PLURILINEAR IMPROVEMENT OF THE HAMMETT EQUATION

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The original Hammett equation, $\Delta = \rho\sigma$, is transformed in a constrained tetralinear relationship where each straight line with variable intercept term correlates one of the following four groups or subsets of dipolar substituents: normal and special substituents (depending on the absence or the presence of a lone electron pair in their atom next to the aromatic ring) and, in each of these classes, separating *meta* and *para* derivatives. There are a total of four fitting parameters in the resulting plurilinear Hammettian transformation (PHT) from which the statistically corrected parameters λ and γ are derived; λ and γ are the asymptotic values in a hyperbolic model for the representation of Δ_4 vs Δ_4/Δ_3. This *meta–para* interrelationship is assumed to hold in the absence of through-resonance effects which, in turn, are allowed for by the use of alternative sigma scales of substituent constants. By applying the PHT to a large number of selected literature data, parameters λ and γ are determined for the ionization equilibria of 3- and 4-monosubstituted benzoic acids, anilinium ions, phenols and pyridinium ions. In these reactions series, parameter λ, which measures the *para/meta* ratio of field/inductive effects, is lower than unity and shows a marked dependence on the basic molecular framework. It is best modelled in terms of a through-space field effect approach. The ratio γ/γ^0, where γ^0 is referred to the unified sigma-zero scale, is shown to correspond to the original Hammett's reaction constant ρ. It is concluded that the PHT constitutes an improved Hammett equation for the analysis of substituent effects in benzene derivatives taking into account statistical errors and making allowance for different transmission coefficients for the field/inductive effect from *meta* and *para* positions in different reaction series.

INTRODUCTION

Hammettian equations

It can be said that correlation studies involving *meta*- and *para*-substituted benzene derivatives were central in the development of linear Gibbs energy relationships. They were undoubtedly at the origin of the Hammett equation.[1] Employing the symbol Δ to represent the experimental effect of a given substituent with respect to the parent compound,[2,3] the original Hammett equation is represented by the straight line passing through the origin:

$$\Delta = \rho\sigma \tag{1}$$

whose slope ρ depends on the reaction series and experimental conditions and where σ is a position-dependent substituent constant.

Refinements of the simple equation (1) were described by Exner[4] and by Shorter.[5] Two main trends are now highlighted. For one, different scales of sigma constants were introduced to account for the proper reactivity of limited classes of aromatic compounds. For another, several multiparametric extensions were devised, aimed at embracing a broader spectrum of reactions. In these developments the question arose of whether an extra term expressing the unavoidable

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inaccuracy of any statistical correlation must be included in all the equations. Shorter presents a lively discussion on this question (Ref. 5, pp. 209–213). If so, the first modification of the Hammett equation is then to add an intercept term δ so that

$$\Delta = \delta + \rho\sigma \tag{2}$$

Although the modern trend is towards multiparametric extensions of equations (1)[6] and (2),[7] in this work we regress to these basic equations and explore a plurilinear approach to their refinement. The first step along this line of investigation goes back to the late 1950s when Hine[8] suggested that there may exist reaction series for which *meta* and *para* derivatives lie on two separate lines. That ρ_3 and ρ_4 need not be measures of the same quantity was statistically validated by Jaffé,[9] and it is now recognized that *meta* and *para* derivatives should be processed separately.[10] Hence, the first plurilinear improvement of the Hammett equation reads

$$\Delta_3 = \delta_3 + \rho_3\sigma_3 \tag{3}$$

$$\Delta_4 = \delta_4 + \rho_4\sigma_4 \tag{4}$$

and we shall refer to the corresponding error-free equations as theoretical relationships.

Meta–para interrelationships

McDaniel's examination[11] of the interrelationship between *meta* and *para* substituent sigma constants stems from Hine's theoretical analysis[8] of equation (1). This and subsequent advances were reviewed by Exner[12] and Shorter.[13] Since these reviews, Pytela[14,15] has re-examined the problem with benzoic acid derivatives by using methods of analysis of latent variables. This author[14] proposes a bundle of three straight lines to interrelate optimized *meta* and *para* substituent constants, one of which corresponds to Exner's equation.[4,12] More recently, based on the unified σ_0-scale,[16] we demonstrated[17] that the appropriate framework to describe the *meta–para* interrelationship of σ^0 constants is the representation σ_4^0 vs σ_4^0/σ_3^0. Substituents were separated into two broad classes according to whether or not they have a pair of lone electrons in the atom next to the benzene ring. The former are named special (s) and the latter, following Exner,[12] normal (n). Then each class was correlated by the appropriate one of the following pair of conjugate rectangular hyperbolae:

$$\sigma_{4n}^0 = \frac{\gamma^0\sigma_{4n}^0/\sigma_{3n}^0 + \varepsilon_n^0}{\sigma_{4n}^0/\sigma_{3n}^0 - \lambda^0} \tag{5}$$

$$\sigma_{4s}^0 = \frac{\gamma^0\sigma_{4s}^0/\sigma_{3s}^0 + \varepsilon_s^0}{\sigma_{4s}^0/\sigma_{3s}^0 - \lambda^0} \tag{6}$$

These conjugate hyperbolae have the common asymptotes $\sigma_4^0/\sigma_3^0 = \lambda^0$ and $\sigma_4^0 = \gamma^0$, which are subjected to the condition

$$\varepsilon_n^0 + \varepsilon_s^0 = -2\gamma^0\lambda^0 \tag{7}$$

In this model σ_3^0 can be explicited as a function of σ_4^0, but the reverse is not true.

In both equations (5) and (6), correlation errors are taken care of by the parameter ε^0. The corresponding theoretical equations are[17]

$$\sigma_{4n}^0(\sigma_{4n}^0 - \gamma^0)/(\sigma_{4n}^0 - 2\gamma^0) = \lambda^0\sigma_{3n}^0 \tag{8}$$

$$\sigma_{4s}^0 = \gamma^0 + \lambda^0\sigma_{3s}^0 \tag{9}$$

It is interesting that equations (8) and (9) can be written in the compact form

$$(\sigma_4^0 - \gamma^0)(\sigma_4^0/\sigma_3^0 - \lambda^0) = \pm\gamma^0\lambda^0 \tag{10}$$

with the plus sign applying to special substituents and the minus sign to normal substituents.

It was further shown[17] that parameter λ^0 is equal to the *para/meta* ratio of transmission coefficients for non-mesomeric or inductive effects, whereas parameter γ^0 is related to limiting values for mesomeric or resonance effects.

The aim of this work is to extent the Hammettian equations (3) and (4) as far as allowed by compliance with our hyperbolic model for the *meta–para* interrelationship. To this end, we resort to extensive literature data on typical ionization reaction series in water and aqueous solvents at 25 °C.

THEORETICAL

General *meta–para* interrelationship

Let us assume that, in the absence of direct or through-resonance effects, the general *meta–para* interrelationship in a given benzene compound conforms to a hyperbolic model similar to that found[17] for the sigma-zero scale. Therefore, the hyperbolic model for the general case is constituted by two conjugate rectangular hyperbolae with asymptotes defined by $\Delta_4/\Delta_3 = \lambda$ and $\Delta_4 = \gamma$, so that the model equations are

$$\Delta_{4n} = \frac{\gamma\Delta_{4n}/\Delta_{3n} + \varepsilon_n}{\Delta_{4n}/\Delta_{3n} - \lambda} \tag{11}$$

$$\Delta_{4s} = \frac{\gamma\Delta_{4s}/\Delta_{3s} + \varepsilon_s}{\Delta_{4s}/\Delta_{3s} - \lambda} \tag{12}$$

$$\varepsilon_n + \varepsilon_s = -2\gamma\lambda \tag{13}$$

Equation (13) expresses the condition for conjugate n and s hyperbolae.

It follows from algebraic restrictions[17] to the exact values for Δ_4 and Δ_4/Δ_3 that $\varepsilon_s^{th} = 0$ and $\varepsilon_n^{th} - 2\gamma\lambda$.

Substitution of these theoretical values into equations (11) and (12) yields

$$\Delta_{4n}(\Delta_{4n} - \gamma)/(\Delta_{4n} - 2\gamma) = \lambda\Delta_{3n} \qquad (14)$$

$$\Delta_{4s} = \gamma + \lambda\Delta_{3s} \qquad (15)$$

which can be condensed to the analogue of equation (10):

$$(\Delta_4 - \gamma)(\Delta_4/\Delta_3 - \lambda) = \pm \gamma\lambda$$

with the plus sign applying to special substituents and the minus sign to normal substituents.

Plurilinear Hammettian transformation

General case

We now consider the following Hammettian transformation:

$$\Delta_{3n} = \delta_{3n} + \rho_{3n}\sigma_{3n}^0 \qquad (16)$$

$$\Delta_{4n} = \delta_{4n} + \rho_{4n}\sigma_{4n}^0 \qquad (17)$$

$$\Delta_{3s} = \delta_{3s} + \rho_{3s}\sigma_{3s}^0 \qquad (18)$$

$$\Delta_{4s} = \delta_{4s} + \rho_{4s}\sigma_{4s}^0 \qquad (19)$$

where ρ and δ are constants. It should be noted that the plurilinear transformation constituted by equations (16)–(19) is very general. In fact, it can account for differences in substituent effects between normal and special classes, between *meta* and *para* positions, and it allows correlations with a non-zero intercept.

Next we establish the conditions under which this transformation is consistent with the general *meta–para* interrelationship in benzene derivatives.

