CROATICA CHEMICA ACTA
CCACAA **81** (3) 487–499 (2008)

ISSN-0011-1643
CCA-3268
Original Scientific Paper

Rules Governing the Effects of Substituents upon Alternant Conjugated Hydrocarbons

Viktorija Gineityte

Institute of Theoretical Physics and Astronomy, Vilnius University, Gostauto 12, LT-01108 Vilnius, Lithuania
(E-mail: gineityte@itpa.lt)

RECEIVED JANUARY 5, 2007; ACCEPTED SEPTEMBER 20, 2007

Keywords
alternant conjugated hydrocarbons
adjacency matrix of molecular graph
charge-bond order matrix
non-canonical molecular orbitals
substituted benzenes
alternating polarity

Explicit algebraic expressions are derived and analyzed for the common charge-bond order matrix and for the related representation matrix of non-canonical molecular orbitals (NCMOs) of substituted alternant hydrocarbons (AHs) in terms of entire blocks of the common Hückel Hamiltonian matrix of parent AHs and thereby of adjacency matrices of graphs of their C-skeletons. Rules governing the effects of substituents upon electronic structures of hydrocarbons are established and supplement the classical results describing the electronic structures of AHs and of their perturbed analogues. In particular, two additive components are revealed within the effect of substituent upon an AH, namely the charge transfer between the above-mentioned subsystems and the intersubset polarization inside the AH [*cf.* the well-known partition of the basis set of $2p_z$ AOs of carbon atoms of AHs into two subsets]. The principal rule governing the first component involves division of the total transferred population equally between the two subsets of AOs of the AH. The intersubset polarization is shown to be governed by the second order analogue of the rule of alternating polarity. Finally, a single principal electron-accepting (donating) orbital is revealed among NCMOs of the parent AH for systems containing an electron-donating (accepting) substituent, *viz.,* the initially-vacant (occupied) NCMO attached to the site of substitution is shown to play this role. The results obtained are illustrated by substituted benzenes as examples.

INTRODUCTION

The well-known rules representing common properties of electronic structures of conjugated alternant hydrocarbons (AHs) are among the principal classical results of quantum chemistry.[1–7] These rules describe constitutions of the usual (canonical) molecular orbitals (MOs) along with relative positions of their one-electron energies,[7] as well as the structures of the respective charge-bond order (CBO) matrices[5,8] in the framework of the simple Hückel model. The Hamiltonian matrices of this model have been related in addition to adjacency matrices of molecular graphs describing the C-skeletons of AHs.[8,9] As a result, a new interpretation of the same rules became possible in terms of molecular topology. Moreover, validity of some of these results beyond the limits of the simple Hückel model has been corroborated.[7,10] Finally, establishment of common properties of non-canonical MOs (NCMOs) of AHs[11] may be mentioned here as a recent achievement in this field.

The so-called perturbed AHs (PAHs)[12–14] form another class of compounds whose electronic structures are expressible in an analogous algebraic form. The famous rule of alternating polarity[1–4,6,13–16] for perturbations of a single Coulomb parameter may be mentioned among the most outstanding examples. This rule represents charge redistributions in PAHs *vs.* those of the parent AHs and also has a graph-theoretical interpretation.[15] Furthermore, the algebraic results for PAHs, concerning alterations in total energies due to perturbation, form the basis of the popular PMO theory of chemical reactivity.[12] Rules governing the reshaping pattern of NCMOs of AHs under the influence of various types of perturbation[16] have also been established recently along with those describing the second order effects of perturbation.[17]

On the whole, rules of the above-mentioned type serve as a tool for representing the most essential peculiarities of electronic structures of a given class of molecules, as well as for comparison of two types of compounds (*e.g.*, AHs and PAHs) with respect to both similarity and dissimilarity of their electronic structures. Moreover, a certain powerful and fruitful approach of quantum chemistry is likely to underlie these rules, which is able to yield new results. The non-trivial examples of similar electronic structures revealed recently among compounds of seemingly different chemical constitution[17] serve to illustrate the above anticipation. That is why extension of the same approach to other types of molecules is an important task.

This paper addresses the derivatives of AHs containing electron-donating and accepting substituents, further referred to as substituted AHs (SAHs). Existence of common rules governing the influence of substituents upon AO populations inside the parent AHs may be foreseen on the basis of both numerical quantum-chemical calculations of particular molecules[6] and experimental facts. Among the latter, the structures of products of the subsequent electrophilic substitution of SAHs[18–21] may be mentioned in the first place. Indeed, an electron-donating substituent is known to favor the formation of *ortho*- and *para*- disubstituted molecules as a result of an electrophilic attack upon the respective substituted benzene, whereas the electron-accepting substituents provide for *meta* orientation of the reagent. Thus, we will look for rules governing the formation of CBO matrices of SAHs.

The CBO matrices of molecules are known to be alternatively obtainable directly without invoking the canonical MOs (CMOs).[22] To this end, the commutation equation for the respective one-electron density matrix should be solved. Moreover, this equation was shown to be closely related[23] to another fundamental non-canonical one-electron problem, namely to the block-diagonalization problem for the Hamiltonian matrix resulting from the Brillouin theorem and determining the relevant NCMOs.[23–29,31] Accordingly, interrelations have been established between CBO matrices and the respective NCMO representation matrices for various types of molecules.[11,16,23,27,30] Charge redistributions then proved to be interpretable in terms of specific reshapings of NCMOs and/or in terms of changes in delocalization. Thus, rules governing the formation of CBO matrices of SAHs (if feasible) are also likely to be accompanied by certain common properties of the relevant NCMOs. Establishing these properties is also among the aims of the present study.

Both the commutation equation and the block-diagonalization problem were shown to be solvable in terms of entire blocks (submatrices) of the initial Hamiltonian matrix.[11,16,23,27–29,31] On this basis, we expect to derive the expressions for the common CBO matrix and for the NCMO representation matrix of SAHs in terms of entire blocks of the common adjacency matrix of molecular graphs referring to C-skeletons of the parent AHs. Inasmuch as the very concept of the substituent implies a sufficiently weak influence of the latter upon the parent hydrocarbon,[6] we are about to confine ourselves to a perturbative treatment of the electron-donating and accepting effects in SAHs. In this connection, we will look for CBO matrices of SAHs and for the relevant matrices of NCMOs in the form of power series. Derivation of the series is based on the application of the so-called non-commutative Rayleigh-Schrödinger perturbation theory (NCRSPT).[23,31,32]

The paper starts with a methodological section devoted to constructing initial Hamiltonian matrices of SAHs and to the principal scheme of the approach applied. Thereupon, general expressions for CBO matrices and for NCMO representation matrices of SAHs are exhibited and analyzed. A certain approximation is then suggested that allows the above-mentioned expressions to be considerably simplified. Finally, the results are illustrated by considering substituted benzenes as examples.

METHODOLOGY

Let us start with initial Hamiltonian matrices of AHs and of their derivatives. In the simple Hückel model, the basis set $\{\chi\}$ of any AH consisting of $2p_z$ AOs of carbon atoms is known to be divisible into two subsets $\{\chi^*\}$ and $\{\chi^\circ\}$, so that the intrasubset resonance parameters take zero values.[5,7–9,33] Given that the Coulomb parameters (α) are additionally assumed to be uniform and the equality $\alpha = 0$ is accepted for convenience, the model Hamiltonian matrices of AHs acquire a common form containing zero submatrices (blocks) in diagonal positions and non-zero blocks in off-diagonal positions, the latter containing the intersubset resonance parameters as exhibited below in Eqs. (1) and (2).

An electron-donating substituent will be represented by a single initially-occupied orbital $\varphi_{(+)d}$ described by a certain one-electron energy γ. For reasons discussed below, the site of the substituent will be assumed to coincide with an orbital of the subset $\{\chi^\circ\}$ *e.g.,* with χ_1°. The resonance parameter δ representing the interaction between orbitals $\varphi_{(+)d}$ and χ_1° is supposed to take a sufficiently small value (*vs.* the remaining parameters) so that it may be included into the first order Hamiltonian matrix. As a result, the total Hamiltonian matrix of the relevant SAHs takes the form:

$$\mathbf{H}_{\rm d} = \mathbf{H}_{\rm d(0)} + \mathbf{H}_{\rm d(1)} = \begin{vmatrix} \gamma & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{B} \\ \mathbf{0} & \mathbf{B}^{+} & \mathbf{0} \end{vmatrix} + \begin{vmatrix} 0 & \mathbf{0} & \mathbf{d} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{d}^{+} & \mathbf{0} & \mathbf{0} \end{vmatrix} . \quad (1)$$

The subscript d here and below refers to systems containing an electron-donating substituent, whilst (0) and (1) are subscripts representing the zero and first order matrices, respectively. The relative order of basis orbitals is chosen to coincide with $\varphi_{(+)\rm d}$, $\{\chi^*\}$ and $\{\chi^\circ\}$ when constructing the Hamiltonian matrix $\mathbf{H}_{\rm d}$. Accordingly, the submatrices $\mathbf{B}$ and $\mathbf{B}^{+}$ contain the intersubset resonance parameters inside the parent AH [The superscript + here and below represents the Hermitian-conjugate (transposed) matrix]. Non-zero elements B_{ij} coincide with resonance parameters referring to the neighboring pairs of AOs. The mean value of these parameters (β) will serve as a (negative) energy unit in our study, *i.e.,* the equality $\beta = 1$ will be accepted. Under this condition, the submatrices $\mathbf{B}$ and $\mathbf{B}^{+}$ coincide with those of adjacency matrices (AMs) of graphs describing the C-skeleton of the parent AH.[8,9] The one-electron energy γ will be assumed to take a positive value in the above-specified negative energy units. Finally, $\mathbf{d}$ is a row-matrix containing a single non-zero element in its first position, *i.e.,* $d_{\rm d1} = \delta$.

For the acceptor-containing SAHs, the substituent will be accordingly represented by a single initially-vacant orbital $\varphi_{(-)\rm a}$ characterized by the one-electron energy $-\mu$ where $\mu > 0$. As opposed to the above-discussed case, the site of the substituent will be assumed to coincide with the orbital $\chi_1{}^*$ belonging to the subset $\{\chi^*\}$. The resonance parameter representing the interaction between orbitals $\varphi_{(-)\rm a}$ and $\chi_1{}^*$ will be denoted by v. Instead of Eq. (1), we then obtain:

$$\mathbf{H}_{\rm a} = \mathbf{H}_{\rm a(0)} + \mathbf{H}_{\rm a(1)} = \begin{vmatrix} \mathbf{0} & \mathbf{B} & \mathbf{0} \\ \mathbf{B}^{+} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & -\mu \end{vmatrix} + \begin{vmatrix} \mathbf{0} & \mathbf{0} & \mathbf{a} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{a}^{+} & \mathbf{0} & 0 \end{vmatrix} , \quad (2)$$

where the subscript a refers to the acceptor-containing SAHs. The order of basis orbitals is chosen now to coincide with $\{\chi^*\}$, $\{\chi^\circ\}$ and $\varphi_{(-)\rm a}$, and $\mathbf{a}$ is a column-matrix containing a single non-zero element $a_{1\rm a} = v$.

