QUANTUM CHEMICAL STUDY OF DISSOCIATION OF *meta* AND *para* SUBSTITUTED BENZOIC ACIDS IN π-ELECTRON APPROXIMATION*

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π-Electron energy changes during ionization (A) have been shown to be correlable with $\sigma_{m,p}$ and σ_R constants of the substituents X. The HMO approximation gives correlation only in the *para* series, whereas the π-SCF-MO method applies for the whole data set. Contribution of π-electrons to classical $+M$ and $-M$ effects of the substituents X and solvation problems are discussed. The Hammett relation between pK values of *meta* and *para* substituted benzoic acids I and log k of alkaline hydrolysis of their esters VI has been interpreted at the π-SCF level.

Ionization of *meta* and *para* substituted benzoic acids I to the corresponding anions II taking place at 298 K according to the following scheme

$$X\text{-}C_6H_4CO_2H + H_2O \rightleftharpoons X\text{-}C_6H_4CO_2^{(-)} + H_3O^{(+)} \qquad (A)$$
$$\quad I \qquad\qquad\qquad\qquad\qquad II$$
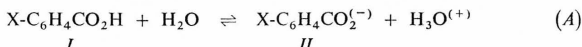
was the basis for the Hammett classical deduction of the well-known correlation equation[1]

$$\log K_X = \varrho\sigma + \log K_H , \qquad (1)$$

where the indices X and H at the equilibrium constants K refer to the substituent X and the unsubstituted standard acid, respectively. With this equation a period was started of quantitative empirical study of substituent effects in organic molecules on the basis of equilibrium and kinetic data. In this approach there exists a remarkable dilemma in that the microprocesses consisting in the electron distribution changes brought about by substituents and reagents are, within discussions of the equations of the type (1), expressed[2] *de facto* in terms of the theory of macrostructures and macroprocesses *i.e.* by means of the rate and equilibrium constants of the type K_X and K_H. Consequently the relations between the macroquantities of the type σ and electronic effects of the substituents X, *i.e.* microquantities, cannot be derived by means of methods of chemical thermodynamics and kinetics alone, but can be derived only with the use of the theories valid for microobjects. In this connection we were interested in the extent to which the standard Hammett's process (A) can be expressed in the terms of organic quantum chemistry. This paper

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deals with the relations between π-electron energy of the reacting substrate *I* and *II* and the empirical parameter σ in Eq. (*1*).

Up to now two different approaches were applied in quantum-chemical interpretations of acidity of benzoic acids *I* using the methods HMO (ref.[3]), EHT (refs[4-6]) and INDO (refs[7,8]). One of them[4,7,8] is based on simple comparison of the calculated characteristics of electron distribution in the region of carboxyl group of the acids *I* with the substituent parameters σ in Eq. (*1*). More significant consonant trends between changes in these two quantities are found[4,7] only for *para* substituted acids *I*. In addition to it, the data obtained by the INDO method[8] were used for independent correlations with the constants σ_m, R and F from which it is deduced[7,8] that resonance and field effects are dominant in the *para* and *meta* series, respectively. The other approach involving the calculated electron energies has been used so far[3,5,6] only within the HMO and EHT methods neglecting electron repulsion. In these cases, too, the correlations were found only for the *para* substituted substrates *I* and *II*. The authors[5] state that the EHT energies of *meta* derivatives can be involved in overall correlation, if the solvation energy contribution is explicitly considered. Besides that it was found[8] that the energies of boundary HOMO and LUMO acids *I* calculated by the INDO method correlate with the Hammett $\sigma_{m,p}$ constants, too.

This paper forms a continuation of our earlier short communication[3] in which it was shown that application of simple HMO method allows to find a linear correlation between the π-electron energy difference of the HMO models *I* and *II* and p*K* values of the acids *I* with the *para* substituents X. On the contrary, in the *meta* series the calculated π-electron contribution is almost zero, so that it could be presumed that only the Hammett σ_p constants involved the π-electron contribution of the substituent effect. Now we have applied the Pople version[10] of SCF—MO method in π-electron approximation to decide whether the above conclusion is due only to the extremely approximative character of the HMO approach.

TABLE I

The Parameters Used in the HMO Method[3,11,12]

Atomic centre	h_Y	Bond	k_{YZ}	Atomic centre	h_Y	Bond	k_{YZ}
N(CH$_3$)	1·0	C—N	0·8	Br	1·5	C—Br	0·3
NH$_2$	1·5	C—N	0·8	N($\equiv$C)	0·5	C$\equiv$N	1·2
OH	2·0	C—O	0·8	N(O$_2$)	1·8	C—N	0·9
OCH$_3$	1·9	C—O	0·8	O($_2$N)	1·5	N—O	1·7
CH$_3$	2·0	C—C	0·7	O($=$C)	1·0	C$=$O	1·0
F	3·0	C—F	0·7	(H)O(CO)	2·0	C—O(H)	0·8
Cl	2·0	C—Cl	0·4	O($_2$C)$^-$	1·5	C—O	1·0

CALCULATIONS

Coulombic and resonance integrals in the simple HMO method were aproximated by usual relations $\alpha_Y = \alpha_C + h_Y\beta_{CC}$ and $\beta_{YZ} = k_{YZ}\beta_{CC}$ in the convention $\alpha_C = 0$ and $\beta_{CC} = 1$ for benzene molecule. With respect to the extensive number of literature data[11,12] the empirical parameters h_Y and k_{YZ} were chosen to obtain the closest possible correlations of the calculated quantum-chemical characteristics with experimental data. For parametrization of the π-SCF-MO method[10] we used refs[13–20]. Tables I and II give the parameter sets used in the HMO and SCF models. In the latter ones we considered the both planar conformations *Ia* and *Ib* for *meta* substituents X differing in the π-electron energy values. Three alternative π-electron configurations of $—CO_2H$ group were considered: *a)* "conjugation" model *A* taking into account the existence of π-bonds between the aromatic nucleus and carboxyl group as well as between the

