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A GENERAL ANALYSIS OF MESOMERIC ELECTRONIC EFFECTS OF SUBSTITUENTS IN AROMATIC SYSTEMS

R. Pollet and R. Van Poucke
Chemical Research Department
Gevaert-Agfa N.V.
Mortsel-Antwerp Belgium

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It was postulated by Hine(1) that the linearity of a plot between the Hammett σ_m and σ_p substituent constants constitutes a check of the general applicability of the Hammett equation, although, as he pointed out, the sigma values from the compilation of McDaniel and Brown (2) do not conform to this statement. Two years later, McDaniel demonstrated [3] that linearity only exists for groups containing a common first atom. In his review of linear free energy relationships, Wells [4] remarked that the basic assumptions and physical significance of this type of analysis are not yet fully understood.

In a recent paper of Exner [5], recognized to be extremely important [6], linearity is shown to apply to +R substituents (electron-withdrawing by resonance) and to substituents of the type $-CH_2X$. The most important conclusion drawn by Exner is that mesomeric effects in mesomeric electron-withdrawing substituents must be negligible.

In this paper we will discuss the deviation from linearity in the above-mentioned plots of -R substituents in benzoic acids, and also the positions of all the substituents of similar plots for systems such as substituted anilines, in which from the mesomeric point of view the reaction centre is electron-donating.

In FIG. 1 meta- and para-substituent constants taken from recent literature data [2,7,8] are plotted against each other. In this plot the substituents, electron-withdrawing by resonance, are linearly related :

$$\sigma_p = 1.142\,\sigma_m + 0.014$$

(correlation coefficient r : 0.993; standard deviation s : 0.033). All the -R substituents in FIG. 1 are situated below the line.

A nearly similar slope and a deviation for -R substituents in the same direction can be obtained for equilibrium data (9) of substituted phenylboric acids and seleninic acids. The result can probably be considered as relatively general, even when applied to different solvent systems and to kinetic data, as demonstrated by the results of Exner [5] and those mentioned in this paper. It has to be mentioned, however, that by a similar treatment of the equilibrium data

FIGURE I

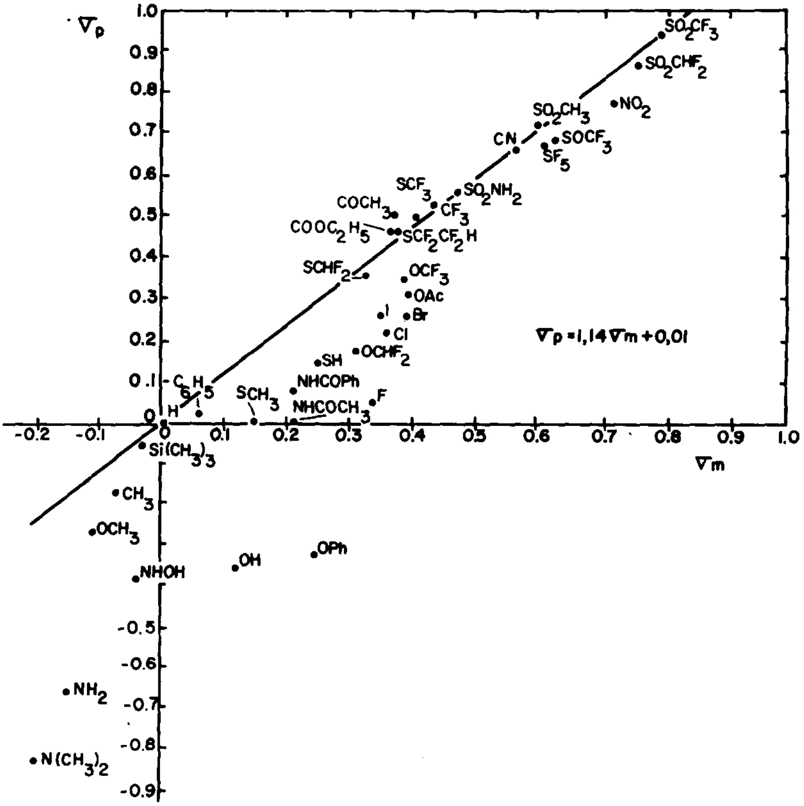

FIG. 1

of pyridines [10] we obtained the following linear relation by correlating the pKa data of the meta- and para-positions for the +R substituents (C_6H_5CO-, $-CN$, $-NO_2$, $-COOMe$) and H:

$$pKa^{para} = 0.916\ pKa^{meta} + 0.492$$

(r = 0.995; s = 0.168).