Let us dwell now on the principal requirements underlying the NCRSPT.[23,31,32] The non-canonical one-electron problems are usually formulated in terms of two subsets of basis orbitals.[24–29] Thus, let us confine ourselves to an analogous particular case of the NCRSPT. The initial basis set of the system(s) under study is then assumed to be divided into two subsets so that the intersubset interactions (resonance parameters) take up small values compared to the intersubset energy gap. Moreover, these subsets are supposed to consist of the initially-occupied basis orbitals (IOBOs) and of the initially-vacant ones (IVBOs). This implies the total Hamiltonian matrix $\tilde{\mathbf{H}}$ to contain a block-diagonal zero order member $\tilde{\mathbf{H}}_{(0)}$ and the first order member $\tilde{\mathbf{H}}_{(1)}$ as follows:

$$\tilde{\mathbf{H}} = \tilde{\mathbf{H}}_{(0)} + \tilde{\mathbf{H}}_{(1)} = \begin{vmatrix} \mathbf{E}_1 & \mathbf{0} \\ \mathbf{0} & -\mathbf{E}_2 \end{vmatrix} + \begin{vmatrix} \mathbf{S}_{(1)} & \mathbf{V}_{(1)} \\ \mathbf{V}^{+}_{(1)} & \mathbf{X}_{(1)} \end{vmatrix} , \quad (3)$$

where submatrices $\mathbf{E}_1 + \mathbf{S}_{(1)}$ and $-\mathbf{E}_2 + \mathbf{X}_{(1)}$ correspond to IOBOs and IVBOs, respectively, and $\mathbf{V}_{(1)}$ represents the intersubset interaction. The minus sign in front of $\mathbf{E}_2$ is introduced for convenience. For Hamiltonian matrices of this particular constitution, both the block-diagonalization problem determining the NCMO representation matrix $\mathbf{T}$ and the commutation equation for the relevant CBO matrix $\tilde{\mathbf{P}}$ have been solved in the form of interrelated power series.[23] Members of these series, in turn, are expressed in terms of certain principal matrices $\mathbf{G}_{(k)}$ determined by the matrix equations:

$$\mathbf{E}_1\mathbf{G}_{(k)} + \mathbf{G}_{(k)}\mathbf{E}_2 + \mathbf{V}_{(k)} = \mathbf{0}\, , \quad (4)$$

where k here and below stands for the order parameter. Matrix $\mathbf{V}_{(1)}$ coincides with the respective submatrix of the Hamiltonian matrix of Eq. (3), whilst other members of the series of matrices $\mathbf{V}_{(k)}$ corresponding to $k > 1$ can be represented in terms of submatrices of lower orders, *e.g.*:

$$\mathbf{V}_{(2)} = \mathbf{S}_{(1)}\mathbf{G}_{(1)} - \mathbf{G}_{(1)}\mathbf{X}_{(1)}\, . \quad (5)$$

It is evident that our initial Hamiltonian matrices for SAHs shown in Eqs. (1) and (2) do not comply with the requirements of the NCRSPT. Nevertheless, the matrices $\mathbf{H}_{\rm d}$ and $\mathbf{H}_{\rm a}$ may be transformed into the form shown in Eq. (3) using the following unitary matrices:

$$\mathbf{C}_{\rm d} = \begin{vmatrix} 1 & \mathbf{0} \\ \mathbf{0} & \mathbf{C} \end{vmatrix} , \quad \mathbf{C}_{\rm a} = \begin{vmatrix} \mathbf{C} & \mathbf{0} \\ \mathbf{0} & 1 \end{vmatrix} \quad (6)$$

containing a common unitary submatrix $\mathbf{C}$. The latter represents the block-diagonalization transformation for the common Hamiltonian matrix of the parent AHs and determines their non-canonical MOs.[11] Matrix $\mathbf{C}$ has been alternatively expressed as follows:

$$\mathbf{C} = \frac{1}{\sqrt{2}} \begin{vmatrix} \mathbf{I} & \mathbf{RB} \\ \mathbf{B}^{+}\mathbf{R} & -\mathbf{I} \end{vmatrix} , \quad \mathbf{C} = \frac{1}{\sqrt{2}} \begin{vmatrix} \mathbf{I} & \mathbf{BQ} \\ \mathbf{QB}^{+} & -\mathbf{I} \end{vmatrix} . \quad (7)$$

The expressions for submatrices $\mathbf{R}$ and $\mathbf{Q}$ of Eq. (7) take the form:

$$\mathbf{R} = (\mathbf{BB}^{+})^{-1/2}\, , \quad \mathbf{Q} = (\mathbf{B}^{+}\mathbf{B})^{-1/2}\, , \quad (8)$$

$\mathbf{I}$ here and below stands for unit matrices and

$$\mathbf{RB} = \mathbf{BQ}. \quad (9)$$

Moreover, the unitarity condition for the matrix yields the relations:

$$\mathbf{RBB}^{+}\mathbf{R} = \mathbf{QB}^{+}\mathbf{BQ} = \mathbf{BQQB}^{+} = \mathbf{B}^{+}\mathbf{RRB} = \mathbf{I}. \quad (10)$$

In terms of designations of Eq. (3), submatrices of the total transformed Hamiltonian matrix $\mathbf{C}_\mathrm{d}^{+}\,\mathbf{H}_\mathrm{d}\,\mathbf{C}_\mathrm{d}$ take the form:

$$\mathbf{E}_{\mathrm{d}1} = \begin{vmatrix} \gamma & \mathbf{0} \\ \mathbf{0} & \mathbf{E}_{(+)} \end{vmatrix}, \quad \mathbf{E}_{\mathrm{d}2} = \mathbf{E}_{(-)}\,,$$

$$\mathbf{S}_{\mathrm{d}(1)} = \frac{1}{\sqrt{2}} \begin{vmatrix} 0 & \mathbf{dQB}^{+} \\ \mathbf{BQd}^{+} & \mathbf{0} \end{vmatrix}, \tag{11}$$

$$\mathbf{V}_{\mathrm{d}(1)} = \frac{1}{\sqrt{2}} \begin{vmatrix} -\mathbf{d} \\ \mathbf{0} \end{vmatrix}, \quad \mathbf{X}_{\mathrm{d}(1)} = \mathbf{0}\,,$$

where $\mathbf{E}_{(+)}$ and $\mathbf{E}_{(-)}$ are the following submatrices:

$$\mathbf{E}_{(+)} = \mathbf{R}^{-1} = (\mathbf{BB}^{+})^{1/2}\,, \quad \mathbf{E}_{(-)} = \mathbf{Q}^{-1} = (\mathbf{B}^{+}\mathbf{B})^{1/2}\,, \tag{12}$$

coinciding with the so-called eigenblocks of the Hamiltonian matrix of the parent AHs.[11]

For the acceptor-containing systems, we accordingly obtain:

$$\mathbf{E}_{\mathrm{a}1} = \mathbf{E}_{(+)}\,, \quad \mathbf{E}_{\mathrm{a}2} = \begin{vmatrix} \mathbf{E}_{(-)} & \mathbf{0} \\ \mathbf{0} & \mu \end{vmatrix}, \quad \mathbf{S}_{\mathrm{a}(1)} = \mathbf{0}\,,$$

$$\mathbf{V}_{\mathrm{a}(1)} = \frac{1}{\sqrt{2}} \begin{vmatrix} \mathbf{0} & \mathbf{a} \end{vmatrix}, \quad \mathbf{X}_{\mathrm{a}(1)} = \frac{1}{\sqrt{2}} \begin{vmatrix} \mathbf{0} & \mathbf{QB}^{+}\mathbf{a} \\ \mathbf{a}^{+}\mathbf{BQ} & 0 \end{vmatrix}. \tag{13}$$

Transformability of our initial Hamiltonian matrices of Eqs. (1) and (2) into the form shown in Eq. (3) implies a straightforward applicability to SAHs of the power series of the NCRSPT in the basis of NCMOs of the parent AHs. Thus, the problem actually resolves itself into analysis and solution of the relevant matrix equations for matrices $\mathbf{G}_{\mathrm{d}(k)}$ and $\mathbf{G}_{\mathrm{a}(k)}$ following from Eq. (4) after substituting Eqs. (11) and (13), respectively. Thereupon, we have to construct the respective CBO matrices $\tilde{\mathbf{P}}_\mathrm{d}$ and $\tilde{\mathbf{P}}_\mathrm{a}$ as well as the NCMO representation matrices $\mathbf{T}_\mathrm{d}$ and $\mathbf{T}_\mathrm{a}$ as described previously[23,31,32] and, subsequently, go back to the basis of $2\mathrm{p}_z$ AOs $\{\chi\}$ again. To the latter end, we invoke the respective inverse transformations for CBO matrices, *viz.,*

$$\mathbf{P}_\mathrm{d} = \mathbf{C}_\mathrm{d}\tilde{\mathbf{P}}_\mathrm{d}\mathbf{C}_\mathrm{d}^{+}\,, \quad \mathbf{P}_\mathrm{a} = \mathbf{C}_\mathrm{a}\tilde{\mathbf{P}}_\mathrm{a}\mathbf{C}_\mathrm{a}^{+}\,, \tag{14}$$

as well as products of respective two transformation matrices for the final NCMO representation matrices $\mathbf{U}_\mathrm{d}$ and $\mathbf{U}_\mathrm{a}$ as follows:

$$\mathbf{U}_\mathrm{d} = \mathbf{C}_\mathrm{d}\mathbf{T}_\mathrm{d}\,, \quad \mathbf{U}_\mathrm{a} = \mathbf{C}_\mathrm{a}\mathbf{T}_\mathrm{a}\,. \tag{15}$$

It is evident that relations of Eqs. (14) and (15) are valid also for separate corrections of matrices involved there.

Expressions for Charge-Bond Order Matrices and for NCMOs

Let us start with the matrix equations of Eq. (4) determining the principal matrices $\mathbf{G}_{(k)}$. Inasmuch as $\mathbf{E}_1$ and $\mathbf{E}_2$ are square matrices, constitution of the matrix $\mathbf{G}_{(k)}$ coincides with that of $\mathbf{V}_{(k)}$. For donor-containing systems, the matrix $\mathbf{V}_{\mathrm{d}(1)}$ is shown in Eq. (11) and contains the row-matrix $-(1/\sqrt{2})\mathbf{d}$ and a square zero matrix. Thus, let us look for the matrix $\mathbf{G}_{\mathrm{d}(1)}$ of the form:

$$\mathbf{G}_{\mathrm{d}(1)} = \begin{vmatrix} \mathbf{g}_{\mathrm{d}(1)} \\ \mathbf{G}'_{\mathrm{d}(1)} \end{vmatrix}, \tag{16}$$

where $\mathbf{g}_{\mathrm{d}(1)}$ is a row-matrix of respective dimensions coinciding with that of the submatrix $\mathbf{d}$ and $\mathbf{G}'_{\mathrm{d}(1)}$ is a certain square matrix. Substituting Eqs. (11), (12) and (16) into Eq. (4) yields the following equation for the row-matrix $\mathbf{g}_{\mathrm{d}(1)}$:

$$\gamma\mathbf{g}_{\mathrm{d}(1)} + \mathbf{g}_{\mathrm{d}(1)}\mathbf{Q}^{-1} - \frac{1}{\sqrt{2}}\,\mathbf{d} = \mathbf{0}\,, \tag{17}$$

and a zero square matrix for $\mathbf{G}'_{\mathrm{d}(1)}$ (Note that matrix equations like that of Eq. (4) yield zero solutions if the respective $\mathbf{G}_{(k)}$ – free term, *i.e.,* $\mathbf{V}_{(k)}$, turns to zero.)[23,29,31] After multiplying the above-obtained equation by $\mathbf{Q}$ from the right-hand side, we obtain an algebraic solution of the form:

$$\mathbf{g}_{\mathrm{d}(1)} = \frac{1}{\sqrt{2}}\,\mathbf{dQ}(\mathbf{I} + \gamma\,\mathbf{Q})^{-1}\,. \tag{18}$$

