An extended model of the S_N2 reaction between a substituted alkane and nucleophile

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Abstract

This paper is devoted to the development of qualitative quantum-chemical models of bimolecular nucleophilic substitution (S_N2 reaction) of substituted alkanes. To this end, we invoke the algebraic expressions for occupation numbers of basis orbitals of heteroatom-containing bonds obtained previously in the form of power series (J. Mol. Struct. (Theochem), 434 (1998) 43). The third-order terms of this series absent in the previous contribution but necessary for investigation of the S_N2 reaction, are additionally derived. The well-known two-orbital model of the reaction (based on taking into account only the direct interaction between the electron-donating orbital of nucleophile ($\varphi_{(+)d}$) and the electron-accepting orbital of the heteroatom-containing bond of the substituted alkane ($\varphi_{(-)a}$)) is shown to follow from second-order terms of the above-mentioned power series. Taking into account the third-order terms of the same series yields an extended model of the reaction, wherein the indirect interactions between orbitals $\varphi_{(+)d}$ and $\varphi_{(-)a}$ also are explicitly included, and orbitals of the nearest (C_α–C_β and C_α–H) bonds with respect to the heteroatom-containing (Z–C_α) bond play the role of the principal mediators of this new interaction. The indirect interactions between orbitals $\varphi_{(+)d}$ and $\varphi_{(-)a}$ are shown to contribute significantly to a greater efficiency of the back attack of the nucleophile vs. the frontal one. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The calculations of potential energy surfaces has become possible now-a-days for more and more chemical reactions. The results of these calculations (if sufficiently accurate) allow certain predictions to be made about the reaction path and transition states (see e.g. Ref. [1]).

This does not imply, however, that simple qualitative approaches and/or models [2–5] lose their significance in this field. Indeed, the question why just the given reaction takes place between the molecules under study may be answered primarily on the basis of qualitative investigations. Moreover, modelling of chemical reactions in terms of quantum chemistry allows us to formulate simple rules governing similar processes within a series of related compounds. In this connection, development of qualitative models of chemical reactions is an important task.

The so-called PMO theory of chemical reactivity of organic compounds [2] based on the Hückel model is among the most popular qualitative approaches. An early stage of the reaction is usually studied in the framework of this method. In particular, bimolecular processes are modelled by formation of an intermolecular bond represented by respective resonance parameters.

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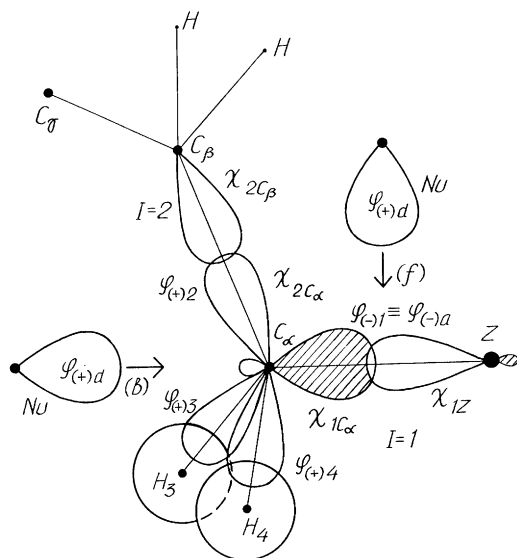*E-mail address:* gineityte@itpa.it (V. Gineityte).

Fig. 1. Diagram representing the two possible directions of the attack of nucleophile (Nu) with respect to the substituted alkane ($ZC_\alpha H_2 C_\beta H_2 C_\gamma \ldots$, where Z stands for a heteroatom), and the principal orbitals participating in the S_N2 reaction: arrows denoted by (f) and (b) indicate the frontal and the back attacks of nucleophile, respectively, and $\varphi_{(+)d}$ stands for its only electron-donating orbital. Numbering of the basis orbitals of the substituted alkane (i.e. of sp^3-hybrid AOs and of $1s_H$ AOs) is also shown. The bonding bond orbitals of the C_α–C_β and C_α–H bonds ($\varphi_{(+)2}$, $\varphi_{(+)3}$ and $\varphi_{(+)4}$) and the antibonding orbital of the Z–C_α bond ($\varphi_{(-)1} \equiv \varphi_{(-)a}$) are defined by Eq. (1). The only dashed basis function χ_{1C_α} coincides with that described by a negative coefficient in the antibonding orbital $\varphi_{(-)a}$.

In the case of reactions between saturated organic molecules, the so-called local models [2,3,6] are used along with the PMO theory. Two points form the basis of these models: firstly, localized two-center bond orbitals (BOs) play the role of basis functions there; secondly, a large number of interorbital interactions (resonance parameters) are considered as irrelevant to the given reaction, especially those between orbitals localized outside the directly contacting fragments.

The above-described approach may be examplified by the simple two-orbital model of the bimolecular nucleophilic substitution of substituted alkanes [2,3,5], i.e. of the S_N2 reaction. The model is based on taking into account the direct interaction (resonance parameter) between the initially occupied (electron-donating) orbital of nucleophile ($\varphi_{(+)d}$) and the initially vacant (electron-accepting) orbital of the

Z–C_α bond of the substituted alkane ($\varphi_{(-)a}$), where Z stands for a heteroatom. Orbitals of the remaining bonds are ignored in this model.

The S_N2 reactions of substituted alkanes are known to be accompanied by inversion of configuration of the attacked carbon atom [2–4,7]. In this connection, a back attack of nucleophile (Fig. 1) and not a frontal one is commonly assumed to give rise to a subsequent reaction process [2–5,7–9]. Hence, accounting for the greater efficiency of the back attack vs. the frontal one is the principal task of the theory of these reactions.

