# CHEMOMETRIC ANALYSIS OF SUBSTITUENT EFFECTS. II. RELATION BETWEEN HAMMETT SUBSTITUENT CONSTANTS $\sigma_m$ AND $\sigma_p$ AND A NEW MODEL FOR QUANTITATIVE DESCRIPTION OF SUBSTITUENT EFFECTS

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The paper presents values of 25 substituent constants $\sigma^i$ obtained by optimizing 46 data series of dissociation constants of substituted benzoic acids in various media. The constants $\sigma^i$ fulfil the general relation between the substituent constants of the Hammett type in *meta* and *para* positions enabling the description of substituent effects from both positions at the same time by a single constant. The Hammett substituent constants are interpreted by means of the $\sigma^i$ constants with an accuracy better than 0.03 units. In addition to it, the validity of general relationship between $\sigma_p$ and $\sigma_m$ was verified on a set of 56 substituents with the prediction accuracy of 0.06 units for $\sigma_p$, and after excluding the probably incorrectly parametrized substituents $NHCOC_6H_5$, $CH_3S$, and F the accuracy has improved to 0.05 units (98% of interpreted variability). The given relationship has served as a basis for suggesting a new model of transfer of substituent effects to a reaction centre: the model involves both the Hammett equation and the Yukawa–Tsuno equation and explains their background. The suggested model uses generalized transmission coefficients to separately describe the transformation of a single primary substituent effect – depending on its structure – into one inductive and two resonance effects which are transmitted through two independent channels to the reaction centre and here transformed into the resulting observable effect. From the model it follows that the substituent constant $\sigma_p$ is not a substituent constant in the true sense of the word since it involves the characteristics of skeleton and of reaction centre.

The description of relationship between substituent effects from *meta* and *para* positions of benzene ring with regard to a side chain containing the reaction centre represents an interesting theoretical problem. Its solution is connected with the understanding of mechanism of formation and separation of substituent effects, of their transmission to the reaction centre, and their superposition in the "target" point causing thus the resultant effect. From this standpoint the problem is a fundamental one, exceeding the primary subject of study. The theme of relationship between substituent effects from *meta* and *para* positions was dealt with by a number of authors[1 – 27], the attention being focused mostly on the description of relationship between the Hammett substituent constants $\sigma_m$ and $\sigma_p$. A roughly linear dependence was found:

$$\sigma_p = C + \lambda \sigma_m , \qquad (1)$$

the intercept $C$ being approximately equal to zero, and the values found for $\lambda$ varied within the interval of 0.95 – 1.19 (1.46) ($\lambda$: 0.95, ref.[15]; 1, ref.[16]; 1.13, ref.[13]; 1.14, refs[6,26]; 1.142, ref.[5]; 1.15, refs[9,12]; 1.19, ref.[23]; 1.46, ref.[23]; for further reference see ref.[18]). The given variety of results predominantly follows from the number, selection, and primary source of the substituent constants adopted. In particular, the relation (*1*) is not obeyed by the substituents possessing a strong $+M$ effect. The disintegration of the data into several classes is especially obvious in the graphical representation of $\sigma_p$ vs $\sigma_m$, refs[2,5,8,15,16,20,27].

In our preceding paper[27] we used the analysis of latent variables of a set of dissociation constants of benzoic acids to show that there probably are three such classes. The first class is formed by substituents exhibiting the inductive effect only, the second class is formed by those substituents which have a free electron pair at the atom adjacent to the aromatic ring, and the third class includes the substituents having a multiple bond between the first and second atoms, its polarity being directed from the aromatic nucleus. The relationship between the effects from *meta* and *para* positions is linear in the individual classes, the respective straight lines intersecting in the isoparametric point having the coordinates $t_m^0$ and $t_p^0$. The dependence of the corresponding latent variables $t$ describing the substituent effects from *meta* and *para* positions was expressed by the formula:

$$(t_p - t_p^0) = (I + \delta \Delta M)(t_m - t_m^0) , \qquad (2)$$

where $I$ and $M$ are parameters describing the inductive and resonance components, respectively, and $\delta$ is a parameter regarding the classification of substituent in one of the three classes: approximately it is $\delta_I = 0$, $\delta_{II} = -2\,\delta_{III}$. The interdependence between the $\sigma_p$ and $\sigma_m$ constants is obviously due to a superposition of two substituent effects – inductive and mesomeric.

