Additive components of heteroatom influence in substituted alkanes. Polarization and depolarization of bonds

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Abstract

The general expression for the common one-electron density matrix (DM) of saturated organic molecules obtained previously in the framework of the Hückel type model (V. Gineityte, J. Mol. Struct. (Theochem) 343 (1995) 183) has been applied to reveal the additive components of the heteroatom influence in substituted alkanes. To this end, the occupation number of a basis orbital has been expressed as a sum of three terms describing the polarization and depolarization of bonds and the intramolecular charge transfer. These terms, in turn, have been related to certain types of direct (through-space) and indirect (through-bond) interactions of bond orbitals (BOs). In particular, changes in the secondary polarization of C–C and C–H bonds under the influence of a heteroatom giving rise to their induced dipole moments has been related to differences in the indirect interaction between the two BOs of the given bond before and after substitution. Additive quantum-chemical analogues of the classical inductive and electron-donating effects have been established. The above-mentioned expressions for the occupation numbers have been also applied to substantiate the implicit postulates of the classical chemistry about additivity of the heteroatom influence in substituted alkanes. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Additive models for evaluation of various observed characteristics make up an important part of the classical theory of the structure of saturated organic molecules. Thus, dipole moments, polarizabilities, energies of formation, etc., are successfully estimated in this case as sums of local increments associated with particular bonds, lone electron pairs and/or functional groups [1–3]. These models are based on explicit assumptions about additivity of properties under study.

Furthermore, numerous implicit postulates of similar nature may be revealed within simple rules of the classical chemistry concerning mutual influence of effective atoms in saturated molecules, in particular within those describing the heteroatom influence in substituted alkanes [4–7].

Thus, heteroatoms are supposed to exert influence upon the electron density distribution in two ways, usually called the inductive and the electron-donating effects. The first of these effects may be traced back to the difference in electronegativities of heteroatoms and of hydrogen and carbon atoms. The electron-donating effect is commonly associated with lone electron pairs of a heteroatom. The two effects under discussion are implicitly assumed to be additive or at least roughly additive. Similarly, the total

influence of several heteroatoms is also expected to be approximately additive. Finally, the total electron density of a substituted molecule is supposed to consist of a sum of two terms, the first one coinciding with the electron density of the parent hydrocarbon and the second one being entirely associated with the heteroatom influence [4].

In this context, a question arises whether quantum-mechanical additive components of the heteroatom influence may be found. These components (if established) are likely to yield a substantiation of the above-mentioned implicit postulates. Moreover, any decomposition of the heteroatom influence into meaningful parts might offer a new tool of interpretation of the electronic structure of substituted alkanes.

It should be noted, however, that a straightforward application of sophisticated quantum-mechanical methods is unlikely to be the most appropriate way of achieving the above-mentioned end. Indeed, additive components of quantum-mechanical characteristics obtained using self-consistent ab initio approaches prove to be too involved in contrast to the extremely simple rules of the classical chemistry. In particular, quantum-mechanical studies of heteroatom influence in substituted alkanes [8–14] showed that several types of intricate interbond interactions make up the quantum-mechanical analogue of the classical inductive effect. But more importantly, the general nature of the classical rules, namely their applicability to any substituted molecule, becomes lost when turning to the relevant exact quantum-mechanical expressions.

The latter aspect may be traced back to the fact that establishing the relation between Schrödinger's equations for molecules containing different numbers of both electrons and nuclei (e.g. mono-substituted alkanes involving a heteroatom of the same type) is not an easy problem in quantum mechanics. Difficulties arise here because the numbers of electrons and nuclei are the principal parameters of the Schrödinger's equation but not of the chemical classification of molecules (the latter is evidently based on definite features of their local constitution [7]). As a result, quantum-mechanical expressions usually refer to a single molecule. It is noteworthy, however, that the problem of the unified description of related molecules becomes less involved if we prefer

simple quantum-chemical models to sophisticated approaches.

The Hückel type models of molecules (see e.g. Refs. [15–17]) may be mentioned here in the first place. This approach allows a simple relation to be established between secular problems for a substituted molecule and for the respective parent hydrocarbon. Indeed, substitution of a carbon (hydrogen) atom by a heteroatom may be modelled here by alteration in a single parameter, namely in the Coulomb integral referring to the site of substitution. This feature of the Hückel model has been used extensively when studying the heteroatom influence both in conjugated molecules [15–17] and in substituted alkanes [18–22]. It should also be noted that the Hückel type models for the inductive effect have been related to characteristics of the so-called bond points within the electron density functions [23].

