

On the direction of the additional dipole of a heteroatom-containing bond due to an external electron-donating effect

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Abstract

The paper continues the search for general rules governing the electron density distribution in organic molecules and molecular systems on the basis of application of the non-canonical method of molecular orbitals. It is devoted to investigation of an electron-donating effect of an external orbital upon a single ($Z-C$) or a double ($Z=C$) heteroatom-containing bond, which is among the widespread effects of organic chemistry (cf. a nucleophilic attack upon substituted alkanes or carbonyl compounds). Use of expressions for occupation numbers of basis orbitals of a $Z-C(Z=C)$ bond derived previously [V. Gineityte, *J. Mol. Struct. (Theochem)* 434 (1998) 43] allows the additional dipole moment of the bond due to the electron-donating effect to be considered as a result of competition between two meaningful components of opposite signs, viz. between the secondary polarization of the given bond owing to the very presence of the electron-donating orbital and the so-called depolarization originating from the dipole-like distribution of the acquired population. The consequent direction of the additional dipole is shown to depend decisively on the relative electronegativity of the heteroatom Z and thereby on the initial polarity of the bond. Predominance of the secondary polarization and thereby coincidence between the directions of the primary dipole of the given bond and of the additional one is obtained for bonds of relatively low initial polarity but not for those of high polarity. This somewhat unexpected result is traced back to alterations in constitution of the antibonding orbital of the $Z-C(Z=C)$ bond when the electronegativity of the heteroatom Z grows that yield a drastic increase of the absolute value of the depolarization dipole. On the basis of the results obtained, the rule of the so-called ‘curly arrow chemistry’ about the universal increase of the dipole moment of a $Z-C(Z=C)$ bond under influence of an electron-donating effect is concluded to be of a limited scope of validity. Moreover, a new accounting is suggested for the well-known experimental fact that highly electronegative heteroatoms usually are bad nucleofuges in S_N2 processes.

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1. Introduction

Search for general rules governing the electron density distributions in molecules and molecular systems is among the principal goals of theoretical chemistry. In particular, rules of this type form the basis of the qualitative way of chemical thinking, the persistent need for which was emphasized recently [1–3]. It is also noteworthy here that simple qualitative approaches and models of electronic structures become of importance in this field.

In respect of their fundamentals, four different types of the above-specified approaches may be distinguished, namely (a) the so-called ‘curly arrow chemistry’ based on the well-known octet rule [4], (b) the simplest qualitative version of the valence bond (VB) method usually referred to as the resonance theory [5], (c) the extremely popular HMO theory [6] based on the Hückel model in the framework of the canonical MO (CMO) method and (d) the Hückel model in the framework of the non-canonical MO (NCMO) method [7–17]. Historically, the above-enumerated approaches originated from rather different fields and problems of chemistry. The same evidently refers to their most outstanding achievements. It is quite likely, therefore,

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that these approaches are characterized by different scopes of validity.

The experience in revealing general rules governing electronic structures shows that consideration of a certain abstract chemical model or situation is preferable in this case to studies of particular molecules [3]. As for instance, the common Hückel type Hamiltonian matrix of the so-called alternant conjugated hydrocarbons may be mentioned [18]. The famous rules describing the MOs and bond order matrices of these systems [18–24] were obtained on the basis of just this model. Consideration of an analogous model for the relevant heteroatom-containing derivatives, in turn, resulted into the rule of alternating signs of orbital-orbital polarizabilities [21–24] describing the influence of a weakly electronegative heteroatom upon the electron density distribution in hydrocarbon fragments.

Situations representable as an electron-donating effect of an external initially-occupied orbital upon a heteroatom-containing ($Z-C$ or $Z=C$) bond may be found almost throughout the theoretical organic chemistry [4,25], where Z here and below stands for a heteroatom. Examples of such an effect are shown in Fig. 1 along with respective ‘curly arrows’. It is seen that a shift of electrons of the $Z-C(Z=C)$ bond towards the more electronegative atom Z is unambiguously predicted by the octet rule in this case. Consequently, an additional polarization of the $Z-C(Z=C)$ bond under influence of the electron-donating effect of the external

orbital is expected to arise, and the direction of this polarization is such that it ensures an increase of the initial dipole of this bond. It should be mentioned finally that the above-discussed shift of electrons towards heteroatom Z is considered as the driving force of the respective (substitution or addition) reactions [4]. Just this fact determines the importance of this effect for theoretical organic chemistry.

In this paper, we are about to study the dependence between the direction of the additional dipole of the $Z-C(Z=C)$ bond and parameters of atoms taking part in the effect. The aim of this study consists in demonstrating that the above predictions of the ‘curly arrow chemistry’ are not self-evident. At the same time, we are going to establish the conditions to be met to ensure the validity of these predictions. Finally, we will discuss the origin and chemical implications of an opposite direction of the additional dipole.

