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HYPERBOLIC MODEL FOR THE *META–PARA* INTERRELATIONSHIP IN BENZENE DERIVATIVES

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A new approach to the long-standing problem of interrelating *meta* and *para* substituent constants is presented. An analysis of the unified σ^0-scale shows that the interrelation between σ_4^0 and σ_4^0/σ_3^0 can be modelled by a pair of conjugate rectangular hyperbolae, one for normal (n) and the other for special (s) substituents. The latter are characterized by a lone electron pair in the first atom. The equations $\sigma_{4n}^0(\sigma_{4n}^0-\gamma^0)/(\sigma_{4n}^0-2\gamma^0)=\lambda^0\sigma_{3n}^0$ and $\sigma_{4s}^0=\gamma^0+\lambda^0\sigma_{3s}^0$ are derived and discussed in terms of Taft's separation of mesomeric and non-mesomeric effects. Asymptotic values $\lambda^0=0{\cdot}960$ and $\gamma^0=-0{\cdot}225$ were obtained by non-linear least rectangles fitting. A non-negligible mesomeric contribution to σ^0 constants for normal substituents is predicted by the hyperbolic model. The present results are at variance with Exner's analysis of the *meta–para* interrelationship in benzene compounds with normal substituents. This divergence is ascribed to opposite views concerning the role of the π-inductive effect.

INTRODUCTION

The successful development over decades of the Hammett equation in its dual and multiparametric extensions[1,2] has not been accompanied by a comparable insight into the relationship linking the reactivities of *meta-* and *para*-substituted benzene compounds. This situation is surprising because a physico-chemical law governing *meta–para* reactivities *within* a single reaction series should be more fundamental than correlations *between* reaction series.

Exner[3] and Shorter[4] reviewed previous attempts to deal with this problem. Based on Hine's theoretical analysis[5] of the original Hammett equation, McDaniel[6] showed that it implied a linear relationship between *para* and *meta* substituent sigma constants passing through the origin. However, this condition was only met by the family of substituents with carbon as first atom.[6] This apparent paradox has been solved by Wold[7] and is well understood in terms of Sjöström and Wold's shell model of substituent.[8] The next significant advance in the search for a *meta–para* reactivity link is due to Exner,[1,9,10] who advocates a direct proportionality law between *para* and *meta* sigma constants for all polar substituents without a lone pair of electrons in the first atom. Although Exner's equation is supported by an impressive body of experimental data,[9-12] it has been criticized on theoretical grounds by several authors.[4,13-15] Notwithstanding these contributions, a comprehensive model for linking *meta* and *para* reactivities is still lacking.

The central idea in this paper is that, in the absence of direct or through resonance, there should exist a general law correlating the *meta* and *para* effect of the same substituent on a given benzene compound. It is sought by analysing the unified sigma zero scale of substituent constants[8] and a hyperbolic model is proposed and discussed.

ANALYSIS OF THE SIGMA ZERO SCALE

Reference system

We consider the unified σ^0-scale proposed in 1976 by Sjöström and Wold[8] (SW) as the best available scale for

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Hammett *meta* and *para* substituent constants. It contains (σ_3^0, σ_4^0) data for 26 substituents which are reproduced in Table 1.

Since the SW scale is the result of a sound statistical treatment of data for a large number of different reaction series, it is not referred to a particular system. It is therefore of interest to characterize the corresponding reference model system. To this end we resorted to Charton's LDR equation.[16] The result of this correlation analysis is shown in Table 2 together with some of Charton's calculations.[16] Judging from the values for parameters η (a measure of the active centre electronic demand) and P_D (the percentage delocalized effect), SW model system resembles closely the ionization of substituted phenylethanoic acids in water (Charton's set P139), as indeed was intended by Sjöström and Wold.[8] Additionally, it is interesting that the alkaline hydrolysis of substituted benzyl benzoates in aqueous propanone (Charton's set P140) could also be regarded as the SW model system.