The interpretation of Hammett substituent constants in terms of substituent constants describing separately the two effects mentioned was also dealt with in a number of studies[2,5,6,8,16,23,24,28 – 32] and sections of reviews[10,14,18,19,21,25,33,34]. Usually used are the substituent constants $\sigma_I$ and $\sigma_R$, and the corresponding expressions have the following forms:

$$\sigma_m = \lambda_m \sigma_I + \alpha \sigma_R \qquad (3)$$

and

$$\sigma_p = \lambda_p \sigma_I + \sigma_R , \qquad (4)$$

where $\lambda_m$ is a constant approximately equal to one (1.10, ref.[19]), $\lambda_p$ is approximately equal to 1.14 (see Eq. (*1*)), and $\alpha$ is approximately 0.33 (refs[28,29]), the value of 0.5 being given for the $\sigma_m^0$, $\sigma_p^0$ scale[2,30]. Similar values were found also for the $\sigma^*$ scale (ref.[24]) and $\sigma_F$, $\sigma_R$ (ref.[23]). Obviously, however, the $\sigma_I$ and $\sigma_R$ scales and similar scales do not represent a fundamental description either, since these substituent constants are also intercorrelated, this correlation being dependent on the structure of substituent[35]. The given proportionality expressed by Eqs (*3*) and (*4*) is obvious also from the analysis of latent variables in sets of substituent constants[20,36]. The location of the individual substituent constants in the plane of the first two latent variables just confirms the well-known fact that all published substituent constants are more or less intercorrelated. In this context a question emerges whether or not there exists a single primary effect of substituent which – due to chemical structure and geometrical arrangement of orbitals in this substituent, to the transmission pathways, and to the reaction centre – is manifested as a superposition of quantitatively describable subeffects. The successful application of neuron network to the prediction of the $\sigma_I$, $\sigma_R$ scales based purely on topological and quantum chemical descriptors[37,38] confirms this presumption.

The aim of the present work, in continuation of the previous one[27], is to use Eq. (*2*) for finding a scale describing the primary effect of substituents in the dissociation of benzoic acids, to compare the results with the conventional scales of the Hammett substituent constants, to verify a potential validity of Eq. (*2*) on a larger set of substituent constants, and to suggest an acceptable model interpreting the relationships found.

## RESULTS AND DISCUSSION

In our earlier report[27] we suggested and verified the relationship (*2*) on the basis of analysis of 46 data sets taken from literature describing the dissociation of monosubstituted benzoic acids in various media. From this relationship it followed[27] that the Gibbs energy of a process taking place in derivatives with *meta* and *para* substituents obeys the relationships:

$$\Delta G_m = \Delta G_{iso}^0 + \rho_{iso} \sigma_m^i \qquad (5)$$

and

$$\Delta G_p = \Delta G_{iso}^0 + \rho_{iso} [\sigma_p^{i0} + (I + \delta \Delta M) (\sigma_m^i - \sigma_m^{i0})] , \qquad (6)$$

where the symbolism is identical with that used in Eq. (*2*), the values of latent variables *t* being transformed into the scale of $\sigma_m^i$ comparable with the scale of the Hammett $\sigma$ constants. Both the equations given are formally and interpretationally identical with the Hammett equation, the only difference consisting in a different standard state and in expressing the $\sigma_p^i$ constant by means of the substituent constant $\sigma_m^i$ and general parameters depending only on the substituent type ($\delta\,\Delta M$, vide infra) or independent of the concrete substituent ($\sigma_m^{i0}$, $\sigma_p^{i0}$, *I*). With the application of the method of conjugated deviations[27,39] to the above-mentioned 46 data sets[27] taken from literature the unknown parameters in Eqs (*5*) and (*6*) were optimized to give the minimum residual standard deviations[39]. The relative residual standard deviation thus obtained had the value $s_{iso}$ = 0.1640 ($S_p^{iso}$ = 19.29, $\nu_R$ = 717, 97.6% interpreted variability), the same data set treated without respecting the inner bond between the data in *meta* and *para* positions only gave $s$ = 0.1609 for the 1st latent variable ($S_R$ = 18.57, $\nu_R$ = 717). The testing criterion for the test of the hypothesis $s^{iso} = s$ has the value $F$ = 1.039. This value falls into the critical region of $F_{0.025}$ = 0.864, $F_{0.975}$ = 1.158, hence the hypothesis is not rejected. For the data analyzed, the validity of Eqs (*5*) and (*6*) can be taken for granted. For comparison, the calculation using the Hammet substituent constant[19] gave the value of total residual standard deviation $s$ = 0.1817 ($S_R$ = 25.35, $\nu_R$ = 768, 96.9% interpreted variability), which is a correlation only slightly less close than that using the "intrinsic" substituent constants in the form of latent variables. The same can be stated about the interpretation adopting the substituent constants $\sigma_I$ and $\sigma_R$ (ref.[19]) which gave the residual standard deviation $s$ = 0.3398 ($S_R$ = 93.38, $\nu_R$ = 722, 89.8% interpreted variability).

