CONCERNING THE TRANSMISSION OF SUBSTITUENT EFFECTS ACROSS THE BENZENE NUCLEUS*

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Experimental and theoretical arguments are presented that the inductive substituent effect is transmitted into the *para* position of the benzene nucleus more effectively than into the *meta* position in the ratio $\lambda = 1 \cdot 13 \pm 0 \cdot 03$. This ratio follows immediately from the dissociation constants of *meta* and *para* substituted benzoic acids (substituents NO_2, CN, SO_2CH_3, SO_2NH_2, SO_2F, $COCH_3$) in three pure solvents; hence the phenomenon is not due to the preferential solvation in mixed solvents. Concordant results are obtained by the statistical analysis based on Eqs (*2a, b*). The opposite conclusions claimed in the literature are explained by the flexibility of the mathematical model which allows transformations of the obtained parameters without affecting the fit. This result implies that the mentioned substituents — and many others — have virtually zero mesomeric effect in substituted benzoic acids. Hence this model is unable to detect their conjugation within the limits of the attainable accuracy and a more suitable model is to be searched for.

Benzene *meta* and *para* derivatives represent a convenient model for studying substituent effects since these effects retain, in the first approximation, their relative values in various reactions. This is expressed in the Hammett equation by the substituent constants σ_m and σ_p which are independent of the reaction within the known range of validity:

$$\log k_m - \log k^0 = \varrho\sigma_m , \qquad (1a)$$

$$\log k_p - \log k^0 = \varrho\sigma_p . \qquad (1b)$$

Note that in this approximation the reaction constant ϱ is identical for both the *meta* and *para* positions[1,2]; the difference is expressed by the unequal values σ_m and σ_p. Hence no information concerning the transmission of substituent effects across the benzene nucleus can be obtained. The second approximation is represented by two Taft equations[3,4] for the two positions:

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$$\log k_m - \log k^0 = \varrho_I^m \sigma_I + \varrho_R^m \sigma_R , \qquad (2a)$$

$$\log k_p - \log k^0 = \varrho_I^p \sigma_I + \varrho_R^p \sigma_R . \qquad (2b)$$

The two substituents constants σ_m, σ_p are replaced by new ones, σ_I and σ_R, while the number of reaction constants is extended to four for each reaction. Equations $(2a, b)$ allow a closer analysis of substituent effects on the one hand, since the constants σ_I and σ_R may be identified with the classic concepts of the inductive and mesomeric effects, respectively. (This interpretation seems to retain its validity although the electronic effects are nearly compensated by the effect of solvent[5].) On the other hand, the constants ϱ reflect some properties of the model itself, *i.e.* the transmission of the inductive (ϱ_I) or mesomeric (ϱ_R) effects to the *meta* (ϱ^m) or *para* (ϱ^p) position, respectively.

In this paper we are dealing with the latter aspect. The main problems are whether the ratios $\varrho_I^m / \varrho_I^p = 1/\lambda$ and $\varrho_R^m / \varrho_R^p = \alpha$ are constant for various reactions, or at least for some groups of related reactions, further what is their physical meaning. The exact value* of λ is relevant for the quantitative separation of inductive and mesomeric effects according to Eqs $(2a, b)$. There are two essentially different ways of determining λ. The statistical approach[4,6-9] is based on Eqs $(2a, b)$ and on experimental values of k_m, k_p for several reaction series, the parameters σ and ϱ being adjusted in agreement with the least-squares criterion. Attention was focused to the values of σ_I and σ_R rather than to the coefficient λ to which the fit is little sensitive[9]. The whole procedure is rather versatile since the constants σ_I and/or σ_R may be either taken from another source or optimized simultaneously; in addition the values obtained are not unique. The alternative approach, more direct but less general, makes use of a single substituent[10-12], or a set of such substituents[13-17], whose mesomeric effects are assumed to be negligible. With $\sigma_R = 0$ Eqs $(2a, b)$ become trivial and the ratio $\lambda = \varrho_I^p / \varrho_I^m$ is obtained immediately from the relation[14]

$$\log k_p - \log k^0 = \lambda(\log k_m - \log k^0) . \qquad (3)$$

The main problem of this approach is the selection of substituents with negligible mesomeric effects; this may be done a posteriori according to the fact that Eq. (3) is fulfilled[14,16].