To determine the second order matrix $\mathbf{G}_{\mathrm{d}(2)}$, the form analogous to that shown in Eq. (16) should be used. Furthermore, Eqs. (11) and (16) should be invoked for constructing the matrix $\mathbf{V}_{\mathrm{d}(2)}$ in accordance with Eq. (5). As a result, the row-matrix $\mathbf{g}_{\mathrm{d}(2)}$ coincides with a zero row-matrix, whilst the square submatrix $\mathbf{G}'_{\mathrm{d}(2)}$ of the matrix $\mathbf{G}_{\mathrm{d}(2)}$ is determined by the matrix equation:

$$\mathbf{G}'_{\mathrm{d}(2)}\mathbf{Q} + \mathbf{R}\mathbf{G}'_{\mathrm{d}(2)} + \frac{1}{\sqrt{2}}\mathbf{RBQd}^{+}\mathbf{g}_{\mathrm{d}(1)}\mathbf{Q} = \mathbf{0}\,. \tag{19}$$

For the acceptor-containing systems, the matrices $\mathbf{G}_{\mathrm{a}(k)}$ of the form:

$$\mathbf{G}_{\mathrm{a}(k)} = \begin{vmatrix} \mathbf{G}'_{\mathrm{a}(k)} & \mathbf{g}_{\mathrm{a}(k)} \end{vmatrix} \tag{20}$$

are sought, where $\mathbf{g}_{\mathrm{a}(k)}$ is a column-matrix referring to the column $(1/\sqrt{2})\mathbf{a}$ of the matrix $\mathbf{V}_{\mathrm{a}(1)}$ of Eq. (13). Instead of Eqs. (18) and (19), we then obtain:

$$\mathbf{g}_{\mathrm{a}(1)} = -\frac{1}{\sqrt{2}}\,(\mathbf{I} + \mu\mathbf{R})^{-1}\mathbf{Ra} \tag{21}$$

and

$$\mathbf{G}'_{\mathrm{d}(2)}\mathbf{Q} + \mathbf{R}\mathbf{G}'_{\mathrm{d}(2)} - \frac{1}{\sqrt{2}}\,\mathbf{R}\mathbf{g}_{\mathrm{a}(1)}\mathbf{a}^{+}\mathbf{BQ}^{2} = \mathbf{0} \tag{22}$$

respectively, whilst $\mathbf{G}'_{\mathrm{a}(1)}$ and $\mathbf{g}_{\mathrm{a}(2)}$ turn to zero.

To write down the NCMOs of SAHs in terms of those of parent AHs, let us define the row-matrices $(\mathbf{\Psi}^{(0)}_{(+)})$ and $(\mathbf{\Psi}^{(0)}_{(-)})$ containing the occupied and vacant NCMOs of the parent AHs denoted by $\mathbf{\Psi}^{(0)}_{(+)i}$ and $\mathbf{\Psi}^{(0)}_{(-)j}$ respectively. Accordingly, the row-matrices $(\mathbf{\Psi}^{(d)}_{(+)})$, $(\mathbf{\Psi}^{(a)}_{(+)})$, $(\mathbf{\Psi}^{(d)}_{(-)})$ and $(\mathbf{\Psi}^{(a)}_{(-)})$ will consist of NCMOs of the respective SAHs attached to occupied and vacant NCMOs of the parent AHs. The NCMOs of the substituted systems originating from the orbitals of substituents $\varphi_{(+)\mathrm{d}}$ and $\varphi_{(-)\mathrm{a}}$ will be correspondingly denoted by $\Phi_{(+)\mathrm{d}}$ and $\Phi_{(-)\mathrm{a}}$. Finally, the above-introduced row-matrices will be used to construct total row-matrices of NCMOs of SAHs. We then obtain:

$$(\Phi_{(+)\mathrm{d}},(\mathbf{\Psi}^{(d)}_{(+)}),(\mathbf{\Psi}^{(d)}_{(-)})) = (\varphi_{(+)\mathrm{d}}, (\mathbf{\Psi}^{(0)}_{(+)}),(\mathbf{\Psi}^{(0)}_{(-)}))\mathbf{T}_{\mathrm{d}},$$

$$((\mathbf{\Psi}^{(a)}_{(+)}),(\mathbf{\Psi}^{(a)}_{(-)}),\mathbf{\Phi}_{(-)\mathrm{a}}) = ((\mathbf{\Psi}^{(0)}_{(+)}),(\mathbf{\Psi}^{(0)}_{(-)}),\varphi_{(-)\mathrm{a}})\mathbf{T}_{\mathrm{a}}\,. \tag{23}$$

The relevant explicit expressions take the form:

$$\Phi_{(+)\mathrm{d}} = \varphi_{(+)\mathrm{d}}[1 - \frac{1}{2}\mathbf{g}_{\mathrm{d}(1)}\mathbf{g}^{+}_{\mathrm{d}(1)}] - (\mathbf{\Psi}^{(0)}_{(-)})\mathbf{g}^{+}_{\mathrm{d}(1)}\,,$$

$$(\mathbf{\Psi}^{(d)}_{(+)}) = (\mathbf{\Psi}^{(0)}_{(+)}) - (\mathbf{\Psi}^{(0)}_{(-)})\mathbf{G}'^{+}_{\mathrm{d}(2)}\,, \tag{24}$$

$$(\mathbf{\Psi}^{(d)}_{(-)}) = \varphi_{(+)\mathrm{d}}\,\mathbf{g}_{\mathrm{d}(1)} + (\mathbf{\Psi}^{(0)}_{(+)})\mathbf{G}'_{\mathrm{d}(2)} + (\mathbf{\Psi}^{(0)}_{(-)})[\mathbf{I} - \frac{1}{2}\mathbf{g}^{+}_{\mathrm{d}(1)}\mathbf{g}_{\mathrm{d}(1)}]\,,$$

and

$$(\mathbf{\Psi}^{(a)}_{(+)}) = (\mathbf{\Psi}^{(0)}_{(+)})[\mathbf{I} - \frac{1}{2}\mathbf{g}_{\mathrm{a}(1)}\mathbf{g}^{+}_{\mathrm{a}(1)}] - (\mathbf{\Psi}^{(0)}_{(-)})\mathbf{G}'^{+}_{\mathrm{a}(2)} - \varphi_{(-)\mathrm{a}}\mathbf{g}^{+}_{\mathrm{a}(1)}\,,$$

$$(\mathbf{\Psi}^{(a)}_{(-)}) = (\mathbf{\Psi}^{(0)}_{(+)})\mathbf{G}'_{\mathrm{a}(2)} + (\mathbf{\Psi}^{(0)}_{(-)})\,,$$

$$\Phi_{(-)\mathrm{a}} = (\mathbf{\Psi}^{(0)}_{(+)})\mathbf{g}_{\mathrm{a}(1)} + \varphi_{(-)\mathrm{a}}(1 - \frac{1}{2}\mathbf{g}^{+}_{\mathrm{a}(1)}\mathbf{g}_{\mathrm{a}(1)}). \tag{25}$$

Accordingly, diagonal elements of matrices $\tilde{\mathbf{P}}_{\mathrm{d}}$ and $\tilde{\mathbf{P}}_{\mathrm{a}}$ yield populations of basis functions, *i.e.,* of NCMOs of the parent AHs along with orbitals of substituents ($\varphi_{(+)\mathrm{d}}$ and $\varphi_{(-)\mathrm{a}}$) in the relevant SAHs. In particular, the actual occupation numbers of orbitals $\varphi_{(+)\mathrm{d}}$ and $\Psi^{(0)}_{(-)j}$ of the donor-containing system are:

$$q_{(+)\mathrm{d}} = 2(1 - \mathbf{g}_{\mathrm{d}(1)}\mathbf{g}^{+}_{\mathrm{d}(1)});$$
$$q_{(-)j} = 2g^{+}_{\mathrm{d}(1),j} \cdot g_{\mathrm{d}(1),j} \tag{26}$$

whilst those of orbitals $\Psi^{(0)}_{(+)i}$ and $\varphi_{(-)\mathrm{a}}$ of acceptor-containing SAHs take the form:

$$q_{(+)i} = 2(1 - g_{\mathrm{a}(1),i} \cdot g^{+}_{\mathrm{a}(1),i});$$
$$q_{(-)\mathrm{a}} = 2\mathbf{g}^{+}_{a(1)}\mathbf{g}_{\mathrm{a}(1)}\,, \tag{27}$$

where $g_{\mathrm{d}(1),j}$ and $g_{\mathrm{a}(1),i}$ are elements of the row-matrix $\mathbf{g}_{\mathrm{d}(1)}$ and of the column-matrix $\mathbf{g}_{\mathrm{a}(1)}$, respectively. Occupation numbers of the remaining orbitals (*viz*., of $\Psi^{(d)}_{(+)i}$ and of $\Psi^{(a)}_{(+)j}$) coincide with their initial values (equal to 2 and 0, respectively) to within the second order terms inclusive. The above expressions indicate that the electron-donating orbital of the substituent $\varphi_{(+)\mathrm{d}}$ becomes primarily delocalized over the vacant NCMOs of the parent AH $\Psi^{(0)}_{(-)j}$ in accordance with the expectation. Analogously, the initially-vacant orbital $\varphi_{(-)\mathrm{a}}$ acquires first order tails over the occupied NCMOs $\Psi^{(0)}_{(+)i}$. Moreover, populations transferred between the same orbitals are in agreement with the above-specified trends in delocalization. This fact may be traced back to the similarity between the CBO matrix $\tilde{\mathbf{P}}$ and the NCMO representation matrix $\mathbf{T}$ in the NCRSPT.[23]

Let us turn finally to CBO matrices of SAHs and their NCMOs in the basis of $2\mathrm{p}_z$ AOs. Like with matrices $\mathbf{C}_{\mathrm{d}}$ and $\mathbf{C}_{\mathrm{a}}$ of Eq. (6), the zero order contributions $\mathbf{P}_{\mathrm{d}(0)}$ and $\mathbf{P}_{\mathrm{a}(0)}$ to the total CBO matrices of SAHs ($\mathbf{P}_{\mathrm{d}}$ and $\mathbf{P}_{\mathrm{a}}$) contain the CBO matrix of the parent AHs ($\mathbf{P}$) as a common submatrix, *viz.,*

$$\mathbf{P}_{\mathrm{d}(0)} = \begin{vmatrix} 2 & \mathbf{0} \\ \mathbf{0} & \mathbf{P} \end{vmatrix}, \quad \mathbf{P}_{\mathrm{a}(0)} = \begin{vmatrix} \mathbf{P} & \mathbf{0} \\ \mathbf{0} & 0 \end{vmatrix} \tag{28}$$

where $\mathbf{P}$ is alternatively expressible as:

$$\mathbf{P} = \begin{vmatrix} \mathbf{I} & \mathbf{RB} \\ \mathbf{B}^{+}\mathbf{R} & \mathbf{I} \end{vmatrix}, \quad \mathbf{P} = \begin{vmatrix} \mathbf{I} & \mathbf{BQ} \\ \mathbf{QB}^{+} & \mathbf{I} \end{vmatrix}. \tag{29}$$