Proposal of a hyperbolic model

An interesting pattern separating substituents into two broad classes is observed when σ_4^0 is plotted vs σ_4^0/σ_3^0 (Figure 1). Following Exner,[3] substituents *without* a lone pair of electrons in the first (or α) atom (numbers 11–26 in Table 1) are referred to as 'normal' (n). In contrast, substituents *with* a lone pair of electrons in the first atom (numbers 1–10 in Table 1) are herein named as 'special' (s). We remark that 'substituent' hydrogen must be excluded from this analysis because $\sigma_{4\text{-H}}^0/\sigma_{3\text{-H}}^0$ became indeterminate. The layout of the points in Figure 1 suggested to us the drawing of a pair of conjugate rectangular hyperbolae: one hyperbola with branches in quadrants 1 and 3 (the latter being empty) for normal substituents, and the other one in quadrants 2 and 4 for special substituents. The behaviour of special substituents $-N(CH_3)_2$ and $-NH_2$ with respect to the hyperbolae in Figure 1 deserves comment. These are the only substituents located in a single branch because their

Table 1. Substituent σ^0 values and standard error h[a]

		meta		*para*		*para/meta*	
No.	Substituent	σ_3^0	h_3	σ_4^0	h_4	σ_4^0/σ_3^0	$h_{4/3}$[b]
	Special						
1	$—N(CH_3)_2$	-0·095	0·010	-0·317	0·013	3·337	0·469
2	$—NH_2$	-0·087	0·006	-0·295	0·010	3·391	0·396
3	—OH	0·023	0·009	-0·221	0·013	-9·609	5·445
4	$—OCH_3$	0·102	0·004	-0·120	0·006	-1·176	0·080
5	—NHAc	0·144	0·012	0·002	0·014	0·014	0·084
6	$—SCH_3$	0·142	0·020	0·063	0·020	0·444	0·154
7	—F	0·335	0·006	0·151	0·006	0·451	0·020
8	—Cl	0·365	0·004	0·242	0·004	0·663	0·013
9	—Br	0·369	0·004	0·265	0·004	0·718	0·013
10	—I	0·343	0·005	0·277	0·005	0·808	0·019
	Normal						
11	$—C(CH_3)_3$	-0·087	0·012	-0·150	0·008	1·724	0·210
12	$—CH_3$	-0·062	0·003	-0·135	0·003	2·177	0·116
13	$—CH(CH_3)_2$	-0·082	0·016	-0·132	0·008	1·610	0·250
14	$—C_2H_5$	-0·077	0·013	-0·127	0·010	1·649	0·273
1	$—CH_2Ph$	-0·047	0·020	-0·058	0·014	1·234	0·562
16	—Ph	0·041	0·016	0·051	0·011	1·244	0·513
17	$—CO_2H$	0·356	0·020	0·440	0·019	1·236	0·087
18	$—CO_2R$	0·349	0·009	0·441	0·008	1·264	0·039
19	—COPh	0·362	0·020	0·456	0·012	1·260	0·069
20	$—COCH_3$	0·360	0·008	0·469	0·011	1·303	0·046
21	—CHO	0·410	0·014	0·473	0·022	1·154	0·071
22	$—CF_3$	0·464	0·007	0·538	0·011	1·159	0·031
23	$—SO_2NH_2$	0·578	0·014	0·582	0·013	1·007	0·033
24	—CN	0·622	0·006	0·714	0·008	1·148	0·018
25	$—SO_2CH_3$	0·685	0·009	0·728	0·011	1·063	0·022
26	$—NO_2$	0·713	0·004	0·814	0·006	1·142	0·011

[a] Data for σ^0 and h taken from Ref. 8.

[b] Calculated by $h_{4/3} = (h_4^2\sigma_4^{0^2} + h_3^2\sigma_3^{0^2})^{1/2}/\sigma_3^{0^2}$.