To achieve these ends, we will apply the non-canonical method of molecular orbitals developed in Refs. [7–17] and based on a general solution of the commutation equation for the one-electron density matrix (bond order matrix) in the form of power series [7]. In particular, we will invoke the expression for occupation numbers of orbitals of a heteroatom-containing bond involved within any chemical compound(s) [10]. This expression takes the form of a sum of three terms representing meaningful components of charge redistribution, viz. the secondary polarization of the given bond owing to the very presence of other bonds and/or lone electron pairs, the increment of the interbond charge transfer and the so-called depolarization of the bond owing to the dipole-like distribution of the lost (acquired) population. On this basis, we are going to reveal the dipole-like component of charge redistribution inside the $Z-C(Z=C)$ bond and to study the dependence between the sign of this component and parameters of the system.

It should be also mentioned here that the above-discussed expressions for occupation numbers were originally derived [9,10,14] and applied [8,15] to study alkanes and their derivatives. For conjugated hydrocarbons and their derivatives, adequacy of the same expressions was verified later [11–13,16,17]. In particular, these formulae have been successfully applied to substituted ethenes [16]. In this connection, our subsequent study embraces both single ($Z-C$) and double ($Z=C$) bonds.

The paper is organized as follows: In Section 2, we discuss the expression for occupation numbers of basis orbitals of a heteroatom-containing bond and formulate a condition to be met to ensure an increase of the total dipole of the bond in terms of signs and relative values of polarization and depolarization. Thereupon, we reformulate the same condition in terms of initial parameters of the system including electronegativities of the involved atoms and consider its validity (Section 3). The final Section 4 is devoted to chemical implications of the obtained results and conclusions.

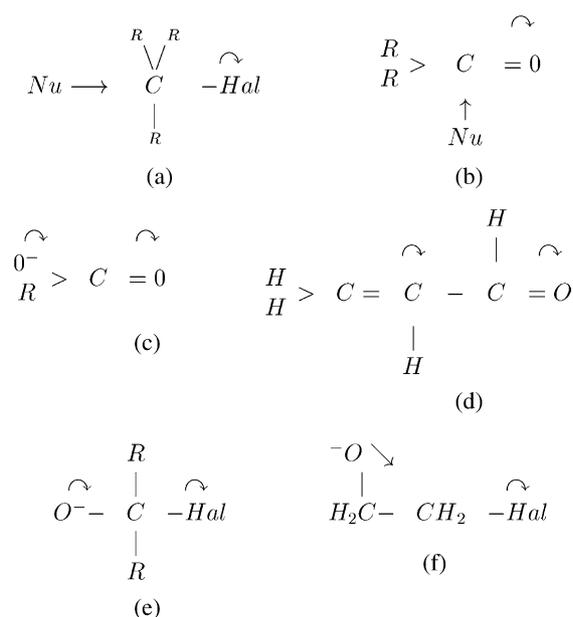


Fig. 1. Examples of an electron-donating effect of an external orbital upon a heteroatom-containing bond along with respective ‘curly arrows’ [4,25]: (i) An attack of nucleophile (Nu) upon an alkyl halogenide (a) and upon a carbonyl group ($R=CH_3, C_2H_5, \dots$ etc.) (b); (ii) Mesomeric effects in the carboxyl anion (c) and acrolein (d); as well as (iii) Electron-donating effects of lone pair orbitals of negatively charged oxygen at geminal (e) and vicinal (f) positions to the leaving halogen atom in intramolecular substitution reactions.

2. Expressions for populations of basis orbitals of a heteroatom-containing bond. The ‘a priori’ negative sign of depolarization

The power series for the one-electron density matrix (DM) [7–10,11] refers to the basis of bond orbitals (BOs), a precise definition which was not required for its derivation. When obtaining the expressions for occupation numbers of sp^3 -hybrid AOs (HAOs) of carbon atoms and $1s_H$ AOs of hydrogen atoms in alkanes and their derivatives [8,10], the relevant BOs have been defined as linear combinations of pairs of HAOs and $1s_H$ AOs corresponding to separate bonds. In the case of a $Z=C$ bond, pairs of respective $2p_z$ AOs may be used in the same definition [11,16,17]. Thus, we may consider a general case of a heteroatom-containing bond represented by two basis orbitals.