Matrix $\mathbf{P}$ has been originally derived by G. G. Hall[5] and is probably the first example of CBO matrices in terms of entire submatrices $\mathbf{B}$ and $\mathbf{B}^{+}$ of the AMs of molecular graphs of C-skeletons of parent AHs. The first and the second order corrections to the CBO matrix $\mathbf{P}_{\mathrm{d}(0)}$ of Eqs. (28) and (29) take the form:

$$\mathbf{P}_{\mathrm{d}(1)} = \sqrt{2}\begin{vmatrix} 0 & -\mathbf{g}_{\mathbf{d(1)}}\mathbf{QB}^{+} & \mathbf{g}_{\mathbf{d(1)}} \\ -\mathbf{BQg}^{+}_{\mathbf{d(1)}} & \mathbf{0} & \mathbf{0} \\ \mathbf{g}^{+}_{\mathbf{d(1)}} & \mathbf{0} & \mathbf{0} \end{vmatrix} \tag{30}$$

and

$$\mathbf{P}_{\mathrm{d}(2)} = \begin{vmatrix} -2\mathbf{g}_{\mathrm{d}(1)}\mathbf{g}^{+}_{\mathrm{d}(1)} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{X}_{\mathrm{d}(2)} + \mathbf{BQg}^{+}_{\mathrm{d}(1)}\mathbf{g}_{\mathrm{d}(1)}\mathbf{QB}^{+} & \mathbf{N}_{\mathrm{d}(2)} - \mathbf{BQg}^{+}_{\mathrm{d}(1)}\mathbf{g}_{\mathrm{d}(1)} \\ \mathbf{0} & \mathbf{N}^{+}_{\mathrm{d}(2)} - \mathbf{g}^{+}_{\mathrm{d}(1)}\mathbf{g}_{\mathrm{d}(1)}\mathbf{QB}^{+} & \mathbf{Z}_{\mathrm{d}(2)} + \mathbf{g}^{+}_{\mathrm{d}(1)}\mathbf{g}_{\mathrm{d}(1)} \end{vmatrix} \tag{31}$$

where submatrices of the second order correction $\mathbf{P}_{\mathrm{d}(2)}$ are expressible as:

$$\mathbf{X}_{\mathrm{d}(2)} = -\mathbf{BQG}'^{+}_{\mathrm{d}(2)} - \mathbf{G}'_{\mathrm{d}(2)}\mathbf{QB}^{+};$$
$$\mathbf{Z}_{\mathrm{d}(2)} = \mathbf{G}'^{+}_{\mathrm{d}(2)}\mathbf{BQ} + \mathbf{QB}^{+}\mathbf{G}'_{\mathrm{d}(2)} \tag{32}$$

$$\mathbf{N}_{\mathrm{d}(2)} = -\mathbf{BQ}\Delta_{\mathrm{d}(2)} = -\Gamma_{\mathrm{d}(2)}\mathbf{BQ}\,, \tag{33}$$

and

$$\Delta_{\mathrm{d}(2)} = \mathbf{G}'^{+}_{\mathrm{d}(2)}\mathbf{BQ} - \mathbf{QB}^{+}\mathbf{G}'_{\mathrm{d}(2)};$$
$$\Gamma_{\mathrm{d}(2)} = \mathbf{BQG}'^{+}_{\mathrm{d}(2)} - \mathbf{G}'_{\mathrm{d}(2)}\mathbf{QB}^{+} \tag{34}$$

The close resemblance between definitions of Eqs. (32) to (34) and those of submatrices of the first order corrections $\mathbf{P}_{(1)}$ for PAHs[16] deserves mentioning. Moreover, the interrelations:

$$\mathbf{X}_{\mathrm{d}(2)} = -\,\mathbf{BQZ}_{\mathrm{d}(2)}\mathbf{QB}^{+}\,; \qquad \boldsymbol{\Gamma}_{\mathrm{d}(2)} = \mathbf{BQ}\boldsymbol{\Delta}_{\mathrm{d}(2)}\mathbf{QB}^{+} \tag{35}$$

established previously for PAHs[16] refer to the SAHs as well. These relations along with Eq. (10) indicate that matrices $\mathbf{X}_{\mathrm{d}(2)}$ and $\mathbf{Z}_{\mathrm{d}(2)}$ as well as $\boldsymbol{\Gamma}_{\mathrm{d}(2)}$ and $\boldsymbol{\Delta}_{\mathrm{d}(2)}$, are connected by unitary transformations. The procedure of deriving matrix equations determining the matrices of Eqs. (32) to (34) directly also resembles the relevant procedure for PAHs. To this end, the matrix equation of Eq. (19) determining the matrix $\mathbf{G}'_{\mathrm{d}(2)}$ should be used. The procedure starts with eliminating the matrix $\mathbf{R}$ from this equation by multiplying it by $\mathbf{B}^{+}$ from its left-hand side and invoking the complex-conjugate counterpart of Eq. (9). After subsequent employment of Eq. (10), we obtain:

$$\mathbf{B}^{+}\mathbf{G}'_{\mathrm{d}(2)}\mathbf{Q} + \mathbf{QB}^{+}\mathbf{G}'_{\mathrm{d}(2)} + \frac{1}{\sqrt{2}}\mathbf{d}^{+}\mathbf{g}_{\mathrm{d}(1)}\mathbf{Q} = \mathbf{0}\,. \tag{36}$$

This relation should be then multiplied by $\mathbf{Q}$ from its left-hand side, whilst its complex-conjugate counterpart will be multiplied by $\mathbf{Q}$ from its right-hand side. After summing up the relations obtained, the matrix equation for the submatrix $\mathbf{Z}_{\mathrm{d}(2)}$ results:

$$\mathbf{QZ}_{\mathrm{d}(2)} + \mathbf{Z}_{\mathrm{d}(2)}\mathbf{Q} + \frac{1}{\sqrt{2}}\mathbf{Q}(\mathbf{d}^{+}\mathbf{g}_{\mathrm{d}(1)} + \mathbf{g}^{+}_{\mathrm{d}(1)}\mathbf{d})\mathbf{Q} = \mathbf{0}\,. \tag{37}$$

Subtracting the same intermediate relations yields the equation for the matrix $\boldsymbol{\Delta}_{\mathrm{d}(2)}$, *viz.*,

$$\mathbf{Q}\boldsymbol{\Delta}_{\mathrm{d}(2)} + \boldsymbol{\Delta}_{\mathrm{d}(2)}\mathbf{Q} + \frac{1}{\sqrt{2}}\mathbf{Q}(\mathbf{g}^{+}_{\mathrm{d}(1)}\mathbf{d} - \mathbf{d}^{+}\mathbf{g}_{\mathrm{d}(1)})\mathbf{Q} = \mathbf{0}. \tag{38}$$

For the acceptor-containing systems, the analogues of Eqs. (30) and (31) take the form:

$$\mathbf{P}_{\mathrm{a}(1)} = -\sqrt{2}\left|\begin{matrix} \mathbf{0} & \mathbf{0} & \mathbf{g}_{\mathrm{a}(1)} \\ \mathbf{0} & \mathbf{0} & \mathbf{QB}^{+}\mathbf{g}_{\mathrm{a}(1)} \\ \mathbf{g}^{+}_{\mathrm{a}(1)} & \mathbf{g}^{+}_{\mathrm{a}(1)}\mathbf{BQ} & 0 \end{matrix}\right| \tag{39}$$

and

$$\mathbf{P}_{\mathrm{a}(2)} = \left|\begin{matrix} \mathbf{X}_{\mathrm{a}(2)} - \mathbf{g}_{\mathrm{a}(1)}\mathbf{g}^{+}_{\mathrm{a}(1)} & \mathbf{N}_{\mathrm{a}(2)} - \mathbf{g}_{\mathrm{a}(1)}\mathbf{g}^{+}_{\mathrm{a}(1)}\mathbf{BQ} & \mathbf{0} \\ \mathbf{N}^{+}_{\mathrm{a}(2)} - \mathbf{QB}^{+}\mathbf{g}_{\mathrm{a}(1)}\mathbf{g}^{+}_{\mathrm{a}(1)} & \mathbf{Z}_{\mathrm{d}(2)} - \mathbf{QB}^{+}\mathbf{g}_{\mathrm{a}(1)}\mathbf{g}^{+}_{\mathrm{a}(1)}\mathbf{BQ} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & 2\mathbf{g}^{+}_{\mathrm{a}(1)}\mathbf{g}_{\mathrm{a}(1)} \end{matrix}\right| \tag{40}$$

where the submatrices of the second order correction $\mathbf{P}_{\mathrm{a}(2)}$ are related to the matrix $\mathbf{G}'_{\mathrm{a}(2)}$ as shown in Eqs. (32) to (35). Accordingly, the analogues of Eqs. (37) and (38) take the form:

$$\mathbf{QZ}_{\mathrm{a}(2)} + \mathbf{Z}_{\mathrm{a}(2)}\mathbf{Q} - \frac{1}{\sqrt{2}}\mathbf{Q}^{2}\mathbf{B}^{+}(\mathbf{g}_{\mathrm{a}(1)}\mathbf{a}^{+} + \mathbf{a}\mathbf{g}^{+}_{\mathrm{a}(1)})\mathbf{BQ}^{2} = \mathbf{0} \tag{41}$$

and

$$\mathbf{Q}\boldsymbol{\Delta}_{\mathrm{a}(2)} + \boldsymbol{\Delta}_{\mathrm{a}(2)}\mathbf{Q} - \frac{1}{\sqrt{2}}\mathbf{Q}^{2}\mathbf{B}^{+}(\mathbf{a}\mathbf{g}^{+}_{\mathrm{a}(1)} - \mathbf{g}_{\mathrm{a}(1)}\mathbf{a}^{+})\mathbf{BQ}^{2} = \mathbf{0}\,. \tag{42}$$

To write down the expressions for NCMOs of SAHs in the basis of $2\mathrm{p}_z$ AOs, it is only required to construct the row-matrices $(\boldsymbol{\Psi}^{(0)}_{(+)})$ and $(\boldsymbol{\Psi}^{(0)}_{(-)})$ containing the NCMOs of the parent hydrocarbons on the basis of the matrix $\mathbf{C}$ of Eq. (7) and to substitute them into Eqs. (24) and (25). As for instance, the orbitals $\Phi_{(+)\mathrm{d}}$ and $\Phi_{(-)\mathrm{a}}$ attached to the substituents take the form

$$\Phi_{(+)\mathrm{d}} = \varphi_{(+)\mathrm{d}}[1 - \frac{1}{2}\mathbf{g}_{\mathrm{d}(1)}\mathbf{g}^{+}_{\mathrm{d}(1)}] - \frac{1}{\sqrt{2}}[(\chi^{*})\mathbf{BQ} - (\chi^{\circ})]\mathbf{g}^{+}_{\mathrm{d}(1)}, \tag{43}$$

$$\Phi_{(-)\mathrm{a}} = \frac{1}{\sqrt{2}}[(\chi^{*}) + (\chi^{\circ})\mathbf{QB}^{+}]\,\mathbf{g}_{\mathrm{a}(1)} + \varphi_{(-)\mathrm{a}}(1 - \frac{1}{2}\mathbf{g}^{+}_{\mathrm{a}(1)}\mathbf{g}_{\mathrm{a}(1)}). \tag{44}$$

Analysis of General Results

It is seen from Eqs. (30) and (39) that intersubsystem bond orders arise within the first order approximation (*i.e.,* bond orders between the orbital of the substituent and AOs of the parent AH). In particular, bond orders between the electron-donating orbital $\varphi_{(+)\mathrm{d}}$ and AOs χ^{*}_{i} and χ°_{j} of the parent AH are:

$$P_{i\mathrm{d}} = -\sqrt{2}\,(\mathbf{BQg}^{+}_{\mathrm{d}(1)})_{i\mathrm{d}}; \quad P_{j\mathrm{d}} = \sqrt{2}\,(\mathbf{g}^{+}_{\mathrm{d}(1)})_{j\mathrm{d}} \tag{45}$$

whilst those between the orbital $\varphi_{(-)\mathrm{a}}$ and the same AOs of the acceptor-containing system take the form:

$$P_{i\mathrm{a}} = -\sqrt{2}\,(\mathbf{g}_{\mathrm{a}(1)})_{i\mathrm{a}}; \quad P_{j\mathrm{a}} = -\sqrt{2}(\mathbf{QB}^{+}\mathbf{g}_{\mathrm{a}(1)})_{j\mathrm{a}}\,. \tag{46}$$

