

QUANTUM-CHEMICAL STUDY OF DISSOCIATION OF *meta* AND *para* SUBSTITUTED BENZOIC ACIDS AT ALL-VALENCE-ELECTRONS LEVEL*

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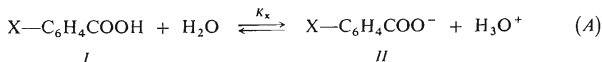
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Relative differences of electronic energies of *meta* and *para* substituted benzoate anions *II* and the parent acids *I* have been correlated with the substituent empirical parameters type σ and with pK_X values of ionization of the acids *I*. The energies obtained by the EHT method only give linear correlation in the *para* substituted series of the studied compounds, whereas the analogous CNDO/2 energies lead to homogeneous correlation for both *meta* and *para* substituents X. Effects of π and σ electrons are discussed as well as effects of electronic repulsion and attraction on the resulting microscopic substitution effect.

In the previous communication¹ it was shown that effects of the substituents X on the equilibrium



can be explained satisfactorily by differences of π -electron energy of the substrates *II* and *I* which can be considered to be a measure of microscopic π -substitution effect in benzene series^{2,3}. From character of the found correlations it was deduced¹ that in the *meta* series' electronic repulsion participates significantly in the transfer of the substituent π -effect. Ponec⁴ came independently to analogous conclusion about significance of the repulsion energy for expression of the *meta*-substituent effect, having applied the perturbation theory of the 2nd order to study of the acids *I* and further series of conjugated compounds in π -electron approximation. For further elucidation of contribution of σ -electron effects to the overall substituent effects in the process (A) we decided to apply the above-mentioned approach¹ at the all-valence-electrons level, too. For this purpose we have now carried out quantum-

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-chemical calculations of the acids *I* and the corresponding anions *II* using the standard methods EHT and CNDO/2. So far the all-valence-electrons calculations of the acids *I* were carried out by the methods EHT (refs⁵⁻⁷), CNDO/2 (refs^{8,9}) and INDO (ref.^{10,11}). Only the reports^{6,7} adopt the approach¹ using the electron energies for evaluation of the equilibria (*A*), but the used way of interpretation^{6,7} was criticized¹.

CALCULATIONS

All the calculations were carried out according to the standard programs (EHT and CNDO/2) using an IBM 370/145 computer. The non-diagonal elements of the *H*-matrix in the EHT method were calculated according to the usual relation $H_{ij} = 1.75S_{ij}(H_{ii} + H_{jj})/2$. The empirical parameters used are given in Table I, the fixed geometrical parameters of MO models of the acids *I* and anions *II* are given in Table II. In the latter cases the bond length C—O in the group —CO_2^- was chosen as a mean of the values of analogous bonds C=O and C—O(H). According to the X-ray diffraction data (refs¹²⁻¹⁵) the plane of the functional groups do not markedly deviate from that of the aromatic ring in the acids type *I* and anions type *II* of the corresponding salts. Hence, for simplicity we chose exclusively the planar MO models of *I* and *II* in which the torsion angles between $\text{—CO}_2\text{H}$ (or —CO_2^-) group and the plane of the aromatic ring corresponded always to planar conformations, i.e. $\theta = 0^\circ$ or 180° . As the differences in the EHT energies of the both planar forms were (in contrast to the situation in the calculations¹ using the π -electron approximation) relatively very small (Table III), the experimental data were only confronted with the minimum E_{EHT} values. The latter corresponded invariably to planar conformers with *syn*-conformation of the C=O and C—X bonds (*meta*-series of the acids *I*) and to conformers with *syn*-orientation of the substituents X = OH, OCH₃ and COOH with respect to the C=O bond (*para*-series of *I*). The groups —CH_3 and —CF_3 were fixed with one C—H (C—F) bond in the plane of the aromatic system. The calculation of the E_{CNDO} energies used the same models as that by the EHT procedure.