For saturated organic molecules, an additional and more important generalization proves to be feasible in the framework of the Hückel-type model. This generalization consists of the possibility of constructing a common model Hamiltonian matrix H for the whole class of compounds under study and of solving the relevant problem for the respective representation of the one-electron density matrix (DM) P [24–31]. The problem under discussion coincides with the commutation equation for matrices P and H that follows from Dirac's equation in the case of the time-independent Hamiltonian [32].

In the basis of bond orbitals (BOs) this problem has been formulated and solved in Refs. [29,30] using certain matrix form of the perturbation theory. The respective general expression for the common DM of saturated organic molecules has been obtained in terms of matrices describing particular types of the direct (through-space) and indirect (through-bond) interactions of BOs (the very concept of these interactions has been suggested in Refs. [33–35]). Application of these expressions to investigate the heteroatom influence in substituted alkanes [30] resulted in an interpretation of the whole effect in terms of the interbond charge transfer being related to the direct (through-space) interactions of BOs.

It is unlikely, however, that the interbond charge transfer is the only consequence of substitution, even more so because heteroatoms are commonly assumed

to give rise to certain induced polarization of the neighboring C–C and C–H bonds [4–7].

In this context, the main aim of the present study consists of revealing all kinds of additive components of the heteroatom influence in substituted alkanes, including the interbond polarization. Moreover, we are about to offer an interpretation of the interbond polarization in terms of indirect (through-bond) interactions of BOs and to substantiate the above-enumerated rules of the classical chemistry concerning additivity of the heteroatom influence.

As it is shown in Ref. [31] devoted to alkanes, passing to the basis of sp^3-hybrid AOs (HAOs) is required for describing the interbond polarization. In Section 2 of this paper we perform an analogous procedure for substituted alkanes.

In contrast to Ref. [31], a local transformation of the two-dimensional DM block corresponding to a particular bond only is carried out, and occupation numbers of the relevant two HAOs are expressed in terms of sums of separate increments. Section 3 deals with substantiation of the classical postulates. In Section 4 the induced dipole moments of C–C and C–H bonds are analyzed in terms of indirect interactions of BOs.

2. Algebraic expressions for occupation numbers of HAOs of a heteroatom-containing bond

Let us consider a separate (Ith) bond containing a heteroatom (Z) and a carbon atom (C) and being involved within a substituted alkane. The HAOs χ_Z and χ_C ascribed to atoms Z and C, respectively, and directed along this bond will be represented by Coulomb parameters α_Z and α_C, whereas the bond itself will be characterized by resonance parameter β. The equalities $\alpha_C = 0$, $\alpha_Z = \alpha$ and $\beta = 1$ will be accepted further for convenience. An equality $\alpha = 0$ will be assumed in addition if we consider the particular case of a C–C or C–H bond (Uniform Coulomb parameters may be ascribed to $1s_H$ AOs of hydrogen atoms and to HAOs of carbon atoms [21,22,24–26] owing to similar values of electronegativities of these atoms [2]).

To obtain the expressions for occupation numbers of HAOs χ_Z and χ_C, we shall use the general form of the DM of saturated organic molecules [29]. To this end, we turn to the basis of BOs at first and invoke the

expressions for occupation numbers of two BOs of a bond and for the bond order between these BOs derived in the above-cited paper. Thereupon we retransform the relevant two-dimensional DM block into the HAO basis again and find its diagonal elements.

Let us define the bonding and antibonding BOs of the Ith bond as eigenfunctions of the respective two-dimensional Hamiltonian matrix block in the basis $\{\chi_Z, \chi_C\}$, i.e.

$$\varphi_{(+)i} = a\chi_Z + b\chi_C; \quad \varphi_{(-)i} = b\chi_Z - a\chi_C \qquad (1)$$

where the coefficients a and b are [22]

$$a = \cos(\gamma/2), \quad b = \sin(\gamma/2),$$

$$\gamma = arctg(2/\alpha), \quad 0 \le \gamma \le (\pi/2) \qquad (2)$$

(More electronegative heteroatoms (Z) versus carbon and hydrogen are considered here and α is assumed to be positive in β units). In the particular case of a C–C (C–H) bond we obtain

$$\alpha = 0, \quad \gamma = \pi/2, \quad a = b = 2^{-1/2} \qquad (3)$$

A pair of BOs like those of Eq. (1) may be evidently defined for any bond in the molecule. Orbitals of lone electron pairs (if any) may be treated similarly to bonding BOs [29].