Again, the tails of NCMOs $\Phi_{(+)\mathrm{d}}$ and $\Phi_{(-)\mathrm{a}}$ over AOs χ^{*}_{i} and χ°_{j} follow from Eqs. (43) and (44). These coincide with relevant elements of the final NCMO representation matrices $\mathbf{U}_{\mathrm{d}}$ and $\mathbf{U}_{\mathrm{a}}$ of Eq. (15), *i.e.,*

$$U_{\mathrm{d},i\mathrm{d}} = -\frac{1}{\sqrt{2}}(\mathbf{BQg}^{+}_{\mathrm{d}(1)})_{i\mathrm{d}}; \quad U_{\mathrm{d},j\mathrm{d}} = \frac{1}{\sqrt{2}}(\mathbf{g}^{+}_{\mathrm{d}(1)})_{j\mathrm{d}};$$

$$U_{\mathrm{a},i\mathrm{a}} = \frac{1}{\sqrt{2}}(\mathbf{g}_{\mathrm{a}(1)})_{i\mathrm{a}}; \quad U_{\mathrm{a},j\mathrm{a}} = \frac{1}{\sqrt{2}}(\mathbf{QB}^{+}\mathbf{g}_{\mathrm{a}(1)})_{j\mathrm{a}}\,. \tag{47}$$

Thus, proportionality between newly-formed bond orders and tails of NCMOs $\Phi_{(+)\mathrm{d}}$ and $\Phi_{(-)\mathrm{a}}$ over the respective AOs is evident. Let us define now the partial delocalization coefficients of these NCMOs as squares of respective tails, *e.g.,*

$$D_{\mathrm{d}i} = (U_{\mathrm{d},i\mathrm{d}})^2; \quad D_{\mathrm{d}j} = (U_{\mathrm{d},j\mathrm{d}})^2, \ etc\,. \tag{48}$$

We then obtain:

$$D_{\mathrm{d}i} = \frac{1}{4}(P_{i\mathrm{d}})^2; \quad D_{\mathrm{d}j} = \frac{1}{4}(P_{j\mathrm{d}})^2;$$

$$D_{\mathrm{a}i} = \frac{1}{4}(P_{i\mathrm{a}})^2; \quad D_{\mathrm{a}j} = \frac{1}{4}(P_{j\mathrm{a}})^2\,. \tag{49}$$

Let us now turn to second order corrections $\mathbf{P}_{\mathrm{d}(2)}$ and $\mathbf{P}_{\mathrm{a}(2)}$ defined by Eqs. (31) and (40). Non-zero submatrices arise both in the diagonal positions of these corrections and in the off-diagonal ones referring to the interaction between subsets $\{\chi^*\}$ and $\{\chi^\circ\}$ inside the AH in contrast to the above-considered first order corrections. Let us start with submatrices taking diagonal positions, diagonal elements of which determine the actual populations of AOs in SAHs. The unitarity condition for the matrix $\mathbf{BQ}$ shown in Eq. (10) along with Eq. (35) yields the relations:

$$\mathrm{tr}\ \mathbf{X}_{\mathrm{d}(2)} + \mathrm{tr}\ \mathbf{Z}_{\mathrm{d}(2)} = 0, \quad \mathrm{tr}\ \mathbf{X}_{\mathrm{a}(2)} + \mathrm{tr}\ \mathbf{Z}_{\mathrm{a}(2)} = 0 \tag{50}$$

indicating that the involved submatrices do not contribute to the total population of the parent AH. Thus, these submatrices describe a certain polarization inside the parent AH due to the very presence of the substituent. [Note that submatrices $\mathbf{X}_{(2)}$ and $\mathbf{Z}_{(2)}$ may be considered as a direct generalization to the case of two subsets $\{\chi^*\}$ and $\{\chi^\circ\}$ of the secondary polarization ($p_{(2)I}$) of a single (Ith) bond under the influence of an external orbital.[34]]. The overall effect represented by submatrices $\mathbf{X}_{\mathrm{d}(2)}$, $\mathbf{Z}_{\mathrm{d}(2)}$, $\mathbf{X}_{\mathrm{a}(2)}$ and $\mathbf{Z}_{\mathrm{a}(2)}$ may be then referred to as the intersubset polarization of the parent AH.

The remaining submatrices taking the diagonal positions within corrections $\mathbf{P}_{\mathrm{d}(2)}$ and $\mathbf{P}_{\mathrm{a}(2)}$ meet the relations:

$$\mathrm{tr}\ (\mathbf{BQg}^{+}_{\mathrm{d}(1)}\mathbf{g}_{\mathrm{d}(1)}\mathbf{QB}^{+}) + \mathrm{tr}\ (\mathbf{g}^{+}_{\mathrm{d}(1)}\mathbf{g}_{\mathrm{d}(1)}) = 2\mathbf{g}_{\mathrm{d}(1)}\mathbf{g}^{+}_{\mathrm{d}(1)}\,,$$

$$\mathrm{tr}\ (\mathbf{QB}^{+}\mathbf{g}_{\mathrm{a}(1)}\mathbf{g}^{+}_{\mathrm{a}(1)}\mathbf{BQ}) + \mathrm{tr}\ (\mathbf{g}_{\mathrm{a}(1)}\mathbf{g}^{+}_{\mathrm{a}(1)}) = 2\mathbf{g}^{+}_{\mathrm{a}(1)}\mathbf{g}_{\mathrm{a}(1)}\,. \tag{51}$$

based on Eq. (10). These relations indicate that the relevant submatrices describe the populations transferred between the substituent and the parent AH and may be interpreted as conservation conditions for total transferred populations. Positive signs of all partial populations acquired by separate AOs of the parent AH from the electron-donating substituent, as well as of all populations donated by individual AOs of the AH to the acceptor, follow from the positive-definite nature of matrices inside the tr signs of Eq. (51) [These matrices can be represented as products $\mathbf{AA}^{+}$ and $\mathbf{A}^{+}\mathbf{A}$ and thereby are positive-definite matrices[35]]. Moreover, the total population donated to the parent AH by the electron-donating substituent ($2\mathbf{g}_{\mathrm{d}(1)}\mathbf{g}^{+}_{\mathrm{d}(1)}$) becomes divided into two equal parts between subsets $\{\chi*\}$ and $\{\chi^\circ\}$. Similarly, the total population withdrawn from the same subsets of the parent AH by the acceptor are also of coinciding values. Intrasubset distributions of these divided populations, in turn, are interrelated by an unitary matrix $\mathbf{BQ}$.

Let us now dwell in more detail on partial populations donated to separate AOs of the AH and on those withdrawn from these AOs. Thus, the partial populations $\Delta q_{\mathrm{d}i}$ and $\Delta q_{\mathrm{d}j}$ donated to AOs χ^*_i and χ°_j equal:

$$\Delta q_{\mathrm{d}i} = (\mathbf{BQg}^{+}_{\mathrm{d}(1)}\mathbf{g}_{\mathrm{d}(1)}\mathbf{QB}^{+})_{ii} = (\mathbf{BQg}^{+}_{\mathrm{d}(1)})_{i\mathrm{d}}(\mathbf{g}_{\mathrm{d}(1)}\mathbf{QB}^{+})_{\mathrm{d}i}\,,$$

$$\Delta q_{\mathrm{d}j} = (\mathbf{g}^{+}_{\mathrm{d}(1)}\mathbf{g}_{\mathrm{d}(1)})_{jj} = g^{+}_{\mathrm{d}(1),j\mathrm{d}} \cdot g_{\mathrm{d}(1),\mathrm{d}j}\,. \tag{52}$$

Comparison of these expressions to those of Eqs. (45) and (49) yields the relations:

$$\Delta q_{\mathrm{d}i} = \frac{1}{2}(P_{i\mathrm{d}})^2 = 2D_{\mathrm{d}i}\,;$$

$$\Delta q_{\mathrm{d}j} = \frac{1}{2}(P_{\mathrm{d}j})^2 = 2D_{\mathrm{d}j}\,. \tag{53}$$

For the case of an acceptor-containing system, we accordingly obtain:

$$\Delta q_{\mathrm{a}i} = -\frac{1}{2}(P_{ia})^2 = -2\,D_{ai}\,;$$

$$\Delta q_{\mathrm{a}j} = -\frac{1}{2}(P_{ja})^2 = -2\,D_{aj}\,. \tag{54}$$

Thus, partial populations acquired (lost) by individual AOs of the parent AH are proportional to the squares of bond orders that are formed between these particular AOs and the orbital of the substituent, as well as to the relevant partial delocalization coefficients of NCMOs $\Phi_{(+)\mathrm{d}}$ and $\Phi_{(-)\mathrm{d}}$. In other words, a local relation is obtained between any intersubsystem bond order and the respective partial transferred population and/or partial delocalization coefficient.

Submatrices taking the off-diagonal positions in the corrections $\mathbf{P}_{\mathrm{d}(2)}$ and $\mathbf{P}_{\mathrm{a}(2)}$ are also of interest. Indeed, elements of these submatrices referring to neighboring pairs of AOs inside the parent AH represent the actual bond orders of the hydrocarbon fragment in the substituted system. Relations like those shown in Eqs. (53) and (54) easily result also for elements of submatrices $\mathbf{M}_{\mathrm{d}(2)}$ and $\mathbf{M}_{\mathrm{a}(2)}$ defined as:

$$\mathbf{M}_{\mathrm{d}(2)} = -\mathbf{BQg}^{+}_{\mathrm{d}(1)}\mathbf{g}_{\mathrm{d}(1)}\,;$$

$$\mathbf{M}_{\mathrm{a}(2)} = -\mathbf{g}_{\mathrm{a}(1)}\mathbf{g}^{+}_{\mathrm{a}(1)}\mathbf{BQ} \tag{55}$$

(see Eqs. (31) and (40)). The above-anticipated relations take the form:

$$M_{\mathrm{d}(2),ij} = \frac{1}{2}P_{i\mathrm{d}}\,P_{j\mathrm{d}}\,;$$

$$M_{\mathrm{a}(2),ij} = -\frac{1}{2}P_{i\mathrm{a}}P_{j\mathrm{a}}\,. \tag{56}$$

It is seen that any alteration in the neighboring bond order originating from the matrix $\mathbf{M}_{d(2)}$ or $\mathbf{M}_{a(2)}$ is determined by the product of two intersubsystem bond orders that are formed between the orbital of the substituent and the AOs of the two carbon atoms involved in the given bond. Thus, a local relation is predicted between intra- and intersubsystem bond orders. In the next section, matrices $\mathbf{M}_{d(2)}$ and $\mathbf{M}_{a(2)}$ will be shown to play a decisive role in the formation of the actual bond orders of the chemically bound pairs of atoms in the SAHs.