RESULTS AND DISCUSSION

Relation between the all-valence-electrons energy and the Hammett $\sigma_{m,p}$ constants and $\text{p}K_{\text{X}}$ values of the acids I: If the operators Δ and δ represent the electron energy change accompanying the ionization $I \rightarrow II$ and that accompanying substitution of *para* or *meta* hydrogen atom in *I* or *II* by the group X, respectively, then the theoretical substituent effect¹⁻³ of the equilibrium (*A*) can be written as follows

$$\delta \Delta E = \Delta E_{\text{X}} - \Delta E_{\text{H}} = \delta E(\text{II})_{\text{X,H}} - \delta E(\text{I})_{\text{X,H}}, \quad (1)$$

where the quantities ΔE represent the energy differences $E(\text{II}) - E(\text{I})$ for X-substituted and non-substituted substrates *I* and *II*. At the same time the expression (1) defines the change of the total electronic energy of the isodesmic process¹⁶:

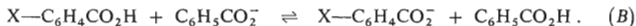


TABLE I
The Parameters Used in the EHT and CNDO/2 Calculations

Atom	$-I_s$, eV	$-I_p$, eV	$-1/2(I_s + A_s)$	$-1/2(I_p + A_p)$	$-\beta^0$	The Slater exponent ^a
H	13.6		7.176		9.0	1.300 (1.200)
C	21.4	11.4	14.051	5.572	21.0	1.625
N	26.0	13.4	19.316	7.275	25.0	1.950
O	32.3 (29.8) ^b	14.8 (12.8) ^b	25.390	9.111	31.0	2.275
F	40.0	18.1	32.272	11.080	29.0	2.425 (2.600)

^a In parenthesis there is a different value for the CNDO/2 method; ^b the values for oxygen in the O—H bond of carboxylic group used in the EHT method^{6,7}.

TABLE II
Geometrical Parameters of the Substituents X Fixed in all the All-Valence-Electrons Calculations of the Acids I and Anions II^a

X	Bond, pm		Bond, pm		Angle, °	Reference
N(CH ₃) ₂	C—N	(142.0)	N—C(H ₃)	(146.0)	CNC(H ₃) (101°33′) C(H ₃)NC(H ₃) (116°)	27
NH ₂	C—N	(140.2)	N—H	(100.1)	CNH (116°) HNH (113°6′)	28
OH	C—O	(136.0)	O—H	(96.0)	COH (109°47′)	29
CH ₃	C—C(H ₃)	(152.0)	C—H	(109.3)	CCH (109°30′)	30
OCH ₃	C—O	(136.0)	O—C(H ₃)	(144.3)	COC (116°48′)	31
F	C—F	(132.0)				30
CF ₃	C—C(F ₃)	(150.0)	C—F	(133.2)	CCF (108°48′)	30
CN	C—C(N)	(142.0)	C≡N	(116.0)	CCN (180°)	30
NO ₂	C—N	(148.0)	N—O	(122.0)	ONO (124°)	32
CO ₂ H	C—C	(152.7)	O—H	(97.2)	HOC (106°18′)	33
	C=O	(121.4)	C—O	(134.4)	OCO (122°48′)	

^a For the anions the mean value of the bond lengths C=O and C—O in carboxylic group were used.

TABLE III
 Comparison of the $\delta\Delta E_{\text{EHT}}$ and $\delta\Delta E_{\text{CNDO}}$ Values^a in Relation (I) for MO Models of the Substrate Forms I and II with the Hammett $\sigma_{\text{m,p}}$ Values of the Substituents X

No	X	$\delta\Delta E_{\text{EHT}}^b$	$\delta\Delta E_{\text{EHT}}^c$	$\delta\Delta E_{\text{CNDO}}^b$	σ_{m}^d	$\delta\Delta E_{\text{EHT}}^b$	$\delta\Delta E_{\text{EHT}}^c$	$\delta\Delta E_{\text{CNDO}}^b$	δ_{p}^d
1	N(CH ₃) ₂	5	1		-0.21	-76	-76		-0.83
2	NH ₂	5	1	1328	-0.16	-72	-72	1992	-0.66
3	OH	4	2	195	0.12	-44	-45	1015	-0.37
4	OCH ₃	4	2	-39	0.12	-45	-45	-157	-0.27
5	CH ₃	4	2	586	-0.07	-19	-19	546	-0.17
6	F	11	2	-1915	0.34	-31	-31	-9.77	0.06
7	COOH	0	-2	-1989	0.37	29	28	-2305	0.45
8	CF ₃	4	1	-3008	0.43	17	17	-3242	0.54
9	CN	2	-8	-2052	0.56	34	34	-2431	0.66
10	NO ₂	5	-3	-4511	0.71	61	61	-4708	0.78

^a All the data are in $\cdot 10^{-4}$ eV; ^b for the *syn*-conformers (Ia); ^c for the *anti*-conformers (Ib); ^d taken from ref.²¹.