To solve this problem, the intermolecular bonding energies and/or the extents of the charge transfer between the two reacting systems are usually compared for both types of the attack [2–5]. In the framework of the two-orbital (local) model, this actually resolves itself to comparison of resonance parameters between orbitals $\varphi_{(+)d}$ and $\varphi_{(-)a}$ for the back attack and for the frontal one, and these are expected to take smaller values in the latter case.

Arguments for such an anticipation are as follows [3]: nucleophile is likely to approach the Z–C_α bond perpendicularly during a frontal attack (Fig. 1). Then the antibonding nature of the electron-accepting orbital $\varphi_{(-)a}$ implies that the overlap integral $\langle \varphi_{(+)d} | \varphi_{(-)a} \rangle$ and thereby the respective resonance parameter contains two contributions of similar absolute values and of opposite signs that almost cancel one another, and the final resonance parameter proves to be small.

This simple explanation, however, is not free from weak points. First, the above-mentioned argument about similar absolute values of two contributions to the overlap integral $\langle \varphi_{(+)d} | \varphi_{(-)a} \rangle$ referring to the frontal attack is undoubtedly valid in the case of a small difference in electronegativities of the atoms Z and C_α but it is not the case for considerable differences in these electronegativities. Second, the frontal attack is not necessarily strongly perpendicular to the Z–C_α bond. The third and the most important point, however, consists in the fact that the overlap integrals under comparison, i.e. those between the orbitals $\varphi_{(+)d}$ and $\varphi_{(-)a}$ referring to the back attack, also are rather small.

The latter conclusion is based on the localized nature of bond orbitals. Let us invoke here the usual definition of these orbitals as bonding and antibonding linear combinations of pairs of sp^3-hybrid AOs directed along the given bond [2,3,5,10–12]. Then only a

small loop of the sp^3-hybrid AO of the C_α atom is directed towards the back-attacking nucleophile (Fig. 1). Consequently, the relevant overlap integral $\langle \varphi_{(+)d} | \varphi_{(-)a} \rangle$ hardly takes a significant value.

Therefore, similar values of resonance parameters between orbitals $\varphi_{(+)d}$ and $\varphi_{(-)a}$ for both types of the attack are quite probable. Then the two-orbital model becomes insufficient to distinguish between the two possible ways of the reaction, and an extended model of this process is required.

To achieve this end, let us recall the results of Ref. [6], wherein the power series for the one-electron density matrix (DM) of saturated organic molecules derived previously [10–12] has been used to investigate the electron density redistribution between two interacting molecules. It is essential that confinement to the second-order terms of the above-mentioned series proved to be equivalent to application of a local model containing orbitals of only two (or several) directly contacting bonds and/or lone electron pairs (the latter are treated similarly in the approach of Ref. [10]).

It may be expected, therefore, that an extended model of the S_N2 reaction may be constructed by invoking the third-order terms of the above-mentioned power series. Such an expectation may be additionally supported by the fact that the third-order corrections to occupation numbers depend on indirect interactions between the electron-donating orbital and the electron-accepting one by means of orbitals of other bonds from their nearest environment [13]. The experience of previous studies of heteroatom-containing molecules shows that indirect interactions contribute significantly to the final picture of the electron density distribution, especially in the cases of comparable increments of direct interactions to populations of orbitals under comparison [13].

Thus, we are about to extend the above-described two-orbital model of the S_N2 reaction of substituted alkanes to the case of explicitly taking into account the orbitals of the neighboring C_α–H and C_α–C_β bonds. The main aim of this study consists in comparison of contributions of indirect interactions between orbitals $\varphi_{(+)d}$ and $\varphi_{(-)a}$ to the additional population acquired by the heteroatom Z under the influence of a frontally and back-attacking nucleophile. The case of similar values of direct interactions between orbitals $\varphi_{(+)d}$ and $\varphi_{(-)a}$ during both types of the attack is of particular interest here. As a result of this investigation, we expect to replenish simple accounting for the advantages of the back attack.

The expressions for occupation numbers of sp^3-hybrid AOs of heteroatom-containing bonds with the second-order terms inclusive have been derived in Ref. [12]. In Section 2 of this paper, we describe briefly these expressions and supplement them with third-order terms. The S_N2 reaction will be studied in Sections 3 and 4.

2. The expressions for occupation numbers of basis orbitals of heteroatom-containing bonds with the third-order terms inclusive

As in Refs. [6,12], let us consider a heteroatom-containing (Z–C) bond involved in any saturated organic system, including several interacting molecules [6]. Let the bond under study coincide with the Ith bond of our system. The bonding BO $\varphi_{(+)i}$ and the antibonding BO $\varphi_{(-)i}$ will correspond to this bond.

Furthermore, the sp^3-hybrid AOs χ_{IZ} and χ_{IC} will be ascribed to atoms Z and C of our bond and directed along it. Let these orbitals be represented by Coulomb parameters α_{IZ} and α_{IC}, whereas the bond itself will be characterized by resonance parameter β_I. The equalities $\alpha_{IC} = 0$, $\alpha_{IZ} = \alpha_I$, and $\beta_I = 1$ will be accepted further for convenience.