TABLE II

The Parameters Used in the SCF Method

Atomic centre	$-I_\mu$, eV	$\gamma_{\mu\mu}$, eV	Bond	$-\beta_{\mu\nu}$, eV	$R_{\mu\nu}$, nm	Z_μ	Ref.
CH	11·16	11·13	C—C	2·386	0·139	1	13
N(CH$_3$)$_2$	21·22	12·98	C—N	2·386	0·140	2	14
NH$_2$	22·60	14·45	C—N	2·090	0·138	2	15
OH	27·17	14·58	C—O	2·550	1·135	2	14
OCH$_3$	26·73	14·58	C—O	2·550	0·135	2	14
C(H$_3$)^a	11·16	11·13	C—H$_3$	1·220	0·152	1	13
H($_3$C)^a	8·50	8·50	C≡H$_3$	3·000	0·045	1	13
SCH$_3$	20·40	10·84	C—S	1·159	0·172	2	14
SH	21·00	10·84	C—S	1·159	0·172	2	14
F	30·24	13·87	C—F	2·486	0·140	2	16, 17
Cl	25·07	9·57	C—Cl	1·927	0·177	2	17, 18
Br	30·00	10·03	C—Br	1·642	0·192	2	19
I	25·00	9·06	C—I	1·141	0·210	2	17
N(≡C)	14·12	12·34	C≡N	2·852	0·120	1	19
C(≡N)	11·16	11·13	C—C(N)	2·386	0·142	1	19
C(NO$_2$)	12·40	11·68	C—N	2·180	0·148	1·1	20
N(O$_2$)	20·40	14·89	C—N	2·180	0·148	1·5	20
O($_2$N)	20·80	16·50	N—O	2·650	0·122	1·2	20
C(O$_2$H)	11·16	11·13	C—C	1·700	0·148	1	13
O(=C)	17·70	15·30	C=O	2·700	0·124^b	1	13, 21
(H)O(CO)	30·46	15·30	C—O(H)	1·800	0·129^b	2	13, 21
O($_2$C)$^{-c}$	24·08	15·30	C—O	2·250	0·126	1·5	

^{a} Parameters of heteroatomic model[13] proved equivalent in the calculations, too; ^{b} for geometry see ref.[21], for X = C$_6$H$_5$ an idealized planar system was used with $R_{CC} = 0·148$ nm and $\beta_{CC} = -1·700$ eV for the bond between the both nuclei; ^{c} oxygen atom in the ionized carboxyl group.

partial fragments C=O and C—OH, b) "aldehyde" model B neglecting the π-bond in the fragment C—OH (ref.[9]) and c) "benzene" model neglecting the π-bond between the aromatic ring and carbonyl group. Thus in the models B and C the π-electron configuration of the acids I is approximated by a π-system of the corresponding aldehydes III and monosubstituted benzenes IV respectively. On the contrary, HMO and SCF models of the anions II involve always explicitly complete conjugation between $-CO_2^{(-)}$ group and aromatic nucleus as well as conjugation within $-CO_2^{(-)}$ group. The geometry of benzoic acid determined by X-diffraction[21] with the modifications shown in Table II were chosen for the SCF calculations[22]. All the quantum-chemical calculations were carried out with the use of a Tesla 200 and an IBM/370—145 computers. Table III gives π-electron energies of the compounds I and II containing usual substituents X which were obtained for the abovementioned HMO and SCF models. Table IV gives some examples of π-electron distribution (π-electron densities q_Y and π-bond orders p_{YZ} for atomic centres Y and Z) calculated for the substrates I and II and model A.

TABLE III

Comparison of some $\Delta\Delta E$ Values in Eq. (3) for the Models A, B, and C of the Substrate Forms I and II with σ_R Constants of Substituents X

X	$\Delta\Delta E_{HMO}$, $\beta \cdot 10^3$			$\Delta\Delta E_{SCF}$, eV $\cdot 10^3$			$\alpha\sigma_R{}^a$
	A	B	C	A	B	C	
p-N(CH₃)₂	0·0	—6·0	31·2	—35·37	—27·81	—98·87	—0·83
p-NH₂	0·1	—4·2	23·6	—31·54	—24·43	—86·13	—0·82
p-OH	0·2	—3·0	17·9	—15·57	—12·22	—44·21	(—0·68)
p-OCH₃	0·2	—3·2	18·8	—16·80	—12·71	—47·59	—0·61
p-CH₃	0·2	—2·2	13·8	—4·14	—2·69	—9·32	—0·11
p-F	0·1	—1·3	9·1	—8·93	—6·44	—23·62	—0·45
p-Cl	0·0	—0·7	4·5	—5·47	—4·08	—15·28	—0·23
p-Br	0·0	—0·6	3·4	—3·28	—2·18	—6·26^b	—0·19
p-CN	—1·2	—0·2	—11·5	10·03	8·86	27·49	0·13
p-NO₂	—1·2	1·0	—17·6	26·41	21·30	66·55	0·15
H	0·0	0·0	0·0	0·00	0·00	0·00	0·00
m-N(CH₃)₂	0·0	0·1	—1·7	—8·58	—7·22	—23·70	—0·274
m-NH₂	0·0	0·1	—1·3	—6·77	—4·98	—18·77	—0·270
m-OH	—0·1	0·0	—1·0	—1·91	—1·15	—7·82	(—0·224)
m-OCH₃	0·0	0·1	—1·0	—2·03	—1·64	—8·75	—0·201
m-CH₃	0·0	0·1	—0·7	—1·62	—1·07	—5·03	—0·036
m-F	0·0	0·0	—0·4	—0·67	0·22	—2·96	—0·149
m-Cl	0·0	0·0	—0·2	—0·99	—0·39	—2·89	—0·076
m-Br	0·0	0·0	—0·2	0·22	0·52	0·45^c	—0·063
m-NO₂	0·1	0·3	—0·2	18·60	15·17	50·19	0·050
m-CN	0·1	0·2	—0·1	7·95	7·11	22·13	0·043

^{a} For *meta* and *para* positions $\alpha = 0.33$ and 1.0, respectively; the values in parenthesis from ref.[23] were not involved in the correlations in Table V. ^{b} for X = p-I calculated $-4.28 \cdot 10^{-3}$ eV; ^{c} for X = m-I calculated $+0.21 \cdot 10^{-3}$ eV.