The effects (*I*) should be identical for the both processes (*A*) and (*B*), provided that the energies of the individual components on the right-hand and left-hand sides of the respective equilibrium equations are not affected by mutual interactions (e.g. by H-bond). Probably this presumption will be fulfilled best in gaseous phase. If there exists a relation between the microscopically defined energy $\delta\Delta E$ and macroscopical free energy $\delta\Delta G$ of the systems (*A*) or (*B*) as

$$\delta\Delta E \sim \delta\Delta G, \quad (2)$$

then it can be expected, at a given temperature, that a proportionality with the Hammett σ parameters also exists ($\delta\Delta E \sim \sigma_{m,p}$), hence it can be written¹

$$\delta\Delta E = a \sigma_{m,p} + b. \quad (3)$$

On condition of validity of the Hammett equation we can write for the thermodynamic quantities $\delta\Delta G$

$$\delta\Delta G = -RT \ln (K_X/K_H) = -2.303RT\sigma_{m,p}. \quad (4)$$

Therefrom it follows that the parameters $\sigma_{m,p}$ are *de facto* generalized equilibrium constants¹⁷ of the process (*A*), i.e. $\sigma_{m,p} = \log K_X - \log K_0$, where K_0 is a statistical value¹⁷ approaching the value K_X for $X = H$. Eq. (3) can be transformed into

$$\delta\Delta E = -a \delta p K_X + b', \quad (5)$$

where $pK_X = -\log K_X$. If the all-valence-electrons MO method is used for calculation of the energy E , then obviously the latter is explicitly expressed predominantly by the first three terms of the relation

$$E = E_\pi + E_\sigma + E_{\pi,\sigma} + E_r, \quad (6)$$

where the term E_r can involve implicitly the effects of non-valence electronic spheres. It can be expected $E_{\pi,\sigma} \approx 0$, because $\sigma-\pi$ separation¹⁸ is a justifiable presumption for planar forms of the substrates *I* and *II*. With respect to the practically identical σ -skeleton of the acids *I* and the corresponding anions *II* (see the isodesmic process (*B*)), furthermore, in the application of the both operators δ and Δ to Eq. (6) it can very likely be expected that $\delta\Delta E_r \approx 0$ even in the case of influence of non-optimum choice of empirical parametrization in the EHT and CNDO/2 procedures. Then the approximation (7) seems reasonable

$$\delta\Delta E = \delta\Delta E_\pi + \delta\Delta E_\sigma. \quad (7)$$

Due to insufficient fulfilment of the presumptions (2) and (6) it must be admitted that the linear relations (3) and (5) will be transformed into mere linear correlations. Statistical examination of closeness of the relations (3) and (5) can thus provide information about fulfilment of namely the presumptions (2) and (7).

Correlation with the EHT energies. In this case the approximation is $\delta\Delta E = \delta\Delta E_{\text{EHT}}$. Botrel and Guérillot showed^{6,7} that these energies correlate according to Eq. (3) with the σ_p parameters but not with the σ_m parameters, and they explained this finding by significant contributions of solvation energy. In the report¹ it was shown that a much more likely reason of the insensitivity of the $\delta\Delta E_{\text{EHT}}$ values towards variation of the substituents X at *meta* position consists in neglect of repulsion part of the electron energy in the Hückel approximation. In accordance with the latter approach, also the HMO data^{1,19} (but not the analogous energies calculated¹ by the PPP method) show similar behaviour in the linear correlations (3) and (5). With the aim to exclude the possibility that the above-mentioned properties of the linear correlations (3) with the EHT energies are connected with ambiguously defined geometry and con-

TABLE IV
The Calculated Characteristics^a of the Studied Correlations (3), (5) and (8)

