CONTRIBUTION TO STUDY OF π-ELECTRONIC EFFECTS IN MONOSUBSTITUTED BENZENES*

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π-Electronic densities in a series of monosubstituted benzenes *I* calculated by the PPP method are discussed in relation to the substitution effect of substituent X, to σ_R^0 or σ parameters and to chemical shifts in NMR spectra. π-Electronic characteristics of the compounds *I* are confronted with electronic and photoelectronic spectra.
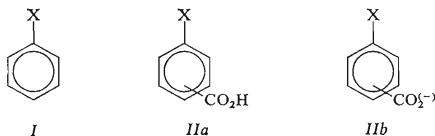
The monosubstituted benzenes *I* are noteworthy in the context of studies of relations between the substituent parameters σ in correlation equations and quantum-chemical characteristics. In principle, the σ parameters can be considered generalized relative enthalpy contributions of rate and equilibrium processes in arrays of reaction series the members of which have the variable part of their molecule denoted conventionally as substituent X. It is easy to show then that[1] physically well-founded quantum-chemical quantities comparable with the empirical parameters σ are differences in electronic energies between the corresponding substrate forms of the given reaction series, *e.g.* molecules of substituted benzoic acids *IIa* and their ionized forms *IIb*.

In the reaction series *I*, so far the correlations of σ parameters are carried out exclusively with quantum-chemical characteristics of electron distribution. Jaffé[2] correlated the Hammett $\sigma_{m,p}$ constants with π-electronic densities. Taft and Lewis[3] developed a modified concept of substitution effect, dual-substituent parameter approach[4,5], with the use of the constants σ_I and $\overline{\sigma}_R$ in which the resonance and the inductive mechanisms of action are differentiated according to the criterion, whether or not a charge transfer between the substituent X and the rest of the molecule occurs. This approach is obviously attractive from the point of view of empirically formulated correlation relations (LFER), but it is difficult to express it by contemporary MO theory derived from the one-electron approximation. Recent *ab initio*[6] and all-valence-electron calculations[7–10] in the series *I* show that electronic charges can only be divided to σ- and π-electron parts, none of these types showing unambiguous relation exclusively to the substituent constant σ_I or $\overline{\sigma}_R$. Therefrom we conclude that alternative interpretation of the substituent effect divided into its σ- and π-electronic component can also be useful, especially so if we try to understand the essence of the quantities type σ_I and $\overline{\sigma}_R$ in terms of quantum-chemical *i.e.* microscopical data.

In this communication it is shown that the PPP calculation of 19 compounds of the series *I* gives the π-electronic charges with similar relations to σ_I and σ_R^0 para-

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meters as in the case of use of *ab initio* method[5,6]. Furthermore it is shown that there are significant intercorrelation relations between the mentioned theoretical character-

istics for individual positions in the molecule *I*, which must be respected in interpretation of connections between π-electron distribution and the proton and $C-13$ chemical shifts in NMR spectra of the studied compounds *I*.

CALCULATIONS

The PPP calculations of the compounds *I* were carried out according to the standard SCF-LCI theory[11,12] (20 monoexcited configurations) with approximation of bicentric repulsion integrals $\varkappa_{\mu\nu}$ according to Mataga and Nishimoto[13] and with identical parametrization and geometry as in the communication[1]. The calculations were carried out with a computer IBM 370 model 145.

RESULTS AND DISCUSSION

π-Energy characteristics. For verification of the calculations the calculated characteristics of electronic absorption bands of the investigated compounds were confronted with experimental data[14] (Table I) and with the formerly published applications of the PPP method to narrower or wider sets of compounds C_6H_5X (refs[15-20]). In most cases satisfactory agreement of the compared data was found. Certain deviations from the experimental absorption curves were observed in cases of simultaneous operation of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions (X = Br, I, SH, SCH_3) and for X = CH_3, $COCH_3$ where perhaps the π-electron approximation does not completely represent the electron effect of the substituent, furthermore for X = C_6H_5 where the used planar conformation corresponds but roughly to real situation. An acceptable relation of the ionisation potentials calculated by the PPP method according to the Koopmans theorem[21] and the experimental ionisation potentials[22-24] is shown in Table II. Halogenobenzenes are the only exception, their splitting of π_3/π_2 orbital energy levels being significant[22,23] and the role of free electron pairs at the halogen atoms being not fully understood. From the correlations found between ionisation potentials and the Hammett σ values it is concluded[25] that the substituent parameters represent a good measure for the HOMO energy.