Let the bond under study coincide with the I th bond of our system. Accordingly, the above-mentioned basis orbitals ascribed to atoms Z and C , respectively, will be denoted by χ_{IZ} and χ_{IC} . These orbitals will be represented by Coulomb parameters α_Z and α_C , whereas the bond itself will be characterized by resonance parameter β_I . The equalities $\alpha_C=0$ and $\beta_I=1$ will be accepted further for convenience. Inasmuch as higher electronegativities usually are peculiar to heteroatoms as compared to carbon atoms [26,27], the parameter α_Z is assumed to be positive in the above-specified energy units. The structure of the remaining part of the system under study is not essential here.

Let the bonding bond orbital (BBO) of the I th bond and the respective antibonding orbital (ABO) to be defined as eigenfunctions of the relevant two-dimensional Hamiltonian matrix block in the basis $\{\chi_{IZ}, \chi_{IC}\}$ [10], i.e.

$$\varphi_{(+i)} = a_I \chi_{IZ} + b_I \chi_{IC}, \quad \varphi_{(-i)} = b_I \chi_{IZ} - a_I \chi_{IC}, \quad (1)$$

where the coefficients a_I and b_I are

$$a_I = \cos(\gamma_I/2), \quad b_I = \sin(\gamma_I/2), \quad a_I > b_I > 0 \quad (2)$$

and

$$\gamma_I = \arctan[2/\alpha_Z], \quad 0 \leq \gamma_I \leq (\pi/2). \quad (3)$$

It is seen that decreasing γ_I values (from $\pi/2$ to 0) correspond to increasing α_Z values (from 0 to ∞ , respectively). Thus, the upper limit $\gamma_I = \pi/2$ refers to 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 owing to similar values of their electronegativities [26,27]).

The occupation numbers X_{IZ} and X_{IC} of orbitals χ_{IZ} and χ_{IC} have been expressed as follows [10]

$$X_{IZ}(X_{IC}) = 1 \pm \cos \gamma_I + \frac{1}{2} \Delta X_{(2)I} \pm p_{(2)I} \pm d_{(2)I}, \quad (4)$$

where the upper signs refer to χ_{IZ} and the lower ones correspond to χ_{IC} . Terms to within the second order inclusive are shown in Eq. (4), and the subscripts (2) are used to denote the second order terms.

Let us consider members of Eq. (4) separately. The only zero order term of this expression coincides with $1 \pm \cos \gamma_I$, where γ_I is defined by Eq. (3). In accordance with the expectation, the population of the HAO χ_{IZ} of the more electronegative heteroatom Z is increased, whereas that of the AO χ_{IC} of the carbon atom is reduced as compared to 1. Thus, a zero order dipole ($\pm \cos \gamma_I$) is inherent in the bond under consideration whatever the structure of the whole molecule. This dipole will be further referred to as the primary one.

The second order term $(1/2)\Delta X_{(2)I}$ does not contribute to the total dipole of the I th bond as Eq. (4) indicates. Nevertheless, it is worth discussing because of its close relation to the last dipole $\pm d_{(2)I}$. Thus, the term $(1/2)\Delta X_{(2)I}$ describes a half of the total population of the I th bond lost (acquired) by this bond owing to the interbond charge transfer [9]. This term may be represented as a sum of contributions $\Delta X_{(2)I(j)}$, each of them associated with certain (J th) bond that plays the role of an acceptor (donor) of the lost (acquired) population. The total population alteration $\Delta X_{(2)I}$ takes the form

$$\Delta X_{(2)I} = \sum_J \Delta X_{(2)I(j)} = 2 \sum_{j \in J} \{(G_{(1)ji})^2 - (G_{(1)ij})^2\}, \quad (5)$$

where the subscript j embraces the two BOs of the J th bond, viz. the BBO $\phi_{(+j)}$ and the ABO $\phi_{(-j)}$. The notation $G_{(1)ij}$ stands for the element of the matrix $G_{(1)}$ [7] describing the direct (through-space) interaction between the BBO $\phi_{(+i)}$ of the I th bond and the ABO $\phi_{(-j)}$ of the J th bond. Similarly, $G_{(1)ji}$ represents the direct interaction between BOs $\phi_{(+j)}$ and $\phi_{(-i)}$. As a result, the positive contribution of the right-hand side of Eq. (5) describes the population acquired by the ABO $\phi_{(-i)}$, whereas the negative increment represents the population lost by the BBO of the same bond after ‘embedding’ the latter into the molecule.

As in Refs. [10,14], let us introduce the following notations for resonance parameters between various types of BOs, the latter being indicated within the bra- and ket-vectors, viz.

$$S_{ij} = \langle \varphi_{(+i)} | \hat{H} | \varphi_{(+j)} \rangle, \quad R_{ij} = \langle \varphi_{(+i)} | \hat{H} | \varphi_{(-j)} \rangle, \quad (6)$$

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

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

$$G_{(1)ij} = -\frac{R_{ij}}{E_{(+i)} - E_{(-j)}}, \quad G_{(1)ji} = -\frac{R_{ji}}{E_{(+j)} - E_{(-i)}}, \quad (7)$$

where the denominators contain differences in one-electron energies of BOs.

