

Interpretation of the inductive effect of heteroatoms in substituted alkanes on the basis of both the one-electron density matrix and localized molecular orbitals

V. Gineityte

Institute of Theoretical Physics and Astronomy, Gostauto 12, 2600 Vilnius, Lithuania

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Abstract

The general relation established previously between the one-electron density matrix (DM) of saturated organic molecules in the basis of bond orbitals and the relevant representation matrix of localized MOs (LMOs) was applied to investigate the inductive effect of heteroatoms in mono- and di-substituted alkanes. Local alterations in the electron density distribution after substitution peculiar to these systems were found to be accompanied by local changes in the extent of delocalization of the LMOs. This allowed the inductive effect to be interpreted in terms of either a perturbed DM or a change in shape of the LMOs compared to the corresponding situations in alkanes. Thus the well-known intuition-based account of the short-range nature of the inductive effect in alkanes being due to weak interbond delocalization was substantiated. The additive nature of the heteroatom influence is related to the additive nature of the interbond delocalization in alkanes.

Keywords: Inductive effect; Localized orbital; One-electron density; Saturated organic molecule; Substituted alkane

1. Introduction

The influence of a heteroatom (substituent) on the properties of the hydrocarbon fragment in substituted alkanes, usually referred to as the inductive effect, has been studied extensively using various physical and chemical methods [1]. An analysis of the information available on this subject shows that there are peculiarities of the effect that are common to the whole class of substituted alkanes. For example, the effect decreases rapidly (i.e. is short-range in nature) and roughly in proportion to the sum of the individual influences of the heteroatoms involved.

The main aim of the quantum theory of the

inductive effect lies in formulating common rules concerning the influence of a heteroatom in terms of its effect on orbitals and their populations and other quantum-chemical characteristics of molecules. Another important task of the theory is to reveal the role that the structural similarity between the initial and the substituted molecules plays in giving rise to the above peculiar effect. Thus the study of quantum-chemical models intended to describe substituted alkanes are of importance in this field.

The Hückel type Hamiltonian matrices for the saturated chain in the framework of the so-called “C-approximation” [2,3] and for a pair of neighbouring (geminal) bonds in substituted alkanes

[4–6] are among the simplest of these models. A closely related approach has been suggested by Del Re [7] and developed by Bhattacharyya and Bhaumik [8]. More sophisticated models of the inductive effect, based on one-electron perturbation theory (PT) in the framework of the semi-empirical Hamiltonian suggested by Parr, Pariser and Pople [9–11] and based on many-particle PT within the basis of the non-orthogonal geminals [12–15], have also been studied. The electron density distribution in systems of interest here has been investigated [9–15], and the results support the short-range nature of the heteroatom influence. Furthermore, simple concepts of the inductive effect in terms of the one-electron PT have been related to characteristics of the so-called “bond points” within the electron density functions [16]. It should be mentioned, however, in the above-mentioned models it is necessary to specify the chain structure, i.e. the number of atoms and/or basis orbitals.

The feasibility of a more general approach to investigating the inductive effect in substituted alkanes followed from the formulation and solving of the common quantum-mechanical problem for saturated molecules [17–22]. The common Hückel-type Hamiltonian matrices for alkanes and their derivatives have been constructed without any restraint regarding the structure of a particular chain.

The relevant common expressions for the one-electron density matrix (DM) of monosubstituted alkanes in the basis of sp^3 -hybridized AOs have been obtained and analysed [17–19]. It has been shown that, whatever the structure of the given molecule, the influence of heteroatom on the DM decreases rapidly and is determined by the interactions (overlaps) between the four sp^3 hybrid AOs and the 1s AOs localized on the perturbed (i.e. heteroatom containing) bond and on the bond under consideration. Therefore, these investigations support the assumption that the influence of a heteroatom is common and short-range in nature.

The most well-known intuition-based account for the short-range nature of the inductive effect originates from the concept of localized chemical bonds in both alkanes and their derivatives [23].

Thus, the weak inter-bond delocalization which is assumed to occur in saturated molecules is expected to prevent the heteroatom influence from extending over the whole system.

The hypothesis that semi-localized chemical bonds exist in saturated molecules is in line with the concept of localized MOs (LMOs) which is widely used in quantum chemistry. The LMOs may be obtained by transforming the occupied canonical MOs into the set of LMOs by using various localization criteria [23], and by direct calculation by means of the Brillouin theorem [20–25]. The optimum LMOs for saturated systems are composed of the main contribution pertaining to one chemical bond or lone pair and tails extending to the neighbouring bonds [26–28]. The tails reflect the extent of delocalization peculiar to the given molecule.

In this connection, basis sets of strictly localized two-centre bond orbitals (BOs) have been used extensively in the quantum chemical investigation of saturated molecules [20–22,24,25,28–39]. Various methods of obtaining BOs have been developed, e.g. optimization on the basis of total-energy minimization [35] and the use of eigenvectors of two-centre blocks of the one-electron DM [38,39]. The non-orthogonality of BOs has been considered explicitly [25,31,32,36,40].

Using the BO basis, the LMOs and DM of both saturated molecules in general [22] and alkanes in particular [20,21] have been shown to be closely interrelated, both being characterized by the same dependence on the structure of the system. Moreover, the two characteristics may be regarded as alternative localized descriptions of the electronic structure of these molecules. Hence, a direct link between local changes in the electron density distribution after introducing a heteroatom and the corresponding changes in the extent of inter-bond delocalization may be expected for saturated molecules.

Furthermore, peculiarities of the electronic structure of the parent hydrocarbons, including the extent of interbond delocalization, are expected to play an important part in producing the observed features of the inductive effect. Hence, the local perturbation of the DM due to the introduction of a heteroatom may also be related to

peculiarities of the LMOs and the DM of the parent alkane.

The aim of the present study was to establish the relationship between the peculiarities of the inductive effect (represented in terms of the perturbed DM) and the nature of the interbond delocalization in both alkanes and their derivatives. To this end, we used the general relationship between the LMOs and the DM of saturated organic molecules established previously [22]. This relation and its main consequences are overviewed briefly in Section 2 of this paper. On this basis, the LMOs and the DM of mono- and di-substituted alkanes were studied; the results are reported in Sections 3 and 4, respectively.