The value of parameter $I$ = 1.135 obtained from the optimization agrees very well with the value of $\lambda$ = 1.14 in Eqs (*1*) and/or (*4*) and indicates that the transmission of inductive effect from *para* position is somewhat more efficient than that from *meta* position. If we adopt the idea of propagation of the inductive effect only through the electrons of $\sigma$ bonds, then assuming a constant weakening at each bond we can arrive at the weakening value of ca 0.57. The additional effect of substituent mediated by the electrons of $\pi$ bonds is expressed by the optimized values $\delta\,\Delta M_{II}$ = 0.599 and $\delta\,\Delta M_{III}$ = –0.290, the classifying of substituents into one of the classes being given in Table I. From the table it is obvious that the classification of substituents is unequivocally connected with their structure. The first class includes the substituents exhibiting only inductive effects; the including of $NO_2$, CN, and $SO_2NH_2$ substituents into this class – already discussed in ref.[27] – stands in accordance with their low abilities to involve the electrons of multiple bonds into the resonance (except for direct conjugation). The second class is formed by substituents possessing a free electron pair at the atom adjacent to the aromatic nucleus. The lower $\delta\,\Delta M_{II}$ value, as compared with $I$ value, can be due to both the "permeability" of transmission pathways and the structures of substituent and reaction centre, and it can only be stated for the time being. The third group includes the substituents having a multiple bond between the first and the second atoms

from the aromatic nucleus, the bond being polarized in the direction from the nucleus; here we must stress the preference of polarizability over the existing polarization. The same effect is exhibited by the substituents such as $CF_3$ which, though having no multiple bonds, nevertheless possess polarizable σ bonds. The $\delta\,\Delta M_{III}$ values have opposite sign and about half magnitude as compared with those of $\delta\,\Delta M_{II}$ ($\delta\,\Delta M_{III}/\delta\,\Delta M_{II} = -0.484$). This indicates that the origin of the effect is the electron-attracting atoms bound at a greater distance from the aromatic nucleus. The effect is manifested the

TABLE I
Comparison of optimized values of substituent constants $\sigma^i \equiv \sigma^i_m$ and the corresponding $\sigma^i_p$ with the Hammett substituent constants $\sigma_m$ and $\sigma_p$ (ref.[19]), $\sigma^i_H = 0.000$

| Substituent | Class | Constants | | | |
|---|---|---|---|---|---|
| | | $\sigma^i_m$ | $\sigma_m$ | $\sigma^i_p$ | $\sigma_p$ |
| $CH_3$ | I | –0.077 | –0.06 | –0.121 | –0.14 |
| $C_2H_5$ | I | –0.096 | –0.08 | –0.143 | –0.13 |
| *tert*-$C_4H_9$ | I | –0.107 | –0.09 | –0.155 | –0.15 |
| $C_6H_5$ | I | 0.038 | 0.04 | 0.010 | 0.02 |
| $CF_3$ | III | 0.432 | 0.46 | 0.504 | 0.53 |
| $CCl_3$ | III | | 0.40 | | 0.46 |
| CN | I | 0.632 | 0.62 | 0.683 | 0.71 |
| CHO | III | 0.459 | 0.41 | 0.527 | 0.47 |
| $COCH_3$ | III | 0.366 | 0.36 | 0.449 | 0.47 |
| COOR | III | 0.314 | 0.35 | 0.404 | 0.44 |
| $NH_2$ | II | –0.115 | –0.09 | –0.589 | –0.57 |
| $N(CH_3)_2$ | II | –0.130 | –0.10 | –0.615 | –0.63 |
| $NHCOCH_3$ | II | 0.129 | 0.14 | –0.166 | –0.09 |
| $N{=}NC_6H_5$ | I | 0.325 | 0.29 | 0.335 | 0.33 |
| $NO_2$ | I | 0.717 | 0.71 | 0.780 | 0.81 |
| $OCH_3$ | II | 0.091 | 0.10 | –0.232 | –0.28 |
| $OCOCH_3$ | II | 0.311 | 0.26 | 0.150 | 0.16 |
| SH | II | 0.299 | 0.25 | 0.129 | (0.15) |
| $SCH_3$ | II | | 0.14 | –0.001 | 0.00 |
| $SO_2CH_3$ | III | 0.654 | 0.68 | 0.691 | 0.73 |
| $SO_2NH_2$ | I | 0.513 | 0.53 | 0.549 | 0.58 |
| F | II | 0.318 | 0.34 | 0.162 | 0.06 |
| Cl | II | 0.372 | 0.37 | 0.256 | 0.22 |
| Br | II | 0.379 | 0.37 | 0.268 | 0.22 |
| I | II | 0.364 | 0.34 | 0.241 | 0.21 |