The bond orbitals $\varphi_{(+)i}$ and $\varphi_{(-)i}$ will be defined as eigenfunctions of the respective 2×2-dimensional Hamiltonian matrix block in the basis of HAOs $\{\chi_{IZ}, \chi_{IC}\}$, i.e.

$$\varphi_{(+)i} = a\chi_{IZ} + b\chi_{IC}, \qquad \varphi_{(-)i} = b\chi_{IZ} - a\chi_{IC} \qquad (1)$$

where the coefficients a and b are [14]:

$$a = \cos(\gamma_I/2), \quad b = \sin(\gamma_I/2), \qquad a > b \qquad (2)$$

and

$$\gamma_I = \mathrm{arctg}(2/\alpha_I), \qquad 0 \le \gamma_I \le (\pi/2) \qquad (3)$$

(More electronegative heteroatoms (Z) versus carbon and hydrogen atoms are considered here and α_I is positive in our negative energy units.) Let us also note that the C–C and C–H bonds may be described by equalities:

$$\alpha_I = 0, \quad \gamma_I = \pi/2, \qquad a = b = 1/\sqrt{2} \qquad (4)$$

(Electronegativities of the C and H atoms and thereby the relevant Coulomb parameters may be assumed to take equal values [15].)

When deriving the expressions for occupation numbers of HAOs χ_{IZ} and χ_{IC} [12], the general form of the power series for the one-electron DM of saturated organic molecules in the basis of BOs [10] has been used. The third-order terms of this series also may be easily obtained as described in Ref. [10]. Thereupon, the 2×2-dimensional block of the DM corresponding to the bond under study and containing terms with the third-order inclusive should be transformed into the basis of HAOs as it was done in Ref. [12].

As a result, the occupation numbers of HAOs χ_{IZ} and χ_{IC} of the *I*th bond may be expressed as follows:

$$X_{IZ}(X_{IC}) = 1 \pm \cos \gamma_I + \tfrac{1}{2} \Delta X_{(2)I} \pm d_{(2)I} \pm p_{(2)I}$$

$$+ \tfrac{1}{2} \Delta X_{(3)I} \pm d_{(3)I} \pm p_{(3)I} \qquad (5)$$

where the upper signs refer to the HAO χ_{IZ} and the lower ones correspond to the orbital χ_{IC}. The subscripts (2) and (3) denote here the second- and the third-order terms, respectively.

The zero-order term of Eq. (5) $(1 \pm \cos \gamma_I)$ describes the occupation numbers of HAOs χ_{IZ} and χ_{IC} of an isolated Z–C_α bond. The population of the HAO χ_{IZ} of a more electronegative heteroatom Z proves to be increased, whereas that of the HAO of the carbon atom is reduced, and this result is not unexpected.

The next term of Eq. (5) describes a half of the second-order contribution to the population of the *I*th bond lost (acquired) by this bond owing to the interbond charge transfer. The total population alteration $\Delta X_{(2)I}$ takes the form:

$$\Delta X_{(2)I} = \sum_J \Delta X_{(2)I(J)} = 2 \sum_{j \ni J} \{(G_{(1)ji})^2 - (G_{(1)ij})^2\} \qquad (6)$$

where the subscript j embraces the two BOs of the *J*th bond $\varphi_{(+)j}$ and $\varphi_{(-)j}$ defined as shown in Eq. (1). The notation $G_{(1)ij}$ stands for an element of certain first order matrix $G_{(1)}$ [10] describing the direct (through-space) interaction between the bonding BO (BBO) $\varphi_{(+)i}$ of the *I*th bond and the antibonding BO(ABO) $\varphi_{(-)j}$ of the *J*th bond.

As in Ref. [12], let us introduce the following nota-

tions for resonance parameters between various types of BOs, the latter being indicated within the bra- and ket-vectors, viz.

$$S_{ij} = \langle \varphi_{(+)i} | \hat{H} | \varphi_{(+)j} \rangle, \qquad R_{ij} = \langle \varphi_{(+)i} | \hat{H} | \varphi_{(-)j} \rangle,$$

$$Q_{ij} = \langle \varphi_{(-)i} | \hat{H} | \varphi_{(-)j} \rangle \qquad (7)$$

and note that $S_{ij} = S_{ji}$, $Q_{ij} = Q_{ji}$ but $R_{ij} \neq R_{ji}$. Then the element $G_{(1)ij}$ takes the form

$$G_{(1)ij} = -\frac{R_{ij}}{E_{(+)i} - E_{(-)j}} \qquad (8)$$

where the denominator of Eq. (8) contains the difference in one-electron energies of BOs $\varphi_{(+)i}$ and $\varphi_{(-)j}$. Given that the subscript *J* describes a lone electron pair and an ABO $\varphi_{(-)j}$ is absent, we obtain

$$\Delta X_{(2)I(L)} = 2(G_{(1)li})^2 > 0 \qquad (9)$$

The next term of Eq. (5) $(\pm d_{(2)I})$ has been expressed as follows [12]:

$$d_{(2)I} = -\left\{ \sum_{j \ni J} \{(G_{(1)ji})^2 + (G_{(1)ij})^2\} \right\} \cos \gamma_I < 0 \quad (10)$$

and it represents the so-called depolarization dipole moment of the *I*th bond. This moment describes the reduction of the primary dipole of the given bond (equal to $1 \pm \cos \gamma_I$) due to the dipole-like distribution of the additional population lost (acquired) by the *I*th bond owing to the second-order interbond charge transfer.