Table I

Comparison of Solution Absorption UV Spectra with PPP Calculations

	Experimental values[14]				PPP Calculations[a]			
	λ_1 (log ε_1)	λ_2 (log ε_2)	λ_3 (log ε_3)	λ_4 (log ε_4)				
$N(CH_3)_2$	296·0 (3·30)	250·0 (4·15)	201·0 (4·34)	177·0 (4·14)	295·0 (3·30)	245·0 (4·20)	190·0 (4·36)	186·0 (4·40)
NH_2	285·0 (3·20)	235·0 (3·90)	198·0 (4·48)	176·0 (4·18)	296·0 (3·23)	249·0 (4·17)	192·0 (4·35)	186·5 (4·38)
OH	270·0 (3·30)	211·0 (3·81)	189·0 (4·75)	—	261·5 (2·86)	211·0 (2·63)	181·5 (4·56)	
OCH_3	271·5 (3·30)	216·5 (3·93)	192·0 (4·70)	—	262·5 (2·92)	212·5 (3·71)	182·0 (4·56)	
CH_3	262·0 (2·40)	205·0 (3·90)	188·0 (4·72)	—	255·5 (1·27)	208·0 (3·69)	188·0 (4·37)	
C_6H_5	—	247·0 (4·26)	200·0 (4·58)	—	—	280·5 (4·36)	213·0 (2·43)	206·5 (0·36)
SCH_3	280·0 (3·18)	254·0 (3·99)	203·0 (4·15)	184·0 (4·41)	254·0 (1·59)	233·5 (3·93)	193·0 (4·38)	186·5 (4·37)
F	260·0 (3·04)	203·0 (3·86)	182·0 (4·68)	—	256·0 (2·39)	203·5 (2·89)	179·0 (4·58)	
SH	276·0 (2·85)	235·0 (3·93)	203·0 (4·34)	185·0 (4·20)	251·0 (0·97)	219·5 (3·84)	187·0 (4·44)	185·0 (4·45)
Cl	261·0 (2·43)	214·0 (3·90)	189·0 (4·79)	—	255·0 (2·00)	202·5 (2·71)	178·5 (4·59)	
Br	261·0 (2·43)	215·0 (3·90)	192·5 (4·54)		253·5 (1·34)	201·0 (1·69)	177·0 (4·58)	
J	260·0 (2·85)	230·0 (4·10)	194·0 (4·45)	178·0 (4·48)	253·5 (1·00)	201·0 (1·75)	177·0 (4·58)	177·0 (4·57)
$COOH$	275·0 (3·00)	232·0 (4·18)	196·0 (4·56)	—	263·0 (2·65)	227·5 (4·06)	196·5 (4·01)	
CHO	281·0 (3·11)	241·0 (4·15)	198·0 (4·43)	—	267·0 (2·67)	237·0 (4·09)	202·0 (3·84)	
CN	270·0 (2·81)	223·0 (4·11)	192·0 (4·72)	—	265·0 (2·73)	234·0 (4·37)	194·0 (4·29)	
NO_2	280·0 (3·18)	252·0 (3·95)	198·0 (4·26)	175·0 (4·49)	277·0 (3·00)	251·0 (4·17)	211·0 (1·33)	204·5 (4·02)
$COCH_3$	280·0 (3·00)	238·5 (4·11)	198·0 (4·49)	—	266·0 (2·62)	235·0 (4·10)	216·0 (3·22)	201·0 (3·89)

[a] The numbers in brackets give log ε = log f + 4·5.

Experimental Values of Ionisation Potentials I.P. (π_3) and Our PPP Values — ε_{HOMO}

X	I.P.[a]	I.P.[b]	I.P.[c]	$-\varepsilon_{HOMO}$
N(CH$_3$)$_2$	7·51		7·37	8·27
NH$_2$	8·04		8·05	8·36
OH	8·75		8·73	9·56
OCH$_3$	8·54		8·39	9·48
CH$_3$	(8·90)	8·82	8·85	10·05
C$_6$H$_5$				9·30
H	9·40	9·25	9·23	10·36
SCH$_3$				9·25
F	(9·50)	9·19		9·97
SH				9·58
Cl	9·31	9·06		10·07
Br	9·25	9·05		10·25
J	8·78	8·67		10·26
COOH				10·52
CHO	9·80			10·55
CN	10·02	9·68	9·72	10·27
NO$_2$	10·26		9·93	10·89
COCH$_3$				10·47
COO$^-$				10·66

[a] Ref.[22] I.P. = 0·899 ($-\varepsilon_{HOMO}$) + 0·202, r = 0·908; [b] ref.[23]; [c] ref.[24] I.P. = 0·858 ($-\varepsilon_{HOMO}$) + 0·494, r = 0·947.