Energy	Parameter (reference)	$a \cdot 10^2$	$b \cdot 10^3$	$ r $	t	n
E_{EHT}	σ_p (21)	0.81	1.61	0.974	12.3	10
E_{EHT}	$\delta\rho K_X$ (22) ^b	0.82	1.41	0.972	10.1	8
E_{EHT}	$\delta\Delta G$ (23) ^b	-1.83	-3.87	0.940	5.5	6
E_{CNDO}	σ_p (21)	-41.75	-60.09	0.964	10.2	10
E_{CNDO}	$\delta\rho K_X$ (22) ^b	-41.83	-62.66	0.955	7.9	8
E_{CNDO}	$\delta\Delta G$ (23) ^b	84.92	24.33	0.940	6.1	7
E_{CNDO}	$\sigma_{m,p}$ (21)	-45.42	-31.80	0.934	10.7	19
E_{CNDO}	$\delta\rho K_X$ (22)	-44.02	-29.88	0.923	8.7	15
E_{CNDO}	$\delta\Delta G$ (23)	88.97	28.40	0.928	8.6	14
E'_{CNDO}	σ_p (21)	-42.23	-59.19	0.964	10.3	10
E'_{CNDO}	$\sigma_{m,p}$ (21)	-45.84	-21.78	0.924	9.9	19
E'_{CNDO}	$\delta\rho K_X$ (22) ^b	-42.52	-62.68	0.955	7.9	8
E'_{CNDO}	$\delta\rho K_X$ (22)	-45.06	-22.13	0.910	7.9	15
E'_{CNDO}	$\delta\Delta G$ (23) ^b	86.42	25.68	0.942	6.3	7
E'_{CNDO}	$\delta\Delta G$ (23)	92.00	40.67	0.924	8.4	14

^a Meaning of the symbols: r correlation coefficient; t the Student test (significance level 0.01); n number of the compared pairs; ^b only for the *para* derivatives.

crete parametrization of the EHT models in the reports^{6,7}, we compared our calculated and the earlier published^{6,7} values $\delta\Delta E_{\text{EHT}}$ with the $\sigma_{m,p}$ parameters. From Fig. 1 and Table III it can be seen that insufficient variability of these values in the *meta*-substituted series of the examined compounds is a general feature of the EHT method, this fact being not changed even by alternative choice of various planar conformations *Ia,b* of the acids *I*. Furthermore, from Table IV it follows that the linear correlations (3) and (5) using the values $\delta\Delta E_{\text{EHT}}$ are almost identical statistically and lead, according to expectation, to practically identical value of the coefficient $a = 8 \cdot 10^{-3}$. As the electron repulsion was neglected here, the expression (7) can be formulated exclusively with the use of the attractive energy components, i.e. $\delta\Delta E_{\text{EHT}} = \delta\Delta E_{\pi,\text{att}} + \delta\Delta E_{\sigma,\text{att}}$. Therefore, we interpret the linear correlations (3) and (5) within these limits as a representation of influence of both π -electron attraction (verified by correlations with the HMO data^{1,19}) and σ -electron attraction (involved, in addition, in the EHT energy quantities).

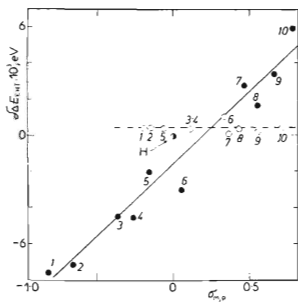


FIG. 1

Dependence of Relative Differences of Calculated Energies $\delta\Delta E_{\text{EHT}}$ on the Hammett $\sigma_{m,p}$ Parameters

For numbers of the substituents see Table III. Full and empty circles belong to the *para* and *meta* series, respectively.

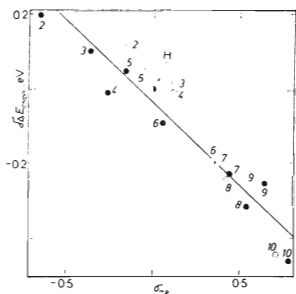
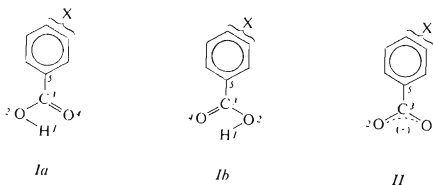


FIG. 2

Dependence of Relative Differences of Calculated Energies $\delta\Delta E_{\text{CNDO}}$ on the Hammett $\sigma_{m,p}$ Parameters

For numbers of the substituents see Table III. Full and empty circles belong to the *para* and *meta* series, respectively.