TABLE IV

Effect of Substituent X on SCF π-Electron Distribution in the Groups COOH and COO$^{(-)}$ of the Compounds *I*, *II* (Model *A*)

All the data in 10^4 of charge unit with respect to X = H: $\Delta q_Y = q_Y(X) - q_Y(H)$ and $\Delta p_{YZ} = p_{YZ}(X) - p_{YZ}(H)$; for benzoic acid itself it is $q_C = 0.6825$, $q_{(O=C)} = 1.4054$, $q_{O(-H)} = 1.9523$, $p_{C=O} = 0.8730$, $p_{C-OH} = 0.2495$, for its anion $q_C = 0.5350$, $q_O = 1.7652$ and $p_{CO} = 0.5816$.

X	Conformation	Acid I^a					Anion II				
		Δq_C	$\Delta q_{O(=C)}$	Δq_{OH}	$\Delta p_{C=O}$	Δp_{C-OH}	Δq_C	$\Delta q_O^{\,b}$		$\Delta p_{CO}^{\,b}$	
m-NH$_2$	*Ia*	−9	47	0	−23	5	−10	4	28	1	−32
	Ib	−3	13	5	−6	−12					
m-CH$_3$	*Ia*	−6	12	1	−6	−1	−2	5	7	−6	−7
	Ib	−4	10	1	−6	−2					
m-F	*Ia*	−9	12	0	−6	2	−3	0	7	0	−6
	Ib	−1	3	2	−5	−3					
m-CN	*Ia*	10	−30	−1	15	2	2	−11	−18	13	21
	Ib	3	−22	−2	12	7					
m-NO$_2$	*Ia*	33	83	−1	42	1	6	−22	−50	25	59
	Ib	4	−46	−8	25	22					
p-NH$_2$	—	26	115	10	−82	−27	77	72		−99	
p-CH$_3$	—	−1	16	2	−11	−3	5	10		−12	
p-F	—	3	34	3	−22	−7	16	20		−26	
p-CN	—	8	−39	−2	16	6	3	−19		21	
p-NO$_2$	—	13	−93	−6	45	16	−6	−50		58	

^{a} Model *A* (see Calculations); ^{b} for *meta* derivatives the first column gives the date concerning the oxygen atom nearer to the substituent X.

RESULTS AND DISCUSSION

Relation between π-electron energy and the Hammett σ constant. As a rule, validity of the Hammett equation (*1*) is based on the presumption that Eq. (*2*) applies for relative change of the Gibbs energies of *meta* and *para* substituted acids *I*.

$$\Delta\Delta G = \Delta G_X - \Delta G_H = -RT \ln \left(K_X / K_H \right) = -2.303 RT\sigma \ . \qquad (2)$$

For an analogous change of relative electron energies of the process (2) it can be written

$$\Delta\Delta E = \Delta E_X - \Delta E_H , \qquad (3)$$

where the terms ΔE_X and ΔE_H correspond to the electron energy changes accompanying the dissociation of an X-substituted and unsubstituted acid I, respectively, to their ionized forms II. Obviously there exists a simple way of comparison of the thermodynamic quantities ΔG with the mentioned electron energies ΔE. This way consists in a presumption of possible parallel changes of the both quantities within a certain series *e.g. para* and *meta* substituted acids I, expressed as

$$\Delta\Delta G \simeq \Delta\Delta E , \qquad (4)$$

so that considering Eqs (2) and (3) we obtain

$$\Delta E_X - \Delta E_H \simeq T\sigma . \qquad (5)$$

For the parameters $\sigma_{m,p}$ usually defined for a certain temperature (298 K) the temperature factor T is eliminated from the relation (5), and for the standard member of the series, *i.e.* the unsubstituted acid I, it is then $\Delta E_H = \text{const}$. For this special case Eq. (4) simplifies to

$$\Delta E_X \simeq \sigma_{m,p} , \qquad (6)$$

which would have to be solved by every quantum-chemical calculation in which the quantity ΔE_X reflects sufficiently precisely the trend in the electron energy changes brought about by introduction of the substituent X in the respective position of benzoic acid and its anion. From this point of view the comparisons of $\sigma_{m,p}$ constants with electron energies carried out up to now[3,5,6,8] can be considered as physically more justified than the comparisons with electron distribution characteristics[4,7,8]. As no π-electrons are assigned to water molecule and oxonium ion in Eq. (A), it can be written

$$\Delta E_X = E(II)_\pi - E(I)_\pi + \Delta E_r , \qquad (7)$$

where the quantities with the index π correspond to π-electron energies of the substrate forms I and II, and the index r denotes the residual energy contribution coming from the other electrons in the molecules of reagents. If the presumption (4) is correct, Eq. (6) would lead to unambiguous linear dependence between the energy ΔE_X and constants $\sigma_{m,p}$. However, if the calculation is carried out only with the first two terms

of Eq. (7), then uncertainty of influence of neglect of the third term ΔE_r can change the linear relation (6) to mere linear correlation:*

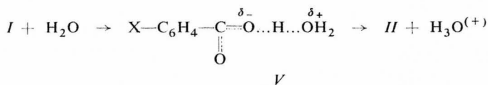$$\Delta E_\pi = E(II)_\pi - E(I)_\pi = a\sigma_{m,p} + b \,, \qquad (8)$$

where the corresponding correlation criteria (correlation coefficient r and the Student distribution t) can be interpreted as significance criteria of the π-electron approximation for study of equilibria of the type (A). A higher statistical probability of the relation (8) indicates an insignificant role of the residual energy ΔE_r and *vice versa*. For investigation of correlations type (8) we chose, first of all, the Hammett $\sigma_{m,p}$ constants for which Eq. (1) is fulfilled very well[23–27]. In this case the obtained correlations (8) are statistically quite equivalent to the analogous relations with pK values given in ref.[3]. Besides that in some cases we investigated also the correlations of energies ΔE_π with so called resonance parameters σ_R involving (according to ref.[24]) the resonance effect *i.e.* π-electron contribution of the substituent effect in equations type (A). The obtained results are summarized in Table V.