The last second-order increment of Eq. (5) $(\pm p_{(2)I})$ describes the so-called induced dipole moment of the *I*th bond arising under the influence of other bonds. This dipole moment equals

$$p_{(2)I} = -2G_{(2)ii} \sin \gamma_I \qquad (11)$$

where $G_{(2)ii}$ is the diagonal element of certain second order matrix $G_{(2)}$ [10]. For further convenience, any element $G_{(2)ij}$ is given below in Eq. (12):

$$G_{(2)ij} = \frac{1}{E_{(+)i} - E_{(-)j}} \left(\sum_l^{BBOs} \frac{S_{il}R_{lj}}{E_{(+)l} - E_{(-)j}} \right.$$

$$\left. - \sum_k^{ABOs} \frac{R_{ik}Q_{kj}}{E_{(+)i} - E_{(-)k}} \right) \qquad (12)$$

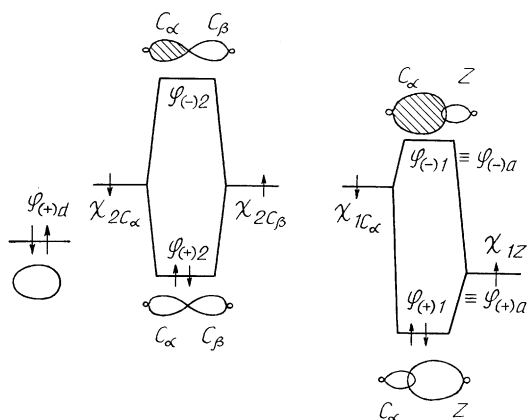and the diagonal element $G_{(2)ii}$ follows from Eq. (12) if

Fig. 2. Diagram reflecting the one-electron energies and the shapes of basis orbitals of nucleophile and of the substituted alkane. The subscripts used for sp³-hybrid AOs $\{\chi\}$ and for bond orbitals $\{\varphi\}$ coincide with those of Fig. 1.

$i = j$. The notations of Eq. (12) coincide with those of Eq. (8). It is seen that the element $G_{(2)ij}$ describes the indirect (through-bond) interaction between the BBO $\varphi_{(+)i}$ of the Ith bond and the ABO $\varphi_{(-)i}$ of the Jth bond by means of other BBOs and/or ABOs.

Let us turn now to the third-order increments of Eq. (5). These may be interpreted similarly to the above-described second-order terms.

The increment $\frac{1}{2}\Delta X_{(3)I}$ describes a half of the third-order contribution to the population lost (acquired) by the Ith bond owing to the interbond charge transfer. The respective expression takes the form:

$$\Delta X_{(3)I} = 4 \sum_{j \ni J} (G_{(1)ji}G_{(2)ji} - G_{(1)ij}G_{(2)ij}) \tag{13}$$

where $G_{(2)ij}$ is defined by Eq. (12). It is seen that products of direct and of indirect interactions of BOs $\varphi_{(+)i}$ and $\varphi_{(-)j}$, as well as of $\varphi_{(-)i}$ and $\varphi_{(+)j}$, are present in Eq. (13) in contrast to Eq. (6).

Similarly, the increment $\pm d_{(3)I}$ may be interpreted as the third-order depolarization dipole moment of the Ith bond. This term may be expressed as follows:

$$d_{(3)I} = -2 \left\{ \sum_{j \ni J} (G_{(1)ji}G_{(2)ji} + G_{(1)ij}G_{(2)ij}) \right\} \cos \gamma_I < 0 \tag{14}$$

And finally, $\pm p_{(3)I}$ is the third-order induced dipole

moment of the Ith bond which takes the form:

$$p_{(3)I} = -2G_{(3)ii} \sin \gamma_I \tag{15}$$

where $G_{(3)ii}$ stands for a diagonal element of the third-order analog of the matrix $G_{(2)}$. This element is equal to

$$G_{(3)ii} = \frac{-1}{E_{(+)i} - E_{(-)i}}$$

$$\times \left\{ \sum_{j}^{BBOs} \sum_{m}^{BBOs} \frac{S_{ij}S_{jm}R_{mi}}{(E_{(+)j} - E_{(-)i})(E_{(+)m} - E_{(-)i})} \right.$$

$$- \sum_{j}^{BBOs} \sum_{r}^{ABOs} \left[\frac{S_{ij}R_{jr}Q_{ri}}{(E_{(+)j} - E_{(-)i})(E_{(+)j} - E_{(-)r})} \right.$$

$$+ \frac{S_{ij}R_{jr}Q_{ri}}{(E_{(+)i} - E_{(-)r})(E_{(+)j} - E_{(-)r})}$$

$$+ \frac{R_{ir}R_{rj}^{+}R_{ji}}{(E_{(+)j} - E_{(-)r})(E_{(+)j} - E_{(-)i})}$$

$$+ \left. \frac{R_{ir}R_{rj}^{+}R_{ji}}{(E_{(+)i} - E_{(-)r})(E_{(+)j} - E_{(-)r})} \right]$$

$$+ \left. \sum_{p}^{ABOs} \sum_{r}^{ABOs} \frac{R_{ir}Q_{rp}Q_{pi}}{(E_{(+)i} - E_{(-)p})(E_{(+)i} - E_{(-)r})} \right\} \tag{16}$$

and $R_{rj}^{+} = R_{jr}$. The element $G_{(3)ii}$ describes the indirect interaction between the BBO $\varphi_{(+)i}$ and ABO $\varphi_{(-)i}$ by means of two mediators.

3. The three-orbital model of the S_N2 reaction

Let us start with investigation of the intermolecular interaction between a mono-substituted alkane ($ZC_{\alpha}H_2C_{\beta}H_2C_{\gamma}...$) and nucleophile (Nu) during its frontal and back attacks (Fig. 1). Our main purpose consists in comparison of populations of the HAO χ_{1Z} of the heteroatom Z for different positions of nucleophile (The number $I = 1$ is ascribed to the Z–C_{α} bond). To this end, the expressions of Section 2 will be used.

