SCF-LCI THEORY OF SUBSTITUENT EFFECT

R.Ponec and J.Málek

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague - Suchdol 2*

The transmission of substituent effects in ground states of various conjugated systems was studied by the SCF-LCI method. The substituent effect was simulated by one-electron perturbation $P_{\mu\mu} \equiv \Delta\alpha_\mu$ only. The results clearly indicate that the SCF-LCI theory, in contrast to HMO and SCF perturbation theory, can describe correctly the transmission of the substituent effect even to the positions which cannot enter into the direct resonance interaction on the given skeleton. The transmission into such positions is a consequence of electron correlation effects with the largest part of the transmission being due to the direct electrostatic interaction (field effect). The SCF-LCI theory may be used to describe the transmission of the substituent effect even in excited singlet and triplet states.

Using HMO perturbation theory we have recently derived an equation[1] formally corresponding to the Hammett equation. The derived equation allowed to interpret ϱ constants in a variety of analogous reactions occurring on different structural skeletons. The validity of the equation was limited owing to the neglect of the electron repulsion in the HMO method; this equation can be applied only to such positions of the substituent relative to the reaction center that allowed their direct resonance interaction on the given skeleton. We tried to remedy this inadequacy by inclusion of the electron repulsion on the level of the Hartree–Fock perturbation theory[2]. The use of the so-called "generalized" atom–atom polarizabilities[3] led then to a solution which was analogous to that in HMO theory. In fact, numerical calculations performed on 1,3- and 1,4-substituted benzene derivatives have shown[2], however, that, despite of certain improvements, the Hartree–Fock perturbation theory is also not able to describe the transmission of the substituent effect into the *meta* position. We have, therefore, decided to employ the SCF-LCI method instead of a perturbation approach.

THEORETICAL

The following equation holds for the ratio of equilibrium (or rate) constants of a reaction of substituted and unsubstituted molecules:

$$\ln K_{\mu v}/K_0 = (\Delta G_0 - \Delta G_\mu)/RT. \tag{1}$$

In the subsequent discussion we shall limit ourselves only to such cases where either $\Delta\Delta S = 0$ or $\Delta\Delta S \sim \Delta\Delta H$. Similarly as in the previous papers[1,2] let us assume that

$$\Delta H_0 = f(\Delta\alpha_v) \tag{2a}$$

and that

$$\Delta H_\mu = f(\Delta\alpha_\mu, \Delta\alpha_v), \tag{2b}$$

but express the energies ΔH_0 and ΔH_μ in terms of the SCF-LCI method. Although this approach could allow one to treat the substituent effect also in excited singlet and triplet states we will deal here only with the substituent effect on the reactivity and equilibria of molecules in ground states.

Let $\mathscr{H}$ represents the Hamiltonian of the unperturbed molecule; then ΔH_0 corresponds to the ground state energy of the perturbed Hamiltonian

$$\mathscr{H}_0 = \mathscr{H} + \mathbf{P}_{vv} \tag{3}$$

and ΔH_μ is the energy corresponding to the Hamiltonian

$$\mathscr{H}_\mu = \mathscr{H} + \mathbf{P}_{\mu\mu} + \mathbf{P}_{vv}. \tag{4}$$

If we express the eigenfunctions of the perturbed Hamiltonians $\mathscr{H}_0$ and $\mathscr{H}_\mu$ in the basis of monoexcited singlet states of the unperturbed Hamiltonian $\mathscr{H}$, then the sets of equations (5) and (6) $(L = 1, 2, \ldots M)$

$$\sum_\varkappa C_\varkappa \{\langle\psi_L|\mathscr{H}|\psi_\varkappa\rangle + \langle\psi_L|\mathbf{P}_{vv}|\psi_\varkappa\rangle - E\delta_{L\varkappa}\} = 0 \tag{5}$$

$$\sum_\vartheta C_\vartheta \{\langle\psi_L|\mathscr{H}|\psi_\vartheta\rangle + \langle\psi_L|\mathbf{P}_{\mu\mu} + \mathbf{P}_{vv}|\psi_\vartheta\rangle - E\delta_{L\vartheta}\} = 0 \tag{6}$$

