PERTURBATION THEORY OF SUBSTITUENT EFFECT. IMPORTANCE OF THE FIELD EFFECT IN TRANSMISSION OF THE SUBSTITUENT EFFECT

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Various quantum chemical approaches to the problem of transmission of the substituent effect were compared. It was shown that inclusion of the electronic repulsion (field effect) was necessary to give a true picture of differences in ϱ constants for reactions of the *cis* and *trans* isomers of substituted unsaturated carboxylic acids; the same holds for an adequate description of transmission of the substituent effect from the meta position on a given skeleton.

On the basis of the second-order HMO perturbation theory, a relation has recently been derived which can be viewed as a quantum chemical analogue of the Hammett equation[1,2]. This relation makes it possible to interpret the reaction constants ϱ for reactions in a series of various structurally similar substrates. However, the major disadvantage of this quantum chemical relation is that its application is restricted only to cases where a direct resonance interaction exists between the substituent and the reaction center on a given skeleton (*para* position). A typical example of a failure of such an HMO approach is the impossibility to describe, even qualitatively, the transmission of the substituent effect from the *meta* position. Another example of an insufficient HMO description is the case of ϱ constants for reactions of the *cis* and *trans* isomers of substituted unsaturated carboxylic acids.

It is clear that all these shortcomings are most likely a result of neglecting the electronic repulsion in the HMO method. A logical attempt at removing these shortcomings led to the inclusion of the electronic repulsion into our model of the substituent effect, namely on the level of the Hartree–Fock perturbation theory[3] and SCF-LCI perturbation theory[4,5].

In this work an attempt has been made to show and emphasize the predominating role of the field effect in transmission of the substituent effect from the *meta* position and to rationalize theoretically the experimental differences in ϱ constants found for reactions of the *cis* and *trans* isomers of unsaturated carboxylic acids.

THEORETICAL

Similarly as in the previous papers, let us assume a simple quantum chemical model where the introduction of a substituent is modelled only by a change in the Coulombic integral $\Delta\alpha_\mu$ at the atom bearing a substituent and where an equilibrium or a rate process is modelled by a change $\Delta\alpha_\nu$ at the reaction center. Then, on the basis of the perturbation theory, the equation (*1*) can be derived that can be considered as a quantum chemical analogue of the Hammett equation[1]

$$\log k_{\mu\nu}/k_{0\nu} = -X_{\mu\nu}/2{\cdot}3RT\,. \tag{1}$$

The quantity $X_{\mu\nu}$ can be expressed on the level of various quantum chemical methods with a different degree of approximation. For the simplest case in the HMO theory the Eq. (*2*) holds

$$X_{\mu\nu} = \pi_{\mu\nu}\,\Delta\alpha_{\mu}\,\Delta\alpha_{\nu}\,, \tag{2}$$

where $\pi_{\mu\nu}$ are the atom–atom polarisabilities[6,7]. Including the electronic repulsion on the level of the Hartree–Fock perturbation theory[3] gives an analogous expression for $X_{\mu\nu}$, only the polarisabilities need to be replaced by the "generalized" polarisabilities defined by Eq. (*3*):

$$\Pi_{\mu\nu} = 4\sum_{i}^{\mathrm{occ}}\sum_{k}^{\mathrm{unocc}}\frac{c_{i\mu}c_{i\nu}c_{k\mu}c_{k\nu}}{\varepsilon_i - \varepsilon_k - \sum_{\alpha,\beta}\left(2c_{i\alpha}c_{i\beta}c_{k\alpha}c_{k\beta} - c_{i\alpha}^2c_{k\beta}^2\right)\gamma_{\alpha\beta}}\,. \tag{3}$$

In the most general case of the SCF-LCI perturbation theory[4,5], $X_{\mu\nu}$ cannot be longer expressed explicitly by means of polarisabilities and needs to be calculated on the basis of the definitional expression (*4*)