The value of λ is certainly near to unit[8,9] but there is no agreement as to its exact value. From the statistical procedures mostly values lower than unit[4,6,7] were obtained (from 0·78 to 0·966) which complied with the concept of σ-inductive effect or perhaps even with the field effect. On the contrary, correlations with selected weakly conjugated substituents (essentially those bearing no lone electron pair in the

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* The symbol λ is also in use with a different meaning[4]. We believe that the best way how to restrict the confusion is to retain our original denotation[14].

α-position) yielded values greater than unit, most frequently[14-17] 1·12−1·13, which must be explained in terms of the π-inductive effect[14]. To explain this discrepancy, attention has been drawn[4] to the fact that most of the latter determinations had been carried out in mixed solvents[14,17] and preferential hydration of the reaction centre was considered responsible[4] for the values $\lambda > 1$. In this paper we firstly bring some new and refer to some previous data[5,18] confirming that Eq. (3) holds with λ greater than unit even in pure solvents. Further it will be shown that the discrepancy between the statistical and the direct approach is only apparent since the former may be modified by transformation of parameters without affecting the overall fit.

EXPERIMENTAL

Substances used: The substituted benzoic acids were the same as previously described[17]. Dimethyl sulphoxide was purified as previously[18]; methanol was dried by anhydrous copper sulphate and rectified; ethylene glycol was dried with calcium oxide and rectified.

The measurement of dissociation constants: Measurement in dimethyl sulphoxide was described[18], in the remaining solvents the same apparatus was used (a glass electrode Radiometer G 2000B and a calomel reference electrode, a bridge filled with saturated lithium chloride solution in methanol). Solutions were titrated with 0·1M tetramethylammonium hydroxide in methanol or ethylene glycol, respectively. The values read off on the mV scale were converted to pK's using the known values for benzoic acid. The results are listed in Table I.

RESULTS

The reexamination of Eq. (3) has been based on apparent dissociation constants of *meta* and *para* substituted benzoic acids in dimethyl sulphoxide, glycol and methanol. Five substituents were chosen, assumed[14,17] to have negligible mesomeric effects
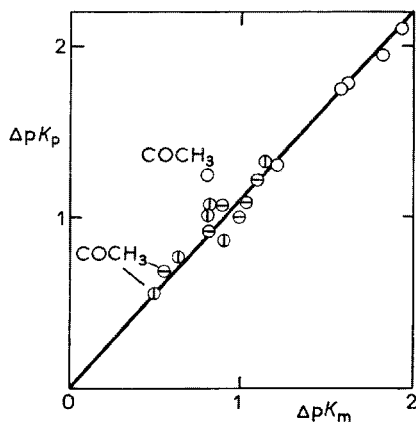
FIG. 1

The Mutual Dependence of Relative Dissociation Constants of *meta* and *para* Substituted Benzoic Acids in Pure Solvents

○ Dimethyl sulphoxide; ⊖ methanol; ⦶ ethylene glycol; the substituents are SO_2NH_2, CN, SO_2CH_3, NO_2, SO_2F, and $COCH_3$, the line has a slope of 1·10.

in this system: NO_2, CN, SO_2CH_3, SO_2NH_2, SO_2F; the assumption is confirmed just by the validity of Eq. (3). The sixth substituent, $COCH_3$, has been found to have a small but finite electron attracting mesomeric effect in the *para* position[14,17]; it was, nevertheless, included for comparison. The relative dissociation constants are plotted in Fig. 1. It is evident that the scatter is greater than in water or in mixed aqueous solvents since the data are certainly less precise. However, some deviations may be real; in particular the deviation upwards is evident at least at one of the points pertinent to the substituent $COCH_3$. The best line going through the origin has the slope λ c. 1·10. The recently published dissociation constants in the gas phase [5] are theoretically still more important, the substituent effects being ten times larger than in water. The two substituents available (CN, NO_2) allow to estimate $\lambda = 1·15 \pm 0·08$. In our opinion the value λ greater than unit is established beyond any doubt. An additional proof based on few substituents but on a great variety of reactions was given previously[14].