2. Relationship between the LMOs and DM of saturated molecules

Let us consider a saturated organic molecule in the basis of orthogonal BOs ϕ . Let these orbitals be defined as the eigenfunctions of separate two-dimensional Hamiltonian matrix blocks associated with either two sp^3 -hybridized AOs or one sp^3 -hybridized AO and the 1s AO of a hydrogen atom belonging to the same chemical bond. Accordingly, the total basis set $\{\phi\}$ consists of bonding BOs (BBOs) $\phi_{(+)}$ and antibonding BOs (ABOs) $\phi_{(-)}$ associated with the chemical bonds of the given molecule. The validity of the assumption of basis-set orthogonality within the model employed here has been discussed previously [40].

Let the first n BOs correspond to BBOs and the remaining n BOs correspond to antibonding BOs (ABOs). Then the common Hückel-type model Hamiltonian matrix \mathbf{H} of saturated organic molecules may be conveniently represented in terms of four blocks of dimensions $n \times n$. The diagonal and off-diagonal blocks of this matrix contain the resonance integrals inside the subspaces of the BBOs and ABOs, and the resonance integrals between the BOs of different types, respectively. As in Ref. [22], let us accept the first-order magnitude of the interactions (resonance integrals) between the BOs of different types as compared to the differences between the BBO and ABO energies. Then the

off-diagonal blocks R of the matrix \mathbf{H} are of first-order magnitude vs. the diagonal ones.

Furthermore, let the two diagonal blocks of the matrix \mathbf{H} to be represented as sums of the corresponding zero-order terms $E_{(+)}$ and $E_{(-)}$ and the corresponding first-order terms S and Q . The subscripts “+” and “-” here, and below, refer to BBOs $\phi_{(+)}$ and ABOs $\phi_{(-)}$. Then the total Hamiltonian matrix \mathbf{H} takes the form

$$\mathbf{H} = \mathbf{H}_{(0)} + \mathbf{H}_{(1)} \quad (1)$$

where

$$\mathbf{H}_{(0)} = \begin{vmatrix} \mathbf{E}_{(+)} & 0 \\ 0 & -\mathbf{E}_{(-)} \end{vmatrix} \quad (2)$$

and

$$\mathbf{H}_{(1)} = \begin{vmatrix} \mathbf{S} & \mathbf{R} \\ \mathbf{R}^+ & \mathbf{Q} \end{vmatrix} \quad (3)$$

are the zero- and first-order Hamiltonian matrices, respectively. The superscript “+” in Eq. (3) designates the transposed matrix, while the minus sign in front of $\mathbf{E}_{(-)}$ in Eq. (2) is introduced for convenience.

The one-electron DM (bond-order matrix) \mathbf{P} of the system described by the Hamiltonian matrix \mathbf{H} (Eqs. (1)–(3)) has been obtained previously [17–22] in the form of a power series:

$$\mathbf{P} = \mathbf{I} + \mathbf{Y} = \mathbf{I} + \mathbf{Y}_{(0)} + \mathbf{Y}_{(1)} + \mathbf{Y}_{(2)} + \dots \quad (4)$$

where \mathbf{Y} is the corresponding residual charge matrix which is connected with \mathbf{P} by the relation $\mathbf{Y} = \mathbf{P} - \mathbf{I}$. The first three terms in the series are

$$\mathbf{Y}_{(0)} = \begin{vmatrix} \mathbf{I}_{(n)} & 0 \\ 0 & -\mathbf{I}_{(n)} \end{vmatrix} \quad (5)$$

$$\mathbf{Y}_{(1)} = -2 \begin{vmatrix} 0 & \mathbf{G}_{(1)} \\ \mathbf{G}_{(1)}^+ & 0 \end{vmatrix} \quad (6)$$

$$\mathbf{Y}_{(2)} = -2 \begin{vmatrix} \mathbf{G}_{(1)}\mathbf{G}_{(1)}^+ & \mathbf{G}_{(2)} \\ \mathbf{G}_{(2)}^+ & -\mathbf{G}_{(1)}^+\mathbf{G}_{(1)} \end{vmatrix} \quad (7)$$

where $\mathbf{I}_{(n)}$ is the n -dimensional unit matrix. The matrices $\mathbf{G}_{(1)}$ and $\mathbf{G}_{(2)}$ have been established to

comply with the matrix equations

$$\mathbf{E}_{(+)}\mathbf{G}_{(1)} + \mathbf{G}_{(1)}\mathbf{E}_{(-)} + \mathbf{R} = 0 \quad (8)$$

$$\mathbf{E}_{(+)}\mathbf{G}_{(2)} + \mathbf{G}_{(2)}\mathbf{E}_{(-)} + \mathbf{V} = 0 \quad (9)$$

where

$$\mathbf{V} = \mathbf{S}\mathbf{G}_{(1)} - \mathbf{G}_{(1)}\mathbf{Q} \quad (10)$$

Alternatively, the same matrices may be represented in integral form

$$\mathbf{G}_{(1)} = \int_0^\infty \exp(\mathbf{E}_{(+)}t)\mathbf{R}\exp(\mathbf{E}_{(-)}t)dt \quad (11)$$

$$\mathbf{G}_{(2)} = \int_0^\infty \exp(\mathbf{E}_{(+)}t)\mathbf{V}\exp(\mathbf{E}_{(-)}t)dt \quad (12)$$

The occupation numbers (populations) of the BOs are

$$\mathbf{X}_{(+i)} = 2 \left[1 - \sum_r^{\text{ABOs}} (\mathbf{G}_{(1)ri}^+)^2 \right] \quad (13a)$$

$$\mathbf{X}_{(-m)} = 2 \sum_i^{\text{BBOs}} (\mathbf{G}_{(1)im})^2 \quad (13b)$$

for the BBOs $\phi_{(+i)}$ and the ABOs $\phi_{(-m)}$, respectively. The subscripts i and j are used here, and below, to denote BBOs, whereas k , m and r refer to ABOs.