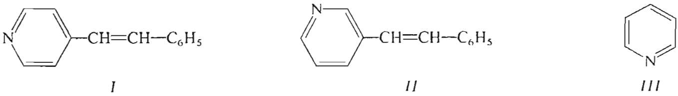
$$X_{\mu\nu} = E_{\mu\nu} - E_{\mu} - E_{\nu} + E_0\,, \tag{4}$$

where E_{μ} and E_{ν} represent the energies of a molecule with a perturbation $\Delta\alpha_{\mu}$ and $\Delta\alpha_{\nu}$, respectively, $E_{\mu\nu}$ represents the energy of a molecule with the perturbation $\Delta\alpha_{\mu} + \Delta\alpha_{\nu}$ and E_0 is the energy of an unperturbed molecule. For the sake of numerical accuracy in calculating $X_{\mu\nu}$, it is useful to set the energy E_0 to zero and to determine E_{μ}, E_{ν} and $E_{\mu\nu}$ in relation to the reference value of E_0. In contrast to the general perturbation method, the SCF-LCI approach offers essentially an accurate solution equivalent to a perturbation theory of an infinite order and can be applied to arbitrary large perturbations. The accuracy of inclusion of the electronic repulsion in this approach depends solely on the extent of the LCI base. The effect of size of the base has been studied in one of our previous works[4]. In the present work, a complete base of monoexcited singlets was used.

As the quantum chemical models for the calculation of generalized polarisabilities $\Pi_{\mu\nu}$ and SCF-LCI quantities $X_{\mu\nu}$ we used the parent unsubstituted molecules of pyridine, 3-styrylpyridine, 4-styrylpyridine, cinnamic acid, α-phenylcinnamic acid and 4-phenyl-1,3-butadienecarboxylic acid in idealized geometries with bond lengths $r_{C-C} = 0{\cdot}14$ nm, $r_{C-N} = 0{\cdot}14$ nm, $r_{C-O} = 0{\cdot}14$ nm and $r_{C=O} = 0{\cdot}125$ nm. The parameters for a part of the SCF calculations were identical with those used in our previous work[5] ($I_C = 11{\cdot}42$ eV, $\gamma_{CC} = 10{\cdot}84$ eV, $\beta_{CC} = -2{\cdot}318$ eV; $I_{\dot{O}} = 32{\cdot}9$ eV, $\gamma_{\dot{O}\dot{O}} = 21{\cdot}53$ eV, $\beta_{C-O} = -1{\cdot}854$ eV*; $I_{\dot{O}} = 17{\cdot}7$ eV, $\gamma_{\dot{O}\dot{O}} = 15{\cdot}23$ eV, $\beta_{C=O} = -2{\cdot}318$ eV; $I_N = 14{\cdot}1$ eV, $\gamma_{NN} = 12{\cdot}3$ eV, $\beta_{CN} = -1{\cdot}854$ eV).

RESULTS AND DISCUSSION

As has already been emphasized in the introduction, the HMO approach does not make it possible to elucidate, even qualitatively, the relative magnitude of transmission of the substituent effect simultaneously from the *meta* and *para* position on a given skeleton. In order to elucidate these differences indicating the fundamental importance of the field effect in transmission of the substituent effect from the *meta* position, it is necessary to turn the attention to methods involving explicitly the electronic repulsion. This may be well documented by an example of ϱ constants for the protonation of 4'-substituted 4- and 3-styrylpyridines (*I*, *II*) (refs[8,9]) (Scheme 1). Experimental values of ϱ constants along with the values of HMO polarisabilities $\pi_{\mu\nu}$ and SCF-LCI quantities $X_{\mu\nu}$ are given in Table I.



SCHEME 1

For the discussion of the experimental results it is decisive that Eq. (*1*) cannot be used, as has already been emphasized[2], for the calculation of the absolute values of ϱ constants. However, on the basis of the Hammett equation and the relation (*1*) it is possible to calculate theoretically the ratio of the experimental ϱ constants (Eq. (*5*)):

$$\varrho_i/\varrho_0 = \pi^i_{\mu\nu}/\pi^0_{\mu\nu}\,. \qquad (5)$$

The relative ϱ constants for the substituted styrylpyridines will be determined in relation to the parent 4-substituted pyridines *III* used as a reference series for which the ϱ constant for protonation determined under comparable conditions can be found in the literature[10]. The data in Table I show that the ratio $\varrho_I/\varrho_{III} = 0{\cdot}15$ for

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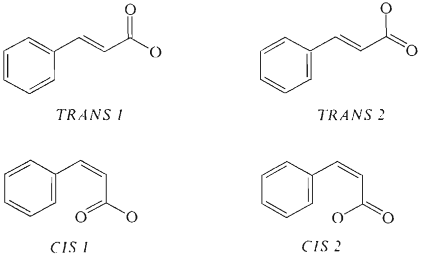
* The value of $-2{\cdot}318$ eV given in the previous work[5] for β_{C-O} was erroneous; for the calculations, however, the correct value, *i.e.* $-1{\cdot}854$ eV was used.