In order to explain the results of the statistical treatment in agreement with the above finding a closer analysis of Eqs (2a, b) is appropriate. Let us assume that the values of $\log k_m$, $\log k_p$ and $\log k^0$ are given for a set consisting of p reactions with q substituents (not including hydrogen); hence the number of all entries (N) equals $2pq$ if the data matrix is full. The constants on the right-hand side of Eqs $(2a, b)$ are to be determined according to the least-squares criterion, *i.e.* to minimize the

TABLE I

Apparent Dissociation Constants of Some Substituted Benzoic Acids in Non-Aqueous Solvents

Substituent	Dimethyl sulphoxide	Methanol	Ethylene glycol
H	11·02[a]	9·41 (9·41[b])	7·65 (7·647[b])
3-COCH$_3$	10·22[a]	8·87	7·15
4-COCH$_3$	9·77[a]	8·72	7·10
3-CN	9·44[a]	8·53	6·84 (5·31[c])
4-CN	9·27[a]	8·34	6·63 (6·59[c])
3-NO$_2$	9·20[a]	8·42 (8·366[b])	6·73 (6·716[b])
3-NO$_2$	9·07[a]	8·41 (8·349[b])	6·59 (6·682[b])
4-SO$_2$CH$_3$	9·41	8·37	6·75
4-SO$_2$CH$_3$	9·25	8·33	6·79
3-SO$_2$NH$_2$	9·81[a]	8·59	7·01
4-SO$_2$NH$_2$	9·71[a]	8·49	6·88
3-SO$_2$F	9·08	8·31	6·51
4-SO$_2$F	8·91	8·18	6·33

[a] Our previous measurements, ref.[18]; [b] ref.[32]; [c] ref.[33].

sum of squared differences between the left-hand and right-hand sides. The various mathematical procedures differ in the additional constraints which may mean either giving some constants particular values or assuming some relations between them. The following models have some physical meaning and have been actually used (Table II):

TABLE II
Models for Calculating Parameters of the Taft Equations (2a, b)

Model	Parameters to determine	M^a	F^b	Possible transformations of parameters^c
1	$\varrho_I^m \varrho_I^p \varrho_R^m \varrho_R^p$ $\sigma_I \sigma_R$	4p + 2q	4	$\sigma_I = A(\sigma_I' \cos\varphi + B\sigma_R' \sin\varphi)$ $\sigma_R = C(\sigma_R' \cos\varphi - \sigma_I' \sin\varphi/B)$ $\varrho_I = (\varrho_I' \cos\varphi + \varrho_R' \sin\varphi/B)/A$ $\varrho_R = (\varrho_R' \cos\varphi - B\varrho_I' \sin\varphi)/C$
2	$\varrho_I^p \varrho_R^p \alpha \lambda$ $\sigma_I \sigma_R$	2p + 2q + 2	4	as ad 1.
3	$\varrho_I^m \varrho_I^p \varrho_R^m \varrho_R^p$ σ_R	4p + q	2	$\sigma_I = \sigma_I', \quad \sigma_R = C(\sigma_R' - B\sigma_I')$ $\varrho_I = \varrho_I' + B\varrho_R', \quad \varrho_R = \varrho_R'/C$
4	$\varrho_I^p \varrho_R^p \alpha \lambda$ σ_R	2p + q + 2	2	as ad 3.
5	$\varrho_I^m \varrho_I^p \varrho_R^m \varrho_R^p$ σ_R	4p + q	3	$\sigma_I = A\sigma_I', \quad \sigma_R = C(\sigma_R' - B\sigma_I')$ $\varrho_I = (\varrho_I' + B\varrho_R')/A, \quad \varrho_R = \varrho_R'/C$
6	$\varrho_I^p \varrho_R^p \alpha \lambda$ σ_R	2p + q + 2	3	as ad 5.
7	$\varrho_I^p \varrho_R^p \varrho_I^m \varrho_R^m$	4p	0	—

^{a} Number of all constants to determine by the least-squares procedure; ^{b} degrees of freedom extant in the model; ^{c} the symbols $\varrho_I(\varrho_R)$ may designate either ϱ_I^m or $\varrho_I^p(\varrho_R^m$ or $\varrho_R^p)$.