Rectangular hyperbolae equations (5) and (6) are of the form

$$\sigma_4^{0^2} - \lambda^0\sigma_3^0\sigma_4^0 - \gamma^0\sigma_4^0 - \varepsilon^0\sigma_3^0 = 0 \qquad (20)$$

Solving equations (16) and (17) [or equations (18) and (19)] for σ_{3n}^0 and σ_{4n}^0 (or for σ_{3s}^0 and σ_{4s}^0), respectively, and inserting the resulting expressions into equation (20) leads to two identical equations for normal and for special substituents having the form

$$\Delta_4^2 - (\rho_4/\rho_3)\lambda^0\Delta_3\Delta_4 - [2\delta_4 - \delta_3(\rho_4/\rho_3)\lambda^0 + \rho_4\gamma^0]\Delta_4$$
$$+ (\rho_4/\rho_3)(\delta_4\lambda^0 - \rho_4\varepsilon^0)\Delta_3 + \delta_4(\delta_4 + \rho_4\gamma^0)$$
$$- \delta_3(\rho_4/\rho_3)(\delta_4\lambda^0 - \rho_4\varepsilon^0) = 0 \qquad (21)$$

On the other hand, equations (11) and (12) can be written as

$$\Delta_4^2 - \lambda\Delta_3\Delta_4 - \gamma\Delta_4 - \varepsilon\Delta_3 = 0 \qquad (22)$$

Relating the parameters in equation (22) with the corresponding parameters in equation (21), and bearing in the mind the assumption of conjugate n and s rectangular hyperbolae, gives

$$\lambda = (\rho_4/\rho_3)\lambda^0 \qquad (23)$$

$$\gamma = 2\delta_4 - \delta_3(\rho_4/\rho_3)\lambda^0 + \rho_4\gamma^0 \qquad (24)$$

$$\varepsilon = -(\rho_4/\rho_3)(\delta_4\lambda^0 - \rho_4\varepsilon^0) \qquad (25)$$

$$0 = \delta_4(\delta_4 + \rho_4\gamma^0) - \delta_3(\rho_4/\rho_3)(\delta_4\lambda^0 - \rho_4\varepsilon^0) \qquad (26)$$

We note that equation (26) expressing the condition for rectangular hyperbolae establishes a dependence between δ_3 and δ_4.

Equations (23)–(26) apply separately to normal and to special substituents. However, the common asymptotic value λ for n and s hyperbolae implies the important constraint

$$\rho_{4n}/\rho_{3n} = \rho_{4s}/\rho_{3s} \qquad (27)$$

It can be further shown that the condition for conjugate n and s hyperbolae expressed by equation (13) is satisfied when ε_n and ε_s are given by equation (25) and common asymptotic values λ and γ by equations (23) and (24), respectively. As a result, the following equation is obtained:

$$\delta_{4s} = 3\delta_{4n} - 2\delta_{3n}\lambda + (\rho_{4s} - \rho_{4n})\varepsilon_s^0/\lambda^0 \qquad (28)$$

in addition to an analogous equation with interchanged subscripts n and s.

Our approach to linear Gibbs energy relationships (LGER) *between* different reactions series of benzene compounds substituted in the *meta* or *para* positions is now clarified. We assume that only LGER consistent with our hyperbolic model for the *meta–para* interrelationship *within* each reaction series are allowed. Although the plurilinear Hammettian transformation constituted by equations (16)–(19) contains eight parameters, we derived four independent equations linking some of these parameters, namely equation (26) applied separately to normal and to special substituents, and equations (27) and (28). Consequently, this general transformation contains four independent parameters.

The present plurilinear Hammettian transformation is based on the sigma-zero scale of substituent constants because it was assumed that no through-resonance effect was operating. However, these effects are important in many benzenoid systems of interest. We shall deal with this problem by resorting to the conventional sigma scales for benzoic acid, minus and plus reactivities on the supposition that the only consequence of using these scales is to counterbalance through-resonance effects.

Theoretical case

From the theoretical point of view, the hyperbolic model equations of interest are equations (8) and (9) for the standard system and equations (14) and (15) for the reaction series under investigation. The corresponding plurilinear transformation is also subjected to some algebraic restrictions. Thus, since we have identified[17] hydrogen as a normal substituent, then $\delta_{3n}^{th} = \delta_{4n}^{th} = 0$ and, from equation (24), $\gamma_n^{th} = \rho_{4n}^{th}\gamma^0$. Additionally, in view

of equation (25), the conditions $\varepsilon_s^{0th} = \varepsilon_s^{th} = 0$ imply $\delta_{4s}^{th} = 0$, so that

$$\gamma_s^{th} = -\delta_{3s}^{th}(\rho_4/\rho_3)\lambda^0 + \rho_{4s}^{th}\gamma^0 \qquad (29)$$

Lastly, the requirement for conjugate n and s hyperbolae, $\gamma_n^{th} = \gamma_s^{th}$, leads to

$$\rho_{3n}^{th} - \rho_{3s}^{th} = -\delta_{3s}^{th}\lambda^0/\gamma^0 \qquad (30)$$

Since the ratio λ^0/γ^0 is negative,[17] equation (30) shows that δ_{3s}^{th} and the difference $\rho_{3n}^{th} - \rho_{3s}^{th}$ have the same sign. We observe that the plurilinear Hammettian transformation is consistent with error-free data for which $\rho_{3n} \neq \rho_{3s}$ and $\rho_{4n} \neq \rho_{4s}$.

Dual electronic effect and the hyperbolic model

Taft equations in the form

$$\sigma_3^0 = \rho_{3M}^0 M + \rho_{3N}^0 N \qquad (31)$$

$$\sigma_4^0 = M + N \qquad (32)$$

were used previously[17] to separate mesomeric (M) and non-mesomeric (N) contributions to σ^0 constants. It was then shown that $\gamma_n^0 = \gamma_s^0$ required transmission coefficients appearing in equations (31) and (32) to have identical values for normal and special substituents. However, separating M and N effects in the general case may necessitate the use of the following equations:

$$\Delta_{3n} = \rho_{3M,n} M + \rho_{3N,n} N \qquad (33)$$

$$\Delta_{4n} = \rho_{4M,n} M + \rho_{4N,n} N \qquad (34)$$

$$\Delta_{3s} = \rho_{3M,s} M + \rho_{3N,s} N \qquad (35)$$

$$\Delta_{4s} = \rho_{4M,s} M + \rho_{4N,s} N \qquad (36)$$

We note that equations (33)–(36), in addition to equations (31) and (32), are theoretical expressions in the sense that they do not contain statistical error terms. Therefore, in the present analysis we shall use the error-free two-parameter hyperbolic model equations (8), (9), (14) and (15).

Dropping the upperscript th, the relevant equations for the theoretical plurilinear transformation are

$$\Delta_{3n} = \rho_{3n} \sigma_{3n}^0 \qquad (37)$$

$$\Delta_{4n} = \rho_{4n} \sigma_{4n}^0 \qquad (38)$$

$$\Delta_{3s} = \delta_{3s} + \rho_{3s} \sigma_{3s}^0 \qquad (39)$$

$$\Delta_{4s} = \rho_{4s} \sigma_{4s}^0 \qquad (40)$$

$$\rho_{4n}/\rho_{3n} = \rho_{4s}/\rho_{3s} \qquad (27)$$

$$\delta_{3s} = (\rho_{3s} - \rho_{3n})\gamma^0/\lambda_0 \qquad (41)$$

Hence this transformation is constituted by four equations with five unknown parameters of which only three are independent.

It has been shown that[17]

$$\lambda^0 = 1/\rho_{3N}^0 \qquad (42)$$

By an analogous procedure one finds

$$\lambda = \rho_{4N,n}/\rho_{3N,n} = \rho_{4N,s}/\rho_{3N,s} \qquad (43)$$

Taft's transmission coefficients appearing in equations (33)–(36) can be expressed in terms of the PHT parameters in equations (37)–(40). The resulting relationships [equations (44)–(55)] are presented in Table 1.

Expressions for γ in terms of Taft's transmission coefficients are readily derived from equations (24), (46) and (47), giving

$$\gamma = \rho_{4M,n} \gamma^0 = \rho_{4N,n} \gamma^0 \qquad (56)$$

Let us pause to comment on these results. If the conventional Taft equations for *meta* and *para* derivatives are applied separately to normal and to special substituents as in equations (33)–(36), then there are eight transmission coefficients to be determined in this system of four equations. However, as a consequence of the theoretical *meta–para* interrelationship, we have derived equations (43) and (52)–(55) (see Table 1) expressing constraints among these parameters. We therefore have a system of four equations with eight unknown quantities, of which only three are independent parameters. This should be compared with the four equations with five unknown quantities of which three are independent that constitute the theoretical plurilinear Hammettian transformation proposed here. Further, equations (44)–(51) (see Table 1) provide direct links between the two sets of parameters. In other words, our plurilinear approach to LGER calls for, and is consistent

Table 1. Expressions for Taft's transmission coefficients in equations (33)–(36)

Normal substituents		Special substituents		Constraints	
$\rho_{3M,n} = \rho_{3n}\rho_{3M}^0$	(44)	$\rho_{3M,s} = \rho_{3s}/\lambda^0 - \rho_{3n}(1 - \lambda^0\rho_{3M}^0)/\lambda^0$	(48)	$\rho_{4N,n}/\rho_{3N,n} = \rho_{4N,s}/\rho_{3N,s}$	(43)
$\rho_{3N,n} = \rho_{3n}/\lambda^0$	(45)	$\rho_{3N,s} = \rho_{3s}/\lambda^0$	(49)	$\rho_{3M,n} = \rho_{3N,n}\lambda^0\rho_{3M}^0$	(52)
$\rho_{4M,n} = \rho_{4n}$	(46)	$\rho_{4M,s} = \rho_{4s}$	(50)	$\rho_{4M,n} = \rho_{4N,n}$	(53)
$\rho_{4N,n} = \rho_{4n}$	(47)	$\rho_{4N,s} = \rho_{4s}$	(51)	$\rho_{3M,s} = \rho_{3N,s} - \rho_{3N,n}(1 - \lambda^0\rho_{3M}^0)$	(54)
				$\rho_{4M,s} = \rho_{4N,s}$	(55)

with, duplicate Taft equations for normal and special substituents while showing that Taft's four original parameters cannot all be independent.