Intercorrelation of Values q in the Sense $y = ax + b$

Meaning of the symbols: r correlation coefficient, t the Student test, p correlation significance level, n number of points.

y	x	a	b	r	t $p = 0.01$	n
q_{para}	q_{ortho}	0·646	0·352	0·995	42·9	19
q_{meta}	q_{ortho}	−0·078	1·078	−0·962	10·6	11[a]
Δq_{ortho}	$\sum\limits_{i \neq X} \Delta q_i$	0·460	−0·000$_3$	0·982	21·2	19
Δq_{para}	$\sum\limits_{i \neq X} \Delta q_i$	0·297	−0·002	0·977	18·7	19

[a] Means the substituents of the 1. class.

We have found that the energies $-\varepsilon_{HOMO}$ calculated by us show an only similar trend of changes during variation of the group X as the parameters type σ do.

Substituent effect and π-electron distribution. It was shown[1] that substituent effect makes itself felt in quantum-chemical π-model quite generally through changes or differences of π-electron energy. In case of an acceptable theoretic model for the investigated series of compounds differing in their substituent X it is possible, in the simplest case, to expect the proportionality

$$\Delta \Delta E_{obs} \approx \Delta \Delta E_{\pi}, \qquad (1)$$

where $\Delta \Delta E = \Delta E(X) - \Delta E(H)$ are differences in observed (obs) or calculated (π) energy changes for an X-substituted and non-substituted members of the series which accompany the followed experimental quantity.*

In order that an observed substituent effect expressed by the quantity $\Delta \Delta E_{obs}$ might be correlated with non-energy quantities, *e.g* π-electron density q_i at the chosen i-th atomic centre, the additional condition (Eq. (2)) must be fulfilled

$$\Delta \Delta E_{\pi} \approx \Delta q_i = q_i(X) - q_i(H) \qquad (2)$$

which does not generally follow from theory. As $\Delta E(H)_{\pi} = const.$ for a given type of experimental data in a given reaction series, the condition of linear dependence (Eq. (3)) is obtained from Eq. (2)

$$\Delta q_i = a' \Delta E(X)_{\pi} + b' , \qquad (3)$$

and if this condition is fulfilled, then it is possible to correlate π-electron density q_i at the chosen i-th reaction centre with the substituent effect brought about by a change of the substituent X.

The condition (3) was verified in some π-MO calculations[26,27], however, often it is not given proper attention. In case of the monosubstituted benzene I we were, in this context, interested in the problem to what extent the values Δq_i for individual positions of the aromatic nucleus can be brought into relations with the substituent parameters $\sigma_{m,p}$ or σ_R which are generalized experimental substituent effects in the conjugated systems. As the mentioned parameters correlate satisfactorily[1] with differences in π-SCF energies

$$\Delta E(II)_{\pi} = E(IIb)_{\pi} - E(IIa)_{\pi} , \qquad (4)$$

* In current MO-LCAO calculations the value $\Delta \Delta E_{\pi}$ is exclusively the electron energy, but the expression (1) can also be fulfilled for experimental data $\Delta \Delta E_{obs}$ expressing proportions of the Gibbs energy or various excitation energies of chemical and physical processes.

for the ionized *IIb* and non-ionized *IIa* forms of *meta* and *para* substituted benzoic acids *II*, it was necessary to verify the condition

$$\Delta q_i(I) = a \, \Delta E(II) + b \qquad (5)$$

obtained from the expressions (3) and (4) by the choice $\Delta E_\pi = \Delta E(II)_\pi$ and $\Delta q_i = = \Delta q_i(I)$ where the last given quantity concerns the compound series *I*. From Fig. 1 it can be seen that the relation (5) is fulfilled very well for *para* positions, and, therefore, in this case π-electron density is a measure of the substituent effect or at least of its π-electronic component. On the contrary, for *meta* positions the relation (5) is not fulfilled satisfactorily for all substituents X (Fig 2), and, hence, π-electron density changes in meta positions cannot be considered to be a measure of operation of the substituent π-effect. These conclusions show noteworthy relation to effects of the substituents X on chemical shifts in NMR spectra where only the para characteristics give reproducible correlations with σ parameters[5,7,29-31].