represent the conditions for eigenenergies ΔH_0 and ΔH_μ and eigenfunctions of the perturbed Hamiltonians. The perturbations $\mathbf{P}$ bring about a mixing of monoexcited states with the ground state. Due to this mixing the energy of the ground state is decreased even below the value obtained from the exact SCF calculation of the perturbed molecules. Hence, this approach makes it possible to include a part of the correlation energy into the calculation. As the further results show, the contributions from the correlation energy are dominant in the transmission into "*meta*-like" positions between which the direct resonance interaction is not possible on a given skeleton. In general, the sum of the energies corresponding to the individual perturbations $\mathbf{P}_{\mu\mu}$ and $\mathbf{P}_{vv}$ is not equal to the energy change of the ground state of the Hamiltonian $\mathscr{H}$ caused by the total perturbation $\mathbf{P} = \mathbf{P}_{\mu\mu} + \mathbf{P}_{vv}$; this reflects the

fact that the substituent effect is not strictly additive. The difference $x_{\mu\nu}$ (Eq. (7))

$$x_{\mu\nu} = E_{\mu\nu} - E_\mu - E_\nu \tag{7}$$

$$(E_{\mu\nu} = \Delta H_\mu, \; E_\nu = \Delta H_0, \; E_\mu = \Delta H(\mathscr{H} + \mathbf{P}_{\mu\mu})),$$
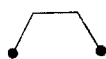
which corresponds to an interaction energy of the perturbations $\mathbf{P}_{\mu\mu}$ and $\mathbf{P}_{\nu\nu}$, is therefore a measure of the substituent effect transmission similarly as the polarizability $\pi_{\mu\nu}(\Pi_{\mu\nu})$ is in the HMO or SCF perturbation theory.

RESULTS AND DISCUSSION

In order to verify the suggested SCF-LCI theory of the substituent effect the following fundamental question has to be answered: does the theory describe adequately the transmission of the substituent effect into the "*meta*-like" positions? The answer comes from the model calculations on 1,3-butadienes, benzenes, and naphthalenes

TABLE I

Transmission of the Substituent Effect in the Series of Substituted 1,3-Butadienes

| Compound[a]	$E_{\mu\nu}$, eV	$x_{\mu\nu}$, eV	$\pi_{\mu\nu}{}^b$, β^{-1}	$\Pi_{\mu\nu}{}^c$, eV^{-1}	$E_{HF}{}^d$, eV
(butadiene structure)	$-2{\cdot}3300$	—	$-0{\cdot}6261$	$-0{\cdot}1627$	$-2{\cdot}2228$
(butadiene structure)	$-2{\cdot}2670$	—	$-0{\cdot}4025$	$-0{\cdot}1308$	$-2{\cdot}1858$
(butadiene structure)	$-4{\cdot}5280$	$0{\cdot}0690$	$-0{\cdot}0447$	$-0{\cdot}0024$	$-4{\cdot}4125$
(butadiene structure)	$-4{\cdot}4283$	$0{\cdot}2317$	$0{\cdot}2683$	$0{\cdot}0208$	$-4{\cdot}3310$

[a] Perturbations on atoms marked by ●: $\Delta\alpha_\mu = \Delta\alpha_\nu = -2$ eV; [b] HMO atom–atom polarizability; [c] SCF "generalized" atom–atom polarizability; [d] Hartree–Fock energy of perturbed molecules (relative to the unsubstituted molecule).