The next term of Eq. (4) ($p_{(2)I}$) describes the second order induced dipole moment of the I th bond due to the very presence of other bonds (lone pairs). This term may be expressed as follows

$$p_{(2)I} = -2G_{(2)ii} \sin \gamma_I \quad (8)$$

where $G_{(2)ii}$ is the diagonal element of the second order matrix $G_{(2)}$ [7] representing the indirect interaction of BOs of the I th bond (i.e. of $\phi_{(+i)}$ and $\phi_{(-i)}$) by means of orbitals of other bonds and/or lone electron pairs playing the role of mediators. Additivity of the matrix element $G_{(2)ii}$ with respect to mediators [7,10,14] allows the secondary polarization $p_{(2)I}$ to be expressed as a sum of partial increments $p_{(2)I(J)}$ like those of Eq. (5), where

$$p_{(2)I(J)} = -\frac{2 \sin \gamma_I}{E_{(+i)} - E_{(-i)}} \left(\frac{S_{ij}R_{ji}}{E_{(+j)} - E_{(-i)}} - \frac{R_{ij}Q_{ji}}{E_{(+i)} - E_{(-j)}} \right). \quad (9)$$

The first fraction within the brackets of Eq. (9) represents the increment of the BBO $\phi_{(+j)}$, whereas the second one describes the relevant contribution of the ABO $\phi_{(-j)}$ (It is evident that only the first fraction of the right-hand side of Eq. (9) remains when describing the influence of a lone electron pair). Differences in one-electron energies of BOs contained within denominators of the right-hand side of Eq. (9) always are positive in our energy units. Thus, the sign of the increment $p_{(2)I(J)}$ depends on relative values and signs of resonance parameters contained within the numerators and it cannot be defined ‘*a priori*’.

The last increment of Eq. (4) ($d_{(2)I}$) is related to the non-uniform distribution among the basis functions χ_{IZ} and χ_{IC} both of the population lost by the BBO $\phi_{(+i)}$ and of that acquired by the ABO $\phi_{(-i)}$ of the I th bond. This term has been expressed as follows [10]

$$d_{(2)I} = \sum_J d_{(2)I(J)} \\ = -\sum_{j \neq I} \{ (G_{(1)ji})^2 + (G_{(1)ij})^2 \} \cos \gamma_I \quad (10)$$

and contains a sum of absolute values of the above-mentioned two increments in contrast to $\Delta X_{(2)I}$. Additive nature of the total dipole $\pm d_{(2)I}$ with respect to contributions of various bonds of the molecule also is seen from Eq. (10). Moreover, an ‘*a priori*’ negative sign of the contribution $d_{(2)I}$ follows from Eq. (10) in contrast to $p_{(2)I}$ of Eqs. (8) and (9). Hence, the orbital χ_{IZ} of the heteroatom Z always loses some population owing to formation of this new dipole, whereas the orbital χ_{IC} acquires an additional population. This implies a certain reduction of the primary dipole of our bond. In this connection, $\pm d_{(2)I}$ has been called the depolarization dipole moment [10]. Vanishing of this dipole for C–C and C–H bonds also is noteworthy (if $\gamma_I = \pi/2$, $\cos \gamma_I = 0$ and $d_{(2)I} = 0$).

Interpretation of opposite signs of the primary dipole ($\pm \cos \gamma_I$) and of the depolarization one ($\pm d_{(2)I}$) also deserves attention here: The primary dipole corresponds to a complete occupation of the BBO $\phi_{(+i)}$ and a zero occupation of the ABO $\phi_{(-i)}$ within the zero order approximation. After taking into account the interbond charge transfer, the BBO $\phi_{(+i)}$ loses some population, whereas the ABO $\phi_{(-i)}$ acquires it as it was seen when

discussing Eq. (5). From the definition of BOs $\phi_{(+i)}$ and $\phi_{(-i)}$ of Eq. (1) and the inequality $a_I > b_I$ of Eq. (2) it is evident that the additional population acquired by the ABO $\phi_{(-i)}$ becomes localized mainly on the orbital χ_{IC} of the carbon atom. Analogously, the loss of population of the BBO $\phi_{(+i)}$ gives rise to a larger reduction of the occupation number of the AO χ_{IZ} of the heteroatom Z as compared to the respective reduction of population of the orbital χ_{IC} of the carbon atom C. Consequently, it is the shapes of BOs that ensure a reduction of the primary dipole moment of the heteroatom-containing bond owing to the interbond charge transfer whatever the structure of the whole system.