The corresponding LMO representation matrix T has also been obtained previously [20–22] in the form of a power series:

$$\mathbf{T} = \mathbf{I}_{(2n)} + \mathbf{T}_{(1)} + \mathbf{T}_{(2)} + \dots \quad (14)$$

where $\mathbf{I}_{(2n)}$ is the $2n$ -dimensional unit matrix, and

$$\mathbf{T}_{(1)} = \begin{vmatrix} 0 & \mathbf{G}_{(1)} \\ -\mathbf{G}_{(1)}^+ & 0 \end{vmatrix} \quad (15)$$

$$\mathbf{T}_{(2)} = \begin{vmatrix} -\frac{1}{2}\mathbf{G}_{(1)}\mathbf{G}_{(1)}^+ & \mathbf{G}_{(2)} \\ -\mathbf{G}_{(2)}^+ & -\frac{1}{2}\mathbf{G}_{(1)}^+\mathbf{G}_{(1)} \end{vmatrix} \quad (16)$$

On the basis of Eq. (14) and (15), the occupied LMO $\Psi_{(+i)}$ and the vacant LMO $\Psi_{(-m)}$, to within first-order terms, may be presented in the form

$$\Psi_{(+i)} = \phi_{(+i)} - \sum_r^{\text{ABOs}} \phi_{(-r)}\mathbf{G}_{(1)ri}^+ \quad (17a)$$

$$\Psi_{(-m)} = \phi_{(-m)} + \sum_j^{\text{BBOs}} \phi_{(+j)}\mathbf{G}_{(1)jm}^+ \quad (17b)$$

The additivity of the delocalization of the LMOs with respect to the contributions from various ABOs (BBOs) may be concluded from Eqs. (17a) and (17b).

As previously [21,22], let us define the positive partial delocalization coefficients of the LMOs $\Psi_{(+i)}$ and $\Psi_{(-m)}$ over the ABO $\phi_{(-r)}$ and the BBO $\phi_{(+j)}$, respectively:

$$d_{(+i),(-r)} = (\mathbf{G}_{(1)ri}^+)^2 \quad (18a)$$

$$d_{(-m),(+j)} = (\mathbf{G}_{(1)jm}^+)^2 \quad (18b)$$

As $\mathbf{G}_{(1)ri}^+ = \mathbf{G}_{(1)ir}$, coupled pairs of equal partial delocalization coefficients are revealed, i.e. $d_{(+i),(-r)} = d_{(-r),(+i)}$.

Accordingly, the total delocalization coefficients of the LMOs $\Psi_{(+i)}$ and $\Psi_{(-m)}$ may be defined as

$$D_{(+i)} = \sum_r^{\text{ABOs}} d_{(+i),(-r)} \quad (19a)$$

$$D_{(-m)} = \sum_j^{\text{BBOs}} d_{(-m),(+j)} \quad (19b)$$

Then the interrelations between the occupation numbers of the BBOs and ABOs (Eqs. (13a) and (13b)) on the one hand, and the total delocalization coefficients $D_{(+i)}$ and $D_{(-m)}$ of the corresponding LMOs $\Psi_{(+i)}$ and $\Psi_{(-m)}$ on the other, follow from Eqs. (18) and (19):

$$X_{(+i)} = 2(1 - D_{(+i)}) \quad (20a)$$

$$X_{(-m)} = 2D_{(-m)} \quad (20b)$$

As a result, the population of the BBO $\phi_{(+i)}$ lost when making up the LMO $\Psi_{(+i)}$ is proportional to the total delocalization of the latter. Similarly, the population $X_{(-m)}$ that the ABO $\phi_{(-m)}$ acquires when making up the LMO $\Psi_{(-m)}$ is proportional to the total delocalization of this LMO.

Alternatively, using Eqs. (19) and (20) we obtain the expressions for the occupation numbers of the BOs in terms of partial delocalization coefficients:

$$X_{(+i)} = 2 \left(1 - \sum_r^{\text{ABOs}} d_{(+i),(-r)} \right) \quad (20c)$$

$$X_{(-m)} = 2 \sum_j^{\text{BBOs}} d_{(-m),(+j)} \quad (20d)$$

Hence, both the population of the BBO $\phi_{(+i)}$ lost when making up the LMO $\Psi_{(+i)}$ and that acquired by the ABO $\phi_{(-m)}$ in the formation of the LMO $\Psi_{(-m)}$ are additive with respect to the contributions from the various ABOs and BBOs of the remaining part of the molecule.

Let us look now at two specific cases.

(i) Let the blocks $\mathbf{E}_{(+)}$ and $\mathbf{E}_{(-)}$ be diagonal matrices with the elements $E_{(+i)}$ and $E_{(-r)}$, respectively. Then the elements of the principal matrix $\mathbf{G}_{(1)}$ take a simple algebraic form

$$G_{(1)ir} = G_{(1)ri}^+ = \frac{-R_{ir}}{(E_{(+i)} + E_{(-r)})} \quad (21)$$

(ii) Let the blocks $\mathbf{E}_{(+)}$ and $\mathbf{E}_{(-)}$ of Eq. (2) to be proportional to the n -dimensional unit matrix $\mathbf{I}_{(n)}$, i.e. $\mathbf{E}_{(+)}^{(a)} = \mathbf{E}_{(-)}^{(a)} = \beta \mathbf{I}_{(n)}$, where β is the negative energy unit. This case corresponds to alkanes and implies identical values of the zero-order energies associated with the BBOs and with the ABOs [20,21]. The superscript (a) here, and below, refers to the case of alkanes. Accordingly, 2β should be substituted for the energy in the denominator in Eq. (21), and the corresponding matrix elements $G_{(1)ir}^{(a)}$ follow.

The elements $G_{(1)ir}$ and $G_{(1)ir}^{(a)}$ describe the direct through-space interaction between the BBO $\phi_{(+i)}$ and the ABO $\phi_{(-r)}$ [20,22]. It should be noted, however, that such an interpretation follows in the basis of orthogonal BOs only.

On the whole, both the partial delocalization coefficients defined by Eqs. (18) and individual contributions to the populations of BOs given by Eqs. (20c) and (20d) may be expected to decrease rapidly when the relevant interbond distance increases. Moreover, transferable values of contributions associated with similarly arranged pairs of identical bonds also follows from the model employed.