RESULTS

Data selection

Guided chiefly by Perrin's tables,[18,19] relative dissociation constants of several *meta*- and *para*-monosubstituted benzenoid acids in water and aqueous solvents at 298 K were collected from the primary literature. Only those substituents used in our analysis[17] of the unified sigma-zero scale[16] were considered. Experimental Δ values are defined as $\Delta = \Delta pK_a = pK_a(H) - pK_a(X)$. Preference was given to ΔpK_a data where values for both substituted (X) and unsubstituted (H) compounds were determined by the same authors and the same method. Data were used as reported and no attempt was made to correct values to zero ionic strength. However, it is well known[20] that if both measurements are made at the same ionic strength, its effect is cancelled by subtraction. Further, ΔpK_a values for these processes are insensitive to differences in temperature of less than 5 °C. The collected data were then slimmed by referring to the least number of research laboratories while covering the maximum number of substituents under study. In the event of having more than one datum for a given substituent, an average value rounded off to the nearest 0.005 unit was taken. We believe that this unbiased selection procedure minimizes inconsistencies arising from the different ΔpK_a values obtained by different authors. Data employed in the present analysis and respective literature sources are recorded in Table 2. Some specific details are as follows.

Sigma constants

Although some compilations of sigma constants are available,[55-57] for the scales sigma-benzoic acid reactivity (σ_4^{BA}), sigma-plus reactivity (σ_4^+) and sigma-minus reactivity (σ_4^-), we preferred the values selected by Exner (Ref. 4, pp. 61–62).

Benzoic acid

Ionization constants for 18 *meta*- and 18 *para*-substituted benzoic acids in 50% (v/v) ethanol–water (BA/50 E-W) and 17 *meta*- and 17 *para*-substituted benzoic acids in 80% (w/w) 2-methoxyethanol—water (BA/80 ME-W) were taken from the tables organized by Exner and co-workers[21-23] which include a few data from other authors.

Anilinium ion

Ionization constants for 20 *meta*- and 21 *para*-substi-

tuted anilinium ions in water were taken from various authors.[24,27,31-34,37,40,45,48] The value for pK_a (3-CO$_2$H) reported by Vandenbelt *et al.*[27] and leading to $\Delta pK_a = 1.66$ was excluded.

Phenol

Ionization constants for 18 *meta*- and 18 *para*-substituted phenols in water were taken from various authors.[25,34,35,41,42,44,46,50,51,53] The substituents NH$_2$, OH and CO$_2$H were not considered in this analysis.

Pyridinium ion

Ionization constants for 21 *meta*- and 20 *para*-substituted pyridinium ions were taken from various authors.[20,26,28-30,36,38,39,43,47,49,52,54] The substituents 4-OH, -CO$_2$H and -CHO were excluded from this analysis.

Fitting experiments

The correlation analysis of experimental data by the plurilinear Hammettian transformation consists of a least-squares regression involving eight unknown quantities, of which only four are independent, in a constrained fitting. The general-purpose optimization program used previously,[17] which is based on the Luus–Jaakola method,[58] was adapted to the present problem. The residual sum of squares (*RSS*) to the fitting of equations (16)–(19) is written in the form

$$RSS = \Sigma_{3n}(\Delta_{3n} - \delta_{3n} - \rho_{3n}\sigma_{3n}^0)^2$$
$$+ \Sigma_{4n}[\Delta_{4n} - \delta_{4n} - (\rho_4/\rho_3)\rho_{3n}\sigma_{4n}]^2$$
$$+ \Sigma_{3s}(\Delta_{3s} - \delta_{3s} - \rho_{3s}\sigma_{3s}^0)^2$$
$$+ \Sigma_{4s}[\Delta_{4s} - \delta_{4s} - (\rho_4/\rho_3)\rho_{3s}\sigma_{4s}]^2 \qquad (57)$$

where σ_{4n} and σ_{4s} represent σ_4^0, σ_4^{BA}, σ_4^- or σ_4^+ as appropriate.

We chose ρ_{3n}, ρ_{3s}, ρ_4/ρ_3 and δ_{4n} as the four independent parameters in equation (57), the other unknown quantities being calculated by

$$\delta_{3n} = \frac{\delta_{4n}[\delta_{4n} + (\rho_4/\rho_3)\rho_{3n}\gamma^0]}{(\rho_4/\rho_3)[\delta_{4n}\lambda^0 - (\rho_4/\rho_3)\rho_{3n}\varepsilon_n^0]} \qquad (58)$$

$$\delta_{4s} = 3\delta_{4n} - 2\delta_{3n}(\rho_4/\rho_3)\lambda^0 + (\rho_4/\rho_3)(\rho_{3s} - \rho_{3n})\varepsilon_s^0/\lambda^0 \qquad (59)$$

$$\delta_{3s} = \frac{\delta_{4s}[\delta_{4s} + (\rho_4/\rho_3)\rho_{3s}\gamma^0]}{(\rho_4/\rho_3)[\delta_{4s}\lambda^0 - (\rho_4/\rho_3)\rho_{3s}\varepsilon_s^0]} \qquad (60)$$

Values for the numerical constants are[17] $\lambda^0 = 0.9602$, $\lambda^0 = -0.2252$, $\varepsilon_n^0 = 0.3416$ and $\varepsilon_s^0 = 0.0909$.

We note that equations (58) and (60) are specialized forms of equation (26), and that equation (59) follows from equation (28).

Table 2. Sigma constants and data for ΔpK_a at 298 K used in this work

No. substituent	Sigma constants[a]					BA/50 E-W[b]		BA/80 ME-W[c]		Anilimium[d]		Phenol[e]		Pyridinium[f]	
	σ^0_3	σ^0_4	σ^{BA}_4	σ^-_4	σ^+_4	Δ_3	Δ_4	Δ_3	Δ_4	Δ_3	Δ_4	Δ_3	Δ_4	Δ_3	Δ_4
Special															
1 N(CH$_3$)$_2$	−0.095	−0.317	−0.63	g	−1.70	−0.20	−1.03	−0.27	−1.05	−	(−2.01)[h]	0.13[i]	−0.24[i]	−1.25[j]	−4.40[j]
2 NH$_2$	−0.087	−0.295	−0.57	g	−1.30	−0.08	−0.785	−0.28	−1.105	−0.33[k]	−1.53[k]	−	−	−0.795[l]	−3.925[m]
3 OH	0.023	−0.221	−0.38	g	−	0.01	−0.445	−0.085	−0.63	0.37[k]	−0.98[k]	−	−	0.40[n]	−
4 OCH$_3$	0.102	−0.120	−0.28	g	−0.78	0.12	−0.255	0.055	−0.385	0.39[o]	−0.725[p]	0.34[q]	−0.215[q]	0.43[r]	−1.38[s]
5 NHAc	0.144	0.002	−0.09	g	−0.60	0.235	−0.06	0.205	−0.12	−	−	−	−	0.86[i]	−0.55[u]
6 SCH$_3$	0.142	0.063	0.00	g	−0.60	−	−	−	−	0.57[v]	0.22[v]	0.56[i]	0.51[i]	0.78[w]	−0.74[w]
7 F	0.335	0.151	0.06	g	−0.07	−	−	−	−	1.075[x]	0.02[v]	0.79[z]	0.09[z]	2.20[aa]	−
8 Cl	0.365	0.242	0.22	g	0.11	0.49	0.46	0.65	0.50	1.125[hh]	0.64[cc]	0.885[q]	0.57[q]	2.365[dd]	1.38[r]
9 Br	0.369	0.265	0.22	g	0.15	0.51	0.34	0.69	0.53	1.16[cc]	0.745[cc]	0.97[q]	0.64[q]	2.345[dd]	1.46[r]
10 I	0.343	0.277	0.21	g	0.13	0.45	0.36	0.60	0.48	1.05[cc]	0.845[cc]	0.94[z]	0.69[i]	1.92[aa]	−
Normal															
11 C(CH$_3$)$_3$	−0.087	−0.150	g	g	−0.26	−	−	−	−	−0.07[cc]	−	−0.08[ff]	−0.23[gg]	−0.65[hh]	−0.82[hh]
12 CH$_3$	−0.062	−0.135	g	g	−0.31	−0.185	−0.26	−0.15	−0.20	−0.11[ii]	−0.475[v]	−0.095[ii]	−0.265[ii]	−0.50[jj]	−0.83[jj]
13 CH(CH$_3$)$_2$	−0.082	−0.132	g	g	−0.28	−	−	−	−	−0.08[cc]	−	−	−	−0.55[hh]	−0.84[kk]
14 C$_2$H$_5$	−0.077	−0.127	g	g	−0.30	−	−	−	−	−0.11[cc]	−0.37[v]	−0.07[ll]	−0.21[ll]	−0.53[hh]	−0.835[kk]
15 CH$_2$Ph	−0.047	−0.058	g	g	−0.27	−0.12	−0.16	−0.13	−0.11	−	−	−	−	−	−0.38[r]
0 H	0	0	g	g	g	0	0	0	0	0	0	0	0	0	0
16 Ph	0.041	0.051	0.02	0.08	−0.18	−	−	−	−	0.42[mm]	0.31[nn]	0.30[oo]	0.38[oo]	0.61[pp]	−0.14[r]
17 CO$_2$H	0.356	0.440	g	0.78	g	−	−	0.54	0.70	−	2.27[k]	−	−	−	−
18 CO$_2$R	0.349	0.441	g	0.74	g	0.60	0.72	−	−	1.05[x]	2.14[v]	0.90[ff]	1.50[gg]	2.12[r]	1.72[r]
19 COPh	0.362	0.456	g	0.86	g	0.55	0.67	0.53	0.68	−	2.43[qq]	−	−	2.03[r]	1.86[r]
20 COCH$_3$	0.360	0.469	g	0.82	g	0.52	0.63	−	−	1.055[rr]	2.48[k]	0.79[ss]	1.93[ss]	1.95[u]	1.70[r]
21 CHO	0.410	0.473	g	0.94	g	−	−	−	−	−	2.91[k]	1.065[ff]	2.395[gg]	−	−
22 CF$_3$	0.464	0.538	g	0.62	g	0.64	0.80	0.78	0.91	1.36[uu]	1.81[uu]	1.05[vv]	1.325[vv]	2.75[ww]	2.58[ww]
23 SO$_2$NH$_2$	0.578	0.582	g	0.89	g	0.83	0.87	0.86	0.93	1.83[k]	−	−	−	−	−
24 CN	0.622	0.714	g	0.99	g	0.88	0.95	1.065	1.11	1.865[xx]	2.921[cc]	1.43[yy]	2.03[yy]	3.85[zz]	3.35[r]
25 SO$_2$CH$_3$	0.685	0.728	g	1.05	g	0.96	1.07	0.97	1.14	2.035[aaa]	3.23[aaa]	1.58[ss]	2.15[ss]	−	3.61[bbb]
26 NO$_2$	0.713	0.814	g	1.25	g	0.94	1.10	1.16	1.34	2.15[bb]	3.605[cc]	1.605[q]	2.835[q]	4.03[r]	3.82[r]