perturbed in 1,3; 1,4 and 1,5; 1,6; 1,7; 1,8 positions, respectively, by one-electron perturbations $\Delta\alpha_\mu$ and $\Delta\alpha_\nu$. The calculations were carried out using a modified version of the PPP method[4,5] in π-electron approximation $(\beta = -2\cdot318\,\text{eV}; \gamma_{11} = 10\cdot84\,\text{eV};$ IP $= 11\cdot42\,\text{eV})$; gamma integrals were approximated according to Mataga[6]. The results of calculations are given in Table I, II, and III; for the purpose of comparison the values of HMO and SCF polarizabilities and the exact values of SCF energies of the perturbed molecules are also included. The calculated values can be verified against *e.g.* the dissociation constants of cyano-substituted pyridines measured in the gas phase[7], because the conditions under which these constants were obtained approximate best the assumpions accepted in quantum chemical calculations $(\Delta\Delta S = 0;$ neglect of solvatation effects). A negative value of the perturbation $\Delta\alpha_\mu$ corresponds to a substitution by an electronegative atom and the protonation process is simulated by a change in $\Delta\alpha_\nu$ similarly as in papers of Chalvet and coworkers[8,9]. For comparison purposes, the corresponding values of $\Delta pK_{\mu\nu}^{\text{G}}(pK_{\mu-\text{CN}}^{\text{G}} - pK_{\text{H}}^{\text{G}})$ are summarized in Table II. The $\Delta pK_{\mu\nu}^{\text{S}}$ values for nitro-substituted quinolines and cyano-substituted pyridines in water[10] are also included into Table II and III.

Despite of the approximative nature of these model calculations (values of -2 eV of the perturbations $\Delta\alpha_\mu = \Delta\alpha_\nu$ apparently do not correspond to any real substituent)
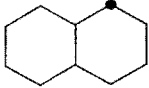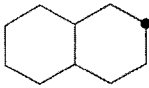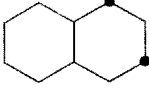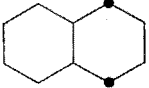
TABLE II

Transmission of the Substituent Effect in the Series of Substituted Benzenes

Compound[a]	$E_{\mu\nu}$, eV	$x_{\mu\nu}$, eV	$\pi_{\mu\nu}{}^{b}$, β^{-1}	$\Pi_{\mu\nu}{}^{c}$, eV^{-1}	$E_{\text{HF}}{}^{d}$, eV	$\Delta pK^{\text{G}\,e}$ eV	$\Delta pK^{\text{S}\,e}$ eV
(benzene)	$-2\cdot2786$	—	$-0\cdot3981$	$-0\cdot1317$	$-2\cdot2091$	—	—
(benzene)	$-4\cdot5428$	$0\cdot0143$	$-0\cdot0093$	$-0\cdot0008$	$-4\cdot4406$	$0\cdot46$	$0\cdot22$
(benzene)	$-4\cdot3875$	$0\cdot1696$	$0\cdot1019$	$0\cdot0187$	$-4\cdot3342$	$0\cdot43$	$0\cdot19$

[a] Perturbations on the atoms marked by ●: $\Delta\alpha_\mu = \Delta\alpha_\nu = -2$ eV; [b] HMO atom–atom polarizability; [c] SCF "generalized" atom–atom polarizability; [d] Hartree–Fock energy of perturbed molecules (relative to the unsubstituted molecule); [e] $\Delta pK = (pK_{\mu-\text{CN}} - pK_{\text{H}})$; G: in the gas phase; S: in the aqueous solution.
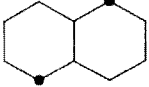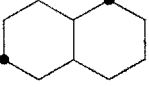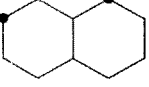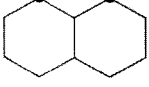
TABLE III