Eq. (5) describes the total populations of HAOs χ_{1Z} and χ_{1C}. To investigate the influence of nucleophile upon the population of HAO χ_{1Z}, studies of the

difference

$$\delta X_{1Z} = X_{1Z} - X^{\circ}_{1Z} \tag{17}$$

proves to be sufficient, where the superscript $^{\circ}$ refers to an isolated substituted alkane. As in Ref. [6], the difference δX_{1Z} may be called the intermolecular part of the total population of the HAO χ_{1Z}.

Let us introduce now the following notations for the principal resonance parameters representing the intermolecular interactions:

$$S_{ad} = \langle \varphi_{(+)a} | \hat{H} | \varphi_{(+)d} \rangle, \ R_{da} = \langle \varphi_{(+)d} | \hat{H} | \varphi_{(-)a} \rangle \tag{18}$$

The relative positions and shapes of BOs of the nearest neighborhood of the fragment Nu$\cdots$C$_\alpha$–Z are shown in Figs. 1 and 2. Nucleophile is modelled here by a single electron-donating orbital $\varphi_{(+)d}$. Inasmuch as the zero-order term of Eq. (5) does not depend on the position of nucleophile, no zero-order increments arise in the difference δX_{1Z}.

The second order contribution $\frac{1}{2}\Delta X_{(2)1}$ to the total population of the HAO χ_{1Z} is additive with respect to increments of particular bonds as shown in Eq. (6). Each of these increments, in turn, depends only on the mutual arrangement of the Ith and Jth bonds (lone pairs). As a result, square of the direct interaction between the electron-donating orbital of nucleophile $\varphi_{(+)d}$ and the electron-accepting orbital of the bond under study $\varphi_{(-)a} \equiv \varphi_{(-)1}$ remains in the difference of Eq. (17) i.e.

$$\delta\left(\tfrac{1}{2}\Delta X_{(2)1}\right) = (G_{(1)da})^2 = \frac{(R_{da})^2}{(E_{(+)d} - E_{(-)a})^2} > 0 \tag{19}$$

It is seen that the population acquired by the HAO χ_{1Z} owing to the second-order intermolecular charge transfer depends on square of the resonance parameter R_{da}. This term may be evidently ascribed to the local two-orbital model of the reaction (Section 1).

The intermolecular part of the depolarization dipole moment $\delta(d_{(2)I})$ describes the actual distribution of the acquired population among the HAOs χ_{1Z} and χ_{1C} of the Z–C$_\alpha$ bond. This term takes the form:

$$\delta(d_{(2)I}) = -(G_{(1)da})^2 \cos \gamma_1 < 0 \tag{20}$$

It is also seen that the sum of the above-discussed two increments

$$\delta Q_{(2)} = \delta(\tfrac{1}{2}\Delta X_{(2)1}) + \delta(d_{(2)I}) = \frac{(R_{da})^2(1 - \cos \gamma_1)}{(E_{(+)d} - E_{(-)a})^2} > 0 \tag{21}$$

remains positive whatever the position of nucleophile and depends on square of the only resonance parameter R_{da}. Hence, taking into account the depolarization dipole moment does not require any extension of the two-orbital model.

Let us turn now to the intermolecular part of the second-order induced dipole moment $\delta(p_{(2)I})$ arising under the influence of nucleophile. This term follows from Eqs. (11) and (12). The electron-donating orbital $\varphi_{(+)d}$ plays the role of mediator of the indirect interaction between the orbitals $\varphi_{(+)a} \equiv \varphi_{(+)1}$ and $\varphi_{(-)a} \equiv \varphi_{(-)1}$ of the Z–C$_\alpha$ bond contained within the element $G_{(2)ii}$. We then obtain

$$\delta(p_{(2)I}) = -2\frac{S_{ad}R_{da}}{(E_{(+)a} - E_{(-)a})(E_{(+)d} - E_{(-)a})} \tag{22}$$

It is seen that three orbitals, viz. $\varphi_{(+)d}$, $\varphi_{(+)a}$ and $\varphi_{(-)a}$, participate in the formation of the induced dipole moment of the Z–C$_\alpha$ bond.

To study the signs of the induced dipole moments $\delta^{(b)}(p_{(2)I})$ and $\delta^{(f)}(p_{(2)I})$ for the back and the frontal attacks, respectively, let us turn to Figs. 1 and 2 and assume that resonance parameters are proportional to respective overlap integrals [16]. This implies a positive (negative) sign of resonance parameters in our negative β units if the overlap integral is positive (negative). Then the following inequalities may be easily established on the basis of Fig. 1:

$$S_{ad}^{(b)} < 0, \qquad R_{da}^{(b)} > 0, \qquad S_{ad}^{(f)} > 0, \qquad R_{da}^{(f)} < 0 \tag{23}$$

Substituting Eq. (23) into Eq. (22) and taking into account the positive sign of any energy difference $E_{(+)i} - E_{(-)j}$ allows us to conclude that

$$\delta^{(b)}(p_{(2)I}) > 0, \qquad \delta^{(f)}(p_{(2)I}) > 0 \tag{24}$$

Thus, the intermolecular part of the induced dipole moment contributes to an increase of the population acquired by the HAO χ_{1Z} of the Z–C$_\alpha$ bond irrespective of the position of the nucleophile.

On the whole, taking into account the second-order terms of the power series for occupation numbers

yields a three-orbital local model of the S_N2 reaction, wherein the lone pair orbital of nucleophile and the two orbitals of the $Z–C_\alpha$ bond are included. The simplest (two-orbital) version of this model follows after neglecting the intermolecular part of the induced dipole moment of the $Z–C_\alpha$ bond.

