ON SEPARATION OF INDUCTIVE AND RESONANCE EFFECT

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On the basis of minimization of the properly defined objective function, a general method for separation of inductive and resonance effect has been proposed. Comparison of the so calculated results with characteristics obtained independently by perturbation theory of substituent effect made it possible to discuss mechanism of the transmission of inductive effect in aromatic and aliphatic series.

One of the basic concepts in physical organic chemistry is the concept of substituent. Its introduction was made possible by the fact that the attachment of a given group to different structural skeletons leads to very similar changes in properties of these skeletons. This finding led to the conclusion that each substituent attached to the molecule shows a certain effect which is an invariant property of this substituent. In such an approach that was most extensively applied in the field of linear free energy relationships, the substituent is characterized by the value of the so called substituent constant σ. The development of theoretical chemistry resulted in that this original concept has been replaced by the more detailed description in which the total substituent effect is expressed in terms of additive contributions that correspond to different mechanisms of intramolecular interaction. This approach became the basis of multiparameter correlation analysis.

In general, we speak of two basic mechanisms of transmission of substituent effect, *i.e.* of inductive and resonance effect. This classification is supported by quantum chemical theory of substituent effect[1]. Nevertheless, all the attempts to separate these effects have been based so far on empirical grounds and classical chemical concepts. Several methods of separation have been proposed, of which especially those of Taft[2], Exner[3], Swain and Lupton[4], and Charton[5] should be mentioned. Empirical basis of all these methods necessitates for achieving this separation to accept a series of complementary assumptions related to the mechanism of transmission of inductive effect (the same mechanism of transmission of inductive effect in aliphatic and aromatic series makes it possible to utilize the common scale of inductive constants) and to the relative intensity of transmission of resonance effect from *meta* and *para* positions. These apriori assumptions can, however, influence markedly the character of the resultant separation.

Therefore, the aim of this work was to suggest a general objective method for separation that would minimize the additional assumptions as much as possible. This made it possible to confront so calculated relative intensities of transmission of inductive and resonance effect from *meta* and *para* position with theoretical values obtained by quantum chemical theory of substituent effect. This approach allows also to discuss eventual differences in the mechanism of transmission of inductive effect in series of aliphatic compounds.

RESULTS AND DISCUSSION

The basic idea of separation of substituent effect starts from the assumption that common Hammett constants σ_p and σ_m can be expressed as a linear combination of certain, so called inductive and resonance constants I and M. The above concept can be formulated mathematically by Eqs $(1a)$ and $(1b)$.

$$\sigma_{p,i} = I_i + M_i, \tag{1a}$$

$$\sigma_{m,i} = \lambda I_i + \alpha M_i. \tag{1b}$$

These constants have not to be inevitably identical with standard set of σ_I and σ_R constants. Parameters α and λ characterize the relative intensity of trasmission of inductive and resonance effect from *meta* position.

Providing that the values of constants α and λ are known, the corresponding inductive and resonance constants I and M can be obtained by solving the set of linear equations $(1a)$ and $(1b)$ for each substituent i. The resultant values of inductive and resonance constants are expressed by Eqs $(2a)$ and $(2b)$.

$$I_i = \frac{\alpha\sigma_{p,i} - \sigma_{m,i}}{\alpha - \lambda}, \tag{2a}$$

$$M_i = \frac{\sigma_{m,i} - \lambda\sigma_{p,i}}{\alpha - \lambda}. \tag{2b}$$

As constants α and λ are *apriori* unknown, their estimation has to be made on the basis of some additional assumptions. Thus, for example, Exner assumed that some substituents (NO_2, CN, CF_3, CCl_3, SO_2CH_3, *etc.*) do not exert resonance effect and starting from ΔpK_m vs ΔpK_p dependence for dissociation of the so substituted benzoic acids he obtained the value of $\lambda \approx 0.87$. The value of α has been assumed to be roughly 0.33. As the reliability of the resultant constants I and M will depend to a great extent on the estimation of λ and α, it becomes clear that this estimation should be based on some objective criteria.

