\epsilon); \\ N_d(\epsilon) = 2\sigma^2\nu(\epsilon) \quad (23)$$

where

$$\begin{aligned}\pi(\epsilon) &= \frac{2a^2bc}{3(\epsilon+1)} + \frac{2a^2bc}{3(\epsilon+2)} > 0 \\ \nu(\epsilon) &= \frac{a^4}{2(\epsilon+2)} + \frac{b^2c^2}{(\epsilon+1)} + \frac{2a^2b^2}{(\epsilon+1)(\epsilon+2)} > 0\end{aligned}\quad (24)$$

are positive functions, whilst the sign of the remaining function

$$\mu(\epsilon) = \frac{a^4}{2(\epsilon+2)} + \frac{b^4}{(\epsilon+1)} - \frac{2a^2b^2}{(\epsilon+1)(\epsilon+2)} \quad (25)$$

is not evident “a priori”.

A detailed study of functions defined by Eqs. (24) and (25) shows that $\mu(\epsilon)$ is positive within the interval $\epsilon = [0; 2]$. Moreover, numerical values of all these functions decrease with increasing ϵ , and their maximal values corresponding to $\epsilon \approx 0$ do not exceed 0.1. Hence, $T_d(\epsilon)$, $M_d(\epsilon)$ and $N_d(\epsilon)$ are small positive corrections only, as was the case with $Q_d(\epsilon)$ and $R_d(\epsilon)$. Orientations of the respective induced dipole moments are shown in Fig. 1. It is seen that the dipole moments D_{oi} and D_{mp} determined by the function $T_d(\epsilon)$ contribute to certain increase of populations of the *ortho* and *meta* positions and to the respective decrease of occupation numbers of $2p_z$ AOs χ_1 and χ_4 . This effect is opposite to the above-discussed differences in the acquired populations of AOs.

Evaluations of functions $\pi(\epsilon)$, $\mu(\epsilon)$ and $\nu(\epsilon)$ show that the dipole moments D_{oi} and D_{mp} when added to the respective acquired populations $Q_d(\epsilon)$ and $R_d(\epsilon)$, yield close values of occupation numbers of all AOs $\chi_1 \dots \chi_6$ provided that ϵ is close to zero, viz.

$$Q_d(\epsilon) - 2T_d(\epsilon) \approx R_d(\epsilon) + T_d(\epsilon), \quad \text{for } \epsilon \approx 0 \quad (26)$$

On the other hand, the dipole moments D_{om} and D_{pi} play an essential role in the formation of an increased total population of AOs χ_2 and χ_4 vs. those of AOs χ_3 and χ_1 , respectively. In other words, it is these dipole moments that determine the increased populations of the *ortho* and *para* positions as compared to the *meta* and *ipso* positions, respectively, in the substituted benzenes containing an electron-donating substituent. As it is seen from Eqs. (24) and (25), the principal contributions to the functions $\mu(\epsilon)$ and $\nu(\epsilon)$ coincide with the second terms of the right-hand sides of these

expressions. The latter, in turn, may be traced back to bond orders between the highest-occupied MO $\varphi_{(+2)}$ and the lowest-vacant MO $\varphi_{(-5)}$ of the phenyl ring arising after substitution. Hence, it is the indirect interactions between these MOs by means of the orbital $\varphi_{(+d)}$ that determines the increased populations of the *ortho* and *para* positions.

Let us consider now an electron-accepting substituent Z_a characterized by an initially vacant orbital $\varphi_{(-a)}$ and the one-electron energy $-\epsilon\beta_0$ (Fig. 2), and by an analogous parameter σ . Instead of Eq. (17) we then obtain

$$(55) = (66) = (56) = 0 \quad (27)$$

Furthermore, the charge transfer terms $Q_a(\epsilon)$ and $R_a(\epsilon)$ are related to the same functions $\kappa(\epsilon)$ and $\rho(\epsilon)$, only minus signs arise in the relevant proportionalities, viz.