Transmission of the Substituent Effect in the Series of Substituted Naphthalenes

Compound[a]	$E_{\mu\nu}$, eV	$x_{\mu\nu}$, eV	$\pi_{\mu\nu}$[b], β^{-1}	$\Pi_{\mu\nu}$[c], eV^{-1}	E_{HF}[d], eV	ΔpK^{Se}, eV
	$-2{\cdot}3220$	—	$-0{\cdot}4428$	$-0{\cdot}1415$	$-2{\cdot}2188$	—
	$-2{\cdot}3084$	—	$-0{\cdot}4049$	$-0{\cdot}1327$	$-2{\cdot}2102$	—
	$-4{\cdot}6108$	$0{\cdot}0196$	$-0{\cdot}0177$	$-0{\cdot}0036$	$-4{\cdot}4573$	$0{\cdot}23$
	$-4{\cdot}4352$	$0{\cdot}2088$	$0{\cdot}1394$	$0{\cdot}0381$	$-4{\cdot}3329$	—
	$-4{\cdot}5539$	$0{\cdot}0801$	$0{\cdot}0232$	$0{\cdot}0034$	$-4{\cdot}4302$	$0{\cdot}13$
	$-4{\cdot}5838$	$0{\cdot}0466$	$-0{\cdot}0064$	$-0{\cdot}0007$	$-4{\cdot}4344$	$0{\cdot}12$
	$-4{\cdot}5501$	$0{\cdot}0803$	$0{\cdot}0323$	$0{\cdot}0066$	$-4{\cdot}4059$	$0{\cdot}14$
	$-4{\cdot}5709$	$0{\cdot}0731$	$-0{\cdot}0267$	$-0{\cdot}0026$	$-4{\cdot}4379$	$0{\cdot}11$

[a] Perturbations on atoms marked by ●: $\Delta\alpha_\mu = \Delta\alpha_\nu = -2$ eV; [b] HMO atom–atom polarizability; [c] SCF "generalized" atom–atom polarizability; [d] Hartree–Fork energy of perturbed molecules (relative to the unsubstituted molecule); [e] $\Delta pK^S = (pK_{\mu-NO_2} - pK_H)$ (in the aqueous solution).

TABLE IV

Values of $x_{\mu\nu}$ Calculated for Substituted 1,3-Butadienes

$x_{\mu\nu}$	Perturbation, $\Delta\alpha^a$, eV			
	$-0\cdot1$	$-0\cdot5$	$-1\cdot0$	$-2\cdot0$
x_{13}	$-0\cdot00004$	$0\cdot0000$	$0\cdot0054$	$0\cdot0690$
x_{14}	$0\cdot0005$	$0\cdot0076$	$0\cdot0510$	$0\cdot2317$

^{a} $\Delta\alpha_{\mu} \equiv \Delta\alpha_{\nu} \equiv \Delta\alpha$.

TABLE V

Values of $x_{\mu\nu}$ Calculated for Substituted Benzenes

$x_{\mu\nu}$	Perturbation, $\Delta\alpha^a$, eV		
	$-0\cdot5$	$-1\cdot0$	$-2\cdot0$
x_{13}	$-0\cdot0011$	$-0\cdot0023$	$0\cdot0143$
x_{14}	$0\cdot0081$	$0\cdot0358$	$0\cdot1696$

^{a} $\Delta\alpha_{\mu} \equiv \Delta\alpha_{\nu} \equiv \Delta\alpha$.

TABLE VI

Values of $x_{\mu\nu}$ Calculated for Substituted Naphthalenes with Different Sizes of the LCI Base

$x_{\mu\nu}$	Perturbation, $\Delta\alpha^a$, eV			
	$-1\cdot0^b$	$-2\cdot0^b$	$-1\cdot0^c$	$-2\cdot0^c$
x_{13}	$-0\cdot0037$	$0\cdot0196$	$-0\cdot0107$	$-0\cdot0637$
x_{14}	$0\cdot0440$	$0\cdot2088$	$0\cdot0619$	$0\cdot2665$
x_{15}	$0\cdot0114$	$0\cdot0801$	$0\cdot0068$	$0\cdot0588$
x_{16}	$0\cdot0031$	$0\cdot0466$	$0\cdot0002$	$0\cdot0256$
x_{17}	$0\cdot0122$	$0\cdot0803$	$0\cdot0187$	$0\cdot0956$
x_{18}	$-0\cdot0027$	$0\cdot0731$	$-0\cdot0040$	$0\cdot0142$

^{a} $\Delta\alpha_{\mu} \equiv \Delta\alpha_{\nu} \equiv \Delta\alpha$; ^{b} extent of configuration interaction NCI $= 5$ (singlets among five highest occupied and lowest unoccupied orbitals); ^{c} NCI $= 4$.