1) All the constants, *i.e.* σ_I and σ_R for each substituent and ϱ_I^m, ϱ_I^p, ϱ_R^m, and ϱ_R^p for each reaction are adjusted without any constraint in order to reach the best fit[6]. This model is apparently simple but mathematically complex and too flexible.

2) The constants σ_I and σ_R are adjusted for each substituent but for the ϱ constants the constraints of constant α and λ are imposed[6]: $\varrho_R^m = \alpha\varrho_R^p$ and $\varrho_I^m = \varrho_I^p/\lambda$. Hence, there are only two constants at disposal for each reaction, in addition it is necessary to find optimum values of α and λ.

3) All the constants σ_I are taken from an idependent source[4,6]; essential for their determination are derivatives of bicyclo[2,2,2]octane-1-carboxylic acid. The goal is to optimize σ_R for each

substituent and ϱ_I^m, ϱ_I^p, ϱ_R^m, ϱ_R^p for each reaction. Since σ_R can be determined from Eq. (2b) more precisely than from Eq. (2a), the procedure was so modified that only the former was exploited to this aim[4]. The experimental data for *meta* derivatives were used only additionally to determine ϱ_I^m and ϱ_R^m from σ_R already known. This model was applied more extensively and at a later date than the others. Hence, we must conclude that it is held by its authors[4] to be the best one.

4) The constants σ_I are taken from an independent source as ad *3* and the constraints are imposed[6] as ad *2*. Hence it is to determine σ_R for each substituent, ϱ_I^p and ϱ_R^p for each reaction, and in addition α and λ.

5) The most difficult step in estimation of σ_I is their scalling; it means that all the constants may be in error by the same factor although their relative values are correct. Hence we suggest an improvement of model *3* requiring that the constants σ_I are not equal to the prefixed values but only proportional to them. Other features of model *3* are retained.

6) The same improvement as ad *5* may be applied to model *4*.

7) Not only the constants σ_I but also σ_R may be taken from an independent source, the calculation being reduced to two multiple regressions with variables σ_I, σ_R, $\log k_m$ and σ_I, σ_R, $\log k_p$, respectively[7].

In addition the various procedures differ in the selection of experimental data ($\log k$). These data may be restricted to dissociation of substituted benzoic acids and to related reactions (the σ_{BA} reactivity[4]), or, on the contrary, to non-conjugated functional groups (the σ^0 reactivity[3,4]), or even relate separately to reactions with donor and acceptor functional groups (the σ^+ and σ^- reactivities). Further consideration will be confined to σ_{BA} and σ^0 reactivities which yield concordant results, in particular if attention is focused to non-conjugated substituents.

The salient feature of all the models are the excessive degrees of freedom. It means that the solution obtained is never unique and from a given optimalized set of parameters (σ_I, σ_R, *etc.*) other sets of new constants (σ_I', σ_R', *etc.*) may be derived by simple algebraic operations, the new set yielding exactly the same predicted values for each combination of substituent and reaction[14,19]. The possible transformations are listed in Table II, last column. Let us consider *e.g.* model *1*. One can easily realize that for any values of the four constants A, B, C, φ the expression ($\varrho_I\sigma_I + \varrho_R\sigma_R$) is invariant so that the fit by Eqs (2a, b) is not affected. The number of these constants (four) is equal to the excessive degrees of freedom (F); for various models this number is listed in Table II, column 4, in addition to the number of all parameters (M) in column 3. The actual degrees of freedom (f) for a concrete example are given as

$$f = N - M + F. \tag{4}$$

Some of the excessive degrees of freedom are commonly used to give certain constants for standard reactions the normalized values, *e.g.* $\varrho_I^p = 1$ and $\varrho_R^p = 1$ for dissociation of benzoic acids in water. However, the remaining degrees of freedom were not exploited in the previous calculations and gave the results some flexibility. This does not impair the predicting power of Eqs (2a, b), however, any discussion of the

values of parameters is invalidated unless the consequences of transformations are examined in detail. Clearly some transformations are less relevant than the others, *e.g.* the constants A and C in Table II, model *1*, are pure scaling factors and cannot influence the values of λ or α. On the contrary, the constants B and φ change completely the physical meaning of the parameters; as an extreme they may convert σ_I into σ_R and *vice versa*. In the following we shall examine the results of previous calculations and show how they can be affected by allowed transformations and made finally compatible with the results of the direct method.