Correlations with HMO *electron energies.* In this case Eq. (7) does not involve both the explicit influence of ΔE_r and the π-electron contribution part of the repulsion character $E_{\pi,\mathrm{rep}}$, *i.e.* the energy relation

$$\Delta E_\pi = E_{\pi,\mathrm{atr}} + E_{\pi,\mathrm{rep}} \qquad (9)$$

is approximated simply as only $\Delta E_\pi = E_{\pi,\mathrm{atr}} \doteq E_{\mathrm{HMO}}$. This simplification could lead to an *a priori* expectation of either complete failure of the correlation (8) or, at least, its non-validity for a certain number of the compared pairs I and II. However, we have found that the result can be affected to a certain extent by proper choice of the corresponding HMO model (Table I). For the model A the ΔE_{HMO} values show the minimum variation within the whole series of the compared compounds (see Table III), so that they practically give no correlation (8). On the contrary, the model B gives good correlation for σ_p constants and fails only in the *meta* series, *i.e.* for σ_m (Fig. 1), where it behaves analogously as the model A. This finding is interpreted by the HMO method over-estimating the π-electron conjugation in all bonds (ref.[11]), in our case mainly between the OH group and the X-C$_6$H$_4$CO residue in the undissociated acid I. Consequently the HMO model of the form I with the resonance integral parameter $\beta_{\mathrm{C-OH}} = 0{\cdot}8\beta_{\mathrm{CC}}$ is too "close" to the HMO model of the form II, and it reflects rather the situation in the reaction course given by formula V:

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* Validity of a quantum-chemical model is presumed enabling $\sigma - \pi$ separation. Otherwise the term ΔE_r would involve a certain part of π-electron contribution.

$$I + H_2O \rightarrow X-C_6H_4-\overset{\overset{\delta-}{|}}{\underset{O}{C}}=\overset{\delta-}{O}...H...\overset{\delta+}{O}H_2 \rightarrow II + H_3O^{(+)}$$

$$V$$

For application of the model A it is then $E(I)_\pi = E(V)_\pi$, and the calculated energy difference for correlation (8) $\Delta E_{\text{HMO}} = E(II)_\pi - E(V)_\pi$ expresses only an insignificant change of π-electron energy between various hydrated ions II and V which, in the HMO method, is not influenced to a decisive extent by the *para* substituent X. On the contrary, in application of the model B, where the HMO model is approximated by the π-electron configuration corresponding to the aldehyde III, the both quantities $E(II)_\pi$ and $E(V)_\pi$ represent equivalent approximations of energy of the anion II, at least so for low values of the resonance intergral β_{C-OH}. In accord with that the correlations of the type (8) involving the energy differences $E(II)_\pi - E(I)_\pi$ and $E(V)_\pi - E(I)_\pi$ are practically equivalent (Table V). The values ΔE_{HMO} for the benzene model C give again a statistically significant correlation only with σ_p constants, which can be interpreted as acceptability of the neglect of conjugation between CO_2H and C_6H_4X groups in the HMO models of the acids I. Absolute insensitivity of all the three models A, B, C to the change of substituent X in *meta* position and, hence, to σ_m constants stands in accord with the conclusion[3] that the HMO method does not reflect that portion of π-electron energy by which the meta substituent X affects the reaction centre CO_2H or $CO_2^{(-)}$. We further used the SCF method to give a true picture to this π-energy contribution.

Correlation with SCF electron energies. In this case calculation can give full expression (9) for energy difference $\Delta E_\pi = \Delta E_{\text{SCF}}$ involving explicitly also the portion of π-electron repulsion, *i.e.* the term $\Delta E_{\pi,\text{rep}}$. As in the HMO procedure[3] and other more perfect calculations[5,8] we found the correlation (8) to be valid for σ_p constants again. With the model A, however, the ΔE_{SCF} quantities (unlike the ΔE_{HMO} values) are sufficiently sensitive to the influence of substituent X (Table V). This circumstance is obviously due to the SCF procedure eliminating the product of the HMO approximation over-estimating the conjugation at C—OH bond in the acids I. The models B and C give also good correlations (8) as it could be expected.

Correlation of ΔE_{SCF} values for the *meta* substituted substrates I and II leads to an ambiguity connected with the two different conformations of unionized forms Ia and Ib or IIa and IIb. This situation in the choice of the models A and B is due to that SCF procedure respects the molecular geometry, whereas the HMO approach respects only the molecular topology. In this context the model C is remarkable, as it does not involve the mentioned conformation problem. From Table V it can be seen that involving of the values ΔE_{SCF} for the *meta* derivatives II into the overall correlation (8) with the $\sigma_{m,p}$ constants does not markedly worsen the correlation criteria r and t of this model. More perfect models A and B would, however, necessi-

tate to accept additional presumptions concerning the choice of the mentioned conformation pairs *Ia, b* resp. *IIIa, b*.