Table 2. Correlation analysis of the σ^0 scale by the LDR equation

System[a]	n[b]	L	S_L[c]	D	S_D[c]	R	S_R[c]	η[d]	P_D[e]	R[f]
meta										
σ_3^0[g]	26	1·03	0·03	0·39	0·02	−0·02	0·11	−0·06	27·5	0·994
P183	17	0·94	0·06	0·46	0·06	0·73	0·37	1·59	32·8	0·980
para										
σ_4^0[g]	26	1·05	0·04	0·78	0·03	−0·26	0·15	−0·33	42·7	0·994
P139	17	0·90	0·03	0·60	0·03	−0·23	0·12	−0·38	40·2	0·994
P140	13	1·10	0·03	0·72	0·05	−0·21	0·20	−0·29	39·6	0·998
P182	18	0·98	0·03	1·00	0·02	0·87	0·17	0·87	50·6	0·998

[a] Charton's primary sets:[16] P183, $-\mathrm{p}K_a$, 3-substituted benzoic acids, water, 25 °C; P139, $-\mathrm{p}K_a$, 4-substituted phenylethanoic acids, 75% (v/v) aq. ethanol, 25 °C; P140, log k, 4-substituted benzyl benzoates + OH^-, 70% (v/v) aq. propanone, 25 °C; P182, $-\mathrm{p}K_a$, 4-substituted benzoic acids, water, 25 °C.

[b] Number of data points.

[c] Standard errors of the regression coefficients.

[d] $\eta = R/D$.

[e] $P_D = 100D/(L+D)$.

[f] Multiple correlation coefficient.

[g] For the substituents listed in Table 1 except —SO_2NH_2 (No. 23). σ^0 Values for —CO_2R (No. 18) were used twice to correlate with Charton's electrical constants for —CO_2CH_3 and —$CO_2C_2H_5$.

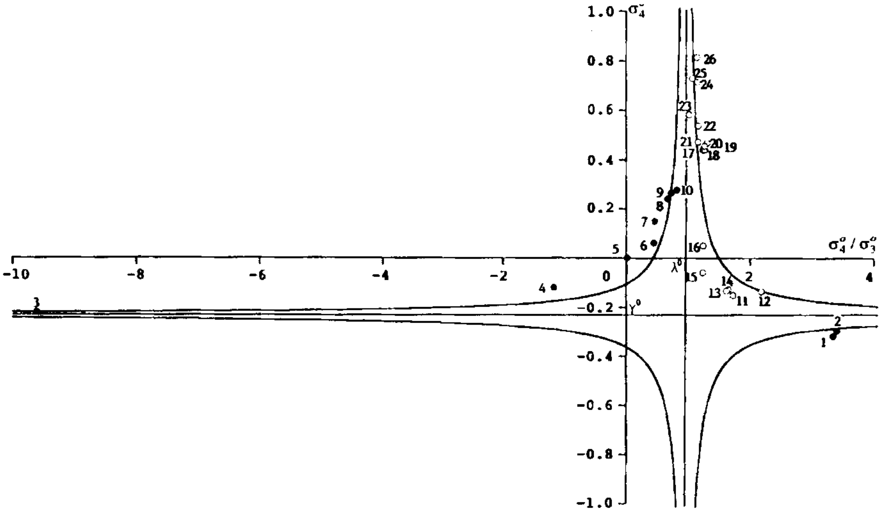

Figure 1. Interrelationship between σ_4^0 and σ_4^0/σ_3^0. Numbering as in Table 1

σ_3^0 and σ_4^0 values are both negative, thus they differ from all other special substituents in Table 1. We note further that the statistical SW values for the σ_4^0 constant of substituents 1 and 2 are near the average of the rather different values previously proposed in the literature and discussed by Hoefnagel and Wepster.[17]

Conjugate hyperbolae have common asymptotes, which in our case are defined by the lines

$$\sigma_4^0/\sigma_3^0 = \lambda^0 \tag{1}$$

$$\sigma_4^0 = \gamma^0 \tag{2}$$

where λ^0 and γ^0 are constants.