π-Electron densities in the compound set I. The π-electronic system of the compounds *I* characterized by a certain distribution of charge density in individual types of the *i*-th positions of aromatic ring ($i = ipso, ortho, meta$ and *para*) can lead to an ambiguity in the relation (5) due to possible intercorrelations between the q_i densities themselves. Comparison of the values q_{para} and q_{ortho} (Fig. 3) shows that there exists a very close linear correlation relation between the two quantities,
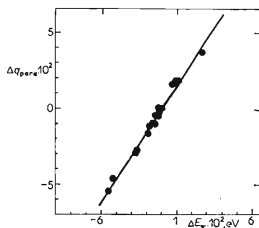

FIG. 1

Relative π-Electron Densities at *para*-Positions of Monosubstituted Benzenes *I vs* Difference of π-Electron Energies[1] of *para*-Substituted Benzoate Anions *IIb* and Corresponding Acids *IIa*

FIG. 2

Relative π-Electron Densities at *meta*-Positions Monosubstituted Benzenes *I vs* Difference of π-Electron Energies[1] of *meta*-Substituted Benzoate Anions *IIb* and Corresponding Acids *IIa*
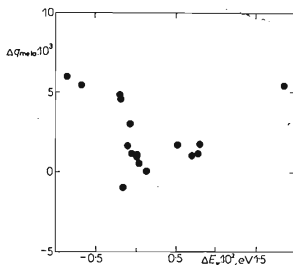
π-electronic densities in *ortho* position being somewhat more sensitive to change of the substituent X. Identical conclusions can be formulated when using the sets of previously published PPP and *ab initio* data[6,19,20], too. Thus it can hardly be decided which of the given densities represent better characteristics of the substituent effects. On the contrary, the quantities q_{meta} show the minimum sensitivity to change of the substituent X, and a certain correlation trend with respect to q_{ortho} values can be observed in their PPP data only for the substituents X of the 1. class (electron-releasing), see Table III. Similar behaviour is also exhibited by the densities q_{ipso} which are rather sensitive to parametrization in semi-empirical SCF model. Furthermore, from Table III it is obvious that the summation $\sum_{i \neq X} q_1$ proposed by the authors[4,5] as a measure of the substituent effect correlates well with the values q_{ortho} and q_{para}. Thus the last given quantities of π-distribution characteristics can be considered to be justified in discussion of the substituent effect of the compounds *I* at least within the semi-empirical SCF theory.

π-Electronic effect of substituents in aromatic conjugated systems should be best expressed (according to the opinions in refs[4,28]) by resonance empirical constants of the $\bar{\sigma}_R$ type. Results of correlations of these parameters with relative changes of π-electronic densities Δq_i are given in Table IV. All the values Δq_{ortho} and Δq_{para} correlate significantly with the substituent parameters σ_R^0, whereas the values Δq_{meta} correlate only for substituents X of the 1. class, the trend being quite different. However, the found correlations of the Δq_1 values with the substituent parameters σ_R^0 could be interpreted unambiguously, if it were not for the close intercorrelation relation q_{para} *vs* q_{ortho} mentioned earlier. Therefore, changes of π-electron densities cannot be excluded *a priori* in *ortho* position during interpretation of correlations with the σ_R^0 parameters. For the sums $\Delta q_{para} + \Delta q_{ortho}$, $\Delta q_{para} + 2\,\Delta q_{ortho}$, and $\sum_{i \neq X} \Delta q_i$ it can be seen from Table IV that they correlate satisfactorily with the σ_R^0 constants. At the same time it can be stated that the correlations of the sums Δq_{para} and Δq_{ortho} are statistically more significant than correlations of the whole sum
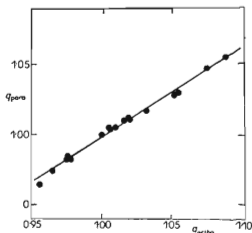

Fig. 3

π-Electron Densities at *para*-Positions of Monosubstituted Benzenes *I* vs π-Electron Densities at *ortho*-Positions

TABLE IV

Correlation of Parameters Type σ with Δq_i Values in the Sense of Equations $y = ax_1 + b$ or $y = ax_1 + bx_2 + c$

y	x_1	x_2	a	b	c	r	t $p = 0.01$	n
Δq_{ortho}	σ_R^0	—	-0.175	-0.015	—	-0.969	13.5	14
Δq_{meta}	σ_R^0	—	0.016	0.002	—	0.995	29.3	10^a
Δq_{para}	σ_R^0	—	-0.116	-0.013	—	-0.958	11.5	14
$\sum\limits_{i \neq X} \Delta \gamma_i$	σ_R^0	—	-0.410	-0.041	—	-0.914	7.8	14
$\Delta q_{para} +$ $+ \Delta q_{ortho}$	σ_R^0	—	-0.289	-0.028	—	-0.966	12.9	14
$\Delta q_{para} +$ $+ 2\,\Delta q_{ortho}$	σ_R^0	—	-0.464	-0.044	—	-0.967	13.2	14
Δq_{para}	σ_p	—	-0.058	-0.011	—	-0.947	11.8	18
Δq_{para}	σ_I	σ_R^0	-0.020	-0.098	-0.003	0.979	—	13
Δq_{meta}	σ_I	σ_R^0	-0.001	0.016	0.003	0.997	—	9^a
Δq_{ortho}	σ_I	σ_R^0	-0.021	-0.158	-0.006	-0.975	—	13
$\sum\limits_{i \neq X} \Delta q_i$	σ_I	σ_R^0	-0.064	-0.329	-0.004	0.931	—	13

[a] Means the substituent of the 1. class.