$$Q_a(\epsilon) = -2\sigma^2\kappa(\epsilon), \quad R_a(\epsilon) = -2\sigma^2\rho(\epsilon) \quad (28)$$

Hence, a lost population stands for an acquired population in this case, and the above-drawn conclusions concerning the acquired populations of AOs refer now to the lost populations. Similarly, the relevant dipole moments are of opposite directions, viz.

$$\begin{aligned}T_a(\epsilon) &= -2\sigma^2\pi(\epsilon) < 0; & M_a(\epsilon) &= -2\sigma^2\mu(\epsilon) < 0; \\ N_a(\epsilon) &= 2\sigma^2\nu(\epsilon) < 0\end{aligned}\quad (29)$$

Hence, the induced dipole moments D_{pi} and D_{om} contribute now to a decrease of relative populations of *ortho* and *para* positions as compared to the *meta* and *ipso* positions. The result represented by Eq. (29) may be accounted for by the fact that contributions to the induced dipole moments of intersubset type defined by Eqs. (7) and (8) contain an initially vacant orbital as a mediator and thereby these contributions acquire a positive sign in contrast to Eq. (20), viz.

$$(ij) = -2G_{(2)ij} = \frac{2\langle\varphi_{(+i)}|\hat{H}|\varphi_{(-a)}\rangle\langle\varphi_{(-a)}|\hat{H}|\varphi_{(-j)}\rangle}{(E_{(+i)} - E_{(-j)})(E_{(+i)} - E_{(-a)})} > 0 \quad (30)$$

whereas the bond order (12) between the two initially occupied MOs $\varphi_{(+1)}$ and $\varphi_{(+2)}$ is negative as it follows from Eq. (6a).

Therefore, the reduced populations of the *ortho* and

para positions as compared to the *meta* and *ipso* positions under the influence of the electron-accepting substituent may be traced back to the induced *ortho–meta* and *para–ipso* dipole moments determined mostly by the indirect interaction between the highest-occupied MO $\varphi_{(+2)}$ and the lowest-vacant MO $\varphi_{(-5)}$ of the phenyl ring by means of the initially vacant orbital of the substituent.

Before finishing this section, let us note that the same final expressions for occupation numbers may be evidently derived using the standard procedure of obtaining the DM by summing up the coefficients within the MOs of the substituted molecule. The advantages of the above-used direct way are as follows: First, the terms contributing to the MOs of the substituted molecule but being absent within the final DM (e.g. those describing an interaction between two initially occupied orbitals) are ignored here from the very outset of solving the problem, and this contributes to a significant simplification of the derivation of the final expressions. Second, the general constitution of occupation numbers shown in Eq. (11) reveals itself after transforming the perturbed DM into the basis of AOs, and the dipole-like increments may be easily distinguished here. And third, the interpretation of the DM elements in terms of direct and indirect interactions developed in Refs. [12–14] becomes useful here.

4. Comparative study of the pyridine-like heterocycles

Occupation numbers of $2p_z$ AOs of a pyridine-like heterocycle also may be found similarly, only the nature of perturbation differs from that of substituted benzene.

Thus, let the AO χ_1 of the heteroatom (e.g. nitrogen) to be described by the Coulomb parameter $\alpha \neq \alpha_0$. As a result, a local perturbation arises in the basis of $2p_z$ AOs. When transformed into the basis of MOs of benzene $\varphi_{(+1)}^s$, $\varphi_{(+2)}^s$, $\varphi_{(-5)}^s$ and $\varphi_{(-6)}^s$, this perturbation takes the form

$$V = \alpha \begin{vmatrix} a^2 & ab & ab & a^2 \\ ab & b^2 & b^2 & ab \\ ab & b^2 & b^2 & ab \\ a^2 & ab & ab & a^2 \end{vmatrix} \quad (31)$$

where the antisymmetric subspace of MOs of benzene ($\varphi_{(+3)}^a$, $\varphi_{(-4)}^a$) is not included because of zero values of respective elements of the matrix V . It is seen that non-zero resonance parameters arise between pairs of MOs of benzene in this case in contrast to substituted benzenes (Section 2). Non-zero resonance parameters, in turn, imply non-zero elements $G_{(1)ik}$ of the first-order matrix $G_{(1)}$ and thereby non-zero direct interactions between occupied and vacant basis orbitals.

