

PERTURBATION THEORY OF SUBSTITUENT EFFECT

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Received October 19th, 1976

Quantum chemical approaches to substituent effect transmission are compared. The approaches differ in the way in which the electron repulsion is treated. Using the example of the dissociation of *meta*- and *para*-substituted benzoic acids it is shown that the repulsion must be taken into consideration in order to get the correct description of substituent effect transmission into the *meta* position.

The Hammett equation has remained to be one of the few successful attempts to describe substituent effects quantitatively. Considerable success has been achieved in mechanistic interpretations of ρ constants of reaction series observed on a given structural skeleton. Interpretation of the ρ constants of a given reaction occurring on different, though similar, structural skeletons had been hindered because the dependence of substituent effect transmission on the type of the skeleton had not been known. Using HMO perturbation theory, we have recently derived the equation¹ which permits such interpretation. With the electron repulsion neglected¹ the equation could not be applied in cases in which the relative position of the substituent and the reaction center prohibits their direct resonance interaction. We have attempted to remedy this inadequacy by inclusion of the electron repulsion on the level of the Hartree-Fock perturbation theory² and SCF-LCI theory³.

In the present paper we will compare all three methods using the example of dissociation of *meta*- and *para*-substituted benzoic acids and we will demonstrate that the inclusion of electron repulsion is necessary for even only qualitatively correct description of substituent effect transmission into the *meta* position.

THEORETICAL

The equation (1) holds for the ratio of equilibrium (or rate) constants of the reactions of substituted and unsubstituted molecules:

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

In the subsequent discussion we shall limit ourselves only to such cases in which either $\Delta\Delta S = 0$ or $\Delta\Delta S \approx \Delta\Delta H$. Similarly, as in the previous papers¹⁻³, we consider the model which describes the substituent effect only by a perturbation $\Delta\alpha_\mu$

(i.e. by a change in the coulombic integral of the substituent bearing atom) and the equilibrium process is described by the perturbation $\Delta\alpha_v$ (i.e. by a change in the coulombic integral of the reaction center). Under these assumptions, relations (2a) and (2b) apply

$$\Delta H_0 = f(\alpha_\mu), \quad (2a)$$

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

The corresponding changes ΔH_0 and ΔH_μ will be expressed on the basis of Scheme 1 quantum chemically. The difference $\Delta H_0 - \Delta H_\mu$ is

$$\Delta H_0 - \Delta H_\mu = E_{\mu\nu} - E_\mu - E_v + E_0. \quad (3)$$

If we also put

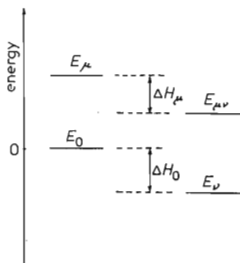
$$E_{\mu\nu} - E_\mu - E_v + E_0 = X_{\mu\nu} \quad (4)$$

then the Eq. (1) can be rewritten in the form

$$\ln K_{\mu\nu}/K_0 = X_{\mu\nu}/RT. \quad (5)$$

Thus the calculation of the transmission of the substituent effect is reduced to the calculation of energies of molecules with perturbations $\Delta\alpha_\mu(E_\mu)$,

$$\Delta\alpha_v(E_v), \quad \text{and} \quad \Delta\alpha_\mu + \Delta\alpha_v(E_{\mu\nu}).$$



SCHEME 1

The $X_{\mu\nu}$ term can be expressed by different quantum chemical methods with a different degree of approximation. To compare the effect of inclusion of the electron repulsion we will give here the expressions for $X_{\mu\nu}$ as derived by HMO and Hartree-