3. Investigation of the inductive effect in monosubstituted alkanes

Let us apply the above-summarized expressions for the DM and LMOs to monosubstituted alkanes containing a single heteroatom Z. The electronegativity of Z is assumed to be higher than that of hydrogen and carbon atoms (electronegativities

of the latter are similar to one another [41]). To simplify the problem, the blocks $\mathbf{E}_{(+)}$ and $\mathbf{E}_{(-)}$ in Eq. (2) are assumed to be diagonal, i.e. it is assumed that the values for the interactions between BOs of different types and interactions inside the subspaces of the BBOs and ABOs are similar. Estimates of such values made previously [5,6] for substituted alkanes bear out this assumption. It is also assumed that no lone pairs of electrons have any effect on the heteroatom Z.

Let $\phi_{(+1)}$ and $\phi_{(-1)}$ be the only BBO and the coupled ABO of the $C_\alpha-Z$ bond, respectively. In accordance with the higher electronegativity of atom Z compared to the hydrogen and carbon atoms, let us assume that the corresponding one-electron energies of the BOs of the $C_\alpha-Z$ bond $E_{(+1)}$ and $-E_{(-1)}$ are situated below the BBO and ABO energies of the remaining hydrocarbon fragment, respectively. The latter, in turn, are taken equal to β and $-\beta$, as for alkanes [20].

Under these approximations, the blocks $\mathbf{E}_{(+)}$ and $\mathbf{E}_{(-)}$ of the zero Hamiltonian matrix $\mathbf{H}_{(0)}$ (Eq. (2)) take the form

$$\mathbf{E}_{(+)} = \beta \begin{vmatrix} \epsilon_{(+)} & 0 \\ 0 & \mathbf{I}_{(n-1)} \end{vmatrix} \quad (22a)$$

$$\mathbf{E}_{(-)} = \beta \begin{vmatrix} \epsilon_{(-)} & 0 \\ 0 & \mathbf{I}_{(n-1)} \end{vmatrix} \quad (22b)$$

where

$$\epsilon_{(+)} = \frac{E_{(+1)}}{\beta} \quad (23a)$$

$$\epsilon_{(-)} = \frac{E_{(-1)}}{\beta} \quad (23b)$$

are positive parameters describing the energies of the BBO $\phi_{(+1)}$ and ABO $\phi_{(-1)}$ in β units (with the negative sign in front of $\mathbf{E}_{(-)}$ in Eq. (2), these negative units yield negative actual values for BBO energies and positive ones for ABO energies). In accordance with the above-accepted relative positions of the energies $E_{(+1)}$ and $-E_{(-1)}$, we obtain

$$\epsilon_{(+)} > 1; \quad \epsilon_{(-)} < 1 \quad (24)$$

Furthermore, let us assume for simplicity that the only change in the Hamiltonian matrix when passing from the parent alkane to the corresponding

substituted molecule consists of replacing 1 by $\epsilon_{(+)}$ and -1 by $-\epsilon_{(-)}$, whilst the first-order Hamiltonian matrices $\mathbf{H}_{(1)}$ (Eq. (3)) are the same for both systems, i.e.

$$\mathbf{H}_{(1)} = \mathbf{H}_{(1)}^{(a)} \quad (25)$$

This approximation resembles those used when discussing the influence of heteroatoms in conjugated hydrocarbons [42], wherein a heteroatom is modelled by changing only the Coulomb integral of the relevant $2p_z$ AO.

As BOs have been defined as eigenfunctions of the Hamiltonian matrix blocks of dimensions 2×2 ascribed to chemical bonds (see Section 2), zero values for the diagonal elements of the matrices \mathbf{R} and \mathbf{R}^+ (Eq. (3)), and thereby of matrices $\mathbf{G}_{(1)}$ ($\mathbf{G}_{(1)}^{(a)}$) (Eq. (21)), are also possible, i.e.

$$R_{ii} = R_{ii}^+ = 0; \quad G_{(1)ii} = G_{(1)ii}^+ = 0; \\ G_{(1)ii}^{(a)} = G_{(1)ii}^{+(a)} = 0 \quad (26)$$

Thus within the framework of this simple approach, only two types of non-diagonal elements of the matrix $\mathbf{G}_{(1)}$ associated with the substituted molecule, viz. $G_{(1)lr}$ ($r = 2, 3, \dots, n$) and $G_{(1)j1}$ ($j = 2, 3, \dots, n$), differ from the corresponding elements for alkanes:

$$G_{(1)lr} = G_{(1)lr}^+ = \frac{-R_{lr}}{(1 + \epsilon_{(+)})}; \\ G_{(1)j1} = G_{(1)j1}^+ = \frac{-R_{j1}}{(1 + \epsilon_{(-)})} \quad (27a)$$

and

$$G_{(1)lr}^{(a)} = G_{(1)lr}^{+(a)} = \frac{-R_{lr}}{2}; \\ G_{(1)j1}^{(a)} = G_{(1)j1}^{+(a)} = \frac{-R_{j1}}{2} \quad (27b)$$

The equality $\beta = 1$ is accepted here, and below, for convenience.

From Eqs. (17a) and (17b) it follows that only the occupied LMO $\Psi_{(+1)}$ and the coupled vacant LMO $\Psi_{(-1)}$ associated with the C_α -Z bond acquire entirely new shapes when a heteroatom is introduced. With regard to the other LMOs, only the partial delocalization coefficients over the BBO $\phi_{(+1)}$ and ABO $\phi_{(-1)}$ change after substitution.

3.1. Characteristics of the C_α -Z bond

The total delocalization coefficients of the LMOs $\Psi_{(+1)}$ and $\Psi_{(-1)}$ follow from Eqs. (18), (19) and (27). The coefficients are given by

$$D_{(+1)} = (1 + \epsilon_{(+)})^{-2} \sum_r^{\text{ABOs}} (R_{1r})^2; \\ D_{(-1)} = (1 + \epsilon_{(-)})^{-2} \sum_j^{\text{BBOs}} (R_{j1})^2 \quad (28a)$$

and

$$D_{(+1)}^{(a)} = \frac{1}{4} \sum_r^{\text{ABOs}} (R_{1r})^2; \quad D_{(-1)}^{(a)} = \frac{1}{4} \sum_j^{\text{BBOs}} (R_{j1})^2 \quad (28b)$$

for the substituted molecule and the parent hydrocarbon, respectively. It can be seen from Eqs. (24), (28a) and (28b) that the total delocalization of the occupied LMO $\Psi_{(+1)}$ decreases, whereas that of the vacant LMO $\Psi_{(-1)}$ increases compared to the corresponding values for the parent alkane, i.e.