4-styrylpyridines is roughly reproduced equally well by the ratio of the HMO polarisabilities $\pi_{I}/\pi_{III} = 0{\cdot}12$ as by that of the SCF-LCI quantities $X_{I}/X_{III} = 0{\cdot}28$. More detailed conclusions cannot be drawn if we realize that we do not know the error in the ratio of the experimental ϱ constants. On the other hand, in the case of substituted 3-styrylpyridines the ratio of the experimental ϱ constants $\varrho_{II}/\varrho_{III} = 0{\cdot}08$ is correctly reproduced only by the ratio $X_{II}/X_{III} = 0{\cdot}15$. The calculation based on the HMO data does not reflect, in addition to a completely unrealistic absolute value of the ratio $\pi_{II}/\pi_{III} = -0{\cdot}0015$, even the sign of the constants.



TRANS 1 *TRANS 2*

CIS 1 *CIS 2*

Scheme 2

Another example, where we encounter with the necessity to take into consideration the field effect, is the difference in the ϱ constants for reactions of the *cis* and *trans* isomers of unsaturated compounds. The available experimental data including dissociation and esterification of the *cis* and *trans* isomers of unsaturated carboxylic

Table I

Experimental Values of ϱ Constants and Calculated Quantities of $\pi_{\mu\nu}$ (HMO) and $X_{\mu\nu}$ (SCF-LCI) for Protonation of 4'-Substituted 3- and 4-Styrylpyridines and 4-Substituted Pyridines

Compound[a]	ϱ	$\pi_{\mu\nu}$, β^{-1}	$X_{\mu\nu}$, eV^{-1} [b]
I	0·85	0·0160	0·0113
II	0·44	−0·0002	0·0060
III	5·71	0·1275	0·0395

[a] *Cf.* Scheme 1; [b] calculated for perturbations $\Delta\alpha_{\mu} = \Delta\alpha_{\nu} = -1$ eV.

acids as well as the hydrolysis of their esters are listed in Table II. Differences between ϱ_{cis} and ϱ_{trans} are small in all cases and it has been recommended to consider them even as statistically unimportant[11]. A reliable decision in this sense is hindered by the fact that most authors do not quote the errors in the experimental values of ϱ constants.

However, from the theoretical point of view it is probable that the subtle differences in the electronic structure of the *cis* and *trans* isomers, which are detectable by a number of other experimental techniques, will find reflection in small differences in the ϱ constants, *i.e.* in the different sensitivity of the *cis* and *trans*-conjugated skeletons to the transmission of the substituent effect. As the Table II shows, in all cases studied is $\varrho_{trans} \geqq \varrho_{cis}$. The sole exception is acrylic acid. It would be interesting to rationalize this finding theoretically. Unfortunately, modelling the substituent effect by the change $\Delta\alpha_\mu$ gives no possibility of differentiating between the *cis*- and *trans*-acrylic acids. From these reasons we were forced to limit ourselves to the interpretation of ϱ constants for the dissociation of cinnamic acid, 4-phenyl-1,3-butadienecarboxylic acid and α-phenylcinnamic acid. It is clear that the simple HMO method, in spite that it has proved to be quite useful in interpreting the ϱ constants for a number of reactions in a series of various structural skeletons, is not capable of describing the subtle differences in the electronic structure of the *cis* and *trans* isomers. It is therefore necessary to turn again the attention to methods including the electronic repulsion.