Therefore, an increased total dipole of the heteroatom-containing bond may be expected under two conditions, namely if $p_{(2)I}$ is a positive quantity and if it exceeds the absolute value of $d_{(2)I}$, i.e. if

$$p_{(2)I} > 0; \quad |p_{(2)I}| > |d_{(2)I}|. \quad (11)$$

In Section 3 we are going to check the validity of these conditions.

3. Comparison of relative extents of polarization and depolarization of bonds

Additivity of expressions for both $p_{(2)I}$ and $d_{(2)I}$ with respect to contributions of the remaining bonds (lone electron pairs) discussed in Section 2 allows us to consider the increment of each external orbital separately. As it is seen from Fig. 1, contribution of a single orbital usually is of interest in chemical situations. This orbital coincides either with the principal electron-donating orbital [15–17] of the nucleophile *Nu* (Fig. 1a and b) or with the lone pair orbital of the formally negatively-charged oxygen (Fig. 1c, e and f) or with the initially-occupied bonding orbital [17] of the $H_2C=CH$ -substituent (Fig. 1d). Let this electron-donating orbital to be denoted by $\phi_{(+d)}$. Accordingly, contributions of this orbital to dipoles $p_{(2)I}$ and $d_{(2)I}$ of the I th bond will be designated by $p_{(2)I(D)}$ and $d_{(2)I(D)}$, respectively. It should be also noted here that the relevant definitions follow from Eqs. (9) and (10) after omitting the increments of the external antibonding orbital, and these take the form

$$p_{(2)I(D)} = -\frac{2S_{id}R_{di} \sin \gamma_I}{(E_{(+i)} - E_{(-i)})(E_{(+d)} - E_{(-i)})} \quad (12)$$

and

$$d_{(2)I(D)} = -\frac{(R_{di})^2 \cos \gamma_I}{(E_{(+d)} - E_{(-i)})^2}, \quad (13)$$

where Eqs. (6) and (7) also are invoked. The resonance parameters S_{id} and R_{di} contained within Eqs. (12) and (13) meet the following inequalities in our negative energy units

$$S_{id}^{(\sigma)} < 0; \quad R_{di}^{(\sigma)} > 0; \quad S_{id}^{(\pi)} > 0; \quad R_{di}^{(\pi)} < 0, \quad (14)$$

where the superscripts (σ) and (π) correspond to the cases of Z–C and Z=C bonds. Two points are taken into consideration along with Eqs. (1) and (2) when obtaining Eq. (14): First, the electron-donating orbital $\phi_{(+d)}$ is assumed to overlap with the AO χ_{IC} of the carbon atom C but not with the AO χ_{IZ} of the heteroatom Z, and, second, the orbital $\phi_{(+d)}$ overlaps with the negative loop of the sp^3 -hybrid AO χ_{IC} [15] owing to its back position with respect to the Z–C bond (Fig. 1).

Substituting Eq. (14) into Eq. (12) shows that both $p_{(2)I(D)}^{(\sigma)}$ and $p_{(2)I(D)}^{(\pi)}$ are positive increments whatever the actual one-electron energies of orbitals $\phi_{(+i)}$, $\phi_{(-i)}$ and $\phi_{(+d)}$. Hence, the secondary polarization due to the very presence of the external orbital $\phi_{(+d)}$ always contributes to an increase of the dipole moment of the given bond irrespective of electronegativities of the involved atoms.

It is noteworthy in this context that the contribution $p_{(2)I(D)}$ proves to be the only term determining the dipole moment of a C–C(C–H) or C=C bond under influence of an external electron-donating effect, e.g. in substituted ethenes D–HC $_{\alpha}$ =C $_{\beta}$ H $_2$, where D stands for an electron-donating substituent (D=OR, NR $_2$, etc.). The above-established positive sign of this contribution then implies a larger occupation number of the $2p_z$ AO of the terminal (C $_{\beta}$) carbon atom as compared to that of the internal atom (C $_{\alpha}$). Consideration of the structure of the non-bonding MO of the hydrocarbon prototype of these molecules [19,28] also yields an increased population of the $2p_z$ AO of the terminal (C $_{\beta}$) carbon atom as compared to that of ethene (the prototype coincides with the allylic anion R $_2$ C $^-$ –C $_{\alpha}$ H=C $_{\beta}$ H $_2$, which ranks among odd alternant hydrocarbon ions). Coincidence of our predictions to those following from the hydrocarbon prototype demonstrates reliability of our approach, on the one hand, and supports transferability of the results based on this prototype to the case of non-hydrocarbon species, on the other hand.