Correlation with the CNDO/2 energies. Within the framework of the CNDO/2 method the energies are formulated usually by two calculation versions differing in expressions of the core-core repulsion²⁰: approximation of the point charges (total energy E_{CNDO}) and presumption of identical core-core and electron-electron repulsion (total energy E'_{CNDO}). We have found that the both approaches are very similar for expression of the substituent effect in the processes (A) and (B) and that the following relation is obeyed

$$\delta \Delta E_{\text{CNDO}} = 0.9744 \delta \Delta E'_{\text{CNDO}} - 0.0121,$$

the correlation coefficient being $r = 0.993$ for 19 compared pairs I and II. From Table IV it is obvious that in accordance therewith the both approaches give almost identical linear correlations (3) and (5), so that the both approximations $\delta \Delta E = \delta \Delta E_{\text{CNDO}}$ and $\delta \Delta E = \delta \Delta E'_{\text{CNDO}}$ can be considered equivalent. Fig. 2 illustrates typical difference between the correlation field of the Eq. (3) approximated by the CNDO/2 energies and that approximated by the EHT energies (Fig. 1). The CNDO/2 method results in homogeneous correlation for the *meta* and *para* substituents X and expresses thus the substituent effect in the *meta*-substituted series of the studied compounds, too. Again this fact can be interpreted as a result of explicit involvement of the electron repulsion in the quantity $\delta \Delta E_{\text{CNDO}}$. The latter are analogies of the values $\delta \Delta E_{\text{SCF}}$ calculated¹ by the PPP method, the only difference being in that obviously the σ -repulsion effects of the electronic structure also participate markedly in the expression of influence of *meta* substitution in the CNDO calculation in the sense of approximative formulation of the relation (7) as

$$\delta \Delta E_{\text{CNDO}} = \delta \Delta E_{\pi, \text{att}} + \delta \Delta E_{\pi, \text{rep}} + \delta \Delta E_{\sigma, \text{att}} + \delta \Delta E_{\sigma, \text{rep}}.$$

Predominance of the fourth term in this expression is documented by the fact that the angular coefficient a in the correlations (3) and (5) not only has a substantially higher absolute value, but it has opposite sign (which is more important) than in the case of application of the EHT energies (Table IV) and PPP energies (see Table V in ref.¹). This fact indicates that the σ -repulsion component $\delta \Delta E_{\sigma, \text{rep}}$ increases in the

same order of the substituents *X* in which the analogous π -component $\delta\Delta E_{\pi,rcp}$ and the both attractive components $\delta\Delta E_{\pi,ait}$ and $\delta\Delta E_{\sigma,ait}$ are decreasing. As far as the term $\delta\Delta E_{\pi,ait}$ expressed by the simple HMO method is concerned, the negative value of the angular coefficient *a* (Table VII) indicates¹ the opposite direction of influence on the transfer of the substituent effect with that of the component $\delta\Delta E_{\sigma,ait}$. This conclusion, of course, applies on the condition that the used¹ "aldehydic" HMO model of the acids *I* is physically correct. These results can hardly be represented sufficiently by the usual symbolism of chemical formulas inclusive of mesomeric structures of the acids *I* or anions *II*. A deeper understanding of transfer of the substituent effect can probably be reached by considering the way in which span of the energy terms of the acids *I* and their ionized forms *II*

TABLE V

Influence of Substitution and Ionization on the CNDO/2 Electronic Charges in COOH and COO⁻ Groups in Compounds *I* and *II* (all the data in 10⁴ multiple of the charge calculated from the relation $Q = Q_X - Q_H$ and $Q_i = Q_i(II) - Q_i(I)$)

X	Acid <i>I</i>					Anion <i>II</i>			Ionization <i>I</i> → <i>II</i>			
	δQ_1	δQ_2	δQ_3	δQ_4	δQ_5	δQ_2	δQ_3	δQ_5	$\delta\Delta Q_2$	$\delta\Delta Q_3$	$\delta\Delta Q_5$	
NH ₂	<i>m</i>	-12	1	-24	26	239	6	-15	216	5	9	-23
	<i>p</i>	-25	-28	31	-109	-372	-52	28	-309	-24	-3	63
OH	<i>m</i>	5	13	-9	38	211	21	5	212	8	14	1
	<i>p</i>	-6	-15	28	-61	-269	-25	24	-230	-10	-4	39
OCH ₃	<i>m</i>	2	-3	-19	34	213	28	0	213	31	19	0
	<i>p</i>	-10	-19	27	-65	-278	-22	23	-224	-3	-4	54
CH ₃	<i>m</i>	-5	0	-9	6	47	4	9	91	4	18	44
	<i>p</i>	-9	-8	6	-32	-100	-1	5	-47	7	-1	53
F	<i>m</i>	26	19	2	62	201	42	4	199	23	2	-2
	<i>p</i>	16	-4	28	-9	-182	8	25	-159	12	-3	23
COOH	<i>m</i>	23	20	15	29	47	47	18	134	43	3	87
	<i>p</i>	23	21	-1	57	128	52	-2	162	37	-1	38
CF ₃	<i>m</i>	45	4	18	60	183	59	23	234	39	5	51
	<i>p</i>	42	15	-1	85	142	64	-4	182	43	-3	40
CN	<i>m</i>	40	11	10	42	14	54	11	107	43	1	93
	<i>p</i>	51	13	-7	54	37	57	-12	137	44	-5	100
NO ₂	<i>m</i>	54	25	22	83	-36	87	29	142	62	7	178
	<i>p</i>	59	32	-26	98	243	98	-34	362	66	-8	119