TABLE II

Experimental Values of ϱ Constants for Reactions of *cis* and *trans* Isomers of Carboxylic Acids[a]

Carboxylic acid	ϱ^b	ϱ^c	ϱ^d
Acrylic acid	2·45 (ref.[12]) 2·19 (ref.[12])	1·77 (ref.[12]) 1·62 (ref.[12])	—
Cinnamic acid	0·57 ± 0·05 (ref.[13]) 0·79 ± 0·05 (ref.[13])	— —	1·12 (ref.[14]) (1.09) (ref.[15]) 1·31 (ref.[14]) (1·24) (ref.[15])
4-Phenyl-1,3-butadiene-carboxylic acid	0·448 (ref.[16]) 0·449 (ref.[16])	— —	— —
α-Phenylcinnamic acid	0·716 (ref.[17]) 0·917 (ref.[17])	0·29 (ref.[17]) 0·54—0·57 (ref.[17])	— —

[a] The upper value pertains to the *cis* and the lower one to the *trans* isomer; [b] dissociation of carboxylic acids at 25°C in various solvents; [c] reaction of carboxylic acids with $(C_6H_5)_2CN_2$ in ethanol at 25°C; [d] hydrolysis of ethyl esters (85% C_2H_5OH/H_2O, 25°C).

The calculated values of generalized polarisabilities $\Pi_{\mu\nu}$ and of SCF-LCI quantities $X_{\mu\nu}$ for cinnamic acid, α-phenylcinnamic acid and 4-phenyl-1,3-butadienecarboxylic acid are given in Table III. The values of $\Pi_{\mu\nu}$ given in Table III reveal that an inclusion of the repulsion on the level of the Hartree–Fock perturbation theory is still insufficient to reflect the differences between ϱ_{cis} and ϱ_{trans} for the dissociation of cinnamic acids. Correct results gave only, in accordance with the expectation, the SCF-LCI perturbation theory. The values of $X_{\mu\nu}$ give a true picture of the differences in the experimental ϱ constants ($\varrho_{cis} < \varrho_{trans}$, $X_{cis} < X_{trans}$) and describe satisfactorily also the ratio of the ϱ constants ($\varrho_{cis}/\varrho_{trans} = 0{\cdot}78 \pm 0{\cdot}11$, $X_{cis}/X_{trans} = 0{\cdot}87$). Also in the case of 4-phenyl-1,3-butadienecarboxylic acid, the values of $X_{\mu\nu}$ reflect correctly the trends in values of the experimental ϱ constants ($\varrho_{cis} \approx \varrho_{trans}$, $X_{cis} \approx X_{trans}$). In these cases, the quantum chemical models for the calculation of $\Pi_{\mu\nu}$ and $X_{\mu\nu}$ were the molecules of the corresponding unsubstituted carboxylic acids. At this point it is worthwhile mentioning that each of the molecules of the *cis*- and *trans*-carboxylic acids may occur yet in two isomeric forms depending upon the orientation of the carboxylic group (Scheme 2). The most stable conformations (*trans* 1, *cis* 1) were used for the calculation of $\Pi_{\mu\nu}$ and $X_{\mu\nu}$.

On the basis of the theoretical values of $X_{\mu\nu}$ thus obtained one can presume that the differences found in the values of ϱ constants for the dissociation of the conjugated *cis*- and *trans*-carboxylic acids do reflect the different sensitivity of the *cis* and *trans* skeletons to the transmission of the substituent effect. Moreover, it is clear that the

TABLE III

Calculated Values of Generalized Polarisabilities $\Pi_{\mu\nu}$ and of SCF-LCI Quantities $X_{\mu\nu}$ for the Dissociation of *cis* and *trans* Isomers of Carboxylic Acids[a]

Carboxylic acid	$\Pi_{\mu\nu}$, eV^{-1}	$X_{\mu\nu}$, eV^{-1}[b]
Cinnamic acid	0·0006	−0·0027
	0·0006	−0·0031
4-Phenyl-1,3-butadienecarboxylic acid	—	−0·0020
	—	−0·0021
α-Phenylcinnamic acid[c]	—	—
	—	−0·0015

[a] The upper value pertains to the *cis* and the lower one to the *trans* isomer; [b] calculated for perturbations $\Delta\alpha_\mu = -1$ eV, $\Delta\alpha_\nu = +1$ eV; [c] the SCF calculation for the *cis* isomer did not converge.

difference between the *cis* and *trans* isomers progressively decreases with the increasing length of the unsaturated chain that is subject to transmission of the substituent effect.

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