TABLE III

Some Selected Substituent Constants σ_I and σ_R According to Different Calculations

Substituent	σ_I			σ_R			
	ref.[4,a]	corrected[b]	ref.[6,c]	ref.[4,d]	corrected[e]	ref.[6,c]	corrected[f]
N(CH$_3$)$_2$	0·06	0·07	—	−0·83	−0·84	—	—
NH$_2$	0·12	0·14	—	−0·82	−0·85	—	—
OCH$_3$	0·27	0·33	0·27	−0·61	−0·67	−0·43	−0·60
CH$_3$	−0·04	−0·05	0·03	−0·11	−0·10	−0·18	−0·22
C$_6$H$_5$	0·10	0·12	—	−0·11	−0·13	—	—
F	0·50	0·61	0·46	−0·45	−0·56	−0·29	−0·48
Cl	0·46	0·56	0·46	−0·23	−0·33	−0·18	−0·35
Si(CH$_3$)$_3$	−0·10	−0·12	—	0·06	0·08	—	—
SOCH$_3$	0·50	0·61	—	0·00	−0·11	—	—
SCF$_3$	0·42	0·51	—	0·04	−0·05	—	—
SOCF$_3$	0·64	0·77	—	0·08	−0·06	—	—
SF$_5$	0·57	0·69	—	0·06	−0·06	—	—
CF$_3$	0·45	0·54	—	0·08	−0·01	—	—
SO$_2$CH$_3$	0·59	0·71	—	0·12	−0·01	—	—
CN	0·56	0·68	—	0·13	0·01	—	—
NO$_2$	0·65	0·79	0·65	0·15	0·01	0·16	0·00
COCH$_3$	0·28	0·34	—	0·16	0·10	—	—
COOR	0·30	0·36	—	0·14	0·08	—	—

[a] Revised values listed in ref.[4]; [b] only the scaling corrected according to Eq. (5); [c] calculated[6] by free fitting, model *1* (Table II); [d] calculated[4] using model *3*; [e] recalculated by us using model *5*; [f] recalculated by us using model *1*.

Most extensive calculations available were done[4] using the model *3*. They were based on an improved set of σ_I constants, specified in detail[4]; some typical values thereof are reproduced in Table III. The most important results were: *a*) the set of σ_R constants, which were positive for assumed acceptors and negative for donors, see Table III; *b*) the following values of λ for six basic set reactions: 1·00, 1·05, 1·04,

1·04, 0·91, 1·07, and the following ones for six other reactions: 0·95, 1·03, 1·07, 0·92, 1·05, 1·18; c) values of α from 0·25 to 0·76 (average 0·49) for the same reactions*. These results differ from those of this paper (Fig. 1) and of previous similar treatments[14−17] in two points: The λ's are lower and σ_R for acceptors have non-zero positive values. The modification of the above result is possible according to the equations in Table II, model 3; two degrees of freedom are available, corresponding to the arbitrary constants B and C. In the original calculation[4] these degrees of freedom were used to normalize the constants $(\varrho_I^p)_1 = (\varrho_R^p)_1 = 1$ for dissociation of benzoic acids in water. In this way B and C are determined and no further transformation is possible. However, while C is only a normalization factor not affecting the physical results, B is not. The constraint $(\varrho_I^p)_1 = 1$ attributed B a definite value and hence determined λ. This is caused by the rigorous presumption that σ_I constants are exactly on the same scale as σ_p. If this is not valid, the determined λ lacks any physical meaning.