[a] σ^0 constants from Ref. 16; σ^{BA}_4, σ^-_4 and σ^+_4 constants from Ref. 4, pp. 61–62.
[b] Ionization of substituted benzoic acids in 50% (v/v) ethanol–water mixture. Data from Refs 21–23 and references therein.
[c] Ionization of substituted benzoic acids in 80% (w/w) 2-methoxyethanol–water mixture. Data from Refs 21–23 and references therein.
[d] Ionization of substituted anilinium ions in water.
[e] Ionization of substituted phenols in water.
[f] Ionization of substituted pyridinium ions in water.
[g] The values σ^0_4 hold.
[h] Data from Ref. 24. Excluded from the final analysis.
[i] Data from Ref. 25.
[j] Data from Ref. 26.
[k] Data from Ref. 27.
[l] Data from Refs 28 (at 20 °C), 29 and 30.
[m] Data from Refs 28 (at 20 °C) and 30.
[n] Data from Refs 20 (at 20 °C) and 29.
[o] Data from Refs 31–33.
[p] Data from Refs 27, 31 and 33.
[q] Data from Refs 34 and 35.
[r] Data from Ref. 30.
[s] Data from Refs 20 (at 20 °C) and 30.
[t] Data from Ref. 29.
[u] Data from Ref. 36 normalized with respect to the value for pK_a (3-NHAc) in Ref. 29.
[v] Data from Ref. 25 with the value for pK_a (H) in Ref. 37.
[w] Data from Ref. 38 (at 20 °C).
[x] Data from Refs 32 and 33.
[y] Data from Ref. 33.
[z] Data from Ref. 35.
[aa] Data from Ref. 39.
[bb] Data from Refs 27, 32, 33 and 40.

[cc] Data from Refs 27 and 33.
[dd] Data from Refs 30 and 39.
[ee] Data from Ref. 32.
[ff] Data from Ref. 41.
[gg] Data from Ref. 42.
[hh] Data from Ref. 43.
[ii] Data from Refs 27 and 31–33.
[jj] Data from Refs 29, 30 and 43.
[kk] Data from Refs 30 and 43.
[ll] Data from Ref. 44.
[mm] Data from Ref. 45 with the value for pK_a (H) in Ref. 31.
[nn] Data from Ref. 31.
[oo] Data from Ref. 46.
[pp] Data from Ref. 47 normalized with respect to the value for pK_a (4-Ph) in Ref. 30.
[qq] Data from Ref. 48 with the value for pK_a (H) in Ref. 32.
[rr] Data from Refs 27 and 32.
[ss] Data from Ref. 34. The value 8.40 derived from Table IV in Ref. 34 was used for pK_a (3-SO$_2$CH$_3$).
[tt] Data from Ref. 49 normalized with respect to the value for pK_a (4-COCH$_3$) in Ref. 30.
[uu] Data from Ref. 40.
[vv] Data from Ref. 50 normalized by equalling the values for pK_a (3-CHO) and pK_a (4-CHO) in Ref. 51 to those in Refs 41 and 42, respectively.
[ww] Data from Ref. 52.
[xx] Data from Refs 27, 32 and 33.
[yy] Data from Ref. 53.
[zz] Data from Refs 29 and 30.
[aaa] Data from Ref. 34 normalized with respect to the value for pK_a (4-NO$_2$) in this table.
[bbb] Data from Ref. 54 (at 20 °C).

Initial values for the fitting parameters were obtained from ordinary linear least squares fits of equations (16)–(19). Their final values were constrained to the verification of the condition

$$| \gamma_n - \gamma_s | < 0.005 | \gamma_n + \gamma_s | \qquad (61)$$

where γ_n and γ_s are calculated from equation (24) by using equations (58)–(60).

The characteristic parameters of the hyperbolic model are obtained as follows. For γ, we take the average between γ_n and γ_s; λ is given by $(\rho_4/\rho_3)\lambda^0$ [equation (23)]; and ε_n and ε_s by specializing equation (25) to

$$\varepsilon_n = -(\rho_4/\rho_3)[\delta_{4n}\lambda^0 - (\rho_4/\rho_3)\rho_{3n}\varepsilon_n^0] \qquad (62)$$

$$\varepsilon_s = -(\rho_4/\rho_3)[\delta_{4s}\lambda^0 - (\rho_4/\rho_3)\rho_{3s}\varepsilon_s^0] \qquad (63)$$

The condition expressed by equation (61) warrants

that the requirement for the common asymptote $\gamma = \gamma_n = \gamma_s$ is verified within 0.5%. In view of equation (13), the departure from strict conjugate n and s hyperbolae behaviour can be evaluated by the relative deviation (RD)

$$RD = -(\varepsilon_n + \varepsilon_s + 2\gamma\lambda)/2\gamma\lambda \qquad (64)$$

We have seen in the Introduction that equations (3) and (4) can be regarded as the first plurilinear improvement of equation (2), the Hammett equation with non-zero intercept. In both cases and for comparison purposes, the hyperbolic model parameters were calculated by means of equations (23), (24) and (62)–(64) which are now greatly simplified.

Three models for the correlation of substituent effects in benzene derivatives, namely, the extended plurilinear Hammettian transformation, separate equations for *meta* and *para* derivatives, and the Hammett

Table 3. Plurilinear analysis of the ionization of 3- and 4-monosubstituted benzoic acids in 50% EtOH–H_2O at 298 K[a]

Quantity	Plurilinear Hammettian transformation[b]		Separate equations for *meta* and *para*[c]		Hammett equation[d]	
	σ_4^{BA} and σ^0	σ^0 only	σ_4^{BA} and σ^0	σ^0 only	σ_4^{BA} and σ^0	σ^0 only
Model parameters						
ρ_{3n}	1.406	1.419	1.443	1.443	1.422	1.459
ρ_{3s}	1.415	1.460	–	–	–	–
ρ_4/ρ_3	1.021	1.016	0.986	1.021	1	1
δ_{4n}	0.000	−0.007	0.019	−0.028	0.004	−0.023
δ_{3s}	0.004	−0.020	−0.018	−0.018	–	–
ε_n	0.500	0.507	0.461	0.541	0.482	0.521
ε_s	0.132	0.145	0.110	0.164	0.126	0.155
λ	0.980	0.975	0.946	0.980	0.960	0.960
γ	−0.324	−0.333	−0.266	−0.370	−0.316	−0.353
RD^e(%)	−0.4	0.5	13.3	3.0	0.0	−0.3
Correlation statistics[f]						
n	38	30	38	30	37	29
p	4	4	4	4	2	2
s	0.067	0.052	0.065	0.051	0.066	0.050
$s\%$	3.13	3.84	3.05	3.74	3.10	3.67
ψ	0.128	0.120	0.124	0.117	0.125	0.115
f	0.104	0.078	0.101	0.076	0.104	0.076
$\mathcal{R}_2, n\text{-}p$	1.004	0.975	1.033	1.000	–	–
$\mathcal{R}_{2, n\text{-}p,95\%}$	1.091	1.122	1.091	1.122	–	–

[a] Data from Table 2.

[b] Equations (16)–(19) constrained by equations (26)–(28) and (61).

[c] Equations (3) and (4) treated as a single correlation.

[d] Equation (2).

[e] Relative deviation from conjugate hyperbolae given by equation (64).

[f] n, number of data points; p, number of independent parameters; s, standard deviation of the fit; $s\%$, relative value of the standard deviation defined by[59] $s\% = 100\, s/\delta\, \Delta pK_a$, where $\delta\, \Delta pK_a$ is the range of variation of ΔpK_a; ψ, Exner's goodness-of-fit statistic defined by[4,60,61] $\psi = s/s_0$, where s_0 is the standard deviation of the data; f, Ehrenson's goodness-of-fit statistic defined by[62] $f = s/RMS$, where RMS is the root mean square of the data; $\mathcal{R}_{2,\, n\text{-}p} = f_2/f_4$ is the f ratio in relation to the Hammett equation; $\mathcal{R}_{2,\, n\text{-}p,95\%}$ is the $\mathcal{R}$ statistic at the 95% confidence level (values taken from Ref· 62).

equation with non-zero intercept, were applied to the data in Table 2. The point for the parent compound lying on the origin of the axes can be considered as corresponding to the 'substituent' hydrogen. It was therefore included twice in plurilinear correlations, one as 3n substituent and the other as 4n substituent. Preliminary experiments showed that correlations were greatly improved if the appropriate scale of substituent sigma constants was employed. As a further test, for each model and reaction series considered, a second fit was performed without the points needing sigma constants different from sigma-zero values. In addition, the ionization of pyridinium ions was studied in terms of sigma-benzoic acid and sigma-plus reactivities. Excepting this latter, the results of these correlation analyses are presented in Tables 3–7, together with the relevant statistics.