Occupation numbers of BOs $\varphi_{(+)i}$ and $\varphi_{(-)i}$ may be expressed as follows [29]

$$X_{(+)i} = 2\{1 - \sum_{r}^{ABOs} (G_{(1)ir})^2\}; \quad X_{(-)i} = 2\sum_{p}^{BBOs} (G_{(1)pi})^2 \qquad (4)$$

where $G_{(1)ij}$ is an element of certain first order matrix $G_{(1)}$ describing the direct (through-space) interaction between the bonding BO (BBO) $\varphi_{(+)i}$ and the antibonding BO (ABO) $\varphi_{(-)j}$ of the Ith and Jth bonds and sums over r and p embrace all the ABOs and all the BBOs of the molecule under study. The element $G_{(1)ij}$ takes the form

$$G_{(1)ij} = -\frac{<\varphi_{(+)i}|\hat{H}|\varphi_{(-)j}>}{E_{(+)i} - E_{(-)j}} \qquad (5)$$

where the numerator contains the element of the Hückel type Hamiltonian matrix (the resonance parameter) between BOs indicated within the bra- and ket-vectors, and the denominator involves the difference in one-electron energies of BOs.

Furthermore, the bond order between the two BOs of the *l*th bond is [29]

$$M_l = -2G_{(2)ii} \tag{6}$$

where $G_{(2)ii}$ is the element of certain second order matrix $G_{(2)}$ representing the indirect (through-bond) interaction between BOs $\varphi_{(+)i}$ and $\varphi_{(-)i}$. This element may be expressed as follows

$$
G_{(2)ii} = \frac{1}{E_{(+)i} - E_{(-)i}}
$$

$$
\times \left\{ \sum_{k}^{BBOs} \frac{<\varphi_{(+)i}|\hat{H}|\varphi_{(+)k}> <\varphi_{(+)k}|\hat{H}|\varphi_{(-)i}>}{E_{(+)k} - E_{(-)i}} \right.
$$

$$
\left. - \sum_{r}^{ABOs} \frac{<\varphi_{(+)i}|\hat{H}|\varphi_{(-)r}> <\varphi_{(-)r}|\hat{H}|\varphi_{(-)i}>}{E_{(+)i} - E_{(-)r}} \right\} \tag{7}
$$

where the meanings of designation coincide with those of Eq. (5).

As a result, the occupation numbers of HAOs χ_Z and χ_C are

$$X_Z = a^2 X_{(+)i} + b^2 X_{(-)i} + 2ab M_l;$$

$$X_C = b^2 X_{(+)i} + a^2 X_{(-)i} - 2ab M_l \tag{8}$$

Using Eqs. (4) and (6), the occupation numbers X_Z and X_C may be rewritten in the form

$$X_Z(X_C) = 1 \pm \cos\gamma + \frac{1}{2}\Delta X_l \pm p_l \pm d_l \tag{9}$$

where the upper signs refer to χ_Z and the lower ones correspond to χ_C. The last three terms of Eq. (9) are

$$\Delta X_l = X_{(+)i} + X_{(-)i} - 2 = 2 \sum_i \{(G_{(1)ji})^2 - (G_{(1)ij})^2\} \tag{10}$$

$$p_l = -2G_{(2)ii} \sin\gamma \tag{11}$$

and

$$d_l = -\left\{ \sum_j (G_{(1)ij}^2 + G_{(1)ji}^2) \cos\gamma \right\} \tag{12}$$

Let us consider the increments of Eq. (9) separately.

The zero order dipole moment ($\pm \cos\gamma$) is inherent in the bond under consideration whatever the structure of the whole molecule (γ is defined by Eq. (2)). This dipole moment coincides with the

respective value for an isolated Z–C bond and it may be called the primary dipole moment. In accordance with the expectation, the population of the HAO χ_Z of the more electronegative atom Z proves to be increased, whereas that of the HAO of the carbon atom is reduced as compared to 1.