more distinctly the greater is the electronegativity difference between the first and further atoms in the substituent chain.

From Eqs (*5*) and (*6*) there follows the existence of a hypothetical substituent with the values $\sigma_m^{i0}$ and $\sigma_p^{i0}$ representing the standard state. The optimized values of $\sigma_m^{i0}$ = 0.595 and $\sigma_p^{i0}$ = 0.642 show that, in contrast to the classic Hammett equation, the standard substituent is not hydrogen, although the respective value is $\sigma_H^i$ = 0.000. The $\sigma^i$ values of other substituents are given in Table I along with the Hammett $\sigma_{m,p}$ constants taken from literature[19]. A comparison of data in the table shows a good agreement between both scales. Quantitatively the relation is described by the regression:

$$\sigma_{m,p} = -(0.000 \pm 0.006) + (0.999 \pm 0.015)\, \sigma_{m,p}^i \qquad (7)$$

$$n = 48,\ s = 0.033,\ r = 0.995,$$

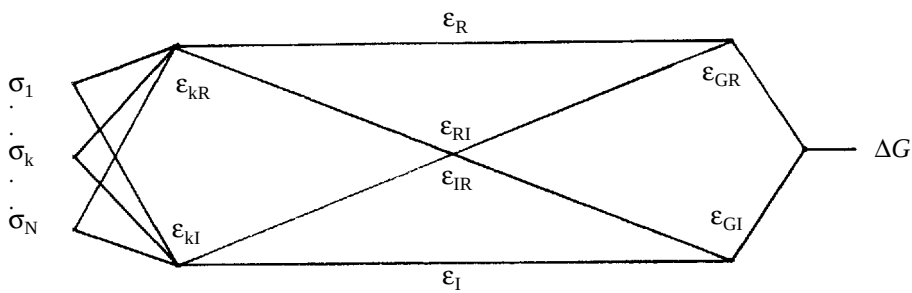
the prediction precision being higher than the declared validity of the Hammett equation[19] (0.05 p*K* units). By means of the Jackknife residua the $\sigma_{m,p}$ values for 4-F (the expected value 0.16) and 4-$NHCOCH_3$ (the expected value –0.17) were indicated as outliers. After rejecting them ($s$ = 0.028, $r$ = 0.997) we obtained for the remote value that for $\sigma_{m,p}$ of 4-CH=O (the expected value 0.53). The substituent constant given in literature for fluorine at *para* position usually somewhat varies; the value of $\sigma_p = 0.15 \pm 0.06$ given in a critical compilation[14] agrees better with the value found by us than does the date from a later work by the same author[19].

With respect to the presented validity of Eq. (*2*) (and Eqs (*5*), (*6*) following therefrom) for primary experimental data, the validity of Eq. (*2*) was verified on a set of 56 Hammett substituent constants $\sigma_m$ and the same number $\sigma_p$ taken from literature[19]. A list of the substituents analyzed and their classification are given in Table II. The optimization of parameters in Eq. (*2*) and classification of the substituents in the individual classes (Table II) gave the residual standard deviation $s$ = 0.059. An extraordinary behaviour was encountered with the $NHCOC_6H_5$ substituent due probably to the strongly underestimated value $\sigma_m$ = 0.02. The result found can easily be understood since the substituent constant for $NHCOCH_3$ is $\sigma_m$ = 0.14 and in water benzoic acid (p$K_a$ = 4.20) is stronger than acetic acid (p$K_a$ = 4.75). Another deviating substituent is $CH_3S$ due probably to the high value of $\sigma_m$ = 0.14 (cf. $\sigma_m$ = 0.10 for $OCH_3$ with more electronegative oxygen). The last distinctly deviating substituent is – traditionally – fluorine, in this case the reason lying obviously in the low value of $\sigma_p$ = 0.06 (the expected value is 0.21). After elimination of the substituents mentioned the residual standard deviation decreased to the value of $s$ = 0.049, the interpreted variability being 98.0%. It can be stated that Eq. (*2*) is valid for a broad spectrum of substituents with a precision comparable to that of the validity of the Hammett equation which is