Given that the resonance parameters of Eq. (18) are of equal absolute values for both types of the attack as discussed in Section 1, i.e.

$$|S_{ad}^{(b)}| = |S_{ad}^{(f)}|, \qquad |R_{da}^{(b)}| = |R_{da}^{(f)}| \qquad (25)$$

the total second-order increments to the population of the HAO χ_{1Z} also coincide with one another. Hence, the second-order terms do not allow us to distinguish between the two ways of the reaction in this case.

4. Contributions of orbitals of the $C_\alpha–C_\beta(C_\alpha–H)$ bonds to population alteration of heteroatom

This section is devoted for the investigation of the third-order terms of Eq. (5). Let us start with the inter-molecular parts of the charge transfer and of the depolarization dipole moment of the $Z–C_\alpha$ bond following from Eqs. (13) and (14).

Additivity of the above-mentioned terms with respect to contributions of various bonds (J) is evident. However, the contributions of the Jth bond (lone pair) to both $\delta(\frac{1}{2}\Delta X_{(3)1})$ and $\delta(d_{(3)1})$ depend not only on the mutual arrangement of the Ith and Jth bonds but also on the structure of the whole molecule. Indeed, the indirect interaction between BOs $\varphi_{(+)i}$ and $\varphi_{(-)j}$, as well as between $\varphi_{(-)j}$ and $\varphi_{(+)j}$, represented by elements $G_{(2)ij}$ and $G_{(2)ji}$, respectively, contain orbitals of other bonds ($\varphi_{(+)l}$ and $\varphi_{(-)k}$) that play the role of mediators of this interaction (see Eq. (12)). As a result, two types of terms remain after taking the difference shown in Eq. (17), namely terms wherein the orbital $\varphi_{(+)d}$ coincides with the jth orbital ($\varphi_{(+)d} \equiv \varphi_{(+)j}$) and those containing $\varphi_{(+)d}$ as mediator in the indirect interactions between orbitals of the Ith bond and those of other bonds.

Let us start with the case $\varphi_{(+)j} = \varphi_{(+)d}$. The respective contributions to the intermolecular parts of the charge transfer and of the depolarization dipole moment of the $Z–C_\alpha$ bond will be denoted by $'$.

These are

$$\delta'\left(\tfrac{1}{2}\Delta X_{(3)1}\right) = 2G_{(1)da}G_{(2)da} \qquad (26)$$

$$\delta'(d_{(3)1}) = -2G_{(1)da}G_{(2)da}\cos\gamma_1 \qquad (27)$$

and their sum

$$\delta'Q_{(3)} = \delta'\left(\tfrac{1}{2}\Delta X_{(3)1}\right) + \delta'(d_{(3)1})$$
$$= 2G_{(1)da}G_{(2)da}(1 - \cos\gamma_1) \qquad (28)$$

where

$$G_{(1)da} = -\frac{R_{da}}{E_{(+)d} - E_{(-)a}} \qquad (29)$$

and

$$G_{(2)da} = \frac{3}{E_{(+)d} - E_{(-)a}}\left(\frac{S_{d2}R_{2a}}{E_{(+)2} - E_{(-)a}} - \frac{R_{d2}Q_{2a}}{E_{(+)d} - E_{(-)2}}\right) \qquad (30)$$

The factor 3 in Eq. (30) is due to three similar increments of bonds $C_\alpha–C_\beta$, $C_\alpha–H_3$ and $C_\alpha–H_4$ of the substituted alkane shown in Fig. 1 to the total element $G_{(2)da}$.

Let us compare now the principal factors of Eq. (28), i.e. $G_{(1)da}$ and $G_{(2)da}$, for the frontal and back attacks of nucleophile. From Eqs. (23) and (29) it follows that

$$G_{(1)da}^{(b)} < 0, \qquad G_{(1)da}^{(f)} > 0 \qquad (31)$$

Hence, the direct interactions between orbitals $\varphi_{(+)d}$ and $\varphi_{(-)a}$ are of opposite signs for both types of the attack. This result may be traced back to different signs of respective resonance parameters R_{da} shown in Eq. (23).

Let us consider now the indirect interaction between orbitals $\varphi_{(+)d}$ and $\varphi_{(-)a}$ described by the element $G_{(2)da}$. The resonance parameter R_{d2} in Eq. (30) may be expected to be of a small value for both types of the attack owing to the equality $a = b$ for C–C(C–H) bonds (see Eqs. (1) and (2)). As a result, the matrix element $G_{(2)da}$ may be approximated as follows:

$$G_{(2)da} \approx \frac{3S_{d2}R_{2a}}{(E_{(+)d} - E_{(-)a})(E_{(+)2} - E_{(-)a})} \qquad (32)$$

and describes the indirect interaction between orbitals

$\varphi_{(+)d}$ and $\varphi_{(-)a}$ by means of bonding BOs of the C_α–$C_\beta(C_\alpha$–H) bonds.

Furthermore, the resonance parameters contained in Eq. (32) meet the following inequalities:

$$S_{d2}^{(b)} > 0, \qquad S_{d2}^{(f)} > 0, \qquad R_{2a}^{(b)} = R_{2a}^{(f)} < 0 \qquad (33)$$

We then obtain

$$G_{(2)da}^{(b)} < 0, \qquad G_{(2)da}^{(f)} < 0 \qquad (34)$$

Hence, the sign of the indirect interaction between orbitals $\varphi_{(+)d}$ and $\varphi_{(-)a}$ does not depend on the position of nucleophile.