Let us drop the above presumption, *i.e.* to proceed to model 5 (Table II) with one constant more (A) representing the scaling factor of σ_I. It is evident that A as well as C are now pure normalization factors which may be disposed of by the conditions $(\varrho_I^p)_1 = (\varrho_R^p)_1 = 1$. The constant B remains and may be used to modify the physical meaning of the results. We suggest the following transformations replacing the calculated constants σ_R, ϱ_I, ϱ_R and the separately determined σ_I by new constants σ_I', σ_R', ϱ_I', ϱ_R':

$$\sigma_I' = 1·210\sigma_I \qquad\qquad \varrho_I' = 0·826\varrho_I + 0·177\varrho_R,$$

$$\sigma_R' = 0·997\sigma_R - 0·214\sigma_I \qquad \varrho_R' = 1·003\varrho_R. \tag{5}$$

The equations are valid for ϱ_I^m, ϱ_R^m and ϱ_I^p, ϱ_R^p as well. The new values of σ_R' are listed in Table III. Four acceptor substituents, believed to be almost non-conjugated[14], have now zero values, three others slightly conjugated $(SF_5, SOCF_3, SCF_3)$ got less precise values near to zero. Also the negative σ_R for SCF_3 seems more reasonable than the previous positive one, while the σ_R constants for donor groups are not appreciably affected. The scaling of σ_I has to be modified in such a manner that all the values must be multiplied with 1·210 to be comparable with σ_p. Previously we derived[14] this factor to be 1·25. The values of λ have now changed to 1·12, 1·13, 1·10, 1·11, 0·95, 1·15 for the basic set and 1·02, 1·12, 1·14, 1·02, 1·20, 1·20 for other reactions; the average is 1·11. The values of α are unaltered. Hence all the results are now in complete agreement with our present and previous[14] conclusions reached by the direct approach.

Models 1 or 2 are apparently simpler and avoid the problem of obtaining and scaling σ_I's since these are determined by free fitting. On the other hand, there are less degrees

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* For two reactions the constants ϱ_R^m and hence also α are given quite differently in Tables XI and XXVII, respectively, of ref.[4]. This discrepancy does not affect further conclusions.

of freedom and a greater variety of possible transformations (Table II). The calculations according to model *1* were based[6] on 12 reaction series of the σ^0 type and on 5 substituents. The number of entries actually available was not given but if the data matrix were complete, there would be 120 entries to determine 54 independent parameters. The following results were obtained[6]: *a*) the sets of constant σ_I and σ_R listed in Table III, columns 4 and 7, respectively; *b*) values of λ from 0·86 to 1·27 (average 1·02), excluding one reaction appertaining virtually to the σ^- type; *c*) values of α from 0·36 to 0·86 (average 0·60). Again the σ_R constant for the nitro group is positive and the values of λ somewhat low. The allowed transformation of parameters (Table II) involve four arbitrary constants. Of these A and C are simply normalization factors and do not influence the main results. The task to choose B and φ in order to get physically meaningful results is rather difficult but for our purpose a partial solution is sufficient. We accepted the condition $\sigma'_R(NO_2) = 0$ and attributed the normalization factors A and C some reasonable values to get σ'_I and σ'_R approximately on their usual scale. The transformation equations obtained have the form:

$$\sigma'_I = \sigma_I + D\sigma_R \qquad\qquad \varrho'_I = 4{\cdot}05(\varrho_I + 0{\cdot}246\varrho_R)/(D + 4{\cdot}05),$$

$$\sigma'_R = 1{\cdot}20(\sigma_R - 0{\cdot}246\sigma_I) \qquad \varrho'_R = 3{\cdot}37(\varrho_R - D\varrho_I)/(D + 4{\cdot}05). \qquad (6)$$

and contain still one undetermined constant (D). This is probably small since the σ_I values (Table III) are reasonable. Fortunately both σ'_R and λ are independent of D and can be directly evaluated. The σ'_R values obtained are listed in Table III, last column and agree reasonably with the previous ones. The constants λ obtained for 11 reactions (excluding one reaction of the σ^- type) were from 0·96 to 1·21 with the average of 1·10 in good agreement with our findings, taking into account few degrees of freedom and complex calculations. The values of α remained undetermined since they depend on D; for small D they would not change appreciably.