Analysis of results

Detection of outliers

Wold and Sjöström[63] recommend a procedure based on normalized residuals R_n for the exclusion of significantly deviating points. Although the tabulated critical values of R_n at the 95% confidence level are for simple linear regressions, we used these values in the analysis of our plurilinear regressions. As a consequence, the ΔpK_a value for 4-dimethylaminoanilinium ion,[24] for which $R_n = 4$ with respect to the Hammett equation was found, was excluded from the final analysis. Here the largest residual in each fit was always less than three times the corresponding standard deviation and often much smaller than the critical normalized residual.

Correlation statistics

The present results were tested for statistical significance by three criteria of goodness of fit. These are Koppel and Palm's relative value of the standard deviation[59] $s\%$, Exner's statistic[4,60,61] ψ and Ehrenson's statistic[62] f. A total of 30 fits with degrees of freedom varying between 24 and 40 were performed. The statistical measures for these fits have values in the following ranges: $s\%$, 2·7–7·4; ψ, 0·10–0·24; and f, 0·06–0·19. Therefore, all these fits can be considered of fair quality.

For each system and data set investigated, the three goodness-of-fit criteria are in total agreement with respect to the best fitting model. Further, they rank the

Table 4. Plurilinear analysis of the ionization of 3- and 4-monosubstituted benzoic acids in 80% $CH_3O(CH_2)_2OH$–H_2O at 298 K[a]

| | Fitting model | | | | | |
| | Plurilinear Hammettian transformation[b] | | Separate equations for *meta* and *para*[c] | | Hammett equation[d] | |
Quantity	σ_4^{BA} and σ^0	σ^0 only	σ_4^{BA} and σ^0	σ^0 only	σ_4^{BA} and σ^0	σ^0 only
Model parameters						
ρ_{3n}	1·620	1·646	1·721	1·721	1·660	1·679
ρ_{3s}	1·784	1·945	–	–	–	–
ρ_4/ρ_3	1·001	1·009	0·959	0·930	1	1
δ_{4n}	−0·020	−0·044	0·007	−0·003	−0·021	−0·047
δ_{3s}	−0·044	−0·099	−0·063	−0·063	–	–
ε_n	0·574	0·615	0·534	0·511	0·587	0·619
ε_s	0·181	0·224	0·137	0·138	0·171	0·198
λ	0·961	0·969	0·921	0·893	0·960	0·960
γ	−0·395	−0·435	−0·299	−0·310	−0·396	−0·427
$RD^c(\%)$	−0·6%	−0·5	21·8	17·2	−0·2	−0·4
Correlation statistics[f]						
n	36	28	36	28	35	27
p	4	4	4	4	2	2
s	0·073	0·049	0·077	0·060	0·082	0·062
$s\%$	2·98	3·02	3·16	3·70	3·35	3·80
ψ	0·117	0·095	0·124	0·116	0·130	0·119
f	0·098	0·064	0·105	0·079	0·112	0·083
$\mathfrak{R}_{2,n-p}$	1·142	1·284	1·074	1·049	–	–
$\mathfrak{R}_{2,n-p,95\%}$	1·098	1·133	1·098	1·133	–	–

[a-f] Footnotes as in Table 3.

Table 5. Plurilinear analysis of the ionization of 3- and 4-monosubstituted anilinium ions in water at 298 K[a]

	Fitting model					
	Plurilinear Hammettian transformation[b]		Separate equations for *meta* and *para*[c]		Hammett equation[d]	
Quantity	σ_4^- and σ^0	σ^0 only	σ_4^- and σ^0	σ^0 only	σ_4^- and σ^0	σ^0 only
Model parameters						
ρ_{3n}	3·063	3·044	2·813	2·813	3·035	3·168
ρ_{3s}	3·411	3·281	–	–	–	–
ρ_4/ρ_3	0·987	1·093	1·125	1·268	1	1
δ_{4n}	−0·045	−0·031	−0·169	−0·179	−0·028	−0·041
δ_{3s}	−0·101	−0·063	0·116	0·116	–	–
ε_n	1·061	1·275	1·397	1·763	1·064	1·121
ε_s	0·343	0·387	0·506	0·629	0·303	0·327
λ	0·948	1·050	1·080	1·218	0·960	0·960
γ	−0·745	−0·796	−1·175	−1·303	−0·713	−0·756
$RD^c(\%)$	−0·5	−0·5	−25·0	−24·6	−0·2	−0·2
Correlation statistics[f]						
n	42	32	42	32	41	31
p	4	4	4	4	2	2
s	0·173	0·191	0·139	0·140	0·178	0·195
$s\%$	3·36	5·19	2·71	3·79	3·46	5·29
ψ	0·142	0·216	0·115	0·158	0·146	0·218
f	0·108	0·180	0·087	0·132	0·113	0·187
$\Re_{2,\,n\text{-}p}$	1·042	1·038	1·293	1·421	–	–
$\Re_{2,\,n\text{-}p,\,95\%}$	1·082	1·113	1·082	1·113	–	–

[a-f] Footnotes as in Table 3.

Table 6. Plurilinear analysis of the ionization of 3- and 4-monosubstituted phenols in water at 298 K[a]

	Fitting model					
	Plurilinear Hammettian transformation[b]		Separate equations for *meta* and *para*[c]		Hammett equation[d]	
Quantity	σ_4^- and σ^0	σ^0 only	σ_4^- and σ^0	σ^0 only	σ_4^- and σ^0	σ^0 only
Model parameters						
ρ_{3n}	2·343	2·361	2·083	2·083	2·071	2·059
ρ_{3s}	1·863	1·872	–	–	–	–
ρ_4/ρ_3	0·926	0·935	1·000	0·866	1	1
δ_{4n}	0·048	0·049	0·108	0·097	0·133	0·133
δ_{3s}	0·139	0·141	0·143	0·143	–	–
ε_n	0·644	0·661	0·608	0·453	0·580	0·575
ε_s	0·107	0·109	0·086	0·061	0·061	0·059
λ	0·890	0·898	0·960	0·831	0·960	0·960
γ	−0·424	−0·431	−0·390	−0·330	−0·328	−0·325
$RD^c(\%)$	−0·5	−0·5	−7·5	−6·5	1·6	1·6
Correlation statistics[f]						
n	38	30	38	30	37	29
p	4	4	4	4	2	2
s	0·146	0·138	0·139	0·125	0·136	0·127
$s\%$	4·69	7·39	4·47	6·66	4·39	6·78
ψ	0·178	0·243	0·170	0·219	0·167	0·222
f	0·124	0·174	0·118	0·157	0·118	0·163
$\Re_{2,\,n\text{-}p}$	0·948	0·936	0·996	1·038	–	–
$\Re_{2,\,n\text{-}p,\,95\%}$	1·091	1·122	1·091	1·122	–	–

Table 7. Plurilinear analysis of the ionization of 3- and 4-monosubstituted pyridinium ions in water at 298 K (benzoic acid reactivity)[a]

	Fitting model					
	Plurilinear Hammettian transformation[b]		Separate equations for *meta* and *para*[c]		Hammett equation[d]	
Quantity	σ_4^{BA} and σ^0	σ^0 only	σ_4^{BA} and σ^0	σ^0 only	σ_4^{BA} and σ^0	σ^0 only
Model parameters						
ρ_{3n}	6·050	6·051	6·168	6·168	5·640	5·320
ρ_{3s}	7·227	6·842	–	–	–	–
ρ_4/ρ_3	0·829	0·779	0·866	0·784	1	1
δ_{4n}	−0·144	−0·083	−0·306	−0·175	−0·160	−0·065
δ_{3s}	−0·394	−0·240	−0·082	−0·082	–	–
ε_n	1·537	1·318	1·835	1·427	2·081	1·880
ε_s	0·572	0·440	0·675	0·476	0·667	0·546
λ	0·796	0·748	0·832	0·753	0·960	0·960
γ	−1·330	−1·180	−1·747	−1·376	−1·437	−1·266
$RD^e(\%)$	−0·5	−0·5	−13·6	−8·2	−0·4	−0·2
Correlation statistics[f]						
n	43	35	43	35	42	34
p	4	4	4	4	2	2
s	0·257	0·198	0·308	0·209	0·378	0·349
$s\%$	3·05	3·75	3·65	3·96	4·49	6·61
ψ	0·134	0·122	0·161	0·129	0·196	0·213
f	0·121	0·095	0·145	0·101	0·181	0·171
$\mathfrak{R}_{2, n-p}$	1·491	1·789	1·244	1·695	–	–
$\mathfrak{R}_{2, n-p, 95\%}$	1·080	1·101	1·080	1·101	–	–

[a]–[f] Footnotes as in Table 3.

three models in the same order but for a single exception in ten comparisons. Differences among the three statistics arise, however, when comparing data sets of different size for the same system. Thus, while ψ and f values run parallel to each other except in one instance, in half of the cases the $s\%$ criterion disagrees with the concordant information from the ψ and f criteria.

Although values of ψ and f are usually appraised by similar scales (up to 0·1 for good and between 0·1 and 0·2 for fair correlations), we obtained $\psi:f$ ratios ranging from 1·1 to 1·5. We refer to Shorter (Ref. 5, p. 219) for the discussion of the conditions leading to complete numerical equivalence between ψ and f. These difficulties are much less pronounced when comparing alternative set fitting by the different statistic ratios. In fact, for an increase in the number of fitting parameters from p to $p + b$, one has

$$s\%_p/s\%_{p+b} = \Psi_p/\Psi_{p+p} = f_p\sqrt{1 - b/(n - p)}/f_{p+b}$$

(65)

By observing that $\mathfrak{R}_{b, n-p} = f_p/f_{p+b}$, the different ratios yield the same information in numerical scales that became equivalent at large number of degrees of freedom. Frequently the only purpose of using statistic f is to discuss $\mathfrak{R}_b$ values. Although the actual f values

for regressions of data not expressed relative to a standard system[64–66] are meaningless (Ref. 5, p. 219), equation (65) shows that the resulting[64–66] $\mathfrak{R}_b$ values are meaningful. A similar situation arose in this work. Since both the representations by the plurilinear Hammettian transformation and the separate lines for *meta* and *para* derivatives make use of more two independent parameters than by the Hammett equation, we obtained values for the $\mathfrak{R}$ statistic slightly smaller than if it were correctly calculated by using identical data sets. These facts explain an awkwardly lower than unity value for $\mathfrak{R}_{2, n-p}$ appearing in Table 6. Nevertheless, this systematic error did not preclude arriving at useful conclusions.