Substituting Eqs. (29) and (32) into Eq. (28) yields the following expression for the sum $\delta'Q_{(3)}$:

$$\delta'Q_{(3)} \approx \frac{-6R_{da}S_{d2}R_{2a}(1 - \cos\gamma_1)}{(E_{(+)d} - E_{(-)a})^2(E_{(+)2} - E_{(-)a})} \qquad (35)$$

Let us consider now the remaining part of the population alteration wherein the orbital $\varphi_{(+)d}$ plays the role of mediator of the indirect interaction. Terms corresponding to $J = 2, 3, 4$ (Fig. 1) evidently make the most significant contributions there. Let us denote the respective increments by $''$. These are

$$\delta''\left(\tfrac{1}{2}\Delta X_{(3)1}\right) = 6(G_{(1)2a}G_{(2)2a} - G_{(1)a2}G_{(2)a2}) \qquad (36)$$

$$\delta''(d_{(3)1}) = -6(G_{(1)2a}G_{(2)2a} + G_{(1)a2}G_{(2)a2})\cos\gamma_1 \quad (37)$$

where

$$G_{(1)a2} = -\frac{R_{a2}}{E_{(+)a} - E_{(-)2}},$$

$$G_{(1)2a} = -\frac{R_{2a}}{E_{(+)2} - E_{(-)a}} \qquad (38)$$

and

$$G_{(2)a2} = \frac{S_{ad}R_{d2}}{(E_{(+)a} - E_{(-)2})(E_{(+)d} - E_{(-)2})} \qquad (39)$$

$$G_{(2)2a} = \frac{S_{2d}R_{da}}{(E_{(+)2} - E_{(-)a})(E_{(+)d} - E_{(-)a})} \qquad (40)$$

Then the sum of increments shown in Eqs. (36) and

(37) becomes

$$\delta''Q_{(3)} \approx \frac{-6R_{da}S_{2d}R_{2a}(1 - \cos\gamma_1)}{(E_{(+)2} - E_{(-)a})^2(E_{(+)d} - E_{(-)a})}$$

$$+ \frac{6R_{d2}S_{ad}R_{a2}(1 + \cos\gamma_1)}{(E_{(+)a} - E_{(-)2})^2(E_{(+)d} - E_{(-)2})} \qquad (41)$$

Let us compare now the separate increments of Eqs. (35) and (41). The following inequalities may be assumed on the basis of Fig. 2:

$$|E_{(+)d} - E_{(-)a}| \ll |E_{(+)2} - E_{(-)a}| \approx |E_{(+)d} - E_{(-)2}|$$

$$\ll |E_{(+)a} - E_{(-)2}| \qquad (42)$$

These relations imply that the second term of the right-hand side of Eq. (41) contains a much larger denominator as compared to the first term. Moreover, the above-discussed small value of the resonance parameter R_{d2} contained in the numerator of the second term of Eq. (41) should be taken into consideration along with the equality $\cos\gamma_1 \ll 1$ established for the majority of heteroatoms Z [14]. We then obtain

$$\delta''Q_{(3)} \approx \frac{-6R_{da}S_{2d}R_{2a}(1 - \cos\gamma_1)}{(E_{(+)2} - E_{(-)a})^2(E_{(+)d} - E_{(-)a})} \qquad (43)$$

Furthermore, comparison of Eqs. (35) and (43) shows that the right-hand sides of these relations contain coinciding numerators ($S_{2d} = S_{d2}$), whilst the denominator of the first increment $\delta'Q_{(3)}$ is considerably smaller. Hence, the increment $\delta'Q_{(3)}$ corresponding to $\varphi_{(+)j} \equiv \varphi_{(+)d}$ seems to be prevalent and we obtain

$$\delta Q_{(3)} \approx \delta'Q_{(3)} = 2G_{(1)da}G_{(2)da}(1 - \cos\gamma_1)$$

$$\approx \frac{-6R_{da}S_{d2}R_{2a}(1 - \cos\gamma_1)}{(E_{(+)d} - E_{(-)a})^2(E_{(+)2} - E_{(-)a})} \qquad (44)$$

Therefore, the sum of the intermolecular parts of the third-order charge transfer and of the third-order depolarization dipole moment of the Z–C_α bond is primarily determined by the product of the direct interaction between orbitals $\varphi_{(+)d}$ and $\varphi_{(-)a}$ and of their indirect interaction by means of the bonding BOs of the C_α–$C_\beta(C_\alpha$–H) bonds. Since only the former type of interaction changes its sign when changing the relative position of nucleophile as Eq. (31) indicates, different signs of $\delta Q_{(3)}^{(b)}$ and $\delta Q_{(3)}^{(f)}$ may be

expected. Using Eqs. (31) and (34) we then obtain

$$\delta Q_{(3)}^{(b)} > 0, \qquad \delta Q_{(3)}^{(f)} < 0 \qquad (45)$$

It is seen that the HAO χ_{1Z} acquires an additional population under the influence of the back-attacking nucleophile, and it loses its population during a frontal attack if third-order terms are included. It is also evident that the inequalities of Eq. (45) should be valid also in the case of explicitly taking into account of the term $\delta Q_{(3)}''$ of Eq. (43).

Let us turn now to the intermolecular part of the third-order induced dipole moment of the $Z–C_\alpha$ bond arising owing to the emergence of the orbital $\varphi_{(+)d}$ as a new mediator for the indirect interaction of BOs $\varphi_{(+)1}$ and $\varphi_{(-)1}$ by means of two mediators. Thus, let us assume that the orbital $\varphi_{(+)d}$ plays the role of the first mediator of this interaction described by Eq. (16).