The calculations according to the model 2 were carried out[6] on the same experimental basis as above and differed only in introducing the constraints of constant λ and α for all reaction series. Hence there are only 32 independent parameters to determine. The results[6] were similar: *a*) the constants σ_I and σ_R were identical as above; *b*) the common value of λ and α were determined to 0·939 and 0·563, respectively. The accuracy dropped about twice compared to model *1*. These results may be modified using again Eqs (6); one get σ_R's as above and the values of $\lambda = 1{\cdot}04 \pm \pm 0{\cdot}02$. The somewhat worse agreement with previous results may be connected with the mentioned presence of one reaction of the σ^- type which influences strongly the average value of λ.

Thus only the calculations[7] according to model *7* cannot be brought to accord with our findings but they are probably the least reliable. They were based on eight donor substituents and the constants σ^* were substituted for σ_I; hence the equations are valid neither for hydrogen nor for methyl since $\sigma^*(CH_3) = 0$. Omitting of acceptor substituents is certainly important, too, so that the value of $\lambda = 0{\cdot}77 \pm 0{\cdot}10$ cannot be given much credit.

DISCUSSION

The experimental results of this and some previous studies[14-17,20,21] may be summarized as follows: There is a group of substituents $(NO_2, CN, SO_2X, CHal_3, CH_2X, C{\equiv}CX, N{=}NAr, SCF_3, SOCF_3, SF_5$, only approximately also COX and COOR, mostly potential acceptors without an α electron pair) whose effects from the *meta* and *para* positions, respectively, are proportional with a good precision. This proportionality holds only unless another substituent (or reaction centre) of the donor type is present in a conjugated position. The proportionality constant $\lambda \cong 1.13 \pm 0.03$ express the greater effect in the *para* position. Its value is fairly constant as far as various reactions are concerned but may be somewhat solvent dependent[14,17]. In any case it is not caused only by preferential solvation in mixed solvents. Recent investigations[5,22] of the gas phase acidities and reactivities revealed close parallelism to water solutions and mixed solvents and it is rather the behaviour in pure aprotic solvents which shows some anomalies. (Note also some anomalous values of α, *e.g.* in benzene solution[4].)

The above facts must be taken into account in any interpretation of substituent effects in benzene derivatives. The simplest explanation[14], which still seems preferable to us, assumes that the mesomeric effects of the mentioned substituents are very small and may be even neglected in compounds like substituted benzoic acids. The constant λ then represents the relative intensity of the inductive effect in the *para* and *meta* positions, respectively, and may be explained in terms of the π-inductive effect[14]. This interpretation is supported by several recent findings[23-28] concerning the small up to negligible conjugation of some of the mentioned substituents; it also complies with Mulliken's theory of conjugation[29] and may be brought into accord with Taft's separation of inductive and mesomeric effects[3,4,6] as shown above. New problems arise particularly with the nitro group whose conjugation seemed to be proved by the arguments concerning the steric inhibition but even in this case the observed facts allow another interpretation[28].

The alternative explanation[30,31] assumes that the mesomeric (including hyperconjugative) effects of the mentioned substituents are perceptible but approximately proportional to their inductive effects. This is difficult to understand with substituents of so different structures but partly only a terminology problem is involved: If two effects are proportional for a half of possible substituents, they may be more reasonable named by a common term, say general inductive effect, and the term mesomeric should be reserved for the remaining substituents.

In our opinion, we must accept that the constants σ_R for almost all acceptor groups are virtually zero if determined from substituted benzoic acids and similar derivatives. Let us stress that this does not mean that these substituents are not capable of conjugation at all, but only that the conjugation is too small in the given compounds to be detected by the experimental approach used. The task is thus to search for a more

efficient model. The simplest possibility seems to be introducing of donor groups into the *para* position; in this way the σ_p^- and σ_R^- constants are defined[4], of course, only for acceptor substituents. In addition, the charge in the α-position in substituted anilinium ions represent a theoretical imperfection of this model.

Another consequence of the above findings concerns the conventional σ_I constants whose scaling is not exact. According to Eq. (5) their values should be multiplied by 1·210, or by 1·09 to be comparable with σ_p or σ_m, respectively. This correction does not affect the separate applicability of σ_I constants in various correlations. Concluding, we may confirm once more the statement that the inductive effect retains its relative magnitude in various systems, while for the mesomeric effect several scales are necessary and even these are applicable only to particular compounds. This is manifested also in the values of α which are much more variable than λ from one reaction to the other.

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