affects position of the equilibrium (*A*). From Fig. 3 it follows that the substituent effect $\delta\Delta E_{\text{CNDO}}$ decreases and increases the gap between the terms $E(II)_{\text{CNDO}}$ and $E(I)_{\text{CNDO}}$ for the electron-attracting ($\sigma_{\text{m,p}} > 0$) and electron-donating ($\sigma_{\text{m,p}} < 0$) substituents X, respectively. According to general quantum-mechanical principles this finding seems physically justifiable. The conversion $II \rightarrow I$ is less favourable energetically in the case of $\sigma_{\text{m,p}} > 0$, and the equilibrium (*A*) can, therefore, be shifted more to the right than in the cases of $\sigma_{\text{m,p}} < 0$. Of course it is noteworthy that if only the π -electron energies are respected, then the result is just opposite (see Fig. 3 in ref.¹), so that the antagonistic effects of π and σ repulsion seem to be more clearly illustrated in the term diagrams.

Relation between calculated and Gibbs free energies. The proportionality (2) can, so far, be presumed on the basis of empirical arguments only. It has not yet been strictly theoretically derived, in spite of the fact that it represents a key relation for confrontation of the microscopically defined quantum-chemical data with the macroscopically defined quantities of chemical thermodynamics. As far as we know the hitherto theoretical studies in this field are predominantly focused on electronic structure of the atom and the therefrom derived concept of chemical bond as a perturbation of the atomic electronic energy (see ref.²⁵ and the references quoted therein). There are certainly other perspective possibilities in the field of statistical thermodynamics²⁶ even though they are still remote from the viewpoint of larger organic molecules. Therefore, it seems reasonable for the time present to accept the relation (2) as a micro-macroscopic theorem³ (MIMAT) which applies to situations in which the thermodynamic quantities ΔG can be successfully interpreted in terms of the chemical microstructure. In the case of the isodesmy (*B*) MIMAT can be tested by examination of the correlation

$$\delta\Delta E = k \delta\Delta G + c, \quad (8)$$

TABLE VI

The Calculated Characteristics of the Correlations (9) for the *i*-th Positions of the Substrate Forms *I* and *II*^a

Correlation	<i>i</i>	<i>a</i> · 10 ²	<i>b</i> · 10 ⁴	<i>r</i>	<i>t</i>	<i>n</i>
(9a)	1	-1.27	2.0	0.962	14.5	19
(9a)	2	-0.70	-3.0	0.858	6.9	19
(9a)	4	-2.23	-7.0	0.792	5.4	19
(9b)	2	-1.20	9.0	0.932	10.6	19

^a For explanation of the used symbols see Table IV.

because the quantities $\delta\Delta G$ were measured²³ in gas phase at the temperature 600 K by the method of high-pressure mass spectrometry. From Table IV it is seen that for a set of fourteen pairs* *I* and *II* the both CNDO/2 energy terms $\delta\Delta E_{\text{CNDO}}$ and $\delta\Delta E'_{\text{CNDO}}$ correlate well with the free energies $\delta\Delta G$. The value of the angular coefficient *k* of Eq. (8) is positive and almost unity, and the value of the additive term *c* is practically negligible, which is noteworthy. Therefore, for the process (*B*) MIMAT in the used MO approximation corresponds roughly to the simple relation $\delta\Delta E = 0.9 \delta\Delta G$. It has been already found³⁴ that for *para* substituted benzoic acids exists

TABLE VII

Type Characterization of the Studied Substituent Effect

Approximation	Slope · 10 ² correlation		The involved electronic contribution	
	(3)	(8)	<i>meta</i> -X	<i>para</i> -X
$\delta\Delta E_{\text{HMO}}^b$	-0.1 ^c	0.95 ^c	—	+A _π
$\delta\Delta E_{\text{PPP}}^b$	3.11	-5.47	-R _π	-A _π < -R _π
δE_{EHT}	0.84	-1.73	—	-A _σ < -A _π
$\delta\Delta E_{\text{CNDO}}$	-45.42	88.84	+R _σ > -R _π	+A _π , +R _σ > -A _σ , -R _π

^a Symbols: A attractive, R repulsive; ^b taken from ref.¹; ^c recalculated for $\beta = -2.318$ eV.