-Fock perturbation theories and by SCF-LCI theory. On the level of HMO method we can write

$$X_{\mu\nu} = \pi_{\mu\nu} \Delta\alpha_\mu \Delta\alpha_\nu, \quad (6)$$

where $\pi_{\mu\nu}$ are "atom-atom" polarizabilities⁴. Analogous expression holds also in Hartree-Fock perturbation theory², only $\pi_{\mu\nu}$ are replaced by the "generalized" polarizabilities⁵ ($\Pi_{\mu\nu}$)

$$X_{\mu\nu} = \Pi_{\mu\nu} \Delta\alpha_\mu \Delta\alpha_\nu. \quad (7)$$

In addition, it was shown² that the explicit inclusion of the electron repulsion leads in a natural way to an expression for the substituent constant $\sigma_{\mu\nu}$ of the Dewar F, M method⁶. When the SCF-LCI formalism is employed it is no longer possible to express $X_{\mu\nu}$ explicitly and its calculation must start from Eq. (4). The values of $E_{\mu\nu}$, E_μ , and E_ν are obtained by solving the set of the secular equations (8a)–(8c),

$$\sum_{\kappa} c_{\kappa} \{ \langle \Psi_L | \hat{\kappa} | \Psi_{\kappa} \rangle + \langle \Psi_L | \hat{P}_\mu | \Psi_{\kappa} \rangle - E_{\mu} \delta_{L\kappa} \} = 0, \quad (8a)$$

$$\sum_{\beta} c_{\beta} \{ \langle \Psi_L | \hat{\beta} | \Psi \rangle + \langle \Psi_L | \hat{P}_\nu | \Psi_{\beta} \rangle - E_{\nu} \delta_{L\beta} \} = 0, \quad (8b)$$

$$\sum_{\lambda} c_{\lambda} \{ \langle \Psi_L | \hat{\lambda} | \Psi_L \rangle + \langle \Psi_L | \hat{P}_\mu + \hat{P}_\nu | \Psi_{\lambda} \rangle - E_{\mu\nu} \delta_{L\lambda} \} = 0, \quad (8c)$$

where $\hat{\kappa}$ represents the hamiltonian of the unperturbed molecule and \hat{P}_μ and \hat{P}_ν are the perturbations. Matrix elements $\langle \Psi_L | \hat{\kappa} | \Psi_{\kappa} \rangle$, $\langle \Psi_L | \hat{P} | \Psi_{\kappa} \rangle_x \dots$ etc. are given by Slater rules⁷; in the ZDO approximation e.g. the matrix element $\langle \Psi_0 | \hat{P}_\mu | {}^1\Psi_{i \rightarrow j} \rangle$ is determined by Eqs (9a) and (9b)

$$\langle \Psi_0 | \hat{P}_\mu | {}^1\Psi_{i \rightarrow j} \rangle = \sqrt{2} \langle i | \hat{P}_\mu | j \rangle, \quad (9a)$$

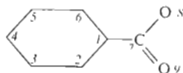
$$\langle i | \hat{P}_\mu | j \rangle = c_{i\mu} c_{j\mu} \Delta\alpha_\mu. \quad (9b)$$

This, SCF-LCI, approach is the most general one and the precision of the inclusion of the electron repulsion is limited only by the size of the CI basis set used. In the studied example we employed the base of all monoexcited singlets. The SCF-LCI method can be also applied to the study of the substituent effect transmission in excited states.

RESULTS AND DISCUSSION

Suitability of different approximations to calculate $X_{\mu\nu}$ was tested on the example of *meta*- and *para*-substituted benzoic acids. The molecule of unsubstituted benzoic

acid (I) was considered as the corresponding model (in the π electron approximation) in which



I

the effect of the substituent and process of ionization are described by the changes $\Delta\alpha_3$, ($\Delta\alpha_4$), and ($\Delta\alpha_8$), resp. The calculations were carried out using HMO and modified PPP (ref.⁸) methods. Idealized geometry was accepted for the carbon skeleton $r_{C-C} = 1.40 \text{ \AA}$, $r_{C-O} = 1.40 \text{ \AA}$ and $r_{C=O} = 1.25 \text{ \AA}$. Gamma integrals were approximated according to Mataga and Nishimoto⁹. Parameters for the HMO calculations were taken from ref.¹⁰ and those for the SCF calculations from ref.¹¹ ($\gamma_{11}^0 = 15.23 \text{ eV}$, $IP_0 = 17.7 \text{ eV}$, $\beta_{C=O} = -2.318 \text{ eV}$, $\gamma_{11}^0 = 21.53 \text{ eV}$, $IP_0 = 32.9 \text{ eV}$, and $\beta_{C-O} = -2.318 \text{ eV}$). The value of -2 eV for $\Delta\alpha_3$ ($\Delta\alpha_4$) corresponds to the substitution by electronegative atoms while the ionization process is represented by the perturbation $\Delta\alpha_8 = +2 \text{ eV}$. The results of the calculations are summarized in Table I. Using the identity (10)