Lastly, fits for the pyridinium ion series with sigma-plus constants led to poor correlations and unrealistic model parameters. These results are not presented in this paper.

DISCUSSION

Comparison of fitting models

Relative dissociation constants of 3- and 4-monosubstituted benzoic acids, anilinium ions, phenols and pyridinium ions in water and aqueous solvents at 25 °C were correlated with appropriate substituent sigma

constants by means of three fitting models: the pluri-linear Hammettian transformation (PHT), separate lines for *meta* and *para* derivatives (m,p) and the Hammett equation (HE), all of them in their statistical version. Examination of statistical functions indicates that the best model for benzoic acids in 80% 2-meth-oxyethanol–water (Table 4) and for pyridinium ions (Table 7) is PHT, for anilinium ions (Table 5) m,p and for benzoic acids in 50% ethanol–water (Table 3) and for phenols (Table 6) HE. On the basis of this statistical evidence, none of the three models studied is revealed as clearly superior to the other two and the classical Hammett equation stands favourably. There are, how-ever, other features to be considered when appraising the different models.

It is important to assess the ability of each model to yield fairly constant model parameters irrespective of the data size. This model performance with respect to derived asymptote values λ and γ can be evaluated from the fits with the whole selected data and with the data requiring only sigma-zero constants as reported in Tables 3–7. Thus, the average deviation in λ values upon point removal is ±4% with PHT and ±8% with m,p, whereas HE imposes a fixed value $\lambda = \lambda^0$ for all systems. In its turn, γ values change by ±7% with PHT, ±18% with m,p and ±8% with HE. Also, for a given system and data set, the average model dependence of λ and γ values referred to PHT values is as follows. In ten comparisons, λ varies ±7% when using both m,p and HE, and γ varies ±28% with m,p and ±8% with HE.

Lastly, the compliance with the hyperbolic model for the *meta–para* interrelationship, as indicated by the quantity RD defined by equation (64), is within ±0.5% for both PHT and HE and within ±14% for m,p.

Emerging from these model comparisons is the clear superiority of the plurilinear Hammettian transform-ation and the better performance of the Hammett equa-tion over separate lines for *meta* and *para* derivatives.

General *meta–para* interrelationship

The plurilinear Hammettian transformation was devel-oped assuming the existence of a hyperbolic relation-ship linking substituent chemical effects from the *meta* and from the *para* positions in the absence of through-resonance. Moreover, parameters for conjugate rec-tangular hyperbolae in the Δ_4 vs Δ_4/Δ_3 representation [equations (11) and (12)] are readily derived from PHT [equations (23)–(25)] and their values are given in Tables 3–7 for the reaction series herein studied. Figures 1–3 illustrate graphs in this representation. Marked points are for the substituents in Table 2 having experimentally determined values for both Δ_3 and Δ_4. Values for *para*-substituted compounds needing sigma constants from scales accounting for direct-resonance effects were subjected to an additional treatment. By entering the corresponding sigma-zero constants into the PHT equations for a given reaction series, the resulting Δ_4 values can be considered as estimated values in the absence of through-resonance. These so-determined
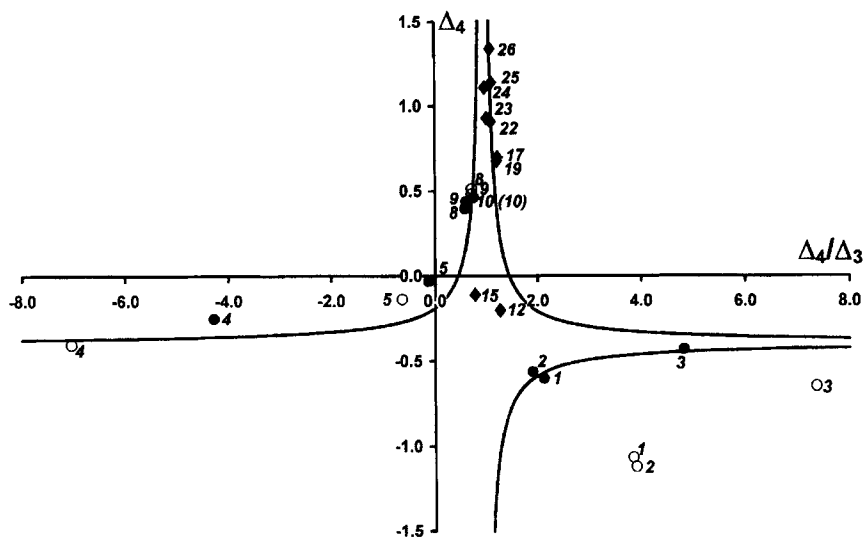

Figure 1. Interrelationship between Δ_4 and Δ_4/Δ_3 for the ionization of benzoic acids in 80% 2-methoxyethanol–water at 25 °C. Diamonds are for normal substituents and circles for special substituents. Filled symbols are for experimental or estimated values without through-resonance contributions and empty symbols are for experimental values that include through-resonance contributions. The lines drawn are for the three-parameter hyperbolae given by the plurilinear Hammettian transformation. Experimental data and substituent numbering from Table 2
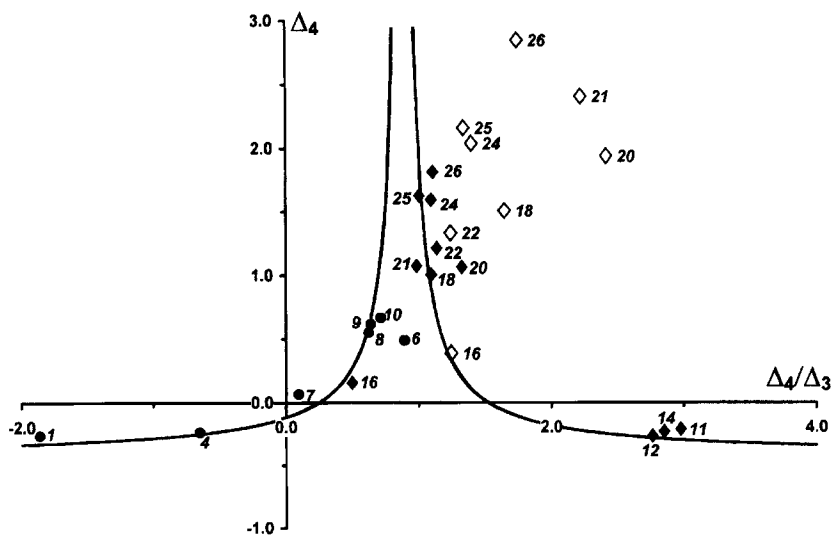
Figure 2. Interrelationship between Δ_4 and Δ_4/Δ_3 for the ionization of phenols in water at 25 °C. Symbols and other explanations as in Figure 1
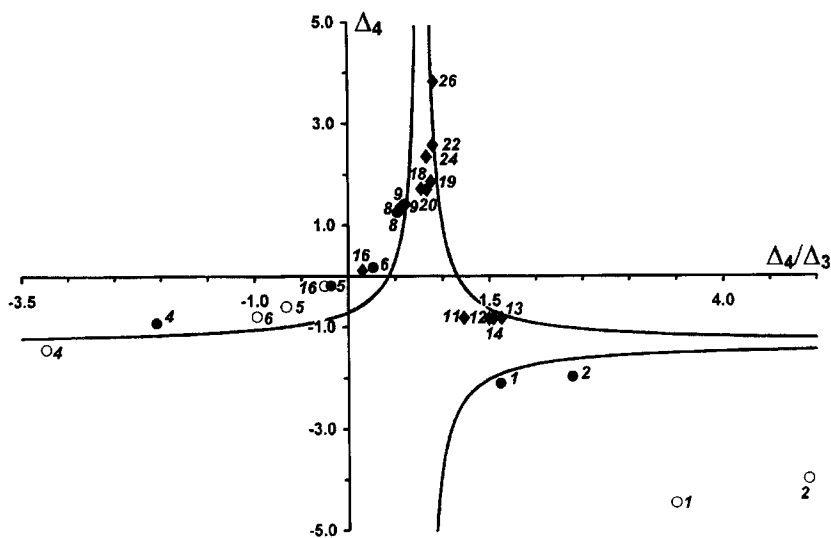

Figure 3. Interrelationship between Δ_4 and Δ_4/Δ_3 for the ionization of pyridinium ions in water at 25 °C. Symbols and other explanations as in Figure 1

values and experimental values without through-resonance contributions are represented by filled symbols in the figures.