One of the possibilities how to achieve this goal is to find such values of α and λ leading to constants I being as close as possible to the scale of common inductive constants σ_I. From mathematical standpoint, it means that we are looking for α and λ values minimizing the objective function $F(\alpha, \lambda)$ (Eq. (3)).

$$\delta F(\alpha, \lambda) = \delta \sum_i (I_i - \sigma_{I,i})^2 = 0. \tag{3}$$

The objective function can be undoubtedly constructed also in many different ways. However, our was stimulated by the effort to retain the same mechanism of transmission of inductive effect in aromatic and bicyclooctane series. Furthermore, the form of function (3) implies the same intensity of transmission of inductive effect in both series. This requirement represents, however, rather limiting condition. More general would be, therefore, to minimize the function $\phi(\alpha, \lambda, c)$ (Eq. (4))

$$\delta \, \phi(\alpha, \lambda, c) = \delta \sum_i (I_i - c\sigma_{I,i})^2 = 0 \qquad (4)$$

expressing by the coefficient c that constants I_i can be only proportional to constants $\sigma_{I,i}$ due to the fact that inductive effect is transmitted with different intensity in both series (although still by the same mechanism).

This method of separation eliminates the original apriori assumption that resonance effect of some substituents is equal to zero. Furthermore, minimization of the objective function demonstrates the statistical character of constants I and M in the sense that they represent the best compromise "averaged" over the whole set of substituents under study.

For practical purposes, it is convenient to rewrite Eq. (4) to the equivalent Eq. (5) that makes it possible to minimize the objective function analytically.

$$\delta \sum_i \left(\frac{I_i}{c} - \sigma_{I,i}\right)^2 = 0 \, . \qquad (5)$$

It holds that

$$\frac{I_i}{c} = \frac{\alpha}{\varepsilon} \sigma_{p,i} - \frac{1}{\varepsilon} \sigma_{m,i} \, , \qquad (6a)$$

where

$$\varepsilon = c(\alpha - \lambda) \, . \qquad (6b)$$

Optimization of the objective function (5) is thus equivalent to search for coefficients α/ε and $1/\varepsilon$ in Eq. (6a) by minimizing the sum (7) by the least squares method.

$$\sum_i \left(\sigma_{I,i} - \frac{\alpha}{\varepsilon} \sigma_{p,i} + \frac{1}{\varepsilon} \sigma_{m,i}\right)^2 \, . \qquad (7)$$

The values of α and ε calculated for the set of substituents studied by us are equal to

$$\alpha = \quad 0.358 \qquad (8a)$$

$$\varepsilon = -0.621 \, . \qquad (8b)$$

At this moment it should be mentioned that although the function ϕ is the function of three variables δ, λ, and c, the physical nature of the problem allows to determine only two independent parameters α and ε. With respect to the validity of Eq. (6), parameters λ and c are interrelated by Eq. (9) that shows that the problem of decomposition of substituent effect to inductive and resonance components has no unique solution. In addition to the value of α which is given unambiguously, one can find from Eq. (9)

$$\lambda = \alpha - \frac{\varepsilon}{c} \qquad (9)$$

for each values of parameter c the corresponding optimum λ and within the framework of empirical separation processes, none of $\lambda - c$ pairs can be preferred.

One should stress that the above ambiguity results from general dependence between λ and c and is not the consequence of Eq. (9). The form of this equation is given by the specific form of the objective function and may change in dependence on the requirements imposed on its construction.

Ambiguity connected with the impossibility to determine the "correct" values λ and c makes it impossible to determine also the unambiguous set of inductive and resonance constants I and M. Although previous methods of separation allow such a determination, one should keep in mind that they do it at the expense of similar, although not always explicitly formulated and verified additional assumptions. Thus, for example, Taft's method of separation presumes that the inductive effect is transmitted identically in aliphatic and aromatic series, $i.e.$ that $c = 1$. In contradistinction to this, Exner presumes that the resonance effect of some substituents is equal to zero. Our intention is not to discuss the correctness of these assumptions but rather to demonstrate that as a consequence such an approach leads to the adjustment of certain values of λ and thus also of c.

From the foregoing discussion it becomes evident that inductive and resonance constants determined by the above methods are ladden with subjectivity that arises from apriori choice of λ or c values. Furthermore, these constants are valid only for the skeleton for which they were derived and cannot be applied to other skeletons. Constants λ and c thus represent certain key molecular characteristics, the determination of which cannot be made within the framework of empirical separation methods and correlation analysis. Therefore, any attempt to determine these constants independently, which can only lead to the solution of the problem of the unambigous separation of substituent effect, must be made on the basis of microscopic description. In this sense, the determination of parameter λ based on SCF perturbation theory of substituent effect seems to be perspective. We start from the fact that the proposed perturbation theory characterizing the substituent only by the change in coulombic integral $\Delta\alpha$, is suitable for description of substituent effect in conjugated and aromatic skeletons. Of the total substituent effect, such a model is thus able

to describe only inductive component, and of it especially the so called π inductive and field effects. However, it does not include the so called I_σ effect which is transferred through the molecule by mechanism of the succesive polarization of σ bonds. Unfortunately, this is just this mechanism that operates in aliphatic series and it is difficult to estimate the magnitude of the error arising from the assumption about the same mechanism of transmission of inductive effect in aromatic and aliphatic series. Nevertheless, let us keep this assumption and make an attempt to determine theoretical values of λ based on our model.