Let us turn again to the Z–C(Z=C) bond. If we recall that $d_{(2)I(D)}$ is a negative quantity for any heteroatom-containing bond, comparison of absolute values of $p_{(2)I(D)}$ and $d_{(2)I(D)}$ defined by Eqs. (12) and (13) proves to be the final aim of our study (see Eq. (11)). The most convenient way of accomplishing such a comparison consists in consideration of the following requirement for an α_Z -dependent ratio $\rho(\alpha_Z)$

$$\rho(\alpha_Z) = \frac{|p_{(2)I(D)}|}{|d_{(2)I(D)}|} > 1. \quad (15)$$

Substituting Eqs. (12) and (13) into Eq. (15) yields the expression

$$\rho(\alpha_Z) = 2 \frac{E_{(+d)} - E_{(-i)}}{E_{(+i)} - E_{(-i)}} \tan \gamma_I \tan \frac{\gamma_I}{2} \quad (16)$$

where the relation

$$\left| \frac{S_{id}}{R_{di}} \right| = \left| \frac{\langle b_I \chi_{IC} | \hat{H} | \phi_{(+d)} \rangle}{\langle \phi_{(+d)} | \hat{H} | (-a_I) \chi_{IC} \rangle} \right| = \frac{b_I}{a_I} = \tan \frac{\gamma_I}{2} \quad (17)$$

also is used along with Eq. (2). One-electron energies contained within the right-hand side of Eq. (16) may be expressed as follows [29]

$$\begin{aligned} E_{(+i)} &= \alpha_Z \cos^2 \frac{\gamma_I}{2} + \sin \gamma_I; \\ E_{(-i)} &= \alpha_Z \sin^2 \frac{\gamma_I}{2} - \sin \gamma_I. \end{aligned} \quad (18)$$

Let the intrabond energy interval $E_{(+i)} - E_{(-i)}$ to be denoted by $\Delta E_I(\alpha_Z)$. We then obtain

$$\begin{aligned} \Delta E_I(\alpha_Z) &= E_{(+i)} - E_{(-i)} = \alpha_Z \cos \gamma_I + 2 \sin \gamma_I \\ &= \frac{2}{\sin \gamma_I}, \end{aligned} \quad (19)$$

where the last expression results after substituting $2/\tan \gamma_I$ for α_Z in accordance with Eq. (3). For the remaining energy difference, we accordingly derive

$$\begin{aligned} \Delta E_D(\alpha_Z) &= E_{(+d)} - E_{(-i)} \\ &= \alpha_d - \alpha_Z \sin^2 \frac{\gamma_I}{2} + \sin \gamma_I \\ &= \alpha_d + \frac{1 - \cos \gamma_I}{\sin \gamma_I} \end{aligned} \quad (20)$$

where the notation $E_{(+d)} = \alpha_d$ is used for simplicity.

Let us start with the case of small values of electronegativity (α_Z) of our heteroatom Z describing bonds of a low initial polarity. We then obtain

$$\gamma_I \rightarrow \frac{\pi}{2}; \quad \tan \gamma_I \rightarrow \infty; \quad \sin \gamma_I \rightarrow 1; \quad \tan \frac{\gamma_I}{2} \rightarrow 1. \quad (21)$$

Given that α_d also is a small quantity close to α_Z , the respective energy intervals $\Delta E_I(\alpha_Z \rightarrow 0)$ and $\Delta E_D(\alpha_Z \rightarrow 0)$ may be correspondingly approximated by 2 and 1 and

$$\rho(\alpha_Z \rightarrow 0) \approx \tan \gamma_I \rightarrow \infty. \quad (22)$$

This result implies that the positive secondary polarization $p_{(2)I(D)}$ predominates over the negative depolarization $d_{(2)I(D)}$ for this particular case. Moreover, the same conclusion refers to larger α_d values as well (An increase of this parameter implies an extension of the energy interval ΔE_D and thereby a further growth of the ratio ρ). Hence, an increase of the total dipole moment of a heteroatom-containing bond follows whatever the relative values of parameters of the external orbital $\phi_{(+d)}$.