It is seen in Figures 1–3 that the *meta–para* interrelationship is described very satisfactorily by our hyperbolic model, provided through-resonance contributions are subtracted from total substituent effects. This is particularly manifested in the phenol series (Figure 2), where even the off-line position estimated for phenyl (No. 16) can be ascribed to a large relative difference between experimental and PHT-calculated values for Δ_3. The location of special substituents hydroxy (No. 3, estimated value) in Figure 1 and dimethylamino (No. 1, experimental value) in Figure 2 is noteworthy. This is because in our analysis[17] of the sigma-zero scale the amino and dimethylamino groups were the only substi-
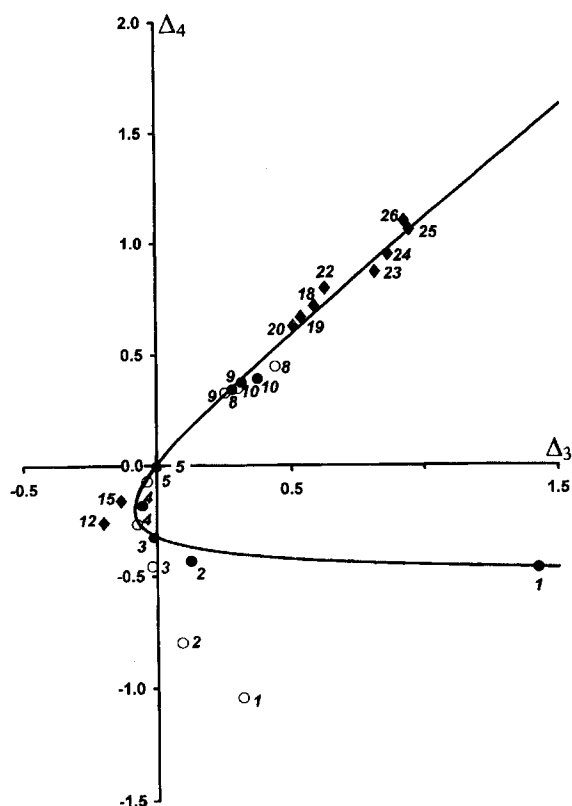
tuents correlated by the hyperbola branch lying in the fourth quadrant (Figure 1 in Ref. 17), such as is now the case for the pyridinium ion series in Figure 3. Therefore, substituents are simply partitioned between normal and special hyperbolae, and no physical significance should be attached to which hyperbola branch they are placed.

The geometrical properties of conjugate n and s rectangular hyperbolae allow us to draw a single hyperbola for the *para* vs *meta* representation. To accomplish this, Δ_{3s} values have to be transposed to $\Delta_{3s,tr}$ values by means of the transformation

$$\Delta_{4s}/\Delta_{3s,tr} = 2\lambda - \Delta_{4s}/\Delta_{3s} \qquad (66)$$

As shown before,[17] this operation amounts to rotate the special hyperbola in turn of its λ asymptote on to the normal hyperbola. The resulting single hyperbola for representing Δ_4 as a function of Δ_3 or $\Delta_{3,tr}$ is expressed by equation (11) and has asymptotes defined by $\Delta_4 = \varepsilon_n/\lambda + \gamma + \lambda\Delta_3$ and $\Delta_4 = -\varepsilon_n/\lambda$. This is exemplified in Figures 4 and 5 for the systems in Tables 3 and 5,
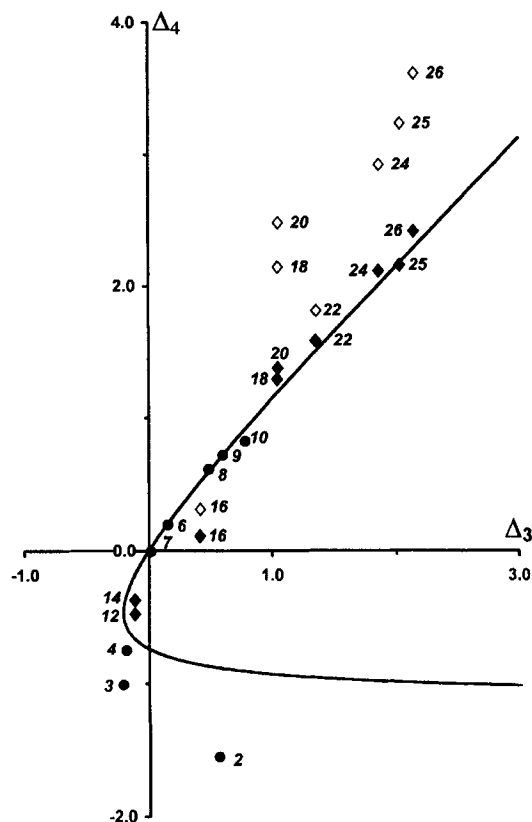

Figure 4. Interrelationship between Δ_4 and Δ_3 or $\Delta_{3,tr}$ for the ionization of benzoic acids in 50% ethanol-water at 25 °C. Diamonds are for normal substituents with coordinates (Δ_{4n}, Δ_{3n}) and circles for special substituents with coordinates (Δ_{4s}, $\Delta_{3s,tr}$). Filled symbols are for experimental or estimated values without through-resonance contributions and empty symbols are for experimental values that include through-resonance contributions. The line drawn is for the three-parameter hyperbola given by the plurilinear Hammettian transformation. Experimental data and substituent numbering from Table 2

Figure 5. Interrelationship between Δ_4 and Δ_3 or $\Delta_{3,tr}$ for the ionization of anilinium ions in water at 25 °C. Symbols and other explanations as in Figure 4

respectively. They illustrate the ability of the plurilinear Hammettian transformation to yield realistic parameter values for the hyperbolic model linking the reactivities of *meta-* and *para-*monosubstituted benzene derivatives in the absence of through-resonance by means of a single hyperbola branch. Also, the above-average deviation for special substituents 2 and 3 in the anilinium ion series (Figure 5) may indicate the operation of through-resonance effects by electron-donating substituents in this system.

Parameter λ

Parameter λ has been interpreted by equation (43) as the *para/meta* ratio of non-mesomeric N substituent effects. Experimental λ values in Table 3–7 are lower than unity and show a marked dependence on the molecular framework. It is of interest to explore the possibility of determining λ theoretically. Current theories for the transmission of non-mesomeric substituent effects were reviewed by Exner and Friedl.[67] If the through-space field effect were the predominant N effect, we may resort to Dewar *et al.*'s FMMF treatment of substituent effects.[68] On the other hand, the through-bond sigma inductive effect has been used recently for this purpose by Soroka and Tomasik[69] and Exner and Fiedler[70] have refined the classical through-bond topological approach.

Following Dewar *et al.*,[68] we consider that the field due to the substituent can be approximated by a point charge q at the nearest ring atom 1, together with a second point charge $-fq$ at the substituent charge centre 2, the resulting potential varying as the inverse of the distance r. The empirical factor f, equated to 0·9 in water by Dewar *et al.*,[68] allows for charge screening by

the solvent. In terms of this model, λ can be calculated by

$$\lambda = \left(\frac{1}{r_{1p}} - \frac{f}{r_{2p}}\right) \bigg/ \left(\frac{1}{r_{1m}} - \frac{f}{r_{2m}}\right) \quad (67)$$

The through-bond inductive model employed by Soroka and Tomasik[69] is based on perturbation of the electronic potential and assumes that the gradient of potential between atoms is proportional to the gradient of the charge at these atoms and to the inverse of the distance measured along the sigma bonds. In terms of this inductive model, λ is given by[69]

$$\lambda = (a + 4b/3 + c)/(a + 3b/2 + c) \quad (68)$$

where a is the average substituent–ring distance, b is the aromatic carbon–carbon length and c is the ring–reactive centre distance.

Since substituent electrical effects are stronger in ions than in neutral molecules, we performed distance calculations for the charged forms. Known crystallographic data[71] were used but substituent effects on the ring geometries were disregarded. For each molecular framework, model calculated λ values reported in Table 8 are the average for the 26 substituted derivatives in Table 2. The standard deviations are small (<0·01) and there is no significant difference between normal and special substituents. The largest individual deviation in the latter class was for iodine (−2·3%) and in the former was for the sulphoxides (−1·4%).

Experimental and calculated λ values are compared in Table 8. The ability of Dewar *et al.*'s model[68] to reproduce experimental λ values is striking. Although the inductive model leads to a good value for the benzoate ion framework, it fails for the pyridinium ion.

Table 8. Parameter λ as a function of the molecular framework: comparison of experimental and theoretical values

Molecular framework	Experimental	λ			Inductive model[b]
		Dewar *et al.'s* model[a]			
		$f = 0.90$	$f = 0.95$	$f = 1.00$	
Benzoate ion	0·97 ± 0·01[c]	0·95[d]	0·97	0·98	0·96[e]
Anilinium and phenoxide ions	0·92 ± 0·03[f]	0·91	0·92	0·92	0·95
Pyridinium ion	0·80[g]	0·84	0·84	0·84	0·94

[a] Calculated by equation (67).
[b] Calculated by equation (68).
[c] Average and mean deviation of PHT λ values in Tables 3 and 4.
[d] Non-rounded value and standard deviation: 0·953 (0·002); Dewar *et al.*[68] reported 0·952.
[e] Non-rounded value and standard deviation: 0·964 (0·001); Soroka and Tomasik[69] reported 0·955.
[f] Average and mean deviation of PHT λ values in Tables 5 and 6.
[g] PHT λ value in Table 7.

Moreover, the built-in empirical factor f of Dewar *et al.*'s model should be useful to rationalize the solvent effect on the field/inductive effect[72-74] and thus on parameter λ.[10] The refined empirical model of the sigma-inductive effect due to the Exner and Fiedler[70] led to an invariant $\lambda = 0.84$ on the basis of a transmission coefficient of 0.36 for the inductive effect across a sigma bond. Although this λ value represents an improvement over $\lambda = 0.64$ as calculated in terms of the unrefined model, these topological approaches suffer from the important drawback of yielding a constant λ value irrespective of differences in molecular framework and substituent skeleton.

The present results clearly show that parameter λ is a function of the molecular framework. This contention lends support to Exner, who first challenged[21,75] Taft and co-worker's assumption[76-79] of equal transmission coefficients for the inductive effect from *meta* and *para* positions in all reaction series of benzene derivatives. On the other hand, our calculations of theoretical λ values have shown that these values vary slightly with the skeleton of individual substituents. An additional variation due to ring deformation upon substitution should have been considered, as Godfrey[80] has remarked. May these facts serve as a reminder that our hyperbolic model for the *meta–para* interrelationship, as well as current correlations of substituent effects, are coarse models that are bound to reveal irreducible deviations at a finer level of analysis.