An Approximate Model for Electronic Structures of SAHs

In this section, we are about to suggest a certain approximation to the above-derived general expressions, which yields a simple and illustrative model for electronic structures of SAHs. To this end, we will invoke the power series for matrices **R** and **Q** of Eq. (8) suggested by G. G. Hall,[5] *viz.,*

$$\mathbf{R} = m^{-1/2}\,(\mathbf{I} + \frac{1}{2}\mathbf{L} + \frac{3}{8}\mathbf{L}^2 + ...)\,,$$
$$\mathbf{Q} = n^{-1/2}\,(\mathbf{I} + \frac{1}{2}\mathbf{K} + \frac{3}{8}\mathbf{K}^2 + ...)\,, \tag{57}$$

where the matrices **L** and **K** along with positive numerical coefficients *m* and *n* were determined by the matrix equations:

$$\mathbf{BB}^+ = m(\mathbf{I} - \mathbf{L}); \quad \mathbf{B}^+\mathbf{B} = n(\mathbf{I} - \mathbf{K})\,. \tag{58}$$

Choice of parameters *m* and *n* was made by imposing an additional condition that eigenvalues of matrices **L** and **K** lie within the interval [–1; +1]. [Just this requirement served to ensure the convergence of the series]. Let us define now the matrices:

$$\mathbf{F}_d = \mathbf{Q}(\mathbf{I} + \gamma\,\mathbf{Q})^{-1}; \quad \mathbf{F}_a = (\mathbf{I} + \mu\,\mathbf{R})^{-1}\,\mathbf{R} \tag{59}$$

and obtain their inverse counterparts. These are:

$$(\mathbf{F}_d)^{-1} = \gamma\,\mathbf{I} + \mathbf{Q}^{-1}; \quad (\mathbf{F}_a)^{-1} = \mu\,\mathbf{I} + \mathbf{R}^{-1}\,. \tag{60}$$

Using the expressions of Eq. (57), we then obtain:

$$(\mathbf{F}_d)^{-1} = (\gamma + n^{1/2})\,\mathbf{I} - \frac{1}{2}n^{1/2}\,\mathbf{K} + ...$$
$$(\mathbf{F}_a)^{-1} = (\mu + m^{1/2})\,\mathbf{I} - \frac{1}{2}m^{1/2}\,\mathbf{L} + ... \tag{61}$$

It is seen that the larger are the (positive) Coulomb parameters γ and μ describing our substituents, the more significant are the zero order terms $(\gamma + n^{1/2})\,\mathbf{I}$ and $(\mu + m^{1/2})\,\mathbf{I}$ *vs.* the remaining terms in the series of Eq. (61). Let us assume our substituents to be described by parameters γ and μ of sufficiently large values so that we may confine ourselves to taking into account the zero order terms of the series of Eq. (61). After returning to matrices $\mathbf{F}_d$ and $\mathbf{F}_a$, we obtain:

$$\mathbf{F}_d \approx \overline{\mathbf{F}}_d = \rho(\gamma)\mathbf{I}, \quad \mathbf{F}_a \approx \overline{\mathbf{F}}_a = \tau(\mu)\mathbf{I}, \tag{62}$$

where

$$\rho(\gamma) = (\gamma + n^{1/2})^{-1} > 0,$$
$$\tau(\mu) = (\mu + m^{1/2})^{-1} > 0 \tag{63}$$

are positive γ- and μ- dependent parameters. Thus, our approximation consists of replacing the matrices $\mathbf{F}_d$ and $\mathbf{F}_a$ of Eq. (59) by $\overline{\mathbf{F}}_d$ and $\overline{\mathbf{F}}_a$, respectively, the latter being proportional to unit matrices. Verification of accuracy of such an approximation is undertaken in the last section.

From Eqs. (18) and (21), we obtain the approximate versions of the principal matrices $\mathbf{g}_{d(1)}$ and $\mathbf{g}_{a(1)}$ denoted by $\overline{\mathbf{g}}_{d(1)}$ and $\overline{\mathbf{g}}_{a(1)}$ respectively, *viz.,*

$$\overline{\mathbf{g}}_{d(1)} = \frac{1}{\sqrt{2}}\,\rho(\gamma)\mathbf{d}; \quad \overline{\mathbf{g}}_{a(1)} = -\,\frac{1}{\sqrt{2}}\,\tau(\mu)\mathbf{a}\,. \tag{64}$$

[Note that overlined characteristics here and below correspond just to the above-described approximation]. It follows from Eq. (64) that the row-matrix $\overline{\mathbf{g}}_{d(1)}$ and the column-matrix $\overline{\mathbf{g}}_{a(1)}$ actually contain non-zero elements in their first positions only. These are equal to $\frac{1}{\sqrt{2}}\,\rho(\gamma)\delta$ and $-\frac{1}{\sqrt{2}}\,\tau(\mu)\nu$, respectively.

Let us now turn to NCMOs of SAHs $\Phi_{(+)d}$ and $\Phi_{(-)a}$ originating from the orbitals of substituents. After substituting $\overline{\mathbf{g}}_{d(1)}$ for $\mathbf{g}_{d(1)}$ into the first expression of Eq. (24), it follows that the electron-donating orbital $\varphi_{(+)d}$ interacts only with a single vacant NCMO of the parent AH when making up the NCMO $\Phi_{(+)d}$, namely with the NCMO $\Psi^{(0)}_{(-)1}$ of the following constitution:

$$\Psi^{(0)}_{(-)1} = \frac{1}{\sqrt{2}}\,[-\chi^{\circ}_{1} + \sum_{i}^{(*)} \chi^{*}_{i}\,(\mathbf{BQ})_{i1}]\,, \tag{65}$$

the latter resulting from Eq. (7). Inasmuch as elements of the matrix **BQ** do not exceed 1,[5,11] the NCMO $\Psi^{(0)}_{(-)1}$ is primarily localized on the site of substitution. It is also seen that the NCMO of Eq. (65) contains no contributions of AOs χ°_{j}, $j \neq 1$. [This NCMO has been conveniently referred to Ref. 11 as that attached to the AO χ°_{1}]. Similarly, the electron-accepting orbital $\varphi_{(-)a}$ interacts only with a single occupied NCMO of the parent AH $\Psi^{(0)}_{(+)1}$ attached to the AO χ^{*}_{1} when making up the NCMO $\Phi_{(-)a}$. This result may be referred to as the two-orbital model for SAHs. It is worth mentioning that this simple model becomes easily constructable just owing to the choice of the sites of the donating and accepting substituents coinciding with the first AOs of subsets $\{\chi^{\circ}\}$ and $\{\chi^{*}\}$ respectively. Indeed, the above-mentioned positions of substituents are compatible with the choice of NCMOs of the parent AHs underlying Eq. (7),[11] in which the occupied and vacant NCMOs are attached to subsets $\{\chi^{*}\}$ and $\{\chi^{\circ}\}$ respectively.

Let us now turn to bond orders defined by Eqs. (45) and (46). After substituting $\bar{\mathbf{g}}_{\mathrm{d}(1)}$ and $\bar{\mathbf{g}}_{\mathrm{a}(1)}$ for $\mathbf{g}_{\mathrm{d}(1)}$ and $\mathbf{g}_{\mathrm{a}(1)}$ respectively, we obtain:

$$\bar{P}_{i\mathrm{d}} = -\rho(\gamma)\delta(\mathbf{BQ})_{i1}, \quad \bar{P}_{j\mathrm{d}}|_{j=1} = \rho(\gamma)\delta, \quad \bar{P}_{j\mathrm{d}}|_{j\neq 1} = 0\,, \qquad (66)$$

$$\bar{P}_{i\mathrm{a}} = \tau(\mu)\nu(\mathbf{QB}^{+})_{j1}, \quad \bar{P}_{i\mathrm{a}}|_{i=1} = \tau(\mu)\nu, \quad \bar{P}_{i\mathrm{a}}|_{i\neq 1} = 0\,. \qquad (67)$$

These results indicate that the largest bond orders arise between the orbital of the electron-donating substituent ($\varphi_{(+)\mathrm{d}}$) and the AO attached to the site of substitution (χ°_{1}), whereas the remaining bond orders $\bar{P}_{j\mathrm{d}}$ take zero values. As far as bond orders between orbitals $\varphi_{(+)\mathrm{d}}$ and χ^{*}_{i} are concerned, these prove to be proportional to bond orders between AOs χ°_{i} and χ^{*}_{i} inside the parent hydrocarbon (the latter are determined by matrix elements $(\mathbf{BQ})_{i1}$. An analogous result follows from Eq. (67) for the case of an acceptor-containing SAH.

Consequences of the approximation of Eqs. (66) and (67) upon partial populations transferred between the substituent and individual AOs of the parent AH may be easily revealed by invoking the expressions for $\Delta q_{\mathrm{d}i}$, $\Delta q_{\mathrm{d}j}$, $\Delta q_{\mathrm{a}i}$ and $\Delta q_{\mathrm{a}j}$ in terms of bond orders shown in Eqs. (53) and (54). Thus, charge proves to be transferred from the orbital $\varphi_{(+)\mathrm{d}}$ to orbitals χ°_{1} and χ^{*}_{i}, as well as from AOs χ^{*}_{1} and χ°_{j} to the orbital $\varphi_{(-)\mathrm{a}}$. This result is in line with constitutions of NCMOs $\Psi^{(0)}_{(-)1}$ (see Eq. (65)) and $\Psi^{(0)}_{(+)1}$ of the parent AHs playing the role of accepting and donating orbitals for the donor- and acceptor-containing SAHs, respectively, in the framework of the two-orbital model.

To show the consequences of our approximation upon the intersubset polarization, let us substitute Eq. (64) into Eqs. (37) and (41) determining matrices $\mathbf{Z}_{\mathrm{d}(2)}$ and $\mathbf{Z}_{\mathrm{a}(2)}$ respectively. We then obtain:

$$\mathbf{Q}\bar{\mathbf{Z}}_{\mathrm{d}(2)} + \bar{\mathbf{Z}}_{\mathrm{d}(2)}\mathbf{Q} + \rho(\gamma)\mathbf{Qd}^{+}\mathbf{dQ} = \mathbf{0}\,, \qquad (68)$$

$$\mathbf{Q}\bar{\mathbf{Z}}_{\mathrm{a}(2)} + \bar{\mathbf{Z}}_{\mathrm{a}(2)}\mathbf{Q} + \tau(\mu)\mathbf{Q}^{2}\mathbf{B}^{+}\mathbf{aa}^{+}\mathbf{BQ}^{2} = \mathbf{0}\,. \qquad (69)$$

Comparison of Eqs. (68) and (69) with matrix equations determining the intersubset polarization matrices of PAHs[16] is of interest. Indeed, local perturbations of Coulomb and/or resonance parameters inside subsets $\{\chi^{\circ}\}$ and $\{\chi^{*}\}$ of AHs give birth to the first order intersubset polarization matrices $\mathbf{Z}^{(\circ)}_{(1)}$ and $\mathbf{Z}^{(*)}_{(1)}$, respectively, conditioned by matrix equations:

$$\mathbf{Q}\mathbf{Z}^{(\circ)}_{(1)} + \mathbf{Z}^{(\circ)}_{(1)}\mathbf{Q} - \mathbf{Q}\mathbf{D}_{(1)}\mathbf{Q} = \mathbf{0}\,, \qquad (70)$$

$$\mathbf{Q}\mathbf{Z}^{(*)}_{(1)} + \mathbf{Z}^{(*)}_{(1)}\mathbf{Q} + \mathbf{Q}^{2}\mathbf{B}^{+}\mathbf{A}_{(1)}\mathbf{BQ}^{2} = \mathbf{0}\,. \qquad (71)$$

where $\mathbf{D}_{(1)}$ and $\mathbf{A}_{(1)}$ stand for the relevant blocks of the first order Hamiltonian matrix for PAHs.[16] Coincidence of overall constitutions of Eqs. (68) and (70), as well as of Eqs. (69) and (71), is evident. Moreover, the products $\mathbf{d}^{+}\mathbf{d}$ and $\mathbf{aa}^{+}$ are square matrices containing non-zero elements δ^{2} and ν^{2}, respectively, in the positions 11 and zero elements elsewhere. As a result, the second order matrices $-\rho(\gamma)\mathbf{d}^{+}\mathbf{d}$ and $\tau(\mu)\mathbf{aa}^{+}$ are proportional to particular first order matrices $\mathbf{D}_{(1)\mathrm{loc}}$ and $\mathbf{A}_{(1)\mathrm{loc}}$ describing local perturbations of Coulomb parameters of AOs χ°_{1} and χ^{*}_{1}, respectively. Consequently, mutual proportionalities may be concluded between matrices $\bar{\mathbf{Z}}_{\mathrm{d}(2)}$ and $\mathbf{Z}^{(\circ)}_{(1)\mathrm{loc}}$ as well as between $\bar{\mathbf{Z}}_{\mathrm{a}(2)}$ and $\mathbf{Z}^{(*)}_{(1)\mathrm{loc}}$, where $\mathbf{Z}^{(\circ)}_{(1)\mathrm{loc}}$ and $\mathbf{Z}^{(*)}_{(1)\mathrm{loc}}$ stand for solutions of Eqs. (70) and (71) referring to local perturbation matrices $\mathbf{D}_{(1)\mathrm{loc}}$ and $\mathbf{A}_{(1)\mathrm{loc}}$ respectively [To show this, it is only required to employ the integral solutions of Eqs. (68) to (71).[23,29,31]].