The value of the slope below unity certainly results here from a more effective transmittance of substituent effects from the meta-position than from the para-position.

Since we felt that the deviations of the -R substituents from linearity have to be a measure of resonance effects, we performed several analyses, one of which led to a very remarkable result. The deviation from linearity of the -R substituents in FIG. 1, parallel with the axis of ordinates and expressed in σ -units, can be symbolized by $\Delta\sigma_p$. By correlating the $\Delta\sigma_p$-values with the "unenhanced resonance parameters" σ_R^o of Taft [11], perfect linearity is obtained for the substituents of Table 1, (the $-N(CH_3)_2$ substituent being excepted), according to the following equation :

$$\Delta\sigma_p = 0.980\sigma_R^o - 0.006$$

$(r = 0.988;\ s = 0.023)$.

The equation, after inclusion of the $N(CH_3)_2$ substituent (σ_m-value of Jaffé [12]) becomes :

$$\Delta\sigma_p = 1.042 + 0.003$$

$(r = 0.988;\ s = 0.027)$.

The correlation is highly significant (0.1 per cent level according to student's t test).

The excellent concordance of the two sets of values is apparent from Table 1.

It is obvious from the identity of $\Delta\sigma_p$ and σ_R^o values, that "normal" resonance substituent parameters can be obtained for all substituents of substitued benzoic acids. For this purpose the pKa values of these acids (in water

TABLE I

Resonance parameters

Substituent	σ^{o}_{R} (a)	$\Delta\sigma_{p}$ (b)
$N(CH_3)_2$	-0.54	-0.60
NH_2	-0.48	-0.49
OCH_3	-0.41	-0.41
F	-0.35	-0.34
$NHCOCH_3$	-0.25	-0.25
SCH_3	-0.24	-0.19
Cl	-0.20	-0.21
Br	-0.19	-0.23
I	-0.12	-0.14
C_6H_5	-0.10	-0.09
CH_3	-0.[illegible]0	-0.10
H	0.00	-0.01

(a) From ref. (11).

(b) Calculated from the equations:

$$\Delta\sigma_{p} = \sigma_{p} - \sigma_{p}\text{ (calc.)}$$

$$\sigma_{p}\text{ calc.} = 1.142\ \sigma_{m} + 0.014$$

σ_m and σ_p-values are taken from ref. (2), except σ_m-$N(CH_3)_2$, taken from ref. (12), and σ_p-I, taken from ref. (8).

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at 25°) have to be known (either by direct measurement or by calculation)for both the meta- and the para-positions. Some $\Delta\sigma_{p}$ resonance parameters of substituents not mentioned in Table I are given in Table II.

TABLE II

Substituent (a)	$\Delta\sigma_p$ (b)	Substituent (a)	$\Delta\sigma_p$ (b)
NHOH	-0.36	$OCHF_2$	-0.19
$NHCOC_6H_5$	-0.18	OCF_3	-0.10
OH	-0.52	$OCOCH_3$	-0.09
OC_6H_5	-0.33	SH	-0.15

(a) Substituent constants needed for the calculations are taken from ref. (2), (7a and d) and (12).

(b) See Table I foot note (b).