Let us demonstrate now that the ratio $\rho(\alpha_Z)$ decreases monotonically when the relative electronegativity α_Z of our heteroatom Z grows. To this end, let us consider the derivative

$$\frac{d\rho(\alpha_Z)}{d\alpha_Z} = \frac{d\rho(\alpha_Z)}{d\gamma_I} \frac{d\gamma_I}{d\alpha_Z}, \quad (23)$$

where the second factor of the right-hand side

$$\frac{d\gamma_I}{d\alpha_Z} = -\frac{2}{(\alpha_Z)^2 + 4} < 0 \quad (24)$$

easily follows from Eq. (3). It is seen that the positive sign of $d\rho(\alpha_Z)/d\gamma_I$ within the interval of γ_I values specified by Eq. (2) is required for the total derivative under interest to take a negative sign. Using Eq. (16) we obtain

$$\begin{aligned} \frac{d\rho(\alpha_Z)}{d\gamma_I} = & \frac{2}{[\Delta E_I(\alpha_Z)]^2} \left\{ \frac{d[\Delta E_D(\alpha_Z)]}{d\gamma_I} \tan \gamma_I \tan \frac{\gamma_I}{2} \Delta E_I(\alpha_Z) \right. \\ & + \Delta E_D(\alpha_Z) \frac{d \tan \frac{\gamma_I}{2}}{d\gamma_I} \tan \frac{\gamma_I}{2} \Delta E_I(\alpha_Z) \\ & + \Delta E_D(\alpha_Z) \tan \gamma_I \frac{d \tan \frac{\gamma_I}{2}}{d\gamma_I} \Delta E_I(\alpha_Z) \\ & \left. - \Delta E_D(\alpha_Z) \tan \gamma_I \tan \frac{\gamma_I}{2} \frac{d[\Delta E_I(\alpha_Z)]}{d\gamma_I} \right\}, \end{aligned} \quad (25)$$

where $\Delta E_I(\alpha_Z)$ and $\Delta E_D(\alpha_Z)$ are defined by Eqs. (19) and (20).

Positive signs of all quantities contained within the right-hand side of Eq. (25) are rather evident except for the derivatives of the energy intervals, viz. $d[\Delta E_I(\alpha_Z)]/d\gamma_I$ and $d[\Delta E_D(\alpha_Z)]/d\gamma_I$. Thus, let us consider them separately. The last expression of Eq. (19) yields

$$\frac{d\Delta E_I(\alpha_Z)}{d\gamma_I} = -\frac{2 \cos \gamma_I}{\sin^2 \gamma_I} < 0. \quad (26)$$

From the last relation of Eq. (20) we accordingly obtain

$$\frac{d\Delta E_D(\alpha_Z)}{d\gamma_I} = \frac{1 - \cos \gamma_I}{\sin^2 \gamma_I} > 0. \quad (27)$$

Substituting Eqs. (26) and (27) into Eq. (25), in turn, indicates the positive sign of the derivative $d\rho(\alpha_Z)/d\gamma_I$ and thereby the negative sign of the derivative being sought, i.e. of $d\rho(\alpha_Z)/d\alpha_Z$.

Therefore, our expectation about the monotonically decreasing nature of the ratio $\rho(\alpha_Z)$ proves to be supported. Moreover, a similar study of the right-hand side of Eq. (13) allows us to conclude that the depolarization dipole moment $d_{(2)I(D)}$ also is a monotoneous function of α_Z (Note that R_{di} is proportional to $\cos(\gamma_I/2)$). As opposed to the ratio $\rho(\alpha_Z)$, however, the absolute value of the depolarization dipole moment grows dramatically with increasing electronegativity of the heteroatom Z.

Let us turn now to heteroatoms of extremely high relative electronegativity ($\alpha_Z \rightarrow \infty$). We then obtain

$$\gamma_I \rightarrow 0; \quad \tan \gamma_I \rightarrow 0; \quad \tan \frac{\gamma_I}{2} \rightarrow 0 \quad (28)$$

and $\rho(\alpha_Z \rightarrow \infty)$ also proves to be a negligible quantity whatever the relative value of the parameter α_d . Hence, the negative depolarization $d_{(2)I(D)}$ exceeds the positive polarization $p_{(2)I(D)}$ in this case, and a reduction of the total dipole of the Z–C(Z=C) bond is obtained.

Let us dwell finally on heteroatoms of medium electronegativity. Let us assume for simplicity that $\alpha_Z=2$. We then obtain

$$\begin{aligned} \gamma_I = \frac{\pi}{4}; \quad \tan \gamma_I = 1; \quad \sin \gamma_I = \cos \gamma_I = \frac{1}{\sqrt{2}}; \\ \tan \frac{\gamma_I}{2} \approx 0.4 \end{aligned} \quad (29)$$

Substituting Eq. (29) into Eqs. (16), (19) and (20) yields

$$\rho(\alpha_Z = 2) \approx 0.8 \frac{\alpha_d + \sqrt{2} - 1}{2\sqrt{2}} \approx 0.8 \frac{\alpha_d + 0.4}{2.8}. \quad (30)$$

It is seen that the condition $\rho(\alpha_Z=2) > 1$ may be met only for sufficiently large α_d values that exceed the α_Z value considerably ($\alpha_d > 3.1$). Hence, only highly-electronegative (hard) donors of electrons are able to ensure an increase of the total dipole moment of the Z–C(Z=C) bond of a medium polarity. Otherwise, a decrease of the total dipole is predicted. The case of coinciding absolute values of polarization and depolarization increments of the total dipole of the Z–C(Z=C) bond will be obtained for $\alpha_d \approx 3.1$ and this implies a zero value of the additional polarization.