From Fig. 2 and Eq. (16), it follows that the anti-bonding BOs $\varphi_{(-)2}$, $\varphi_{(-)3}$ and $\varphi_{(-)4}$ are not efficient second mediators for the indirect interaction of BOs $\varphi_{(+)1}$ and $\varphi_{(-)1}$ owing to both the relatively large energy differences $E_{(+)a} - E_{(-)2}$ and $E_{(+)d} - E_{(-)2}$ and small resonance parameter R_{d2}. Thus, let us exclude these orbitals from consideration. Then, three similar pairs of bonding orbitals $(\varphi_{(+)d}, \varphi_{(+)2})$, $(\varphi_{(+)d}, \varphi_{(+)3})$ and $(\varphi_{(+)d}, \varphi_{(+)4})$ play the role of the most efficient mediators of the indirect interaction between the orbitals $\varphi_{(+)1}$ and $\varphi_{(-)1}$. This implies that the first double-sum of Eq. (16) yields the main contribution to the element $G_{(3)11}$ determining the additional induced dipole moment $\delta p_{(3)1}$. Moreover, two cases should be considered here, namely $j = (+)d$, $m = (+)2$ and $j = (+)2$, $m = (+)d$. We then obtain

$$\delta p_{(3)1} \approx \frac{6(S_{ad}S_{d2}R_{2a} + S_{a2}S_{2d}R_{da})\sin \gamma_1}{(E_{(+)2} - E_{(-)a})(E_{(+)a} - E_{(-)a})(E_{(+)d} - E_{(-)a})} \qquad (46)$$

It is seen that products of three resonance parameters come from the numerator of Eq. (46). Moreover, use of Eqs. (23) and (33) along with additional inequalities:

$$S_{a2}^{(b)} = S_{a2}^{(f)} > 0, \qquad S_{2d}^{(b)} > 0, \qquad S_{2d}^{(f)} > 0 \qquad (47)$$

allows us to conclude that only one of every three resonance parameters, viz. S_{ad} and/or R_{da}, changes its sign within the above-mentioned products when

passing from the frontal to the back attack. As a result, different signs of $\delta p_{(3)1}^{(b)}$ and $\delta p_{(3)1}^{(f)}$ follow, viz.

$$\delta p_{(3)1}^{(b)} > 0, \qquad \delta p_{(3)1}^{(f)} < 0 \qquad (48)$$

Comparison of Eqs. (45) and (48) shows that the total third-order increment to the population of the HAO χ_{1Z} is positive for the back attack of nucleophile and negative for the frontal one.

It is essential to note that the absolute values of the third-order increments are not necessarily small as compared to those of the second-order increments. Two points form the basis of the latter expectation: firstly, the resonance parameter $S_{d2} \equiv S_{2d}$ contained in Eqs. (44) and (46) is likely to be sufficiently large owing to the bonding nature of the orbital $\varphi_{(+)2}$; secondly, the factor 6 in the expressions for third-order terms owing to three geminal neighbors of the $Z–C_\alpha$ bond also contributes essentially to an increase of the relative values of the third-order contributions to population of the HAO χ_{1Z}.

Hence, the third-order increments may play a decisive part in distinguishing between the two possible ways of the S_N2 reaction, especially if the second-order increments are of similar absolute values as discussed in Section 3. Moreover, the third-order terms always contribute to the greater efficiency of the back attack of nucleophile as compared to the frontal one even if the relevant second-order increments take equal values.

5. Conclusions

The application of the power series for occupation numbers of basis orbitals of saturated organic molecules to investigate an intermolecular interaction between a nucleophile and a substituted alkane allowed us to extend the most popular two-orbital model of the S_N2 reaction to the case of explicitly taking into account orbitals of the $C_\alpha–C_\beta$ and/or $C_\alpha–H$ bonds. Moreover, different models of the reaction proved to be attributable to confinement to terms of different order within the above-mentioned power series:

1. Taking into account terms with the second-order inclusive yields a local model of the reaction, which involves the electron-donating orbital of

nucleophile ($\varphi_{(+)d}$) and the two orbitals of the Z–C_α bond ($\varphi_{(+)a}$) and ($\varphi_{(-)a}$). The simplest two-orbital model containing only the orbitals $\varphi_{(+)d}$ and $\varphi_{(-)a}$ corresponds to a particular case of the former.

2. An extended model of the reaction, wherein orbitals of the nearest C_α–C_β(C_α–H) bonds also are explicitly included, corresponds to an additional taking into account the third-order terms of the same power series. These orbitals play the role of mediators in the indirect interaction between orbitals $\varphi_{(+)d}$ and $\varphi_{(-)a}$, as well as between $\varphi_{(+)a}$ and $\varphi_{(-)a}$, contained in the third-order corrections to occupation numbers.

These results indicate an unambiguous hierarchy of models.

Studies of the extended model indicate that a larger absolute value of the direct interaction (overlap) between the electron-donating orbital of nucleophile ($\varphi_{(+)d}$) and the electron-accepting orbital of the Z–C_α bond ($\varphi_{(-)a}$) is not a necessary condition for a greater total intermolecular interaction as it is commonly believed on the basis of the two-orbital model. The point is that the indirect interactions between orbitals $\varphi_{(+)d}$ and $\varphi_{(-)a}$, as well as between $\varphi_{(+)a}$ and $\varphi_{(-)a}$, also contribute significantly to the total interaction. Moreover, the above-mentioned indirect interactions by means of orbitals of the C_α–C_β(C_α–H) bonds lead to a larger population acquired by the heteroatom Z under the influence of the back-attacking nucleophile as compared to the frontally attacking one even if the direct interactions are of coinciding absolute values.

Therefore, the greater efficiency of the back attack of nucleophile vs. the frontal one (assumed on the basis of experimental facts [2–5,7–9]) might be related either to the larger direct interaction between orbitals $\varphi_{(+)d}$ and $\varphi_{(-)a}$, or to the decisive role of indirect (through-bond) interactions.

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