$$\frac{pK_0 - pK_{m-x}}{pK_0 - pK_{p-x}} = \left(\frac{\sigma_m}{\sigma_p} \right)_x = \frac{X_{38}}{X_{48}} \quad (10)$$

the calculated $X_{\mu\nu}$ values can be compared with the experimental dissociation constants of *meta*- and *para*-nitrobenzoic acids as determined in the gas phase¹². It is clear from the results in Table I that the HMO method does not describe the transmission of the substituent effect into the *meta* position even qualitatively. From the

TABLE I

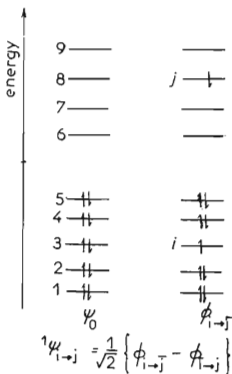
Results of Different Quantum Chemical Methods of Description of Substituent Effect Transmission

Acid	$\pi_{\mu\nu}, \beta^{-1} \text{ }^a$	$\Pi_{\mu\nu}, \text{eV}^{-1} \text{ }^b$	$X_{\mu\nu}, \text{eV} \text{ }^c$	$\Delta pK_G, \text{eV} \text{ }^d$
<i>meta</i> -Nitrobenzoic	-0.0001	+0.0001	-0.0079	-0.39
<i>para</i> -Nitrobenzoic	+0.0042	+0.0008	-0.0245	-0.48

^a HMO atom-atom polarizability; ^b "generalized" polarizability of Hartree-Fock perturbation theory; ^c SCF-LCI theory; ^d $\Delta pK_G = (pH_H - pK_{\mu-NO_2})$; the pK unit corresponds to 0.0588 eV at 300°C.

sign of π_{38} follows that *meta*-nitrobenzoic acid should be a weaker acid than benzoic acid. In contrast to the finding of a similar study³ of basicities of substituted pyridines, the inclusion of the electron repulsion on the level of the Hartree-Fock perturbation theory leads to a considerable improvement and to the correct sign of Π_{38} in the present case. On the other hand, the ratio $X_{38}/X_{48} \sim 0.12$ is still not in a good agreement with the expected value $(\sigma_m/\sigma_p)_{NO_2} \sim 0.9$. As expected, the best agreement with the experimental data is achieved when the SCF-LCI theory is employed ($X_{38}/X_{48} \sim 0.3$). Larger discrepancies than in the ratio X_{38}/X_{48} are observed between the absolute values of $X_{\mu\nu}$ on one side and the corresponding ΔpK^G values on the other. Certainly, some part of the differences can be assigned to the model values of the perturbations but the imperfections of the model used (neglect of σ electrons and mesomeric effect) are responsible for the larger part. Despite that, the calculations clearly demonstrate the usually assumed parallelism between the π inductive and mesomeric effects¹³. The approximation of substituent effects by the change $\Delta\alpha$ is based on this parallelism. In addition, this SCF-LCI method is capable of giving (in the terms of the so-called configurational analysis¹⁴⁻¹⁶) a very illustrative picture of the changes caused in the parent molecule by the perturbation. For example the dissociation of benzoic acid (modeled by the change $\Delta\alpha_8 = +2$ eV) leads to the wave function of the ground state (Scheme 2)

$$\Psi'_0 = 0.997\Psi_0 - 0.053^1\Psi_{3\rightarrow 6} - 0.039^1\Psi_{3\rightarrow 8} + 0.027^1\Psi_{2\rightarrow 6} + 0.022^1\Psi_{2\rightarrow 8} + \dots \quad (11)$$



SCHEME 2

Here Ψ_0 corresponds to the configuration of the ground state of the unperturbed molecule, ${}^1\Psi_{i \rightarrow j}$ stand for polarization contributions of monoexcited states to the

ground state. Owing to its simplicity and generality, the method gives an alternative description of the so-called "static orbital mixing"¹⁷ which is, from the point of view of accuracy, more suitable than those which are provided by common perturbation approaches.

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Translated by J. Schraml.