Explicit equations for rectangular hyperbolae n and s are

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

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

and the condition for conjugate hyperbolae is

$$\varepsilon_\mathrm{n}^0 + \varepsilon_\mathrm{s}^0 = -2\gamma^0\lambda^0 \tag{5}$$

The fitting of σ^0 constants by equations (3) and (4) is now discussed. Since the variables σ_4^0 and σ_4^0/σ_3^0 are interdependent, none of them is a suitable independent variable for least-squares regression analysis. This fact was appreciated by Kalfus *et al.*,[11] who, for a linear correlation, took the arithmetic mean of the regression coefficients for the direct and the inverse least-squares correlations. We believe that the correct approach to this problem is to find the minimum sum of the rectangle area defined by the distances between the experimental point and the fitting curve along both axes. This statistical treatment is known as the least rectangles method.[18] It has the important property of yielding identical regression parameters when both variables are interchanged. If applied to a linear correlation, it gives the principal axis or orthogonal regression line whose regression coefficient is the geometric mean of the two regression coefficients obtained by ordinary least-squares fitting.[18]

The assumption of conjugate n and s hyperbolae permits us to fit jointly the whole data because a point belonging to hyperbola s with coordinates $(\sigma_{4s}^0, \sigma_{4s}^0/\sigma_{3s}^0)$ can be transposed to the point $(\sigma_{4s}^0, \sigma_{4s}^0/\sigma_{3s,tr}^0)$, where

$$\sigma_{4s}^0/\sigma_{3s,tr}^0 = 2\lambda^0 - \sigma_{4s}^0/\sigma_{3s}^0 \qquad (6)$$

falling on hyperbola n. In this way, points in quadrants 2 and 4 are transposed to quadrants 1 and 3, respectively.

Each rectangle area in our hyperbolic model is given by

$$R = \left(\frac{\sigma_4^0}{\sigma_3^0} - \frac{\lambda^0\sigma_4^0 + \varepsilon_n^0}{\sigma_4^0 - \gamma^0}\right)\left(\sigma_4^0 - \frac{\gamma^0\sigma_4^0/\sigma_3^0 + \varepsilon_n^0}{\sigma_4^0/\sigma_3^0 - \lambda^0}\right) \qquad (7)$$

where σ_4^0 stands for both σ_{4n}^0 and σ_{4s}^0, and σ_3^0 is either σ_{3n}^0 or $\sigma_{3s,tr}^0$. For a hyperbola lying in the first and third quadrants, it follows from geometrical reasons that both distances defining rectangle area R have the same sign, thus ensuring that each term calculated by equation (7) is positive. The availability of standard errors h for the unified σ^0 constants[8] enable us to weight R terms by a weighting factor $w = 1/h_4 h_{4/3}$. The sum to minimize is thus

$$S = \sum_i w_i R_i$$

Since a general-purpose non-linear algorithm is required to obtain this least rectangle area sum, we wrote a program based on the Luus–Jaakola method,[19] the technical details of which are given in the Appendix.

Some algebraic restrictions follow from the peculiar variables we are using. Thus, if $\sigma_{4s}^0 = 0$ then $\sigma_{4s}^0/\sigma_{3s}^0 = 0$ provided $\sigma_{3s}^0 \neq 0$. Hence one should have the theoretical value $\varepsilon_s^{0th} = 0$ in equation (4) and the hyperbola s would degenerate to the straight line

$$\sigma_{4s}^0 = \gamma^0 + \lambda^0\sigma_{3s}^0 \qquad (8)$$

In its turn, the theoretical value $\varepsilon_s^{0th} = 0$ together with equation (5) leads to $\varepsilon_m^{0th} = -2\gamma^0\lambda^0$ and, by equation (3), to

$$\sigma_{4n}^0(\sigma_{4n}^0 - \gamma^0)/(\sigma_{4n}^0 - 2\gamma^0) = \lambda^0\sigma_{3n}^0 \qquad (9)$$