$$D_{(+1)} < D_{(+1)}^{(a)}; \quad D_{(-1)} > D_{(-1)}^{(a)} \quad (29)$$

Similarly, from Eqs. (20) and (29) it follows that

$$X_{(+1)} > X_{(+1)}^{(a)}; \quad X_{(-1)} > X_{(-1)}^{(a)} \quad (30)$$

Therefore, due to the decreased delocalization of the LMO $\Psi_{(+1)}$, the population of the BBO $\phi_{(+1)}$ is lost to a smaller extent when building up the substituted molecule than in the parent alkane. Alternatively, more charge is acquired by the ABO $\phi_{(-1)}$ in the substituted molecule than in the parent alkane owing to the increased delocalization of the LMO $\Psi_{(-1)}$. As a result, the total population of the C_α -Z bond is increased after the introduction of a heteroatom.

The occupation numbers $X_{(+1)}$ and $X_{(-1)}$ may also be related to the values of the total delocalization coefficients in the parent alkanes ($D_{(+1)}^{(a)}$ and $D_{(-1)}^{(a)}$). Thus, on the basis of Eqs. (28) we obtain

$$D_{(+1)} = pD_{(+1)}^{(a)}; \quad D_{(-1)} = qD_{(-1)}^{(a)} \quad (31)$$

where

$$p = \frac{4}{(1 + \epsilon_{(+)})^2} < 1; \quad q = \frac{4}{(1 + \epsilon_{(-)})^2} > 1 \quad (32)$$

Accordingly, the changes in the occupation numbers of the BBO $\phi_{(+)1}$ and the ABO $\phi_{(-)1}$ after substitution are

$$\Delta X_{(+)1} = X_{(+)1} - X_{(+)1}^{(a)} = 2(1 - p)D_{(+)1}^{(a)} > 0 \quad (33)$$

and

$$\Delta X_{(-)1} = X_{(-)1} - X_{(-)1}^{(a)} = 2(q - 1)D_{(-)1}^{(a)} > 0 \quad (34)$$

and prove to be proportional to the delocalization coefficients of the LMOs $\Psi_{(+)1}^{(a)}$ and $\Psi_{(-)1}^{(a)}$ in alkanes.

Therefore, the more delocalized the LMOs of the C–H bond are before substitution, the stronger the inductive effect will be expected to be in the corresponding substituted molecule. This result is in line with the intuitive ideas about the important role that the interbond delocalization in alkanes plays in the peculiarities of the inductive effect (see Section 1).

Let us consider in more detail the case where there are small differences in the electronegativities of the carbon, hydrogen and Z atoms. The following approximate expressions for $\epsilon_{(+)}$, $\epsilon_{(-)}$, p and q may be accepted in this case

$$\epsilon_{(+)} \approx \epsilon_{(+)}^{(0)} = 1 + \alpha; \quad \epsilon_{(-)} \approx \epsilon_{(-)}^{(0)} = 1 - \gamma \quad (35)$$

$$p \approx p^{(0)} = 1 - \alpha, \quad q \approx q^{(0)} = 1 + \gamma \quad (36)$$

where α and γ are parameters that are small compared to 1. The differences in the occupation numbers (Eqs. (33) and (34)) become

$$\Delta X_{(+)1}^{(0)} = 2\alpha D_{(+)1}^{(a)}; \quad \Delta X_{(-)1}^{(0)} = 2\gamma D_{(-)1}^{(a)} \quad (37)$$

As in the case of conjugated hydrocarbons [42], the self-polarizabilities of the BOs $\phi_{(+)1}$ and $\phi_{(-)1}$ may be introduced

$$\Pi_{(+)1,(+)1} = 2D_{(+)1}^{(a)}; \quad \Pi_{(-)1,(-)1} = 2D_{(-)1}^{(a)} \quad (38)$$

and these also prove to be proportional to the total delocalization of the corresponding LMOs in the initial alkane.

Let us turn again to the changes in the populations $\Delta X_{(+)1}$ and $\Delta X_{(-)1}$ after the introduction of a heteroatom of any electronegativity. These differences in the occupation numbers may be also expressed in terms of differences in the partial delocalization coefficients (Eqs. (20c) and (20d)). As a result, the changes in the population of the C_α –Z bond after substitution proves to be additive with respect to the contributions of all the C–C and C–H bonds in the hydrocarbon fragment of the molecule. A similar rule has been established in the basis of sp^3 -hybridized AOs and H1s AOs [43].

If we take into account the interactions between the BOs belonging to the C_α –Z bond and those of the nearest-neighbour (geminal) bonds only, the changes in the population of the C_α –Z bond ($\Delta X_{(+)1}$ and $\Delta X_{(-)1}$) are transferable because the number of these neighbouring bonds is always 3 in all substituted alkanes. This situation is analogous to that for the dipole moments of C_α –Z bonds containing the same heteroatom Z, a situation which has been confirmed experimentally [1,41] for various substituted alkanes. However, if we consider also the contributions of the second-neighbour (vicinal) bonds, certain deviations from a direct transferability of values might be expected for the population changes $\Delta X_{(+)1}$ and $\Delta X_{(-)1}$.

These deviations are likely to be largest when passing from substituted methanes to ethanes. Indeed, the latter molecules contain additional second-neighbour (vicinal) C–H bonds with respect to the C_α –Z bond and thus additional contributions to the population changes $\Delta X_{(+)1}$ and $\Delta X_{(-)1}$. Therefore, there is an increase in $X_{(-)1}$ and a decrease in $X_{(+)1}$ for substituted ethanes compared with the corresponding populations of the BOs $\phi_{(+)1}$ and $\phi_{(-)1}$ in substituted methanes. As, according to Eq. (32), $q > p$, the increases in both $D_{(-)1}$ and $X_{(-)1}$ exceed the absolute values of the corresponding changes in $D_{(+)1}$ and $X_{(+)1}$. Thus an increase in the total occupation of the C_α –Z bond in substituted ethanes over that in substituted methanes follows from our model. These additional population changes, however, may be

expected to be smaller than the strength of the inductive effect itself.