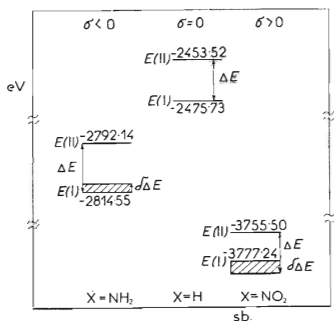


FIG. 3

Influence of Character of the Substituent X on Energies of the Substrate Forms *I* and *II* Calculated by CNDO/2 Method
sb. substitution.

* The case of X = *p*-OH was excluded from the correlation, since this group undergoes easier dissociation in gas phase than carboxylic group^{23,24}.

very close linear correlation between $\delta\Delta G$ values^{2,3} and $\delta\Delta E$ values calculated by means of *ab initio* method. On the contrary, the EHT method gives, in accordance with the previous findings, a certain correlation for only the *para* substituted derivatives, whereas in the *meta* series the correlation (8) is meaningless due to negligibly low value of k . Respecting of the electron repulsion is thus one of the critical factors for formulation of MIMAT.

Effects of electron distribution. Table V gives changes in CNDO/2 charge densities δQ at the reaction centres $-\text{CO}_2\text{H}$ and $-\text{CO}_2^-$ brought about by substitution of the hydrogen atom at *para* or at *meta* position of benzoic acid and benzoate anion by a substituent X and changes $\delta\Delta Q$ between the charges at equivalent atomic centres of the substrate forms *II* and *I*. It is seen that greater changes in electron distribution due to substitution are encountered in the individual positions of the *para* substituted series of the studied compounds. The authors⁵ studying the acids *I* by the EHT method also came to similar conclusion. Generally it can be stated that the charge densities calculated by the CNDO/2 method in this report and those calculated by the PPP method¹ are very similar in their trends, so that transition from the π -electron approximation to the all-valence-electrons level does not bring any substantial new aspects of the electron distribution changes caused by the substituent effect in the substrate forms *I* and *II*. Also the values obtained earlier by the CNDO/2 method^{8,9} and INDO method^{10,11} have very similar trends with those of the now obtained CNDO/2 charges.

It can be stated that for representation of the theoretical substitution effect the maximum variable quantities are suitable which correlate^{2,3} with the theoretical substitution effects in the sense of the relations

$$\delta Q_i = a \delta\Delta E + b \quad (9a)$$

$$\delta\Delta Q_i = a \delta\Delta E + b. \quad (9b)$$

From Table VI it follows that these presumptions are fulfilled satisfactorily for the atomic centres 1, 2 and 4. Direction of the found correlations (9a) agrees with the analogous ones (δQ vs $\sigma_{m,p}$) presented in refs^{10,11}. It is worth mentioning that the authors^{10,11} found, for the positions 1, 2 and 4, correlations of the $\sigma_{m,p}$ constants with the INDO charges, which is obviously an indirect consequence of the existence of the corresponding relations type (9). However, in this study no correlations type (9) have been found for the positions 3 and 5 and, therefore, the electronic charges at these centres obviously are not suitable for expressing the theoretical substitution effect. This conclusion is also supported by the finding that the π -electron charges do not correlate here in the sense of the relations (9), too. Correlations of the CNDO/2 charges with the pK values^{8,9} lead to a similar conclusion.

Classification of substituent effects. The microscopically defined substituent effects can be classified according to the above-mentioned knowledge as follows: 1) according to the type of the valence electrons (π and σ) and 2) according to the physical character of the interaction (attractive, repulsive). Positive effect (+) is ascribed to the case when the quantities $\delta\Delta E$ change in accordance with the free energies, as e.g. in the isodesmy (B), the opposite case being negative (-). As the relation between the quantities $\delta\Delta G$ and $\sigma_{m,p}$ is (provided the Hammett equation is obeyed) unambiguously defined, the sign of the coefficient in the correlation (3) is decisive for direction of the effect. Magnitude of the effect in the given process can then be represented by absolute value of this coefficient expressed in a universal energy scale. On the basis of these aspects Table VII gives an attempt of classification of the substituent effects calculated by semiempirical methods for the ionization processes (A) and (B).