Diagonal elements of matrices $\mathbf{Z}^{(\circ)}_{(1)\mathrm{loc}}$ and $\mathbf{Z}^{(*)}_{(1)\mathrm{loc}}$ were shown to determine[16] the relevant polarizabilities of the atom-atom type,[1–4,6] widely used when describing the effects of local perturbations in AHs. Hence, diagonal elements of matrices $\bar{\mathbf{Z}}_{\mathrm{d}(2)}$ and $\bar{\mathbf{Z}}_{\mathrm{a}(2)}$ and thereby the population alterations due to the intersubset polarization in SAHs are proportional to the relevant atom-atom polarizabilities in the parent AH. Using the above-mentioned integral solutions,[23,29,31] diagonal elements of matrices $\bar{\mathbf{Z}}_{\mathrm{d}(2)}$ and $\bar{\mathbf{Z}}_{\mathrm{a}(2)}$ may be expressed as:

$$\bar{Z}_{\mathrm{d}(2),\,jj} = -\,\rho(\gamma)\delta^{2}\int_{0}^{\infty}\{(\exp[-\mathbf{Q}t]\mathbf{Q})_{j1}\}^{2}\,\mathrm{d}t\,, \qquad (72)$$

$$\bar{Z}_{\mathrm{a}(2),\,jj} = -\,\tau(\mu)\nu^{2}\int_{0}^{\infty}\{(\exp[-\mathbf{Q}t]\mathbf{Q}^{2}\mathbf{B}^{+})_{j1}\}^{2}\,\mathrm{d}t \qquad (73)$$

and prove to be of negative signs. By contrast, $\bar{X}_{\mathrm{d}(2),ii}$ and $\bar{X}_{\mathrm{a}(2),ii}$ take positive values as it may be demonstrated on the basis of the first relation of Eq. (35).[16] The overall result is:

$$\bar{Z}_{\mathrm{d}(2),jj} < 0, \quad \bar{Z}_{\mathrm{a}(2),jj} < 0, \quad \bar{X}_{\mathrm{d}(2),ii} > 0, \quad \bar{X}_{\mathrm{a}(2),ii} > 0 \qquad (74)$$

and it is nothing more than the analogue of the rule of the alternating polarity for SAHs. It is seen that the intersubset polarization gives rise to negative and positive alterations in populations of AOs of subsets embracing the sites of electron-donating and accepting substituents, *i.e.,* of subsets $\{\chi^{\circ}\}$ and $\{\chi^{*}\}$ respectively, whilst the population alterations of AOs of opposite subsets are of opposite signs. Hence, the effect of an electron-donating (accepting) substituent resembles that of a heteroatom of a lower (higher) electronegativity *vs.* the carbon atom in respect of the intersubset polarization.

It is evident that total population alterations of particular AOs inside the parent AHs are made up of sums of increments originating from the intersubset polarization and from the intersubsystem charge transfer. As a result, positive population alterations unambiguously follow for all AOs χ^{*}_{i} of the donor-containing system, and negative total alterations result for all AOs χ°_{j} of the acceptor-containing system. As far as subsets of AOs embracing the sites of substitution are concerned, the respective total population alterations are determined by the intersubset polarization except for the very site of substitution, where a significant charge transfer is also expected. As a result, alterations in populations of AOs $\chi_i^{\circ} (j \neq 1)$ and $\chi_i^{*} (i \neq 1)$ take negative and positive signs for the donor- and acceptor-containing systems, respectively. Consequently, the rule of alternating polarity is unambiguously predicted to be valid also for total population alterations of AOs of SAHs, except for those at the very site of substitution.

Furthermore, substituting Eq. (64) into Eqs. (38) and (42) yields zero matrices for both $\overline{\Delta}_{d(2)}$ and $\overline{\Delta}_{a(2)}$ and thereby for submatrices $\overline{\mathbf{N}}_{d(2)}$ and $\overline{\mathbf{N}}_{a(2)}$ taking the off-diagonal positions in the second order corrections to CBO matrices $\overline{\mathbf{P}}_{d(2)}$ and $\overline{\mathbf{P}}_{a(2)}$ (see also Eq. (33)). Consequently, alterations in bond orders inside the parent AHs due to substitution prove to be determined by elements of matrices $\overline{\mathbf{M}}_{d(2)}$ and $\overline{\mathbf{M}}_{a(2)}$ following from Eq. (56) after replacing the bond orders P_{id}, P_{jd}, *etc.* by respective approximate versions shown in Eqs. (66) and (67). It is seen that non-zero products $P_{id}P_{jd}$ and $P_{ia}P_{ja}$ and thereby significant alterations primarily arise for orders of bonds attached to the site of substitution in the framework of our approximate model. Inasmuch as positive values were obtained for elements of the matrix **BQ** referring to nearest-neighboring pairs of AOs in AHs,[11] the inequality $(\mathbf{BQ})_{i1} > 0$ may be expected for AOs χ_i^{*} taking the nearest-neighboring positions with respect to the site of the electron-donating substituent. Thus, both $\overline{P}_{id}$ and $\overline{M}_{d(2),i1}$ are negative quantities and thereby reduction of bond orders attached to the donating substituent follows. For the case of an electron-accepting substituent, the same conclusion may be drawn on the basis of the positive sign of $\overline{P}_{ja}$ and of the negative sign of $\overline{M}_{a(2),j1}$.

Illustration of the Results

In this section, we are about to illustrate the above-obtained algebraic results using substituted benzenes as an example.

Scheme 1. Numbering of $2p_z$ AOs of carbon atoms for substituted benzenes containing an electron-donating substituent (D) and an electron-accepting substituent (A). Carbon atoms containing AOs of subsets $\{\chi^{*}\}$ and $\{\chi^{\circ}\}$ are accordingly denoted by * and °.

Numbering of $2p_z$ AOs of carbon atoms inside the phenyl ring (see Scheme 1) will be chosen so as to ensure the anti-block-diagonal structure of the relevant submatrices of Hamiltonian matrices of Eqs. (1) and (2). [Non-zero resonance parameters referring to chemical bonds should be found in the off-diagonal blocks **B** and $\mathbf{B}^{+}$ in this matrix]. Matrices **Q**, **R** and $\mathbf{QB}^{+}$ for the ring then take the form:[16]

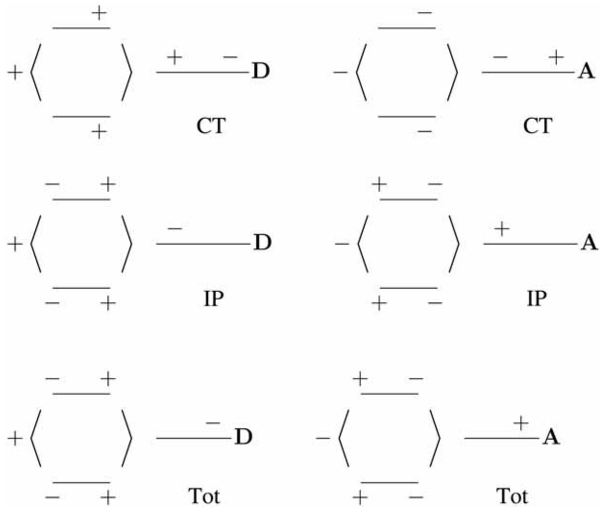
$$\mathbf{Q} = \mathbf{R} = \frac{1}{6}\begin{vmatrix} 5 & -1 & -1 \\ -1 & 5 & -1 \\ -1 & -1 & 5 \end{vmatrix}, \quad \mathbf{QB}^{+} = \frac{1}{3}\begin{vmatrix} 2 & 2 & -1 \\ -1 & 2 & 2 \\ 2 & -1 & 2 \end{vmatrix}. \quad (75)$$

Let us start with verification of Eq. (62). Matrices $\mathbf{Q}^{-1}$ and $\mathbf{R}^{-1}$ contained within Eq. (60) are equal to:

$$\mathbf{Q}^{-1} = \mathbf{R}^{-1} = \frac{1}{3}\begin{vmatrix} 4 & 1 & 1 \\ 1 & 4 & 1 \\ 1 & 1 & 4 \end{vmatrix}. \quad (76)$$

Diagonal elements of this matrix are four times larger compared to the off-diagonal ones. After adding the increments $\gamma\mathbf{I}$ and $\mu\mathbf{I}$ $(\gamma > 0, \mu > 0)$ in accordance with Eq. (60), the resulting matrices $(\mathbf{F}_d)^{-1}$ and $(\mathbf{F}_a)^{-1}$ become even closer to their approximate versions proportional to unit matrices.

Let us now turn to the substituted benzenes. The electron-accepting substituent (A) will be placed at the first position of the phenyl ring represented by the AO χ_1^{*} (Scheme 1). Again, the electron-donating substituent (D) will be attached to the fourth position, which coincides with the first position of the subset $\{\chi^{\circ}\}$. Scheme 2 represents the signs of population alterations in these derivatives of benzene due to the intersubsystem charge transfer and to the intersubset polarization separately, as well as of their total values. It is evident that *ortho-* and *para-*positions correspond to AOs χ_i^{*} of the D-substituted molecule, as well as to AOs χ_j° of the acceptor-containing system. Accordingly, it is predicted that the population is donated to the above-enumerated positions by the substituent D and withdrawn from the same positions by the acceptor A. The *ipso* positions χ_4° and χ_1^{*} are embraced by the effect too.



Scheme 2. Signs of population alterations caused by the intersubsystem charge transfer (CT) and by the intersubset polarization (IP), as well as those of total population alterations (Tot) for derivatives of benzene containing electron-donating substituents (D) and electron-accepting substituents (A).

Signs of population alterations caused by the intersubset polarization follow from Eq. (74). On the basis of superposition of these two components of the effect, increased total populations of *ortho*- and *para*-positioned carbon atoms are predicted along with reduced occupation numbers of AOs of the *meta*-positioned atoms in the D-substituted benzenes. At the same time, reduced and increased occupation numbers refer to *ortho*/*para* and *meta* positions, respectively, in the case of an acceptor-containing system. These results are in line both with numerical calculations by means of the simple Hückel method and trends in chemical reactivity of substituted benzenes.[18–21]

A more detailed consideration of the same systems becomes possible after invoking the NCMOs. Let us confine ourselves to the case of an electron-donating substituent for simplicity. The basis orbital $\varphi_{(+)\mathrm{d}}$ of this substituent interacts mostly with the NCMO $\Psi^{(0)}_{(-)4}$ of the phenyl ring of the following constitution:

$$\Psi^{(0)}_{(-)4} = \frac{1}{\sqrt{2}}\left[-\chi_4 + \frac{2}{3}(\chi_1 + \chi_2) - \frac{1}{3}\chi_3\right], \qquad (77)$$

the latter following from Eq. (7) after employment of the matrix $\mathbf{OB}^+$ of Eq. (75). It is seen that the orbital $\Psi^{(0)}_{(-)4}$ is localized on *ipso*-, *ortho*- and *para*-positions with respect to the substituent. Relative values of the partial delocalization coefficients of the resulting NCMO $\overline{\Phi}_{(+)\mathrm{d}}$ over the above-enumerated positions are correspondingly proportional to 1, 4/9 and 1/9. Partial populations donated by the substituent D to these positions are also proportional to the same numbers in accordance with Eq. (54).