it is clear that qualitatively the values x_{13} and x_{14} describe correctly the substituent effect; this confirms the frequently assumed proportionality between the π-inductive and mesomeric effects. In contrast to the transmission into the *para* position, which is well described both by polarizability $\pi_{14}(\Pi_{14})$ and by x_{14} values, the transmission of the substituent effect into the *meta* position (or generally into the "*meta*-like" positions) is qualitatively correctly described only by the corresponding values of $x_{\mu\nu}$ in the LCI approach with a complete base of monoexcited singlets (Table VI). In this approach the inclusion of correlation energy contributions leads first of all to an increase in relative contribution of the „field" effect into the „*meta*-like" positions. Nevertheless, the calculated values of x_{13} and x_{14} are considerably smaller than the corresponding differences $\Delta pK_{\mu\nu}^G$. However, the whole discrepancy cannot be ascribed to the simulated values of the perturbations $\Delta\alpha_\mu$ and $\Delta\alpha_\nu$, for in such a case the magnitude of the perturbations would become unrealistic. It seems more likely that this discrepancy is due to an inadequacy of the model used (neglect of mesomeric effect, simulation of protonation by a change in $\Delta\alpha_\nu$ only) for a quantitative treatment of the substituent effect. As it is apparent from Tables IV − VI, the "correctness" of the values $x_{\mu\nu}$ depends on the magnitude of perturbations $\Delta\alpha_\mu$ and $\Delta\alpha_\nu$ and on the type of the skeleton. Since the delocalization and correlation effects are closely connected[11], this fact confirms the importance of correlation effects for the transmission of substituent effects into the „*meta*-like" positions.

The values of $\Delta pK_{\mu\nu}^S$ for cyano-substituted pyridines and nitro-substituted quinolines can be compared with the calculated values of $x_{\mu\nu}$ only very roughly. Despite of it, one can see that the values of $x_{\mu\nu}$ reproduce correctly the trend in $\Delta pK_{\mu\nu}^S$ in both series of compounds. Moreover, in the isoquinoline and quinoline series the SCF-LCI theory differentiates between 4- and 3-positions, respectively, which was possible neither with Dewar F, M method[12,13], nor with HMO or SCF perturbation theory. At the same time this result demonstrates that the F and M constants of the Dewar F, M method are not exactly transferable from one to another molecule.

The above results clearly show that the SCF-LCI theory is able to give qualitatively good description of the substituent effect transmission on any conjugated skeleton. Moreover, it can be assumed that after inclusion of the mesomeric effect this theory will also be able to provide a quantitative account of the substituent effect. Such calculations are now in progress in our laboratory.

REFERENCES

1. Ponec R., Chvalovský V.: This Journal *39*, 3091 (1974).
2. Ponec R.: This Journal *41*, 1105 (1976).
3. Pople J. A.: Proc. Roy. Soc. A *233*, 233 (1955).
4. Pariser R., Parr R. G.: J. Chem. Phys. *21*, 466 (1953).
5. Pople J. A.: Trans. Faraday Soc. *49*, 1375 (1953).
6. Mataga N., Nishimoto K.: Z. Phys. Chem. (Frankfurt am Main) *13*, 140 (1957).

7. Koppel I. A., Karelson M. M.: Organic Reactivity *11*, 985 (1975).

8. Bertran J., Chalvet O., Daudel R.: Theor. Chim. Acta *14*, 1 (1969).

9. Constanciel R., Chalvet O., Rayez J.: Theor. Chim. Acta *37*, 305 (1975).

10. Albert A. in the book: *Physical Methods in Heterocyclic Chemistry* (A. Katritzky Ed.), Chap. 1. Academic Press, New York 1963.

11. Salem L.: *Molecular Orbital Theory of Conjugated Systems*, Chap. 2. W. A. Benjamin, New York 1966.

12. Dewar M. J. S., Grisdale P.: J. Amer. Chem. Soc. *84*, 3546 (1962).

13. Wells P. R.: *Linear Free Energy Relationships*, p. 30. Academic Press, London 1968.