Parameter γ

The physical meaning of γ^0, the parameter γ for the sigma-zero scale, has been given before[17] as the non-zero σ_4^0 value to which a zero-value σ_3^0 substituent constant corresponds. Hence γ for a given reaction series can be interpreted as the Δ_4 value subtracted from possible through-resonance contributions for which the corresponding Δ_3 value is zero.

From equations (29), (50), (51) and (56), the ratio γ/γ^0 can be expressed by

$$\gamma/\gamma^0 = \rho_{4M,n} = \rho_{4M,s} - \delta_{3s}\lambda/\gamma^0$$
$$= \rho_{4N,n} = \rho_{4N,s} - \delta_{3s}\lambda/\gamma^0 \quad (69)$$

We note that the $-\delta_{3s}\lambda/\gamma^0$ term appearing in equation (69) is a consequence of our option for separate Taft equations for normal and special substituents. Notwithstanding this, equation (69) allows us to interpret the ratio γ/γ^0 as measuring the sensivity of the reaction centre to mesomeric and non-mesomeric effects of substituents from the *para* position. Values for γ/γ^0 calculated by means of PHT equation (24) can thus be regarded as improved Hammett reaction constants that take into account proper statistical considerations and the fact that parameter λ generally differs from unity.

Values for the ratio γ/γ^0 are compared with ρ values

in Table 9. Differences between these parameters are not appreciable for the reaction series of benzoic acids and pyridinium ions. However, if γ/γ^0 were a more reliable measure than ρ, then the reaction constant for the ionization of anilinium ions has been underestimated and that for the ionization of phenols has been overestimated.

Separation of M, N and R effects

Taft equations (33)–(36) are the expression of a dual substituent parameter approach. To deal with through-resonance effects, a third parameter should be accommodated without altering its basic assumptions. Let R designate the through-resonance substituent effect that can only operate from the *para* position. Then sigma constants in the different scales can be defined by $\sigma_4' = \sigma_4^0 + R'$, where the prime stands for benzoic acid, plus or minus reactivities. Taft equations (34) and (36) should thus be substituted by equations having the form

$$\Delta_4 = \rho_{4M}M + \rho_{4N}N + \rho_{4R'}R'$$

so that γ becomes given by the value for $\Delta_4 - \rho_{4R'}R'$ when $\Delta_3 = 0$.

Because of constraints (53) and (55) (see Table 1), it can also be shown that $\rho_{4R',n} = \rho_{4n}$ and $\rho_{4R',s} = \rho_{4s}$. Therefore, the PHT approach assumes identical transmission coefficients for the M, N and R effects from a substituent in the *para* position. Hence this approach should fail in reaction series for which the resonance demand by the reaction centre differs considerably from that in the reaction series used to define the respective sigma scale, i.e. when $\rho_{4R'} \neq \rho_{4M} = \rho_{4N}$. We suspect that this is the reason why the dissociation of pyridinium ions was poorly correlated by the sigma-plus scale as referred to in the subsection on results analysis.

Taft's parameter α is given by the ratio ρ_{3M}/ρ_{4M}. From expressions in Table 1 we write for normal

Table 9. Comparison of γ/γ^0 with the Hammett reaction constant ρ

Reaction series[a]	$\gamma/\gamma^{0\,b}$	ρ This work[b]	Literature
BA/50 E-W	1.439	1.422	1.522[c]
BA/80 ME-W	1.755	1.660	1.68[c]
Anilinium ion	3.308	3.035	2.889[c]
Phenol	1.884	2.071	2.229[c]
Pyridinium ion	5.905	5.640	5.714[d]

[a] For identification of reaction series, see footnotes b–f in Table 2.
[b] From Tables 3–7.
[c] Ref. 4, p. 71.
[d] Ref. 29.

substituents

$$\alpha_n = \rho_{3n}\rho_{3M}^0 / \rho_{4n} \qquad (70)$$

Noting that for the sigma-zero scale[17] $\alpha^0 = \rho_{3M}^0$, it follows from equations (23) and (70) that

$$\lambda\alpha_n = \lambda^0\alpha^0 = \text{constant} \qquad (71)$$

For special substituents, expressions in Table 1 lead to

$$\alpha_s = [\rho_{3s} - \rho_{3n}(1 - \lambda^0\rho_{3M}^0)]/\lambda^0\rho_{4s}$$

which can be transformed to

$$\lambda\alpha_s = (\rho_{3n}/\rho_{3s})(\lambda^0\alpha^0 - 1) + 1 \qquad (72)$$

Since $\rho_{3n} \approx \rho_{3s}$, equations (71) and (72) are very similar. They show that possible values for parameters α and λ are closely linked. Examination of λ values in Table 8 shows further that α values should not vary much in reaction series of benzene derivatives. Indeed, since Taft and co-workers[76-79] arbitrarily fixed $\lambda = 1$, then α would also be a constant, as it was originally assumed.[77] However, it is well known that a variable parameter α (a different constant for each reaction series) was empirically introduced on the grounds that better fittings were obtained.[78,81] We suspect that such a variation of parameter α may compensate for the use of non-separate M and R effects.

Comparison with other approaches

McDaniel[11] showed that Hine's theoretical interpretation[8] of the unmodified Hammett equation implied a linear correlation with zero intercept between the *para* and *meta* sigma constants for the same substituent. Since this behaviour was not supported by experiment,[11] it remained a paradox until solved by Wold.[82] Here we have obtained evidence supporting Wold's analysis.[82] In fact, we demonstrated that, in the absence of through-resonance, the Hammett equation is consistent with a hyperbolic relationship between Δ_3 and Δ_4, even though too much restrictive with respect to the asymptotic λ values.

The plurilinear Hammettian transformation is based on the realization that if there is a hyperbolic relationship linking the reactivities of corresponding *meta* and *para* substituents *within* a reaction series, then it can be incorporated into relationships correlating reactivities *between* reaction series. A similar examination along different lines was recently carried out by Pytela.[15] This author[14] modelled the *para* vs *meta* relationship of optimized sigma constants for the benzoic acid reactivity by means of three straight lines intercepting in a single point. Interestingly, the substituent classes so defined are closely related to our own normal and special classes. Thus, Pytela's Class 2 is for special substituents. Since there is a good linear correlation between σ_{4s}^{BA} and σ_{4s}^0 constants ($r = 0.992$ for the data in Table 2), in view of equation (9) an approximately

linear relationship is expected to hold between σ_{4s}^{BA} and σ_{3s}^0. Normal substituents are subdivided into Classes 1 and 3 in Pytela's analysis,[14] and correlated in the representation σ_4 vs σ_3 by two straight lines with not too different slopes. This we consider an amelioration of Exner's equation.[4,12,21,75,83] However, we[17] were able to describe the *meta–para* behaviour of normal-substituent constants by means of equation (8), which requires only two adjustable parameters. Further, these are the same as employed to describe special-substituent constants by equation (9). Although it may prove difficult to decide empirically which is the best model, ours is certainly the most economical in fitting parameters.

Finally, we recall the controversy in the 1960s and 1970s on the proper scale to describe the pyridine reactivity, as summarized by Sawada *et al.*[84] Our observations on the apparent failure of the PHT treatment while using sigma-plus substituent constants are related to this controversy and will be dealt with elsewhere.

CONCLUSIONS

The plurilinear Hammettian transformation (PHT) introduced here is a constrained tetralinear improvement of the original Hammett equation. Substituents are first classified as special or normal according to whether or not there is a lone electron pair in the substituent atom attached to the aromatic ring. Second, in each of these classes *meta* and *para* derivatives are treated separately, a procedure in agreement with modern usage.[10] The resulting four linear equations have parameters linked by constraints derived from a general hyperbolic model for the *meta–para* interrelationship applying to benzene derivatives in the absence of through-resonance effects. These are taken care of by means of conventional reactivity scales of substituent constants. A total of four fitting parameters ensure proper treatment of statistical errors. The PHT model is regarded as an improved Hammett equation that incorporates a hyperbolic relationship[17] connecting *meta* and *para* substituent constants of the unified sigma-zero scale.[16]

By performing a non-linear correlation analysis of extensive selected literature data, the PHT characteristic parameters λ and γ were obtained for several reaction series involving dissociation equilibria of benzene derivatives in the liquid phase. We conclude that the Hammett equation is a model too restrictive with respect to possible values for λ whereas the bilinear model with separate and independent straight lines for *meta* and *para* derivatives is too little constrained. Concerning the link between the effect of a given substituent from the *meta* and from the *para* position, the constrained tetralinear PHT model emerges as a compromise between the rigidity of the Hammett equation and the inherent unrelatedness in the unconstrained bilinear

model. Moreover, the PHT treatment is able to yield realistic parameters for the *meta–para* interrelationship in reaction series for which data are available for only a limited number of substituents in at least three of the four groups or subsets considered here.

The parameter λ measures the *para/meta* ratio of non-mesomeric or field/inductive effects. PHT-derived λ values for the reaction series of benzoic acid, anilinium ion, phenol and pyridinium ion are lower than unity and a function of the molecular framework (Table 8). These λ values are best modelled by the through-space field effect approach of Dewar *et al.*,[68] which approximates dipolar substituents as two electrical point charges of opposite sign. Hence their effect on the electrical energy at the reaction centre of these proton transfer processes vary as the inverse of the through-space distance. According to this model, it can be expected that λ values for pole or charged and for dipolar or non-charged substituents should differ noticeably from each other. Also, since the non-mesomeric substituent effect on NMR chemical shifts and on IR intensities of double bond stretching absorptions is an effect on the field intensity, the effect of a charge at a substituent should follow an inverse square distance law,[68] leading to different λ values. Both of these aspects are in accordance with Topsom's theoretical analysis[85] of electronic substituent effects. We conclude that the good modelling of PHT λ values by current electrostatic theories of field/inductive effects provides evidence for the soundness of our hyperbolic model for the *meta–para* interrelationship.

Finally, in the PHT improvement of the Hammett equation, the ratio γ/γ^0 is a statistically adequate measure of the original Hammett's reaction constant ρ (Table 9).

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