Another way of obtaining the same result involves consideration of bond orders formed between the electron-donating orbital $\varphi_{(+)\mathrm{d}}$ and AOs of benzene. These follow from Eq. (66) after invoking Eq. (75) and are equal to:

$$\overline{P}_{4\mathrm{d}} = \rho(\gamma)\delta, \quad \overline{P}_{5\mathrm{d}} = \overline{P}_{6\mathrm{d}} = 0, \quad \overline{P}_{1\mathrm{d}} = \overline{P}_{2\mathrm{d}} = -\frac{2}{3}\rho(\gamma)\delta,$$

$$\overline{P}_{3\mathrm{d}} = \frac{1}{3}\rho(\gamma)\delta. \qquad (78)$$

Populations donated to particular carbon atoms result from the squares of these bond orders in accordance with Eq. (54) and also prove to be proportional to 1, 4/9 and 1/9 for AOs $\overset{\circ}{\chi}_4$, $\overset{*}{\chi}_1$ and $\overset{*}{\chi}_3$ respectively.

Let us now turn to alterations in orders of chemical bonds inside the phenyl ring due to substitution. As already mentioned, these bond orders are determined by elements of the matrix $\overline{\mathbf{M}}_{\mathrm{d}(2)}$ defined by Eq. (55) in the framework of our approximation. Using Eq. (78) within Eq. (56) yields the following result:

$$\overline{M}_{\mathrm{d}(2),14} = \overline{M}_{\mathrm{d}(2),24} = -\frac{1}{3}[\rho(\gamma)\delta]^2, \qquad (79)$$

whilst the remaining elements of the same matrix take zero values. Thus, a local reduction of bond orders attached to the site of substituent may be concluded.

On the whole, a simple and illustrative model is obtained for substituted benzenes on the basis of our results. To present an independent verification of the model, let us invoke the results of direct numerical calculations of substituted benzenes by means of the simple Hückel method.[6] Thus, bond orders between the AO of the nitrogen atom and those of the phenyl ring of the aniline molecule (Ph–NH$_2$) were shown to take the following values:

$$P^{(\mathrm{c})}_{4\mathrm{d}} = 0.291, \quad P^{(\mathrm{c})}_{5\mathrm{d}} = P^{(\mathrm{c})}_{6\mathrm{d}} = -0.032,$$
$$P^{(\mathrm{c})}_{1\mathrm{d}} = P^{(\mathrm{c})}_{2\mathrm{d}} = -0.167, \quad P^{(\mathrm{c})}_{3\mathrm{d}} = 0.127, \qquad (80)$$

where the superscript (c) here and below refers to calculated characteristics. It is seen that both the signs and the relative values of bond orders of Eq. (80) closely resemble those of Eq. (78).

Furthermore, bond orders inside the phenyl ring of the same aniline molecule were also calculated in the same study.[6] These are:

$$P^{(\mathrm{c})}_{14} = P^{(\mathrm{c})}_{42} = 0.637, \quad P^{(\mathrm{c})}_{25} = P^{(\mathrm{c})}_{16} = 0.673,$$
$$P^{(\mathrm{c})}_{34} = P^{(\mathrm{c})}_{36} = 0.663, \quad P^{(\mathrm{c})}_{\mathrm{benz}} = 0.667, \qquad (81)$$

where the last bond order ($P^{(\mathrm{c})}_{\mathrm{benz}}$) represents the relevant value for the parent benzene molecule. It is seen that the orders of bonds attached to the site of the substituent (*viz*., $P^{(\mathrm{c})}_{14}$ and $P^{(\mathrm{c})}_{42}$) are reduced most significantly, as predicted by our approximate model. It is also noteworthy that the formation of elements $\overline{M}_{\mathrm{d}(2),ij}$ on the basis of Eq. (56) by replacing $P_{i\mathrm{d}}$ and $P_{j\mathrm{d}}$ by respective numerical values of Eq. (80) yields the following result:

$$\overline{M}'_{\mathrm{d}(2),14} = \overline{M}'_{\mathrm{d}(2),24} = -0.024,$$
$$\overline{M}'_{\mathrm{d}(2),16} = \overline{M}'_{\mathrm{d}(2),25} = 0.003,$$
$$\overline{M}'_{\mathrm{d}(2),35} = \overline{M}'_{\mathrm{d}(2),36} = -0.002. \qquad (82)$$

The alterations in the neighboring bond orders determined by Eq. (82) are even closer to the relevant exact values of Eq. (81).

Thus, our two-orbital model of substituted benzenes is also supported by the results of numerical calculations.

CONCLUSIONS

Rules governing the effects of substituents in SAHs are:

(i) The effect of substituent of any type upon the electronic structure of an AH consists of two additive components, *viz*., of the charge transfer between the above-mentioned subsystems and of the intersubset polarization inside the AH due to the very presence of the substituent.

(ii) The total population transferred between a substituent and an AH becomes divided up equally between the two subsets of AOs of the AH.

(iii) The partial population transferred between the substituent and an individual $2p_z$ AO of the AH is proportional to the square of the respective bond order, as well as to the extent of delocalization of the orbital of the substituent over the AO under consideration when making up the respective NCMO.

(iv) The total transfer of population from (or to) the substituent can be approximately represented as an electron-donating (accepting) effect of its orbital upon a single NCMO of the parent AH attached to the site of substitution. Accordingly, the relative extents of populations donated to (or withdrawn from) separate AOs of the AH are determined by the shape of the above-specified principal NCMO.

(v) The intersubset polarization inside the AH due to substitution is governed by the second order analogue of the rule of alternating polarity. For an electron-donating (accepting) substituent, the relevant component of the total charge redistribution resembles that caused by a heteroatom of lower (higher) electronegativity.

(vi) Alterations in bond orders between chemically-bound pairs of atoms of the AH due to substitution are proportional to the products of two newly-formed intersubsystem bond orders between the orbital of the substituent and the $2p_z$ AOs of carbon atoms involved in the given bond. Predominant weakening of bonds attached to the site of substitution is actually observable.

REFERENCES

1. C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. London, Ser. A* **191** (1947) 39–60.
2. C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. London, Ser. A* **192** (1947) 16–32.
3. C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. London, Ser. A* **193** (1948) 447–464.
4. C C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. London, Ser. A* **195** (1948) 188–197.
5. G. G. Hall, *Proc. Roy. Soc.*, *London, Ser. A* **229** (1955) 251–259.
6. M. V. Basilevskii, *Metod Molekuliarnych Orbit i Reaktsionnaya Sposobnost Organitcheskich Molekul*, Khimia, Moscow, 1969 (in Russian).
7. S. Huzinaga, *The MO Method*, Mir, Moscow, 1983 (in Russian).
8. N. Trinajstić in: G. A. Segal (Ed.), *Semiempirical Methods of Electronic Structure Calculations*, Part A, *Techniques*, Plenum Press, New York and London, 1977.
9. D. M. Cvetkovic, M. Doob, and H. Sachs, *Spectra of Graphs. Theory and Application*, VEB Deutscher Verlag der Wissenschaften, Berlin, 1980.
10. J. A. Pople, *Trans. Faraday. Soc.* **50** (1954) 901–911.
11. V. Gineityte, *Int. J. Quant. Chem.* **101** (2005) 274–282.
12. M. J. S. Dewar and R. C. Dougherty, *The PMO Theory of Organic Chemistry*, Plenum Press, New York, 1975.
13. M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry*, McGraw Hill, New York, 1969.
14. R. Zahradnik and R. Polak, *Elements of Quantum Chemistry*, Plenum Press, New York, 1980.
15. I. Gutman, *Z. Naturforsch., A* **36** (1981) 1112–1114.
16. V. Gineityte, *Int. J. Quant. Chem.* **105** (2005) 232–245.
17. V. Gineityte, *Int. J. Quant. Chem.* **106** (2006) 2145–2160.
18. J. March, *Advanced Organic Chemistry, Reactions, Mechanisms and Structure*, Wiley, New York, 1985.
19. A. S. Dnieprovskii and T. I. Temnikova, *Fundamentals of Organic Chemistry*, Khimia, Leningrad, 1981 (in Russian).
20. H. G. O. Becker, Einfürung *in die Elektronentheorie Organisch Chemischen Reaktionen*, Deutscher Verlag der Wissenschaften, Berlin, 1974.
21. K. F. Reid, *Properties and Reactions of Bonds in Organic Molecules*, Longmans, Green and Co, London, 1968.
22. M. M. Mestechkin, *Metod matricy plotnosti v teorii molekul*, Naukova Dumka, Kiev, 1977.
23. V. Gineityte, *J. Mol. Struct.* (*Theochem*) **343** (1995) 183–194.
24. I. Mayer, *Chem. Phys. Lett.* **89** (1982) 390–394.
25. P. R. Surjan, I. Mayer, and M. Kertesz, *J. Chem. Phys.* **77** (1982) 2454–2459.
26. I. Mayer and P. R. Surjan, *J. Chem. Phys.* **80** (1984) 5649–5658.
27. V. Gineityte, *J. Mol. Struct.* (*Theochem*) **288** (1993) 111–118.
28. V. Gineityte, *J. Mol. Struct.* (*Theochem*) **333** (1995) 297–306.
29. V. Gineityte, *Int. J. Quant. Chem.* **72** (1999) 559–570.
30. V. Gineityte, *J. Mol. Struct.* (*Theochem*) **364** (1996) 85–96.
31. V. Gineityte, *Int. J. Quant. Chem.* **68** (1998) 119–127.
32. V. Gineityte, *Lithuanian J. Phys.* **44** (2004) 219–236.
33. V. Gineityte, *J. Mol. Struct.* (*Theochem*) **487** (1999) 231–240.
34. V. Gineityte, *J. Mol. Struct.* (*Theochem*) **434** (1998) 43–51.
35. R. A. Horn and C. R. Johnson, *Matrix Analysis*, Cambridge Univ. Press, Cambridge, 1986.

SAŽETAK

Pravila koja određuju djelovanje substituenata na alternatne konjugirane ugljikovodike

Viktorija Gineityte

Izvedeni su eksplicitni algebarski izrazi i analizirane matrice naboja i reda veze te srodne matrice reprezentacije ne-kanonskih molekularnih orbitala substituiranih alternatnih konjugiranih ugljikovodika pomoću blokova Hückelove matrice ne-supstituiranih ugljikovodika. Hückelova matrica odgovara matrici susjedstva grafa, koji predstavlja ugljikov kostur molekule. Postavljena su pravila koja određuju djelovanje supstituenata na elektronsku strukturu ugljikovodika koja dopunjuju klasična pravila. Valja istaknuti da je pri tome ustanovljeno da postoje dvije aditivne komponente unutar djelovanja supstituenata na alternatni ugljikovodik. To su prijenos elektronskoga naboja između navedenih blokova i međublokovska polarizacija unutar ugljikovodika. To odgovara particiji temeljnoga skupa $2p_z$ atomskih orbitala u dva podskupa. Pravilo koje određuje utjecaj prve komponente sastoji se od jednake raspodjele naboja između dva podskupa atomskih orbitala ugljikovodika. Pokazano je da polarizaciju između dva podskupa određuje analog pravila o alternirajućoj polarizaciji drugoga reda. Sve navedeno ilustrirano je na supstituiranim benzenima.