Now we note that if equation (6) is solved for σ_{3s}^0 and this result is inserted into equation (8), then one obtains a relationship between σ_{4s}^0 and $\sigma_{3s,tr}^0$ with the form of equation (9). Also, it can be shown that equation (9) represents a non-rectangular hyperbolic relationship between σ_{4n}^0 and σ_{3n}^0 with asymptotes $\sigma_{4n}^0 = -\gamma^0 + \lambda^0\sigma_{3n}^0$ and $\sigma_{4n}^0 = 2\gamma^0$.

The foregoing analysis shows that the relevant parameters in our hyperbolic model are the asymptotic values λ^0 and γ^0 defined by equations (1) and (2), respectively. However, because we are dealing with statistical quantities (Ref. 1, p. 59), a three-parameter fit was performed giving $\lambda^0 = 0{\cdot}960$, $\gamma^0 = -0{\cdot}225$ and $\varepsilon_n^0 = 0{\cdot}342$ ($\varepsilon_m^{0th} = 0{\cdot}433$). The resulting hyperbola is shown in Figure 2, where points for special substituents have abscissae transposed by means of equation (6).

The theoretical hyperbola linking *para* and *meta* substituent constants is represented by two-parameter equation (9) and it is shown in Figure 3. Points for special substituents corresponding to the linear equation (8) are rather scattered and are not shown. Instead, we used $\sigma_{3s,tr}^0$ values, which fit equation (9) nicely. This situation is readily explained by Wold's conclusion[7] that 'small deviations within one framework can correspond to large deviations within another framework.' Figure 3 deserves further comment. First we note that points for normal and special substituents are correlated by a single branch of the theoretical hyperbola. In particular, the peculiar location of substituents 1 and 2 observed in Figures 1 and 2 does not show up in the representation used in Figure 3. The three-parameter hyperbola [equation (3)] with asymptotes $\sigma_4^0 = \varepsilon_n^0/\lambda^0 + \gamma^0 + \lambda^0\sigma_3^0$, where $\varepsilon_n^0/\lambda^0 + \gamma^0 = 0{\cdot}131$, and $\sigma_4^0 = -\varepsilon_n^0/\lambda^0 = -0{\cdot}356$ would give a slightly improved correlation. Second, it is interesting that the curve passes through the origin, i.e. the point for hydrogen which should then be classified as a normal substituent. It can be further shown that this geometrical property is also present in the three-parameter hyperbola. Finally, by differentiating equation (9) with respect σ_{3n}^0 the indeterminate value for $\sigma_{4\text{-H}}^0/\sigma_{3\text{-H}}^0$ is fixed equal to $2\lambda^0$. This is the slope of the tangent to the hyperbola of Figure 3 at the origin.

Dual electronic effect and the hyperbolic model

Following the original work by Taft[20] on a dual-parameter extension of the Hammett equation, several improvements and other similar treatments have been published.[1,4] Their common feature is to consider two independent mechanisms for transmitting the electronic effect of a substituent in a *meta* or *para* position, here referred to as M (loosely standing for mesomeric) and