The above conclusions also correlate with the experimentally observed trends: a definite increase in the dipole moment of the $C_{\alpha}-Z$ bond is observed when passing from substituted methanes to substituted ethanes [1]. Moreover, the electron spectroscopy for chemical analysis (ESCA) spectra of chloromethanes and chloroethanes [44] indicate an increased population of chlorine atoms in the latter case.

3.2. Characteristics of the C–C and C–H bonds

Populations of BBOs $\phi_{(+)i}$ ($i \neq 1$) belonging to the hydrocarbon fragment are also described by Eqs. (20). As only the term $d_{(+)i,(-)1} = (G_{(1)1i}^+)^2$ differs from the corresponding terms for alkanes in the sum of Eq. (20c), let us rewrite the total delocalization coefficient $D_{(+)i}$ of the LMO $\Psi_{(+)i}$ in the form

$$D_{(+)i} = D_{(+)i}^{(a)} + \Delta D_{(+)i} \quad (39)$$

where the difference

$$\begin{aligned} \Delta D_{(+)i} &= \frac{1}{4}(q-1)(R_{i1})^2 = (q-1)(G_{(1)1i}^{(a)})^2 \\ &= (q-1)d_{(+)i,(-)1}^{(a)} \\ &= (q-1)d_{(-)1,(+)i}^{(a)} > 0 \end{aligned} \quad (40)$$

describes the change in the delocalization coefficient $D_{(+)i}$ after substitution. Equations (18) and (21) for alkanes were used to obtain Eq. (40), and the equality $d_{(+)i,(-)1} = d_{(-)1,(+)i}$ following from Eq. (18) was employed.

Since $q > 1$, as shown by Eq. (32), increased delocalization, as compared to that in the corresponding LMO $\Psi_{(+)i}^{(a)}$ of the parent alkane, is peculiar to the LMO $\Psi_{(+)i}$ of the substituted molecule. This additional delocalization originates from the increased partial delocalization coefficient of the LMO $\Psi_{(+)i}$ over the ABO $\phi_{(-)1}$. Alternatively, the difference $\Delta D_{(+)i}$ (Eq. (40)) proves to be proportional to the initial value of the partial delocalization coefficient in the parent alkane and, because of the equality $d_{(+)i,(-)1}^{(a)} = d_{(-)1,(+)i}^{(a)}$, this difference may also be regarded as being proportional to the mutual delocalization of BOs $\phi_{(+)i}^{(a)}$ and $\phi_{(-)1}^{(a)}$.

The difference in the population of the BBO $\phi_{(+)i}$ before and after substitution follows from Eqs. (20a), (39) and (40):

$$\begin{aligned} \Delta X_{(+)i} &= X_{(+)i} - X_{(+)i}^{(a)} = \frac{1}{2}(1-q)(R_{i1})^2 \\ &= 2(1-q)d_{(+)i,(-)1}^{(a)} = 2(1-q)d_{(-)1,(+)i}^{(a)} < 0 \end{aligned} \quad (41)$$

As a result, the population of the BBO $\phi_{(+)i}$ decreases after substitution, whatever the position of the C–C (C–H) bond being studied and whatever the structure of the molecule which contains it.

Similarly, the total delocalization coefficient $D_{(-)m}$ of a vacant LMO $\Psi_{(-)m}$ may be shown to decrease after substitution, the decrease being due to the reduced partial delocalization of this LMO over the BBO $\phi_{(+)1}$. Accordingly, the change in the occupation number of the ABO $\phi_{(-)m}$ follows from Eq. (20b):

$$\begin{aligned} \Delta X_{(-)m} &= X_{(-)m} - X_{(-)m}^{(a)} = \frac{1}{2}(p-1)(R_{1m})^2 \\ &= 2(p-1)d_{(+)1,(-)m}^{(a)} \\ &= 2(p-1)d_{(-)m,(+)1}^{(a)} < 0 \end{aligned} \quad (42)$$

Hence, the occupation number of the ABO $\phi_{(-)m}$ decreases after substitution, the decrease being proportional to the mutual partial delocalization of the BOs $\phi_{(+)1}^{(a)}$ and $\phi_{(-)m}^{(a)}$ in the parent alkane.

On the whole, it may be concluded that the total populations of the C–C and C–H bonds are reduced after substitution, a finding which is in line with the electron-accepting nature of the heteroatom Z.

In the case of a heteroatom Z with an electronegativity that insignificantly differs from those of the carbon and hydrogen atoms, the approximations given in Eqs. (35) and (36) may be used to reformulate Eqs. (41) and (42). We then obtain

$$\begin{aligned} \Delta X_{(+)i}^{(0)} &= -2\gamma d_{(+)i,(-)1}^{(a)} \\ &= -2\gamma d_{(-)1,(+)i}^{(a)} < 0 \end{aligned} \quad (43a)$$

$$\begin{aligned} \Delta X_{(-)m}^{(0)} &= -2\alpha d_{(+)1,(-)m}^{(a)} \\ &= -2\alpha d_{(-)m,(+)1}^{(a)} < 0 \end{aligned} \quad (43b)$$

Accordingly, the relevant orbital–orbital polarizabilities may be introduced:

$$\begin{aligned}\Pi_{(-)1,(+)i} &= \Pi_{(+)i,(-)1} = -2d_{(-)1,(+)i}^{(a)} \\ &= -2d_{(+)i,(-)1}^{(a)}\end{aligned}\quad (44a)$$

$$\begin{aligned}\Pi_{(+)1,(-)m} &= \Pi_{(-)m,(+)1} = -2d_{(+)1,(-)m}^{(a)} \\ &= -2d_{(-)m,(+)1}^{(a)}\end{aligned}\quad (44b)$$

Hence, in contrast to the self-polarizabilities of BOs defined by Eq. (38), the orbital-orbital polarizabilities involve partial delocalization coefficients rather than the total ones.

Finally, definite conclusions may be drawn regarding the relative values of the various changes in the populations of the C–C and C–H bonds. Because of the through-space nature of the partial delocalization coefficients, absolute values of the differences $\Delta X_{(+)i}$ and $\Delta X_{(-)m}$ decrease rapidly when the distance between the C_α –Z bond and the bond under consideration increases. Hence, the well-known short-range nature of the inductive effect is borne out by our investigation and the intuition-based account of this phenomenon in terms of the interbond delocalization in alkanes is supported.