Presuming that the alternative ionizations in the *meta* series $Ia \rightleftarrows II$ and $Ib \rightleftarrows II$ will be much faster than establishing of the conformation equilibrium $m(Ia) \rightleftarrows n(Ib)$, the overall ionization can be expressed as $m(Ia) + n(Ib) \rightleftarrows (m + n) II$. If another simplification is accepted that for the meta substituted acids I it will be $m \doteq n \doteq 1$, which seems likely, then three types of ΔE_{SCF} values can be taken into account in the correlation (8) for the model A: $\Delta E_{SCF,a} = E(II)_\pi - E(Ia)_\pi$, $\Delta E_{SCF,b} = E(II)_\pi - E(Ib)_\pi$, and an "average" value $\Delta E_{SCF,a,b} = E(II)_\pi - 0.5(E(Ia)_\pi + E(Ib)_\pi)$. The last expression corresponds to a transformation $\frac{1}{2}(Ia) + \frac{1}{2}(Ib) \rightleftarrows II$, and it is easily applicable also for the model B in the form $\Delta E_{SCF,a,b} = E(II)_\pi - 0.5(E(IIIa)_\pi + E(IIIb)_\pi)$, the "non-average" values being $\Delta E_{SCF,a} = E(II)_\pi - E(IIIa)_\pi$ and $\Delta E_{SCF,b} = E(II)_\pi - E(IIIb)_\pi$. Thus it is seen that the correlations type (8) for the *meta* substituted substrates I and II are less lucid with respect to possible conformational non-homogeneity of the unionized forms I as compared with the *para* series.

TABLE V

The Calculated Characteristics of the Studied Correlations (8)

Energy[a]	Model	σ	$a . 10^3$	$b . 10^3$	r	t	n
$\Delta\Delta E_{HMO}$	B	σ_p	0.412	−1.91	0.971	4.0	10
		σ_R	0.658	0.22	0.900	2.1	9
$\Delta\Delta E_{HMO}$	C	σ_p	−2.92	−8.32	0.987	6.2	10
		σ_R	−4.62	8.83	0.923	6.3	9
$\Delta\Delta E_{SCF}$	A	$\sigma_{m,p}$	3.11	−6.20	0.930	14.1	33
		σ_p	3.38	−6.87	0.958	12.4	16
		σ_m	2.23	−3.97	0.842	5.8	16
		$\alpha_{m,p}\sigma_R$	4.57	5.58	0.934	13.1	27
		$\alpha_p\sigma_R$	4.65	6.08	0.946	9.7	13
$\Delta\Delta E_{SCF}$	B	$\sigma_{m,p}$	2.49	4.75	0.937	15.0	33
		σ_p	2.69	−5.13	0.960	12.8	16
		σ_m	1.87	−3.32	0.869	6.6	16
		$\alpha_{m,p}\sigma_R$	3.56	4.44	0.923	12.0	27
		$\alpha_p\sigma_R$	3.66	5.53	0.947	9.8	13
$\Delta\Delta E_{SCF}$	C	$\sigma_{m,p}$	8.44	−1.78	0.934	14.6	33
		σ_p	9.16	−1.93	0.960	12.9	16
		σ_m	6.22	−1.26	0.852	6.1	16
		$\alpha_{m,p}\sigma_R$	12.38	1.43	0.938	13.5	27
		$\alpha_p\sigma_R$	12.75	1.81	0.960	11.4	13

[a] Meaning of the symbols: $\Delta\Delta E = \Delta E_\pi$ (for X $\neq$ H) $- \Delta E_\pi$ (for X = H).

A somewhat more complicated situation is encountered with the acids I (or their "aldehyde" models III) having the *para* substituent X = COOH or CHO which can assume different conformations $Ic, d(IIIc, d)$. In these cases it was necessary to use analogous values $\Delta E_{SCF,c}$, $\Delta E_{SCF,d}$ and $\Delta E_{SCF,c,d}$ for the *para* series, too. For the corresponding *meta* substituted analogues three SCF models Ie, f, g $(IIIe, f, g)$ must be taken into account, the respective conformation equilibria being Ie(or $IIIe$) + If (or $IIIf$) $\rightleftarrows IIe$ and If (or $IIIf$) + Ig (or $IIIg$) $\rightleftarrows IIf$; the respective "average" energy differences $\Delta E_{SCF,e,f}$ and $\Delta E_{SCF,f,g}$ are determined as it follows: $\Delta E_{SCF,e,f} = E(IIe)_\pi - 0.5(E(Ie)_\pi + E(If)_\pi)$, $\Delta E_{SCF,f,g} = E(IIf)_\pi - 0.5(E(If)_\pi + E(Ig)_\pi)$ and analogous expressions with the quantities $E(IIIe)_\pi$, $E(IIIf)_\pi$, and $E(IIIg)_\pi$.

It is remarkable that the mentioned conformational aspect has not yet been given attention in the correlation analysis[4-8]. This circumstance is probably insignificant in comparison of the $\sigma_{m,p}$ constants with the electron distribution characteristics of the acids I (ref.[4,7,8]), since the distribution parameters depend usually little on conformation of carboxyl group in the planar forms (ref.[28]). On the contrary, the EHT electron energies of the conformation forms type Ia and Ib somewhat differ depending on the chosen geometry[29].
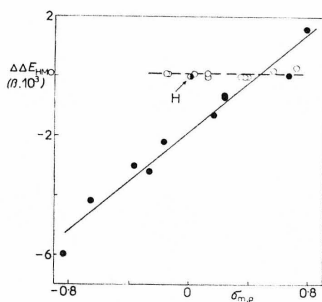
Fig. 1

Dependence of Relative π-Electron Energy Differences $\Delta \Delta E_{HMO}$ (model B) on the Hammett $\sigma_{m,p}$ Parameters

Substituents X: N(CH$_3$)$_2$, NH$_2$, OH, OCH$_3$, CH$_3$, H, F, Cl, Br, CN and NO$_2$; light and dark points denote *meta* and *para* positions, respectively; the arrow indicates the data for the non-substituted benzoic acid.
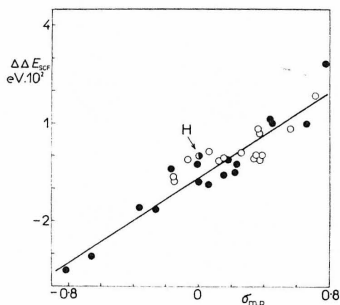
Fig. 2

Dependence of Relative π-Electron Energy Differences $\Delta \Delta E_{SCF}$ (model A) on the Hammett $\sigma_{m,p}$ Parameters

Substituents X: N(CH$_3$)$_2$, NH$_2$, OH, OCH$_3$, CH$_3$, C$_6$H$_5$, H, SCH$_3$, F, SH, Cl, Br, I, COOH, CHO, CN and NO$_2$; for description of points see Fig. 1.