Before finishing this section, let us dwell on the actual values of the relative electronegativity α_Z of various heteroatoms Z. Although, the results of the relevant estimations depend on the set of parameters used [8], the majority of heteroatoms are expected to be described by α_Z values inside the interval $0 \leq \alpha_Z \leq 2$ [28]. For example, $\alpha_O \approx 1.0$ is obtained for the O=C bond after invoking the relevant parameters of the Hückel model of Ref. [28]. Furthermore, evaluations like those of Ref. [8] yield $\alpha_F \approx 1.7$ for the F–C bond in alkyl fluorides, and this case is rather close to that described by Eq. (30).

4. Discussion of the principal result of the study and conclusions

The principal result of our study may be formulated as follows:

The direction of the total additional dipole of a heteroatom-containing bond under influence of an electron-donating effect of an external orbital decisively depends on the actual value of the relative electronegativity of the given heteroatom and thereby on the initial polarity of the bond. For bonds of a low polarity, the total dipole moment always becomes increased under influence of the electron-donating effect whatever the remaining parameters of the system. However, this trend gradually goes into reverse when the electronegativity of the heteroatom and thereby the initial polarity of the bond grows. Indeed, even for bonds of a medium polarity a decrease of the total dipole moment is predicted (except for the case of hard electron-donating groups represented by orbitals of a high electronegativity), to say nothing about the highly polar bonds.

The above-mentioned overturn of the direction of the additional dipole of a heteroatom-containing bond when the electronegativity of the heteroatom grows may be accounted for by a rather drastic increase of the absolute value of the negative depolarization dipole moment. Inasmuch as this moment describes the dipole-like distribution inside the Z–C(Z=C) bond of the additional population acquired from the electron-donating orbital $\phi_{(+)}d$, the relevant alterations in constitution of the initially-vacant (antibonding) orbital of this bond prove to be responsible for the above-predicted effect. Indeed, the larger is the relative electronegativity of the heteroatom Z, the more pronounced is the trend towards localization of this antibonding orbital on the carbon atom. As a result, more and more population is acquired by the carbon atom relatively to that acquired by the heteroatom when the electronegativity of the latter grows. Finally, the growing absolute value of the negative depolarization increment reaches and exceeds the positive polarization increment. As a result, the total additional polarization of the bond takes a negative sign and thereby a decrease of the final dipole moment is obtained.

Therefore, predictions of the ‘curly arrow chemistry’ about the universal increase of the dipole moment of a heteroatom-containing bond under influence of an electron-donating effect of an external orbital proves to be supported only for weakly polar bonds but not for highly polar ones. This implies a limited scope of validity of the rules referred to as the ‘curly arrow chemistry’ and based only on the octet condition for electrons of the carbon atom. Such a conclusion causes no surprise because this simple rule predicts a definite shift of electrons without consideration whether or not the appropriate orbitals are present in the particular system that are able to accept the shifted electrons.

It should be noted finally that the above-established limited validity of the ‘curly arrow chemistry’ hardly implies a limited adequacy of the octet rule. On the other hand, a reverse prediction about a decreased dipole of the Z–C(Z=C) bond and thereby about a larger population acquired by the carbon atom vs. that of the heteroatom owing to an electron-donating effect of an external orbital seems to run counter to this rule. Therefore, the most reasonable way out of this situation lies in an assumption about a low (or even zero) rates of the relevant reactions in the range of invalidity of the ‘curly arrow chemistry’, e.g. of the S_N2 processes of substituted alkanes (Fig. 1a) containing highly electronegative substituents.

On the whole, the results of this paper yield an accounting for the well-known experimental fact that highly electronegative heteroatoms (or their groups) usually are bad nucleofuges in the S_N2 processes, e.g. the fluorine atoms in alkyl fluorides [4,25,30–33]. Indeed, the formation of an induced dipole of the heteroatom-containing bond such that it is able to contribute to its appropriate heterolytic

dissociation, is not ensured in this case, and this peculiarity of highly electronegative heteroatoms serves to account for their low nucleofugality. Similarly, the fact that reactants containing highly electronegative (hard) nucleofuges predominantly react with hard nucleophiles [33] may be traced back to our conclusion that only highly electronegative donors of electrons are able to ensure an increase of the total dipole moment of the Z–C(Z=C) bonds of medium polarity.

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