TABLE V

Linear Correlation of the Proton and ^{13}C-NMR Chemical Shifts with π-Electron Charges

y	x	a	b	r	t $p = 0.01$	n
$^1H_{ortho}$	Q_{ortho}	-12.549	-0.255	-0.964	11.5	12^a
$^1H_{para}$	Q_{para}	-13.181	-0.004	-0.989	21.5	12^a
$^{13}C_{ortho}$	Q_{ortho}	-143.049	1.406	-0.716	4.2	19^b
$^{13}C_{para}$	Q_{para}	-215.658	0.381	-0.972	17.0	19^b

[a] The experimental data according to ref.[32]; [b] the experimental data according to ref.[33].

$\sum\limits_{i \neq X} \Delta q_i$. Thus it is obvious that if the sum $\sum\limits_{i \neq X} \Delta q = \sum \Delta q_i$ is used, then the correlations with σ_R^0 constants are less significant as compared with the situations in which only the expressions Δq_{ortho} and Δq_{para} or their sums are correlated. With respect to these circumstances it is possible, in our opinion, to formulate the resonance constants σ_R^0 as a measure of transfer of π-charge (brought about by introduction of the substituent X into the benzene molecule) rather to *ortho* and *para* positions than to all positions according to the presumptions of the authors[8].

Hehre, Taft and Topsom[5] applied the dual-substituent parameter approach (DSP) and found that the π-electronic charges at carbon atoms in *meta* and *para* positions depend on the σ_I values. They interpret this finding as theoretical evidence of the π-inductive effect and express its measure in the *i*-th position as $\lambda_i = a/b$ from two-parameter correlations of the type $\Delta q_i = a\sigma_I + b\sigma_R$. The authors[5] found on the basis of *ab initio* calculations that *meta* position shows a relatively smaller dependence on the π-inductive effect formulated in this way as compared with *para* position, the characteristic property of the Δq_{meta} and Δq_{para} values being their inverse dependence on the conjugation effect of the substituent. From the data of Table IV we obtained λ_{ortho} 0·134, λ_{meta} 0·048, and λ_{para} 0·195. From these values it is seen that the use of the PPP method leads to analogous results.

Intercorrelation in Fig. 3 has an inevitable consequence for interpretation of relations between π-electronic charges Q_i and the proton or ^{13}C-chemical shifts, δ_j. From Table V it can be seen that, in accord with refs[29-31], close correlations of the type Eq. (6) can be stated for $i = j$. In Fig. 4 it is shown that in the case of the proton chemical shifts[32] analogous correlation (6)
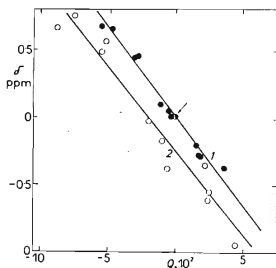
$$\delta_j = aQ_i + b \qquad (6)$$

FIG. 4

Relation between the Proton Chemical Shifts[32] in NMR Spectra of Monosubstituted Benzenes *I* and π-Electron Charges at Corresponding Positions of Aromatic Nucleus

Full and empty circles give the data for *para* and *ortho* positions, respectively. The arrow denotes the data for benzene itself.

can be found between the values δ_j and Q_i for $i = j = ortho$, too, eventhough a certain scattering of the correlation field is influenced by the existence of local anisotropy of the near substituent on the chemical shift δ_j. In the case of the ^{13}C chemical shifts[33] operation of the anisotropic factor is obviously so important that the linear correlation (6) looses its meaning for $i = j = ortho$. The existence of the intercorrelation in Fig. 3, however, makes it possible to interpret the relation (6) not only for the cases $i = j$ but also for the case $i \neq j$ with the same justification.

The generally given conclusion about linear correlation of chemical shifts exclusively in *para* position[5,7,29,31,34,35] with π-electronic charges can be, on the basis of the abovementioned facts, modified by the following postulate: in *ortho* and *para* positions of monosubstituted benzenes, in which change of the substituent brings about identical trend of changes of π-electronic charges, analogous trend in changes of the proton chemical shifts takes place, too.

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