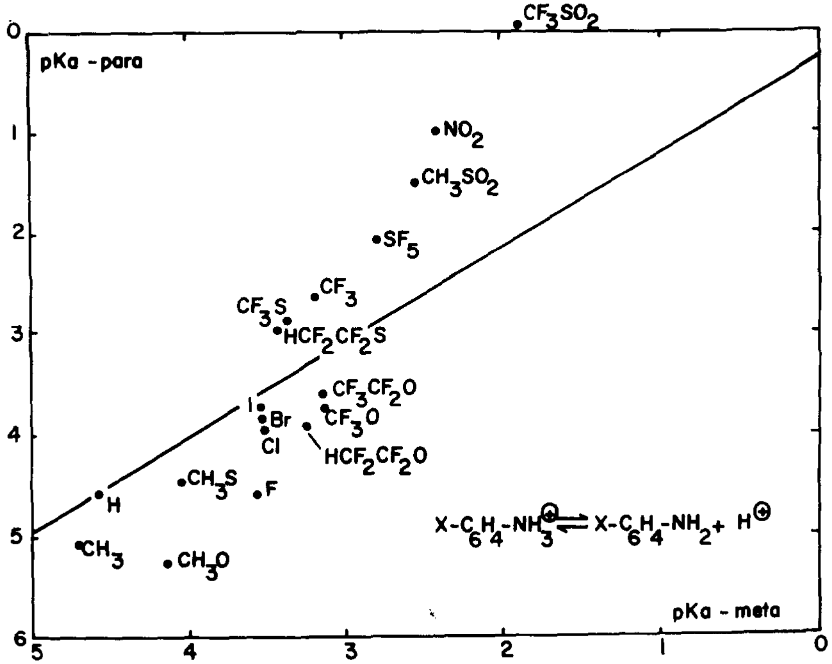
In other solvent systems [i.e. 50 % ethanol or 80 % ethyleneglycolmonomethylether (Methylcellosolve)] the ΔpKa para values, which are analogous to the $\Delta\sigma_p$ values, are also related to the σ^o_R values, although not linearly.

In order to evaluate resonance effects in every type of reaction one can plot equilibrium data (log K) or kinetic date (log k) for para-substituents against the same data for meta-substituents. In this analysis the +R substituents must be linearly related and the deviation from linearity of the -R substituents must be a measure of resonance effects.

We should like to mention that in the plots of any systems we investigated, the position of the CH_3 substituent is indicative for a hyperconjugative effect.

Turning our attention to systems with a mesomeric electron-donating reaction center, linearity of a meta-para plot for -R substituents could be expected. Such a result, although only for well defined classes of substituents, has been obtained with respect to fluorine nuclear magnetic resonance shielding in meta- and para-substitued fluorobenzenes [13]. A plot of pKa-para against pKa-meta values for substituted anilines (7b)(14) is presented in FIG. 2.

FIGURE II



Because linearity could not be observed, we drew a line of slope 1.14 through the point for the hydrogen substituent. By this procedure the +R substituents (above the line) are perfectly separated from the -R substituents (below the line), without any exception, and this also constitutes an extremely interesting result. One could suppose that all the points should be situated on the line; the +R substituents, however, deviate because of direct conjugation with the reaction centre and the -R substituents as a result of the well known "saturation" or "leveled" effects (15) The same result can be obtained by using pKa data of phenols, thiophenols and even phenylacetic acids. This supports the suggestion of Taft (16) that σ^n values (15) for mesomeric electron-donating groups are too low. The following conclusions can be drawn from the studies to which we referred and from the results presented in this paper.

(1) A linear correlation of points in a $\sigma_p - \sigma_m$ plot or a pKa para-pKa meta plot constitutes a linear free energy relationship, in which only polar effects, in the sense of a Taft equation (17), are operative. One of the two following conditions must be fulfilled for an exclusive operation of polar effects :

   a) Somewhere in the molecule conjugative effects must be blocked : this probably happens in substituents such as $X{-}CH_2{-}$, X-CO-, $X{-}SO_2{-}$, $X_3C{-}O{-}$, $X_3C{-}S{-}$, $X_3C{-}SO_2$.

   b) Both the substituent and the reaction centre in the aromatic system must be electron-withdrawing, by resonance. This according to the results obtained, excludes the appearance of mesomeric effects involving both groups simultaneously.

2) The so-called saturation effect is operating in every aromatic system containing two -R substituents. A

conjugative interaction exists here, due to an uninterrupted π -electron system, resulting in the non-applicability of a linear free energy relationship between meta- and para-data, which must be determined solely by polar effects.

3) For the applicability of the Hammett equation to the equilibrium or kinetic data of a given aromatic system, a linear meta-para relation must exist in the latter for +R substituents, and the deviations from linearity of the -R substituents must be of the same importance as for substituted benzoic acids.

4) A quantitative study of resonance effects for +R as well as for -R substituents, must be possible by using the method described in this paper. A similar treatment of data for heterocyclic systems that can be substituted at two positions with respect to the reaction center would also be interesting.

Further investigation of the principles exposed here is in progress.

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