The second order term ($\frac{1}{2}\Delta X_l$) describes half of the total population alteration of the *l*th bond due to the interbond (or lone pair-bond) charge transfer [30]. It is seen that ΔX_l contains a sum of contributions each of them associated with a bond (lone pair) *J* being present in the given molecule. Thus, ΔX_l may be expressed as follows

$$\Delta X_l = \sum_{J \neq l} \Delta X_{l(J)} \tag{13}$$

where

$$\Delta X_{l(J)} = 2\left\{ (G_{(1)ji})^2 - (G_{(1)ij})^2 \right\} \tag{14}$$

is the increment of the *J*th bond (lone pair). (Note that $G_{(1)ii} = 0$ in accordance with the definition of BOs and $\Delta X_{l(l)} = 0$ in Eq. (13)). The increment $\Delta X_{l(J)}$ depends on the difference between squares of the direct (through-space) interactions of the BBO $\varphi_{(+)i}$ and of ABO $\varphi_{(-)j}$, on the one hand, and the BBO $\varphi_{(+)j}$ and ABO $\varphi_{(-)i}$, on the other hand. Hence, this contribution is actually determined by the mutual arrangement of the two involved bonds and it is independent of the constitution of the rest of molecule.

The second order dipole moment $\pm p_l$ shown in Eq. (11) proves to be related to the indirect (through-bond) interaction between the BBO $\varphi_{(+)i}$ and ABO $\varphi_{(-)i}$ of the *l*th bond by means of BBOs and ABOs of other bonds (lone pairs) defined by Eq. (7). In this connection, the above-discussed term describes a secondary polarization of bonds.

Additivity of the dipole moment $\pm p_l$ of the *l*th bond with respect to contributions of the remaining bonds (lone pairs) follows from additivity of the indirect interaction of BOs $\varphi_{(+)i}$ and $\varphi_{(-)i}$ with respect to mediators (BBOs and ABOs). Thus, on the basis of Eqs. (7) and (11), we obtain an expression for p_l like that of Eq. (13), and the partial increment of the *J*th bond (lone electron pair) equal to

$$
p_{l(J)} = -\frac{2\sin\gamma}{E_{(+)i} - E_{(-)i}} \left[\frac{S_{ij}R_{ji}}{E_{(+)j} - E_{(-)i}} - \frac{R_{ij}Q_{ji}}{E_{(+)i} - E_{(-)j}} \right] \tag{15}
$$

where the following designations are introduced

$$S_{ij} = \; <\varphi_{(+)i}|\hat{H}|\varphi_{(+)j}>, \quad R_{ij} = \; <\varphi_{(+)i}|\hat{H}|\varphi_{(-)j}>,$$

$$Q_{ij} = \; <\varphi_{(-)i}|\hat{H}|\varphi_{(-)j}> \qquad (16)$$

(Since $R_{ii} = 0$, $p_{I(i)} = 0$, i.e. no self-contribution is present within the expression for p_I).

From Eq. (15) it follows also that $p_{I(J)}$ may be further decomposed into two terms describing the contributions of the BBO $\varphi_{(+)j}$ and of the ABO $\varphi_{(-)j}$, i.e.

$$p_{I(J)} = p_{I(J+)} + p_{I(J-)} \qquad (17)$$

where

$$p_{I(J+)} = - \frac{2 S_{ij} R_{ji} \sin \gamma}{(E_{(+)i} - E_{(-)i})(E_{(+)j} - E_{(-)i})}$$

$$+ p_{I(J-)} = \frac{2 R_{ij} Q_{ji} \sin \gamma}{(E_{(+)i} - E_{(-)i})(E_{(+)i} - E_{(-)j})} \qquad (18)$$

The last dipole moment $\pm d_I$ shown in Eq. (12) is related to the non-uniform distribution among the HAOs χ_Z and χ_C of the population lost (acquired) by both the BBO $\varphi_{(+)i}$ and the ABO $\varphi_{(-)i}$ of the Ith bond. Indeed, comparing Eqs. (4), (11) and (12) shows that $d_I = 0$ if no charge transfer refers to both the BBO $\varphi_{(+)i}$ and ABO $\varphi_{(-)i}$, i.e. if both $\sum_j (G_{(1)ij})^2 = 0$ and $\sum_j (G_{(1)ji})^2 = 0$. On the other hand, a non-zero dipole moment $\pm d_I$ is allowed in the case of zero total population ΔX_I lost (acquired) by the Ith bond and defined by Eq. (10).