In Fig. 2 the values $\Delta\Delta E_{SCF} = \Delta\Delta E$ in the relation (3) (calculated with the use of all *para* and *meta* "average" energy differences of the type ΔE_{SCF} within the model *A*) are plotted against the Hammett $\sigma_{m,p}$ constants. It is immediately obvious that there is a close linear correlation between the both compared quantities. Besides that, in this context we take for significant that the values $\Delta\Delta E_{SCF}$ have the same signs (Table III) when compared with the resonance parameters $\sigma = \alpha\sigma_R$ in Eq. (5) there being only two exceptions (X = *m*-Br and *m*-I) due probably to inaccurate parametrization. This fact indicates that all the three π-SCF models *A*, *B*, *C* are physically justified. Fig. 3 illustrates the way in which typical substituents X influence the value $E(II)_\pi -$ $- E(I)_\pi$ in Eq. (7). In contrast to correlations with ΔE_{HMO} quantities (Fig. 1), in Fig. 2 the correlation area is not divided in two parts (*para* and *meta* substitution). Choice of the "average" and "non-average" values type ΔE_{SCF} has an only limited effect on scattering of the points from the regression straight line. The values $\Delta E_{SCF,a,b}$, $\Delta E_{SCF,c,d}$, $\Delta E_{SCF,e,f}$, and $\Delta E_{SCF,f,g}$ give better correlation for those substituents for which the calculated π-energy differences between the corresponding conformation pairs *Ia, b, Ic, d*, and *Ie, g* are relatively large, *i.e.* for X = *m*-N(CH$_3$)$_2$, *m*-NH$_2$, *m*-NO$_2$ and *p*-COOH. For the other substituents it is immaterial whether the "average" value or some of the energies ΔE_{SCF} of ionization of the chosen conformer is used. An analogous correlation to that in Fig. 2 was found also for the model *B* (Table V). Considerable similarity of the SCF models *A* and *B* thus contrasts with the abovementioned difference between the corresponding HMO models and is due obviously to the improved orbital energies in the SCF method. The presence and the absence of divided correlation area in the HMO and SCF treatments, respectively (Figs 1 and 2), is probably due to the neglect if the decisive portion of π-electron repulsion in the Hückel approximation by which the *meta* substituent X, which is closer in space to the reaction centre, can affect its ability to ionize. This is supported
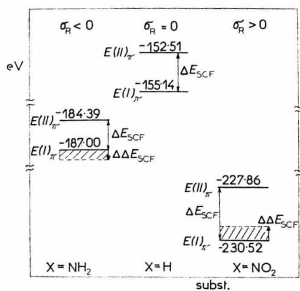

FIG. 3

Influence of Character of the Substituent X on π-Electron Energy of the Substrate Forms *I* and *II* Calculated by SCF Method

by our comparison of the independent correlations (8) for the *meta* series with both the values $\Delta E_{\text{SCF,a}}$ and $\Delta E_{\text{SCF,b}}$. Slope of the regression straight line (8) is *e.g.* positive and higher ($a = 3 \cdot 87 \cdot 10^{-2}$ eV) for the conformers *Ib*, having the π-electron system of the substituent X closer to the reaction centre C—OH, than for the conformers *Ib* ($a = 4 \cdot 9 \cdot 10^{-3}$ eV). This space factor is obviously manifested in the repulsion integrals type $\gamma_{\mu\nu}$ through which the π-SCF wave functions and the eigenvalues themselves are more sensitive to the change of the *meta* substituent X than analogous HMO characteristics.

Contribution of π-electrons in $+M$ and $-M$ effects of substituents X. The electronic effects $+M$ and $-M$ derived from macroscopic correlation data are usually discussed in terms of the electron shifts within the molecule and, therefore, we took it for useful to compare them for the substrate forms *I* and *II* with the calculated characteristics of π-electron distribution. From Table IV it can be seen that effect of the substituent X on π-electron densities q_Y and orders of π-bonds p_{YZ} is somewhat smaller in the region of the reaction centre of the acids *I* than for the anions *II*. However, the effects is substantially higher in the *para* series than in the *meta* series. Hence it is concluded, that in the case of the *meta* substituted substrates *I* and *II* the substituent effect is predominantly transmitted by another mechanism, different from classical π-electron shifts from the substituent to the reaction centre or back. This effect consists in repulsion of π-electrons of those parts of the substituent X which are closer in space to the reaction centre COOH or $CO_2^{(-)}$ and which was completely neglected in the simple version of the HMO method. Therefore, the values ΔE_{HMO} cannot depend on the character of the *meta* substituent X, which is demonstrated in Fig. 1. From the point of view of Eq. (9), then, for the para substituent effects it holds $\Delta E_{\pi,\text{atr}} \gg \Delta E_{\pi,\text{rep}}$, and Eq. (9) can be replaced by an acceptable approximation $\Delta E_\pi \approx \Delta E_{\pi,\text{atr}}$. In this case the HMO approximation is sufficient. On the contrary, for the *meta* substituent effects it is $\Delta E_{\pi,\text{rep}} \gg \Delta E_{\pi,\text{atr}}$, and a suitable approximation for (9) can be $\Delta E_\pi \approx \Delta E_{\pi,\text{rep}}$. In this case the SCF procedure is indispensable. This presumption is supported by the fact that in all cases[30-32] of correlations of σ_m constants with HMO data special additional parametrization had to be chosen for a number of further reaction centres as a mean for involving a part of repulsion effect into the original HMO model not involving this effect.