usually given as 0.05 p*K* units[19]. Also interesting is the placing of substituents into the individual classes (Table II): here we can say roughly the same as above for the set in Table I. The including of $P(C_6H_5)_2$, $SeCH_3$, $SCOCH_3$, and $SOCH_3$ substituents in the class I might attract notice since according to their structure these substituents rather belong to the class II. This can be explained in two ways: either the free electron pair is not sufficiently localized at the respective atom (probably $P(C_6H_5)_2$, $SCOCH_3$ due to resonance with chemical environment, $P(C_6H_5)_2$, $SeCH_3$ due to small overlap with relatively loose valence electrons of bulky atom) or the data for these substituents are less reliable.

The found general relationships can contribute to the interpretation of nature of substituent effects. Let us presume that a substituent has a number of properties which are superposed as the inductive and resonance outputs and further transmitted by means of $\sigma$ and $\pi$ electrons to the reaction centre where they make themselves felt as the property measured. Moreover let us presume for greater universality that the transmission pathways are not orthogonal. The described situation can be represented by Scheme 1 where $\sigma_k$ are the primary effects of substituent, $\varepsilon$ are generalized transmission coefficients – $\varepsilon_{kR}$ is the *k*-th contribution to the resonance effect of substituent, $\varepsilon_{kI}$ is the *k*-th contribution to the inductive effect of substituent, $\varepsilon_R$ and $\varepsilon_I$ describe the transmission of resonance and inductive effects of substituent through the skeleton, respectively, $\varepsilon_{RI}$ and $\varepsilon_{IR}$ refer to the interactions between the $\sigma$ and $\pi$ electrons of the transmission pathways, $\varepsilon_{GR}$ and $\varepsilon_{GI}$ are the resonance and inductive components of substituent effect, respectively, which affect the reaction centre, and $\Delta G$ is the change observed. First let us presume that the interactions $\varepsilon_{RI}$ and $\varepsilon_{IR}$ are not manifested. For the observed effect of substituent from *para* position with regard to the side chain containing the reaction centre it can be written:

$$\Delta\Delta G_p = (\Delta G_p - \Delta G^0) = \sum_{k=1}^{N} \sigma_k \varepsilon_{kI} \varepsilon_I^{para} \varepsilon_{GI} + \sum_{k=1}^{N} \sigma_k \varepsilon_{kR} \varepsilon_R^{para} \varepsilon_{GR} . \qquad (8)$$




SCHEME 1

Similarly for the substituent effect from *meta* position:

$$\Delta\Delta G_m = (\Delta G_m - \Delta G^0) = \sum_{k=1}^{N} \sigma_k \varepsilon_{kI} \varepsilon_I^{meta} \varepsilon_{GI}, \qquad (9)$$

with the presumption that the resonance interaction does not operate from this position. This presumption is arbitrary at this phase and contradicts Eq. (*3*), and its justifiability can only be verified by the ability of final results to describe known experimental facts. The ratio of both effects after modification (for simplicity the indexes at the sum symbol were omitted) reads as follows:

$$\Delta\Delta G_p = \left( \frac{\varepsilon_I^{para}}{\varepsilon_I^{meta}} + \frac{\varepsilon_R^{para} \varepsilon_{GR}}{\varepsilon_I^{meta} \varepsilon_{GI}} \frac{\sum \sigma_k \varepsilon_{kR}}{\sum \sigma_k \varepsilon_{kI}} \right) \Delta\Delta G_m . \qquad (10)$$

If now it were admitted that there is a significant interaction between the transmission pathways *I* and *R*, the difference between them would disappear, at the same time the difference between $\varepsilon_{kR}$ and $\varepsilon_{kI}$ would also disappear, and a single linear dependence would result according to Eq. (*10*). As this is not the fact, there is no significant interaction between both pathways. This statement agrees with the well-known principle of $\sigma$–$\pi$ separation used in simple quantum-mechanic methods. A single linear dependence