It is also noteworthy that the dipole moment $\pm d_I$ refers to Z–C bonds only and it turns to zero for C–C and C–H bonds (if $\gamma = \pi/2$ as shown in Eq. (3), $\pi_I = 0$ in accordance with Eq. (12)).

It is seen that d_I is negative. Hence, the HAO χ_Z pertinent to the heteroatom Z loses its population owing to the formation of the dipole $\pm d_I$, whereas the HAO χ_C of the carbon atom acquires an additional population. Therefore, the primary dipole moment ($\pm \cos \gamma$) of the Ith bond becomes reduced after 'embedding' this bond into a molecule. In this connection, the term $\pm d_I$ may be called the depolarization dipole moment.

Opposite orientations of the primary dipole moment and of the depolarization one may be accounted for by the fact that the population acquired by the Z–C bond becomes localized mainly on the ABO $\varphi_{(-)i}$ [30]. Hence, it is the shape of this ABO

that is responsible for the orientation of the depolarization dipole moment. This shape, in turn, follows from Eq. (1). Inasmuch as $a > b$, the HAO χ_C of the carbon atom acquires more population as compared to the HAO χ_Z of the heteroatom.

From Eq. (12), it also follows that the depolarization dipole moment $\pm d_I$ of the Ith bond is additive with respect to contributions of other bonds (lone pairs), and the partial increment of the Jth bond (lone pair) is equal to

$$d_{I(J)} = -(G_{(1)ij}^2 + G_{(1)ji}^2)\cos \gamma \qquad (19)$$

On the whole three additive components reveal themselves within the populations of HAOs of substituted alkanes, as shown in Eq. (9), and these describe the intramolecular charge transfer, the secondary polarization of bonds and depolarization of heteroatom-containing bonds. Moreover, each of these contributions may be represented as the sum of partial increments of various bonds (lone electron pairs) of the given molecule.

3. Substantiation of the classical rules concerning additivity of the heteroatom influence

Let us dwell in this section on the main features of the heteroatom influence in substituted alkanes. Let us compare the electron density distribution of a substituted molecule to that of the parent hydrocarbon.

The occupation number of the HAO χ_k of the substituted molecule may be represented in the form

$$X_k = X_k + X_k^o - X_k^o = X_k^o + \delta X_k \qquad (20)$$

where X_k^o is the respective occupation number for the parent hydrocarbon and

$$\delta X_k = X_k - X_k^o \qquad (21)$$

is the difference under interest.

Let the heteroatoms under study (Z) be described by the difference in the electronegativities of orbitals (HAOs) pertinent to the Z–C bond, as discussed in Section 2, and contain lone electron pairs in addition. Then from the additivity of the occupation numbers of HAOs with respect to various bonds and lone electron pairs it follows that any population alteration δX_k contains a sum of two terms traced back to the above-mentioned two peculiarities of heteroatoms

separately. Since the influences of the latter upon the final electron density distribution are called the inductive and electron-donating effects, the correction δX_k consists of two terms representing the partial increments of these effects, i.e.

$$\delta X_k = \delta X_k^{(ie)} + \delta X_k^{(ede)} \tag{22}$$

Both terms of the right side of Eq. (22) and thereby the total alteration in the occupation number δX_k turn to zero if we resubstitute the heteroatoms by hydrogen atoms. Hence, the correction δX_k may be entirely ascribed to the heteroatom influence.

It may be concluded, therefore, that substitution gives rise to extra terms within the expression for the occupation numbers that should be added to those of the parent hydrocarbon.

The C–C and C–H bonds in alkanes have been established to be described by transferable occupation numbers of HAOs and $1s_H$ AOs [24–26]. Hence, the corrections X_k^o of Eq. (20) may be regarded as transferable characteristics of various parent hydrocarbons. Then the population alteration δX_k associated with the heteroatom influence may be studied in the general case without regard for the structure of a particular molecule. This result serves to substantiate the general nature of rules governing the heteroatom influence in substituted alkanes commonly assumed in classical chemistry.