Thus, the matrix $G_{(1)}$ describing the direct intersubset interactions in pyridine-like heterocycles follows from Eqs. (5) and (31) and takes the form

$$G_{(1)} = -\alpha \begin{vmatrix} \frac{1}{3}ab & \frac{1}{4}a^2 \\ \frac{1}{2}b^2 & \frac{1}{3}ab \end{vmatrix} \quad (32)$$

As a consequence, first order contributions arise within the bond orders between MOs $\varphi_{(+i)}$ ($i = 1, 2$) and $\varphi_{(-j)}$ ($j = 5, 6$) for pyridine-like heterocycles as it is seen from Eq. (7). Thus, the above-mentioned bond orders are

$$\begin{aligned} (15) = (26) &= \frac{2}{3} \alpha ab; & (16) &= \frac{1}{2} \alpha a^2; \\ (25) &= \alpha b^2 \end{aligned} \quad (33)$$

It should be also noted here that no more first-order contributions are present within the DM of pyridine-like molecules as it is seen from Eqs. (4a), (4b) and (6a), (6b). Hence, first order dipole-like terms $T_{(1)}$, $M_{(1)}$ and $N_{(1)}$ prove to be peculiar to these molecules which resemble the second order dipoles of substituted benzenes. These terms may be found on the basis of Eqs. (13) and (33), viz.

$$\begin{aligned} T_{(1)} &= -\frac{8}{3} a^2 bc \alpha; & M_{(1)} &= -(a^4 + 2b^4) \alpha; \\ N_{(1)} &= -(a^4 + 2b^2 c^2) \alpha \end{aligned} \quad (34)$$

These dipole-like terms are negative, as it was the case with electron-accepting substituents in substituted benzenes (Section 2).

As a result, the final populations of basis orbitals χ_1 , χ_2 , χ_3 and χ_4 of the pyridine-like system are

$$\begin{aligned} X_1 &= 1 - 2T_{(1)} - M_{(1)} = 0.398\alpha > 0; \\ X_2 &= 1 + T_{(1)} + N_{(1)} = -0.157\alpha < 0; \\ X_3 &= 1 + T_{(1)} - N_{(1)} = 0.009\alpha > 0; \\ X_4 &= 1 - 2T_{(1)} + M_{(1)} = -0.101\alpha < 0 \end{aligned} \quad (35)$$

to within the first-order terms inclusive. Eq. (35) demonstrates the validity of the rule of alternating polarity [8–11] for pyridine-like heterocycles. It is also seen that the dipole-like terms $T_{(1)}$, $M_{(1)}$ and $N_{(1)}$ are the additive components of the atom-atomic polarizabilities in this case.

Therefore, similarity of the electron density distributions in substituted benzenes containing an electron-accepting substituent and in the pyridine-like heterocycles proves to be supported on the basis of our approach. This similarity takes place owing to the analogous dipole-like additive components of the electron density of both molecules. Two points serve to account for the emergence of common additive components of heteroatom influence in substituted benzenes and pyridine-like heterocycles: The first one consists in the dependence of the nature of these components on the structure of the transformation matrix C contained within Eq. (3), and the second one lies in the applicability of the same matrix C for both types of molecules coinciding with that of Eq. (1) and containing coefficients of MOs of benzene in the basis of $2p_z$ AOs. The latter peculiarity of molecules under study reflects their relation to common parent hydrocarbon, namely to the benzene molecule.