TABLE II
Distribution of substituents into classes according to electronic structure participating in interaction with reaction centre

| Class | Substituents |
|---|---|
| I | H, D, $CH_3$, $C_2H_5$, iso$C_3H_7$, *tert*-$C_4H_9$, C≡CH, C≡C$C_6H_5$, cyclo$C_3H_5$, $C_6H_5$, $CH_2C_6H_5$, $CH_2CN$, $CH_2OR$, $CH_2Cl$, $Si(CH_3)_3$, N=N$C_6H_5$ CN, $NO_2$, $SO_2NH_2$, $P(C_6H_5)_2$, $SeCH_3$, $SCOCH_3$, $SOCH_3$ |
| II | $NH_2$, $N(CH_3)_2$, $NHCOCH_3$, $NHCOC_6H_5$, $NHCOCF_3$, NCS, $N_3$, $OCH_3$, $OC_6H_5$, $OCF_3$, $OCOCH_3$, SH, $SCH_3$, SCN, F, Cl, Br, I |
| III | CHO, $COCH_3$, $COC_6H_5$, $CONH_2$, COOH, COOR, $PO(C_6H_5)_2$, $PO(OC_2H_5)$, $SO_2CH_3$, $SO_2F$, $IO_2$, $B(OH)_2$, $CF_3$, $CCl_3$, $SF_5$ |

would also be obtained if in Scheme 1 all $\varepsilon_{kR}$ terms (or, inversely, all $\varepsilon_{kI}$ terms) were equal to zero, but this is not the fact either. Furthermore let us presume that the disintegration of set of substituents into classes is only due to the structure of substituents, and the (unique) structure of transmission pathways and the (unique) reaction centre make no contribution. In this case all the transmission coefficients of Eq. (*10*) are constant except for $\varepsilon_{kR}$ and $\varepsilon_{kI}$, and the substituents of the class I (Table II) have $\varepsilon_{kR} = 0$. According to Eq. (*10*) the existence of the remaining two classes can be explained in several ways. According to the most general variant there exist two primary effects $\sigma_1$ and $\sigma_2$ connected with $\varepsilon_{kR}$ and $\varepsilon_{kI}$ which are nonzero and constant for the given class of substituents. With regard to the electronic structure of substituents in Table II, however, it is more likely that only one type of transformation described by a single pair of transmission coefficients, $\varepsilon_{kR}$ and $\varepsilon_{kI}$, operates with one type of substituent. In this case the sums in Eq. (*10*) become meaningless, and also meaningless is the differentiation between the individual primary effects of substituents $\sigma_k$, and it can well be presumed that there is only a single primary effect. Thus the relation (*10*) can be rewritten as in Eq. (*11*)

$$\Delta\Delta G_p = \left( \frac{\varepsilon_I^{para}}{\varepsilon_I^{meta}} + \frac{\varepsilon_R^{para}\,\varepsilon_{GR}}{\varepsilon_I^{meta}\,\varepsilon_{GI}\,\varepsilon_{kI}}\;\varepsilon_{kR} \right) \Delta\Delta G_m \,. \qquad (11)$$

As the transformation of inductive effect is geometrically invariant with respect to structure of substituent, the observed disintegration into classes is due to the way the electrons of substituent interact with the resonance channel of skeleton.

The expressions (*2*) and (*11*) are evidently similar and the presumptions introduced seem to be justified. At the same time, it is possible – by comparing Eqs (*5*), (*6*), and (*11*) – to make a conclusion that the substituent constant $\sigma_p$ in the Hammett equation also involves the components describing the skeleton and reaction centre. Therefrom it follows that the validity of the Hammett equation is limited to the molecules with the same ratio of transmission coefficients as it is the case with benzoic acid. A change of skeleton or of transmission coefficients at the reaction centre will be manifested by changes in $\sigma_p$ in the way described by the Yukawa–Tsuno equation. From Eqs (*5*), (*6*), and (*11*) it can be deduced that the Hammett equation and cognate relations describe – in the reaction constant – only the sensitivity of reaction centre to the inductive effect of substituent, the deviations from the Hammett equation for *para* substituents indicating another character of the resonance interaction as compared with the standard benzoic acid.

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