Additivity of the occupation numbers of basis orbitals with respect to increments of separate bonds (lone electron pairs) allows us also to conclude that influences of several heteroatoms on the occupation numbers associated with HAOs of the hydrocarbon fragment of a polysubstituted molecule are additive with respect to partial increments of these heteroatoms. Indeed, for a molecule containing N heteroatoms we obtain

$$\delta X_k^{(N)} = \sum_{p=1}^{N} \delta X_k^{(p)} \tag{23}$$

The left side of Eq. (23) describes the population alteration of the HAO χ_k referring to the hydrocarbon fragment of the polysubstituted molecule, whereas the right side contains the sum of N corrections, each of them describing the influence of a particular (pth) heteroatom. The terms of Eq. (23) may be further decomposed into contributions of the inductive and electron-donating effects of each heteroatom separately.

It is evident that the above conclusions are true not only for total occupation numbers but also for separate additive components ΔX_l, d_l and p_l shown in Eq. (9). Alternatively, the two terms of the right side of Eq. (22) referring to the inductive and electron-donating effects may be represented as sums of three additive components describing the intramolecular charge transfer, the polarization and the depolarization of bonds. Hence, the inductive and the electron-donating effects both manifest themselves as sums of three terms describing the above-mentioned intramolecular interactions. These additive components may be regarded as making up the quantum-chemical content of both classical effects in the framework of the employed model. These conclusions also indicate that these effects are of similar nature although of different origin. The fact that the electron-donating effect of a heteroatom gives rise to an additional polarization of bonds has been observed previously [36].

Therefore, we have substantiated the postulates of the classical chemistry concerning additivity of the heteroatom influence in substituted alkanes.

4. Analysis of the secondary (induced) dipole moments of C–C (C–H) bonds in terms of indirect interactions of BOs

The above results show that the influence of a heteroatom upon the hydrocarbon fragment of a substituted molecule resolves itself into a sum of the interbond charge transfer and of the secondary polarization of bonds. The first of these effects has been studied in Ref. [30] in detail. Hence, let us dwell on the secondary polarization in this Section.

From Section 2 it follows that additional (induced) dipole moments of C–C (C–H) bonds arise if the secondary polarization of the given bond changes after substitution. The origin of such a change (if any) lies in the respective alteration in the indirect interaction of BOs of the bond under study by means of other BOs of the molecule.

To illustrate this general expectation, let us consider the C_α–C_β or C_α–H bond located near the site of substitution. It is evident that the changing nature of BOs of the bond under substitution and appearance of lone pair orbitals of heteroatoms as additional mediators are both likely to contribute to changes

in the indirect interaction of BOs of the given C–C (C–H) bond.

Let the heteroatom Z be located in the 1st ($J1$) position of the Jth (Z–C$_\alpha$) bond (Fig. 1). Then

the alteration (Δp_I) in the dipole moment of the Ith C$_\alpha$–C$_\beta$ (C$_\alpha$–H) bond due to substitution is