In this context it is possible to make a certain conclusion about physical meaning of so called reasonance constants σ_R (refs.[33-35]). From Table V it can be seen that the correlation (8) for σ_R is approximately as close as for the Hammett $\sigma_{m,p}$ constants. Therefrom it is concluded that the σ_R constants reflect the classical resonance effect only for *para* substituents X. In the *meta* series they reflect the non-classical effect of π-electron repulsion, *i.e.* repulsion influence of π-electrons through the space between the reaction centre and the substituent X, which is close to the idea about the so called field-effect.

Solvation effects. If the given conclusions are correct, then the relations type (6) cannot be homogeneous for the *meta* and *para* substituted acids I, as far as the ΔE_X values are calculated by a method neglecting the electron repulsion, *i.e.* HMO or EHT. The authors[5] state that division of data can be replaced by additional introduction of solvation, and they use Eq. (10) instead of (7)

$$\Delta E_X = E(II) - E(I) + \Delta E_{solv}, \qquad (10)$$

where the first two terms represent the overall electron energies of the compounds I and II calculated by the EHT method, and the third term is the energy contribution of solvation calculated according to the obtained electron distribution. In the calculations[5] the first two terms of Eq. (10) involve only 10.8% of the calculated energy difference ΔE_X, so that the term ΔE_{solv} is predominant. In this context we were interested in a comparison of experimental[36] $\Delta\Delta G$ values for the ionization

$$\text{X-C}_6\text{H}_4\text{COOH} + \text{C}_6\text{H}_5\text{COO}^{(-)} \ \rightleftarrows \ \text{X-C}_6\text{H}_4\text{COO}^{(-)} + \text{C}_6\text{H}_5\text{COOH} \qquad (B)$$
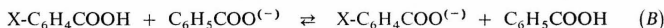
taking place in gas phase without solvation effects with the calculated[5] energies ΔE_X according to Eq. (4). From Fig. 4 it can be seen that difference of the first two terms of Eq. (10) shows the expected division of data into *meta* and *para* series when correlated with the $\Delta\Delta G$ data, and introduction of the calculated[5] value ΔE_{solv} removes the differences between the both data sets again. Character of the correlation area is maintained, too, if the energies calculated by the iterative EHT procedure[6] are used. Hence it is obvious, that the considered term ΔE_{solv} does not reflect the solvation effect according to the original presumptions[5] but rather a certain effect
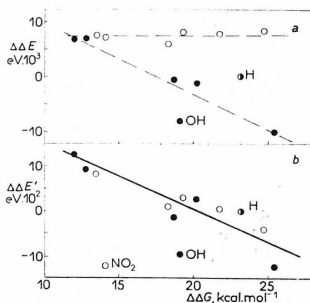

Fig. 4

Relative Differences of Electron Energies of the Substrate Forms I and II Calculated[5] by EHT Method against Relative Differences of the Gibbs Energies $\Delta\Delta G$ Measured[36] for Equilibrium (2) in Gas Phase

For description of points see Fig. 1; $a\ \Delta\Delta E = E(II)_{X\neq H} - E(I)_{X\neq H} - E(II)_{X=H} + E(I)_{X=H}$; $b\ \Delta\Delta E' = \Delta\Delta E + \Delta\Delta E_{solv}$.

of electron distribution and, thereby, perhaps a part of repulsion effects, too. Of course, on the basis of recent semiempirical calculations[37] as well as *ab initio* treatment[38] convincing arguments were presented that $\sigma_{m,p}$ parameters involve solvation effect to a greater or smaller extent. In the case of our substrates *I* and *II* it is, however, impossible to draw the conclusions that the correlations (8) cannot be interpreted by means of pure π-electron effects. The fact that pK values of the acids *I* correlate very well with the $\sigma_{m,p}$ constants in various solvents[39−42] indicates that the solvation
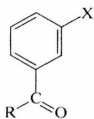
Ia, R = OH
IIIa, R = H
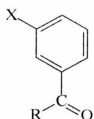
Ib, R = OH
IIIb, R = H
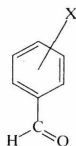
III

IV

Ic, IIIc

Id, IIId
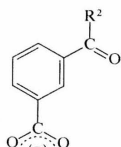
Ie, IIIe

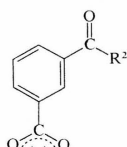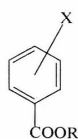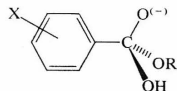*If, IIIf*

Ig, IIIg

IIe
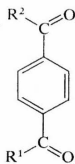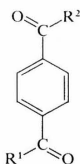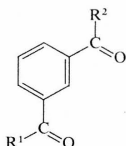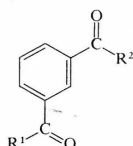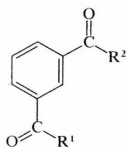
IIf

VI

Ic−g, R¹ = OH, R² = H   or   OH
IIe,f, R² = H   or   OH
IIIc−g, R¹ = H, R² = H   or   OH

VII

effect in the process (A) is either slight or correlates with the substitution parameters in the same direction as the other terms. The former possibility is supported by the fact[36] that the $\Delta\Delta G$ values for gas phase correlate very well with the Hammett $\sigma_{m,p}$ constants, smaller deviations being observed only for the substituents $X = OH$ and NH_2, which form hydrogen bonds in condensed phases. Separation of solvation terms in Eq. (7) is made considerably doubtful also by the circumstance that the HMO and π-SCF methods are parametrized to give satisfactory agreement with experiments in liquid solvents.