Theoretical determination of parameter λ starts from Eq. (10) where π_m and π_p stand for atom–atom polarizabilities in a given skeleton. In accordance with Taft's

$$\lambda = \frac{\pi_m}{\pi_p} \tag{10}$$

and Exner's separation method, we have chosen the dissociation of substituted benzoic acids as standard reaction. π_m and π_p correspond then to polarizabilities $\pi_{3,8}$ and $\pi_{4,8}$, the numbering of atoms being given in Scheme 1.
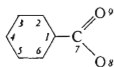
SCHEME 1

Our earlier perturbation theory proved that the transmission of substituent effect from position *meta* is not fully described by SCF perturbation theory and that one has to use SCF–LCI perturbation theory[6,7]. In terms of this theory, the expression

TABLE I

Calculated values of SCF–LCI quantities X and of parameter λ for dissociation of benzoic acid in dependence on the magnitude of perturbations, $\Delta\alpha_3 = \Delta\alpha_4 = -k$; $\Delta\alpha_8 = +k$ (eV)

k	X_m, eV	X_p, eV	λ
3	-0.0410	-0.1076	0.38
2	-0.0079	-0.0245	0.32
1	$-9.4 \cdot 10^{-4}$	$-4.25 \cdot 10^{-3}$	0.22
0.5	$-7.0 \cdot 10^{-5}$	$-6.5 \cdot 10^{-4}$	0.11

for parameter λ is given by Eq. (*11*), the corresponding quantities X being defined in

$$\lambda = \frac{X_m}{X_p} \qquad (11)$$

the work cited. With regard to the fact that the magnitude of X_m and X_p depends on the absolute values of perturbations $\Delta\alpha$, it is necessary to extrapolate X value to zero perturbation, to achieve the consistency from Eq. (*6*).

However, this limit procedure is not advantageous for numerical calculation, as for small perturbations close to zero, also X values are close to zero, so that the real values can be easily distorted by rounding-off errors that accumulate during the calculation. Therefore, we have approximated parameter λ by the quotient of quantities X calculated for several small, but finite perturbations. For purposes of illustration, the calculated values are presented in Table I. It is seen that the magnitude of perturbations affects not only X_m and X_p values but also the parameter λ. For the smallest perturbations, for which one would expect the best λ values according to Eq. (*7*), the distortion due to rounding-off errors in quantities X plays a role. For that reason, the correct "limit" value of λ can be hardly determined. The reasonable compromise are then the values of λ corresponding to perturbations $|\Delta\alpha| \sim 1-2$ eV, *i.e.* $\lambda \doteq 0{\cdot}20 - 0{\cdot}30$. According to Eq. (*9*), the values of c corresponding to the above λ values then lie in the interval -4 to -10. These values are not acceptable since the $c < 0$ represents the situation where the substituent acting inductively as a donor on the aromatic skeleton will act as an acceptor in bicyclooctane and *vise versa*. With respect to the fact that the above perturbation theory proved frequently useful in describing substituent effect in aromatic series, it seems likely that the λ value determined by us will not be much unrealistic. From the foregoing it follows that the unacceptable value of the corresponding c results from Eq. (*9*) that was based on the assumption about identical mechanism of inductive effect transmission in aliphatic and aromatic series. As mentioned earlier in connection with discussion of our model of substituent effect, this assumption is not fully justified since our model neglects I_σ effect. This neglect plays likely only insiginificant role in aromatic series in which the contribution of I_σ would be roughly constant, if not even neglectable. On going to bicyclooctane series, the importance of I_σ effect can increase to such a degree that it becomes dominant mechanism of inductive effect transmission. In order to describe quantitatively the role of I_σ effect in aliphatic series, the perturbation theory should be extended behind the framework of π approximation on the level of methods working with all valence electrons.

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Translated by J. Hetflejš.