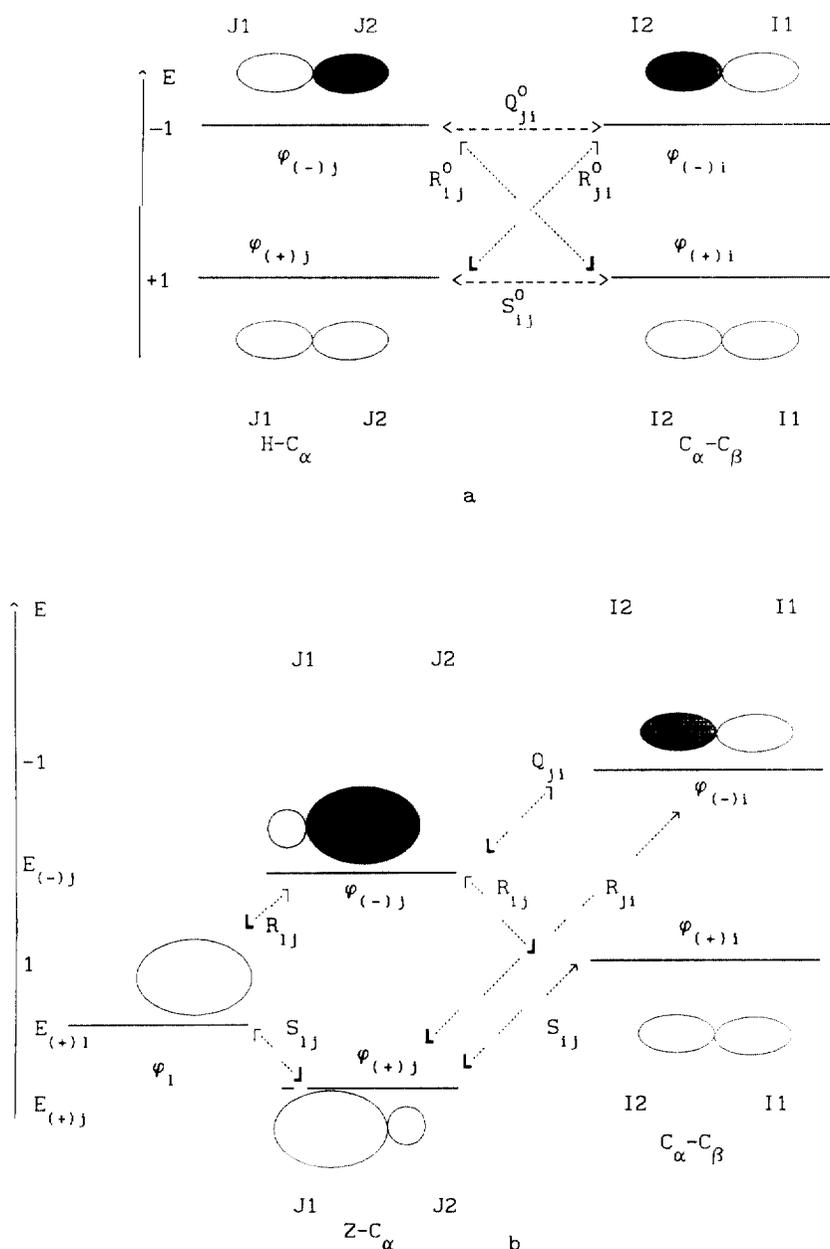$$\Delta p_I = \Delta p_{I(J)} + \Delta p_{I(L)} \qquad (24)$$

Fig. 1. Diagram reflecting the one-electron energies of BBOs $\varphi_{(+)}$ and of ABOs $\varphi_{(-)}$ of the Z–C$_\alpha$ (Jth) and C$_\alpha$–C$_\beta$ (C$_\alpha$–H) (Ith) bonds, and the shapes of these orbitals. Meanings of the resonance parameters S_{ij}, R_{ij}, R_{ji} and Q_{ij} are shown in Eq. (16). Diagram (a) describes the parent hydrocarbon, whereas (b) corresponds to the substituted molecule.

where

$$\Delta p_{I(J)} = \Delta p_{I(J)} - p_{I(J)}^o; \quad \Delta p_{I(L)} = p_{I(L)} \tag{25}$$

are the increments of the Jth (Z–C$_\alpha$) bond and of the lone electron pairs of the heteroatom, respectively (the superscript o refers to the parent hydrocarbon).

Let us start with the first increment $\Delta p_{I(J)}$ of Eq. (24). Inasmuch as $\gamma = \pi/2$ and thereby $\sin \gamma = 1$ may be substituted into Eqs. (15)–(18) determining $p_{I(J)}$ and $p_{I(J)}^o$ for the Ith C$_\alpha$–C$_\beta$ bond, and the energy differences $E_{(+)i}^o - E_{(-)i}^o$, $E_{(+)i}^o - E_{(-)i}^o$, $E_{(+)i}^o - E_{(-)i}^o$ for hydrocarbon along with $E_{(+)i} - E_{(-)i}$ for the substituted molecule may be taken to equal 2 (in negative β units), we obtain

$$\Delta p_{I(J)} = \Delta p_{I(J+)} + \Delta p_{I(J-)} \tag{26}$$

where

$$\Delta p_{I(J+)} = \frac{1}{2} S_{ij}^o R_{ji}^o - \frac{S_{ij} R_{ji}}{E_{(+)i} - E_{(-)i}} \tag{27}$$

$$\Delta p_{I(J-)} = \frac{R_{ij} Q_{ji}}{E_{(+)i} - E_{(-)j}} - \frac{1}{2} R_{ij}^o Q_{ji}^o \tag{28}$$