Quantum-chemical description of the Hammett correlation. The classical Hammett correlation[43] is based on the linear dependence of pK values of *meta* and *para* substituted acids I on logarithms of rate constats of alkaline hydrolysis of the esters VI, *i.e.* on the proportionality $\log k \approx \log K$. Its π-SCF quantum-chemical description consists (as it is the case for the HMO interpretation[3]) in the validity of the analogous relation $A_{SCF} \approx \Delta E_{SCF}$. The quantity A_{SCF} corresponds to the Wheland localization energy for a nucleophilic attack at the carbonyl carbon atom of the acids I having the same π-electron structure as the esters VI, and it reflects the π-electron component of the activation energy of the process $VI + OH^{(-)} \rightleftarrows VII \rightarrow II + RO^{(-)}$. The energy portion corresponding to the ionization (A), *i.e.* $\Delta E_{SCF} = \Delta E_{\pi}$, is defined in the sense of Eq. (8) for the models A and B. From Fig. 5 it is seen that the linear correlation of the quantities A_{SCF} and ΔE_{SCF} is very close and still closer to a strict linear dependence than that of the HMO quantities[3]. Therefore, it is supposed that the HMO and π-SCF models of the substrates I and II reflect correctly the π-electronic disposition of these substances to behave in accord with the macroscopic description by means of Eq. (1).
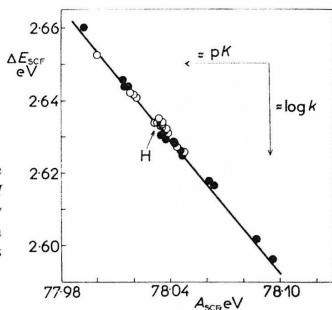
FIG. 5

Dependence of π-Electron Energy Difference of SCF Models of the Substrate Forms I and II on the Wheland Localization Energy for Nucleophilic Attack at Carbonyl Carbon Atom of the SCF Models of Alkylbenzoates VI

For description of points see Fig. 1.

REFERENCES

1. Hammett L. P.: J. Amer. Chem. Soc. *59*, 96 (1937).
2. *Advances in Linear Free Energy Relationships* (N. B. Chapman, J. Shorter, Eds), Editor's Introduction and p. 35, 130, 239 and 245. Plenum Press, London and New York, 1972.
3. Kuthan J., Skála V.: Z. Chem. *8*, 340 (1968).
4. Krayushkin M. M., Gagarin S. G., Sevastyanova V. V.: Izv. Akad. Nauk SSSR *1970*, 37.
5. Botrel A., Guerillot C. R.: C. R. Acad. Sci. Ser. C *276*, 1663 (1973).
6. Botrel A., Guerillot C. R., J. Chim. Phys. Physicochim. Biol. *71*, 974 (1974).
7. Kang S., Beveridge D. L.: Theoret. Chim. Acta *22*, 312 (1971).
8. Kang S., Cho M. H.: Int. J. Quant. Chem. *7*, 319 (1973).
9. Reetz M.: Tetrahedron Lett. *1967*, 1549.
10. Pople J. A.: Trans. Faraday Soc. *49*, 1375 (1953).
11. Streitwieser A., jr: *Molecular Orbital Theory for Organic Chemists*. Wiley, New York 1961.
12. Güsten H., Klasinc L.; Tetrahedron *23*, 2923 (1967).
13. Smeyers Y. G., Sieiro C.: Theoret. Chim. Acta *28*, 355 (1973).
14. Fabian J.: Tetrahedron *29*, 2449 (1973).
15. Zahradník R., Tesařová I., Pancíř J.: This Journal *36*, 2867 (1971).
16. Kwiatkowski J. S.: Theoret. Chim. Acta *10*, 47 (1968).
17. Hinze J., Jaffé H. H.: J. Amer. Chem. Soc. *84*, 540 (1962).
18. Kysel' O., Zahradník R., Belluš D., Sticzay T.: This Journal *36*, 2867 (1971).
19. Dobáš I., Eichler J.: This Journal *38*, 2602 (1973).
20. Gordon M. D., Neumer J. F.: J. Phys. Chem. *78*, 1868 (1974).
21. Sim G. A., Robertson J. M., Goodwin T. H.: Acta Cryst. *8*, 157 (1955).
22. Mataga N., Nishimoto K.: Z. Phys. Chem. (Frankfurt am Main) *13*, 140 (1957).
23. Exner O.: see ref.[2], p. 1.
24. Ehrenson S., Brownlee R. T. C., Taft R. W.: Progress Phys. Org. Chem. *10*, 1 (1973).
25. McDaniel D. H., Brown H. C.: J. Org. Chem. *23*, 420 (1958).
26. Eaborn C., Parker S. H.: J. Chem. Soc. *1954*, 939.
27. Humffray A. A., Ryan J. J., Warren J. P., Yung Y. H.: Chem. Commun. *1965*, 610.
28. Kuthan J., Musil L.: This Journal *41*, 3282 (1976).
29. Kuthan J., Danihel I.: Unpublished results.
30. Sixma F. L. J.: J. Chem. Phys. *19*, 1209 (1951).
31. Sixma F. L. J.: Rec. Trav. Chim. Pays-Bas *72*, 273, 538, 543, 673 (1953).
32. Sixma F. L. J.: Rec. Trav. Chim. Pays-Bas *73*, 243 (1954).
33. Taft R. W., Lewis I. C.: J. Amer. Chem. Soc. *80*, 2436 (1958).
34. Taft R. W., Lewis I. C.: J. Amer. Chem. Soc. *81*, 5343 (1959).
35. Taft R. W.: J. Phys. Chem. *64*, 1805 (1960).
36. Yamdagni R., McMahon T. B., Kebarle P.: J. Amer. Chem. Soc. *96*, 4035 (1974).
37. Hermann R. B.: J. Amer. Chem. Soc. *91*, 3152 (1969).
38. McKelvey J. M., Alexandratos S., Streitwieser A. jr, Abbond J. L. M., Hehre W. J.: J. Amer. Chem. Soc. *98*, 244 (1976).
39. Kalfus K., Večeřa M., Exner O.: This Journal *35*, 1195 (1970).
40. Kolthoff I. M., Chantooni M. K.: J. Amer. Chem. Soc. *93*, 3845 (1971).
41. Kalfus K., Večeřa M.: This Journal *37*, 3607 (1972).
42. Exner O., Kalfus K.: This Journal *41*, 569 (1976).
43. Hine J.: *Physical Organic Chemistry*. McGraw-Hill, New York 1956.