5. Conclusions

1. The electron density distribution in substituted benzenes is determined by the superposition of five terms, two of them describing the intramolecular charge transfer and the remaining ones representing the induced dipole moments of the phenyl ring, viz. the *para-ipso* dipole moment, the *ortho-meta* dipole moment and the *ipso-ortho (meta-para)* dipole moments. In the case of pyridine-like heterocycles, only the above-enumerated dipole moments suffice to describe the heteroatom influence. Hence, the intramolecular charge transfer and the above-enumerated induced dipole moments may be regarded as additive components of the heteroatom influence in the molecules under study. Moreover, these are virtually similar to the additive components of the heteroatom influence in substituted alkanes [14].
2. The above-described general constitution of electron density distribution of both substituted benzenes and pyridine-like heterocycles is condi-

tioned by the structure of MOs of benzene. This conclusion serves to account for the observed similarity of the principal pictures of the electron density distribution in pyridine-like heterocycles and in substituted benzenes containing an electron-accepting substituent. Moreover, the concept of classical chemistry about benzene molecule being a common parent hydrocarbon of both types of heteroatom-containing systems proves to be supported on the basis of our approach.

3. The main difference between substituted benzenes and pyridine-like heterocycles consists in different orders of their induced dipole moments and thereby in relations of these moments to different intramolecular interactions. Thus, the induced dipole moments of pyridine-like heterocycles are described by first order terms of power series for occupation numbers and related to direct interactions between the initially occupied and initially vacant MOs of benzene. Alternatively, the analogous dipole moments of substituted benzenes are described by second order terms associated with indirect interactions of the same orbitals by means of orbitals of the substituent.
4. The induced *para-ipso* and *ortho-meta* dipole moments play the principal role in the formation of the observed picture of the electron density distribution in the molecules under study, viz. of an increase (reduction) of the occupation numbers of the *ortho* and *para* positions after introducing an electron-donating (accepting) substituent. These dipole moments, in turn, are determined mainly by (direct or indirect) interactions between the highest occupied and the lowest vacant MOs of benzene.

References

- [1] J. March, *Advanced Organic Chemistry, Reactions, Mechanisms and Structure*, Wiley, New York, 1985.
- [2] A.S. Dnieprovskii, T.I. Temnikova, *Fundamentals of Organic Chemistry*, Khimia, Leningrad, 1991 in Russian.
- [3] H.G.O. Becker, *Einführung in die Elektronentheorie Organisch Chemischen Reaktionen*, Deutscher Verlag der Wissenschaften, Berlin, 1974.
- [4] K.F. Reid, *Properties and Reactions of Bonds in Organic Molecules*, Longmans, Green and Co, London, 1968.
- [5] V.F. Traven, *Electronic Structure and Properties of Organic Molecules*, Khimia, Moscow, 1989 in Russian.

- [6] L. Pauling, *The Nature of Chemical Bond*, Goskhimizdat, Moscow, 1947 in Russian.
- [7] M.V. Basilevskii, *The Method of Molecular Orbitals and Chemical Reactivity of Organic Molecules*, Khimia, Moscow, 1969 in Russian.
- [8] C.A. Coulson, H.L. Longuet-Higgins, *Proc. R. Soc. A* 191 (1947) 39.
- [9] C.A. Coulson, H.L. Longuet-Higgins, *Proc. R. Soc. A* 192 (1947) 16.
- [10] C.A. Coulson, H.L. Longuet-Higgins, *Proc. R. Soc. A* 193 (1948) 447 see also p. 456.
- [11] C.A. Coulson, H.L. Longuet-Higgins, *Proc. R. Soc. A* 195 (1948) 188.
- [12] V. Gineityte, *J. Mol. Struct. (Theochem)* 343 (1995) 183.
- [13] V. Gineityte, *J. Mol. Struct. (Theochem)* 430 (1998) 97.
- [14] V. Gineityte, *J. Mol. Struct. (Theochem)* 434 (1998) 43.
- [15] M.M. Mestechkin, *The Density Matrix Method in the Theory of Molecules*, Naukova Dumka, Kiev, 1977.
- [16] V. Gineityte, *J. Mol. Struct. (Theochem)* 333 (1995) 297.
- [17] V. Gineityte, *J. Mol. Struct. (Theochem)* 288 (1993) 111.