From Fig. 1 it follows that $E_{(+)i} - E_{(-)i} > 2$, whilst $E_{(+)i} - E_{(-)i} < 2$. Inasmuch as the 'center of gravity' of the BBO $\varphi_{(+)i}$ becomes shifted towards the heteroatom Z after substitution, the inequalities

$$0 < S_{ij} < S_{ij}^o, \quad R_{ji}^o < R_{ji} < 0, \quad |R_{ji}| < |R_{ji}^o| \tag{29}$$

follow and this implies a negative sign of $\Delta p_{I(J+)}$. On the other hand, the 'center of gravity' of the ABO $\varphi_{(-)i}$ is shifted towards the Ith bond and we obtain

$$Q_{ji} > Q_{ji}^o > 0, \quad R_{ij} < R_{ij}^o < 0, \quad |R_{ij}| > |R_{ij}^o| \tag{30}$$

and $\Delta p_{I(J-)} < 0$. Hence, a negative sign of the total induced dipole $\Delta p_{I(J)}$ follows. As a result, the HAO χ_{II} of the carbon atom C$_\beta$ loses its population, and an additional positive charge appears on this atom.

The contribution of the lone pair orbital $\varphi_{(+)II}$ to the indirect interaction of BOs $\varphi_{(+)i}$ and $\varphi_{(-)i}$ and thereby to the induced dipole moment of the Ith bond is

$$\Delta p_{I(L)} = -\frac{S_{ii} R_{li}}{E_{(+)II} - E_{(-)i}} \tag{31}$$

and it proves to be positive as $R_{li} < 0$. Hence, the electron-donating effect of the heteroatom contributes to a negative charge of the atom C$_\beta$. This conclusion is

in line with the results of Ref. [37] as well as with the expectation expressed in Refs. [38,39] that the so-called charge alternation in substituted alkanes following from certain numerical calculations might be due to overestimation of the electron-donating effect in the employed method.

It is seen, therefore, that contributions of the inductive and electron-donating effects of the heteroatom to the induced dipole moment of the C$_\alpha$–C$_\beta$ (C$_\alpha$–H) bond are of opposite signs, and the final result depends on their relative absolute values. In addition, the increment of the intramolecular charge transfer should be taken into consideration when looking for the total charge of the atom C$_\beta$ in the substituted molecule (see Eq. (9)).

The C–C (C–H) bonds have been established to lose their populations after substitution [30]. Hence, the charge transfer contributes to the positive charge of the atom C$_\beta$. Since the above-mentioned atom is commonly expected to be charged positively in the classical chemistry [4–7] on the basis of indirect experimental studies, the contribution of the electron-donating effect is likely to be a small correction only. This result is also borne out by evaluations of relative contributions of the inductive and electron-donating effects made in Ref. [37].

5. Conclusions

The results of the present study indicate the large extent of additivity of the heteroatom influence in substituted alkanes:

1. Substitution of hydrogen atoms by heteroatoms gives rise to extra terms being added to occupation numbers of HAOs of the parent hydrocarbon to obtain the respective occupation numbers for the substituted molecule.
2. These extra terms, in turn, are additive with respect to increments of separate heteroatoms so far as the C–C and C–H bonds of the substituted molecule are concerned.
3. Quantum-chemical analogues of the classical inductive and of the electron-donating effects of heteroatom within the population alteration due to substitution also prove to be additive.
4. Three additive components reveal themselves

within the quantum chemical analogues of the classical effects, and the relevant terms of the occupation numbers describe the secondary polarization and depolarization of bonds and the intramolecular charge transfer.

5. Each of the above-enumerated three intramolecular interactions has been expressed as the sum of partial increments of separate bonds and lone electron pairs being present in the given molecule.

The additive components of the classical effects have been studied in more detail. Thus, depolarization of bonds (i.e. a decrease of the primary dipole moment of the given bond after 'embedding' it into a molecule) proved to be peculiar to heteroatom-containing bonds only. As a result, populations of HAOs of C–C and C–H bonds in substituted alkanes are determined by the sum of intramolecular charge transfer and of the secondary polarization. The first of these increments leads to a decrease of the total population of the C–C (C–H) bond under study after introducing a heteroatom [30]. The secondary polarization gives rise to an emergence of an induced dipole moment of the given C–C (C–H) bond after substitution. This effect is related to the difference in the indirect interaction of the two BOs of this bond by means of BOs of the H–C (Z–C) bond before and after substitution.

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