The relative values of the two differences in the populations of BOs ($\Delta X_{(+)i}$ and $\Delta X_{(-)m}$) depend only on the spatial arrangement of two bonds, i.e. the C_α –Z bond and the bond under study. This conclusion is in line with the results of studies [17–19] done in the basis of sp^3 -hybridized AOs and H1s AOs. The through-space nature of the heteroatom influence found here also serves to support early models of the inductive effect (see Section 1) which either neglected completely the C–H bonds (the so-called “C-approximation”) or considered only the four orbitals of two bonds.

4. Influence of heteroatoms in disubstituted alkanes

Let us consider a disubstituted alkane containing two identical heteroatoms Z_1 and Z_2 in positions 1 and 2, respectively. The following treatment

applies to any mutual arrangement of these heteroatoms.

The heteroatoms Z_1 and Z_2 are supposed to be described by the parameters $\epsilon_{(+)}$ and $\epsilon_{(-)}$ in Eq. (23). The conditions given by Eqs. (24)–(26) are also assumed to be valid for the disubstituted molecule. In particular, we assume that there is no change in the resonance integrals on passing from mono- to disubstituted molecules; i.e. $\tilde{H}_{(1)} = H_{(1)} = H_{(1)}^+$, where terms associated with disubstituted molecule are denoted here, and below, by \sim . Then five types of non-diagonal elements of the matrix $\tilde{G}_{(1)}$ (namely $\tilde{G}_{(1)1r}$, $\tilde{G}_{(1)2r}$ ($r = 3, 4, \dots, n$), $\tilde{G}_{(1)j1}$, $\tilde{G}_{(1)j2}$ ($j = 3, 4, \dots, n$) and $\tilde{G}_{(1)12}$) differ from the corresponding elements for the parent alkanes:

$$\begin{aligned}\tilde{G}_{(1)1r} &= \tilde{G}_{(1)r1}^+ = \frac{-R_{1r}}{(1 + \epsilon_{(+)})}; \\ \tilde{G}_{(1)j1} &= \tilde{G}_{(1)1j}^+ = \frac{-R_{j1}}{(1 + \epsilon_{(-)})}\end{aligned}\quad (45a)$$

$$\begin{aligned}\tilde{G}_{(1)2r} &= \tilde{G}_{(1)r2}^+ = \frac{-R_{2r}}{(1 + \epsilon_{(+)})}; \\ \tilde{G}_{(1)j2} &= \tilde{G}_{(1)2j}^+ = \frac{-R_{j2}}{(1 + \epsilon_{(-)})}\end{aligned}\quad (45b)$$

$$\tilde{G}_{(1)12} = \tilde{G}_{(1)21}^+ = \frac{-R_{12}}{(\epsilon_{(+)} + \epsilon_{(-)})}\quad (45c)$$

Let us start by discussing the BOs associated with the hydrocarbon fragment of the molecule. Consider the population $\tilde{X}_{(+)i}$ of the BBO $\tilde{\phi}_{(+)i}$ ($i \neq 1$ or 2). In contrast to the case of the monosubstituted molecule, two terms of the sum in Eq. (20c), namely $\tilde{d}_{(+)i,(-)1} = (\tilde{G}_{(1)1i}^+)^2$ and $\tilde{d}_{(+)i,(-)2} = (\tilde{G}_{(1)2i}^+)^2$, differ from the corresponding terms for the parent alkanes.

The change in the occupation number of the BBO $\phi_{(+)i}$ is then

$$\Delta \tilde{X}_{(+)i} = 2(1 - q)(d_{(+)i,(-)1}^{(a)} + d_{(+)i,(-)2}^{(a)}) < 0\quad (46)$$

Comparison of Eqs. (41) and (46) shows that the total change in the population of the BBO $\phi_{(+)i}$ after introducing two heteroatoms Z_1 and Z_2 is additive with respect to the partial increments due to the first and second heteroatoms. An analogous

rule has been established on the basis of sp^3 -hybridized AOs and H1s AOs [43].

Similarly, the change in the population of the ABO $\phi_{(-)m}$ ($m \neq 1$ or 2) is given by

$$\Delta \tilde{X}_{(-)m} = 2(p-1)(d_{(+1),(-)m}^{(a)} + d_{(+2),(-)m}^{(a)}) < 0 \quad (47)$$

Therefore, it may be concluded that the total effect of two heteroatoms on the hydrocarbon fragment is the sum of the two individual effects and originates from the through-space nature of the heteroatom influence.

These results are in line with the characteristics observed in the ESCA spectra of dichloroethanes [44]: the chemical shifts ascribed to the C_β atoms in these spectra are roughly proportional to the number of chlorine atoms at the C_α atom.

Let us turn now to populations of BOs belonging to the $C-Z_1$ and $C-Z_2$ bonds in disubstituted alkanes. Consider one of these bonds, e.g. the $C-Z_1$, bond. Two terms ($\tilde{d}_{(+1),(-)2}$ and $\tilde{d}_{(-1),(+2)}$) in the sums of Eq. (19) differ from those for monosubstituted alkanes. On the basis of Eqs. (18), (24), (27a) and (45c) we then obtain

$$\tilde{D}_{(+1)} > D_{(+1)}; \quad \tilde{D}_{(-1)} < D_{(-1)} \quad (48)$$

Thus the total delocalization coefficients of the LMOs $\tilde{\Psi}_{(+1)}$ and $\tilde{\Psi}_{(-1)}$ are somewhat increased and decreased, respectively, in the disubstituted molecule compared to the corresponding coefficients $D_{(+1)}$ and $D_{(-1)}$ for the monosubstituted alkane. Nevertheless, $\tilde{D}_{(+1)}$ remains lower than $D_{(+1)}^{(a)}$ in the parent alkane, whereas $\tilde{D}_{(-1)}$ remains higher than $D_{(-1)}^{(a)}$. The reason for this lies in the fact that all the partial delocalization coefficients of the LMO $\Psi_{(+1)}$ decrease when passing from the parent alkane to the monosubstituted molecule (see Section 3), and only one of them ($d_{(+1),(-)2}$) increases again on introducing the second heteroatom. Similarly, all the partial coefficients of the LMO $\Psi_{(-1)}$ increase after the first substitution, whereas only one of them ($d_{(-1),(+2)}$) reduces again on the second substitution.