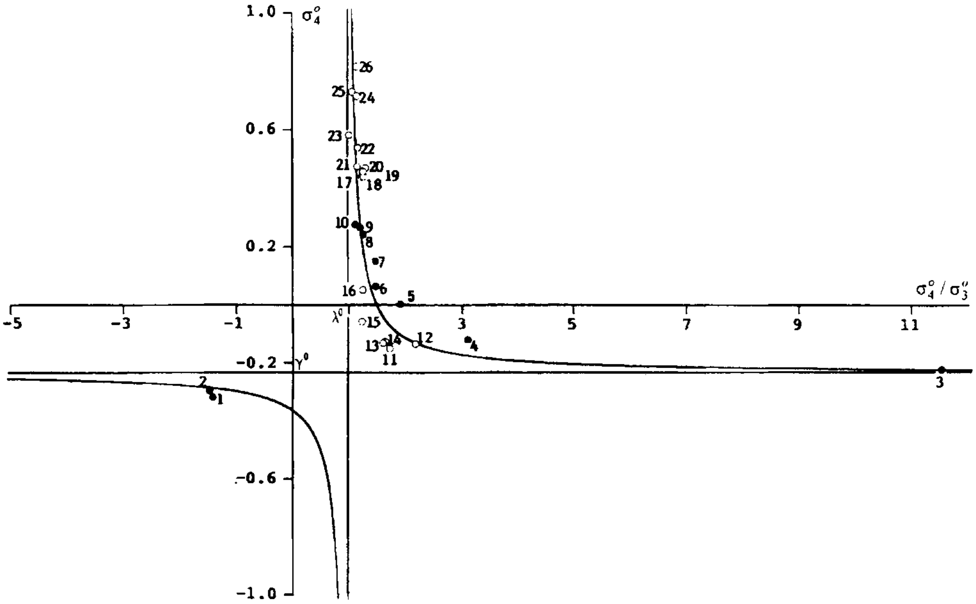

Figure 2. Interrelationship between σ_4^0 and σ_4^0/σ_3^0 [equation(3)]. o, Normal substituents with coordinates (σ_{4n}^0, $\sigma_{4n}^0/\sigma_{3n}^0$); •, special substituents with coordinates (σ_{4s}^0, $\sigma_{4s}^0/\sigma_{3s,tr}^0$). Numbering as in Table 1

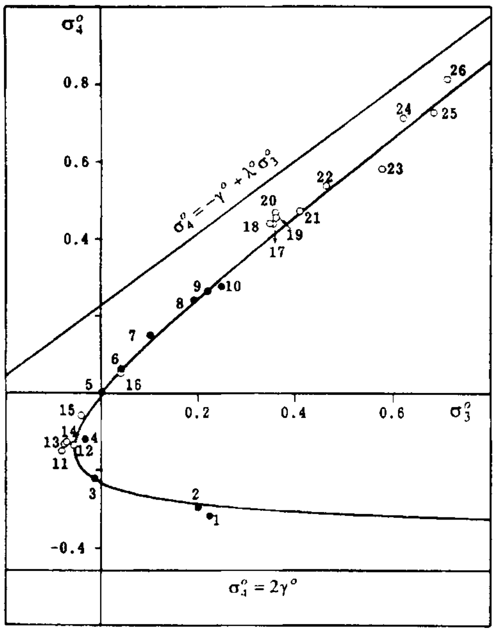

Figure 3. Interrelationship between σ_4^0 and σ_3^0 or $\sigma_{3,tr}^0$; o, Normal substituents with coordinates (σ_{4n}^0, σ_{3n}^0); •, special substituents with coordinates (σ_{4s}^0, $\sigma_{3s,tr}^0$). The lines drawn are for the theoretical two-parameter hyperbola [equation (9)] and its asymptotes. Numbering as in Table 1

N (for non-mesomeric) without going into details. For the present purpose, we have only to accept that *N* can be increased indefinitely whereas *M* is limited by finite upper and lower values.

By adapting Hine's clear presentation[15] of the dual separation method, we write in self-evident notation for σ^0 constants of both normal and special substituents

$$\sigma_3^0 = \rho_{3M}^0 M + \rho_{3N}^0 N \qquad (10)$$

$$\sigma_4^0 = M + N \qquad (11)$$

thus fixing $\rho_{4M}^0 = \rho_{4N}^0 = 1$. It follows from equations (10) and (11) that

$$\sigma_4^0 = (1 - \rho_{3M}^0/\rho_{3N}^0)M + (1/\rho_{3N}^0)\sigma_3^0 \qquad (12)$$

It is also well known[3] that relationships between σ_3^0 and σ_4^0 for the same substituent are matched by relationships between *M* and *N*.