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REFERENCES

1. Kuthan J., Danihel I., Skála V.: This Journal 43, 447 (1978).
2. Danihel I., Kuthan J.: This Journal 44, 873 (1979).
3. Kuthan J., Danihel I.: *Fourth International Symposium on Physical Organic Chemistry*, September 4th to 8th, 1978, York, England.
4. Ponec R.: This Journal 42, 2772 (1977).
5. Krayushkin M. M., Gagarin S. G., Sevastyanova V. V.: *Izv. Akad. Nauk SSSR* 1970, 37.
6. Botrel A., Guérillot C. R.: *C. R. Acad. Sci. Ser. C* 276, 1663 (1973).
7. Botrel A., Guérillot C. R.: *J. Chim. Phys. Physicochim. Biol.* 71, 974 (1974).
8. Nagata Ch., Nagata H., Tanaka S.: *J. Chem. Soc. Jap.* 1975, 2045.
9. Nagata Ch., Hasegawa T., Tanaka S.: *J. Chem. Soc. Jap.* 1977, 1087.
10. Kang S., Beveridge D. L.: *Theor. Chim. Acta* 22, 312 (1971).
11. Kang S., Cho M.-H.: *Int. J. Quantum Chem.* 7, 319 (1973).
12. Lai T. F., March R. E.: *Acta Crystallogr.* 23, 885 (1967).
13. Manoslovic L.: *Acta Crystallogr. Sect. B*, 24, 326 (1968).
14. Colapietro M., Domenicano A.: *Acta Crystallogr. B*, 33, 2240 (1977).
15. Colapietro M., Domenicano A.: *Acta Crystallogr. B*, 34, 3277 (1978).
16. Hehre W. J., Ditchfield R., Radom L., Pople J. A.: *J. Amer. Chem. Soc.* 92, 4796 (1970).
17. Exner O. in the book: *Advances in Linear Free Energy Relationships* (N. B. Chapman, J. Shorter, Eds), Chap. 1. Plenum Press, London and New York 1972.
18. Kutzelnigg W., Del Re G., Berthier G.: *Fortschr. Chem. Forsch.* 22, 1 (1971).
19. Kuthan J., Skála V.: *Z. Chem.* 8, 340 (1968).
20. Pople J. A., Beveridge D. L.: *Approximate Molecular Orbital Theory*. McGraw-Hill Book Co., 1970.
21. McDaniel D. H., Brown H. C.: *J. Org. Chem.* 23, 420 (1958).
22. Albert A., Serjeant E.: *Konstanty Ionizacii Kyslot i Osnovanií*. Russian translation. Izd. Khimiia, Moscow 1964.
23. Yamadagni R., McMahon T. B., Kebarle P.: *J. Amer. Chem. Soc.* 96, 4035 (1974).

24. McMahon T. B., Kebarle P.: *J. Amer. Chem. Soc.* **99**, 2222 (1977).
25. Lindeberg J.: *Quantum Chem. Suppl.* **1**, 12, 267 (1977).
26. Zahradník R., Polák R.: *Základy kvantové chemie*. Published by SNTL, Prague 1976.
27. Vilkov L. V., Timasheva T. P.: *Dokl. Akad. Nauk SSSR* **161**, 351 (1965).
28. Lister D. G., Tyler J. K., Høg J. H., Wessel-Larsen N.: *J. Mol. Struct.* **23**, 253 (1974).
29. Seidel H., Köhler H. J., Fruwert J., Geisler G.: *Z. Physik. Chem. (Leipzig)* **258**, 508 (1977).
30. Brownlee R. T. C., Taft R. W.: *J. Amer. Chem. Soc.* **92**, 7007 (1970).
31. Bryan R. F.: *J. Chem. Soc. (B)* **1967**, 1311.
32. Gordon M. D., Neumer J. F.: *J. Phys. Chem.* **78**, 1868 (1974).
33. Bobik M., Kohler F., Heger G., Lishka H., Schuster P.: *Chem. Phys. Lett.* **40**, 66 (1976).
34. Mezey P. G., Reynolds W. F.: *Can. J. Chem.* **55**, 1567 (1977).

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