Therefore, the changing nature of the bond at the position of the second substitution gives rise to changes in the extent of delocalization of the LMOs associated with the $C_\alpha-Z_1$ bond, and this

determines the relevant differences in the populations, viz.

$$\begin{aligned} \Delta \tilde{X}_{(+1)} &= \tilde{X}_{(+1)} - X_{(+1)} \\ &= -2(\tilde{d}_{(+1),(-)2} - d_{(+1),(-)2}) < 0 \end{aligned} \quad (49a)$$

$$\begin{aligned} \Delta \tilde{X}_{(-1)} &= \tilde{X}_{(-1)} - X_{(-1)} \\ &= 2(\tilde{d}_{(-1),(+2)} - d_{(-1),(+2)}) < 0 \end{aligned} \quad (49b)$$

The negative signs of the population changes in Eqs. (49) imply a decreased total occupation of the $C_\alpha-Z$ bond in the disubstituted alkane compared with that in the monosubstituted molecule.

Therefore, a mutually suppressing effect of two heteroatoms may be concluded to take place, the extent of the effect of this depending on the mutual arrangement of the $C-Z_1$ and $C-Z_2$ bonds and on the relevant interbond distance but independent of the remainder of the molecule. As a result, the mutual influence of two heteroatoms may be expected to decrease when the interbond distance increases and to be transferable for a given pair of heteroatoms, whatever the structure of the rest of molecule.

As the populations $\tilde{X}_{(+1)}$ and $\tilde{X}_{(-1)}$ in the disubstituted alkane remain higher than the corresponding values ($X_{(+1)}^{(a)}$ and $X_{(-1)}^{(a)}$) in the unsubstituted alkanes, owing to the inequalities $\tilde{D}_{(+1)} < D_{(+1)}^{(a)}$ and $\tilde{D}_{(-1)} > D_{(-1)}^{(a)}$, the mutually suppressing influence of two heteroatoms may be concluded to be weaker than the inductive effect itself. It should be noted that the mutually suppressing influence of two geminal heteroatoms has been observed experimentally when comparing the relevant dipole moments of the $C_\alpha-Z$ bonds [1].

In the case of a small difference between the electronegativity of the heteroatom and the electronegativities of the carbon and hydrogen atoms, the changes of the occupation numbers $\Delta \tilde{X}_{(+1)}$ and $\Delta \tilde{X}_{(-1)}$ given in Eqs. (49) are now expressed in terms of the orbital-orbital polarizabilities defined by Eqs. (44):

$$\begin{aligned} \Delta \tilde{X}_{(+1)}^{(0)} &= -\frac{1}{2} \gamma (R_{12})^2 = -2\gamma d_{(+1),(-)2}^{(a)} \\ &= \gamma \Pi_{(+1),(-)2} \end{aligned} \quad (50a)$$

$$\begin{aligned}\Delta\tilde{X}_{(-)1}^{(0)} &= -\frac{1}{2}\alpha(R_{12})^2 = -2\alpha d_{(-)1,(+)2}^{(a)} \\ &= \alpha\Pi_{(-)1,(+)2}\end{aligned}\quad (50b)$$

Hence the mutual suppressing influence of two slightly electronegative heteroatoms Z_1 and Z_2 is proportional to the orbital–orbital polarizabilities of BOs $\phi_{(+)1}^{(a)}$ and $\phi_{(-)2}^{(a)}$ in addition to the $\phi_{(-)1}^{(a)}$ and $\phi_{(+)2}^{(a)}$ in the parent alkane: the larger these polarizabilities are, the stronger the mutual influence of the heteroatoms on the disubstituted molecule.

Let us now compare the effect of a single slightly electronegative heteroatom Z_1 on the C–C or C–H bond in position 2 of the monosubstituted alkane and the mutual influence of two heteroatoms in positions 1 and 2 in the disubstituted molecule. In accordance with Eqs. (43) and (44), the population changes $\Delta X_{(+)2}^{(0)}$ and $\Delta X_{(-)2}^{(0)}$ in BOs $\phi_{(+)2}$ and $\phi_{(-)2}$ in the monosubstituted case are equal to $\gamma\Pi_{(-)1,(+)2}$ and $\alpha\Pi_{(-)2,(+)1}$, respectively; the same expressions follow for the changes $\Delta\tilde{X}_{(+)2}^{(0)}$ and $\Delta\tilde{X}_{(-)2}^{(0)}$ for the disubstituted molecule. Therefore, it will be expected that the stronger the effect of a given heteroatom on the hydrocarbon fragment, the stronger the mutual influence of two similar heteroatoms will be. An analogous conclusion has been drawn previously [45] in the basis of four sp^3 -hybridized AOs belonging to two geminal bonds.

On the whole, both the additive and non-additive aspects of the inductive effect reveal themselves when studying disubstituted molecules, i.e. the additive influence of two heteroatoms upon the hydrocarbon fragment goes together with their mutually suppressing influence.

5. Conclusions

The inductive effect of heteroatoms in substituted alkanes may be interpreted either in terms of a perturbed electron density distribution or in terms of LMOs that have changed shape relative to those of the parent alkanes. Changes in the electron density after the introduction of heteroatoms are accompanied by corresponding changes in the degree of delocalization of the LMOs. The latter

perturbations are proportional to the values of the LMO delocalization coefficients in the parent alkanes. As a result, the short-range nature and other peculiarities of the inductive effect may be concluded to originate from a weak interbond delocalization in alkanes.

Additive aspects of the inductive effect reveal themselves when studying substituted alkanes. Changes in the populations of BOs belonging to the C_α –Z bond are additive with respect to the individual contributions of the C–C(C–H) bonds of the whole hydrocarbon fragment. Furthermore, the total influence of two heteroatoms on the hydrocarbon fragment appears to be additive with respect to the partial increments associated with each individual heteroatom. These peculiarities of the inductive effect may be concluded to be related to the additivity of the interbond delocalization in saturated molecules.

On the whole, the common peculiarities of the inductive effect in substituted alkanes are borne out by the results of our investigation and are accompanied by a similarity in the delocalization patterns in these systems.

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