Inserting equations (10) and (11) into theoretical equation (8) leads, for special substituents, to

$$M_s = \frac{\gamma^0}{1 - \lambda^0\rho_{3M}^0} - \frac{(1 - \lambda^0\rho_{3N}^0)N_s}{1 - \lambda^0\rho_{3M}^0} \qquad (13)$$

Given our reasonable assumption on the range of possible values for *M* and *N*, then from equation (13)

$$\lim_{N_s \to \infty} \frac{M_s}{N_s} = -\frac{1 - \lambda^0\rho_{3N}^0}{1 - \lambda^0\rho_{3M}^0} = 0$$

Hence, provided $\rho^0_{3N} \neq \rho^0_{3M}$, the above limit condition can only be fulfilled if

$$\lambda^0 = 1/\rho^0_{3N} \tag{14}$$

This result, besides conferring a theoretical meaning to the parameter λ^0, allows the simplification of equation (13), leading to

$$M_s = \gamma^0/(1 - \lambda^0\rho^0_{3M}) \tag{15}$$

which means that the value for the M-effect is a constant in all special substituents. It should be stressed that this conclusion follows directly from Taft's dual parameter model equation (12) combined with equation (14) and the linear relationship between σ^0_{4s} and σ^0_{3s} in the form of equation (8). Additionally, equation (15) suggests that parameter γ^0 of our hyperbolic model is intimately related to the M-effect.

It follows from equations (9)–(11) and (14) that

$$M_n\left[M_n - \frac{(1-2\lambda^0\rho^0_{3M})\gamma^0}{1-\lambda^0\rho^0_{3M}}\right] \Big/ \left(M_n + \frac{\lambda^0}{1-\lambda^0\rho^0_{3M}}\right) = -N_n \tag{16}$$

Equation (16), interrelating M and N values for normal substituents, is a hyperbola with asymptotes $M_n = 2\gamma^0 - N_n$ and $M_n = -\gamma^0/(1 - \lambda^0\rho^0_{3M})$.

The ubiquity of the transmission coefficient ρ^0_{3M} in the equations in this section is striking. Its value can only be fixed by means of the much debated[21–24] scaling of electronic substituent constant values. However, an upper bounding value for ρ^0_{3M} can be inferred from our hyperbolic model. First we note that the hyperbola for normal substituents represented by equation (16) passes through the origin, which corresponds to hydrogen, where

$$(\mathrm{d}M_n/\mathrm{d}N_n)_H = 1/(1 - 2\lambda^0\rho^0_{3M}) \tag{17}$$

Since one should expect to find points in the third quadrant (those for normal substituents with $M < 0$ and $N < 0$), this derivative must be finite and positive. Hence, from equation (17), $\rho^0_{3M} < 1/2\lambda^0$. Because ρ^0_{3M} is a non-negative parameter, by using our best estimate for λ^0 we obtain

$$0 < \rho^0_{3M} < 0{\cdot}52 \tag{18}$$

Further, these boundary values ensure that the curve interrelating M and N values also has points in the first ($M > 0$, $N > 0$) and fourth ($M < 0$, $N > 0$) quadrants, and predict a vacant second quadrant ($M > 0$, $N < 0$). Equation (15) for special substituents and equation (16) for normal substituents, together with the latter's asymptotes, are illustrated in Figure 4 on the basis of an arbitrarily chosen $\rho^0_{3M} = 1/3$.

DISCUSSION

Parameter λ^0

Exner's equation for expressing the *meta–para* interrelationship is restricted to normal substituents. It reads

$$\sigma_{4n} = \lambda\sigma_{3n} \tag{19}$$

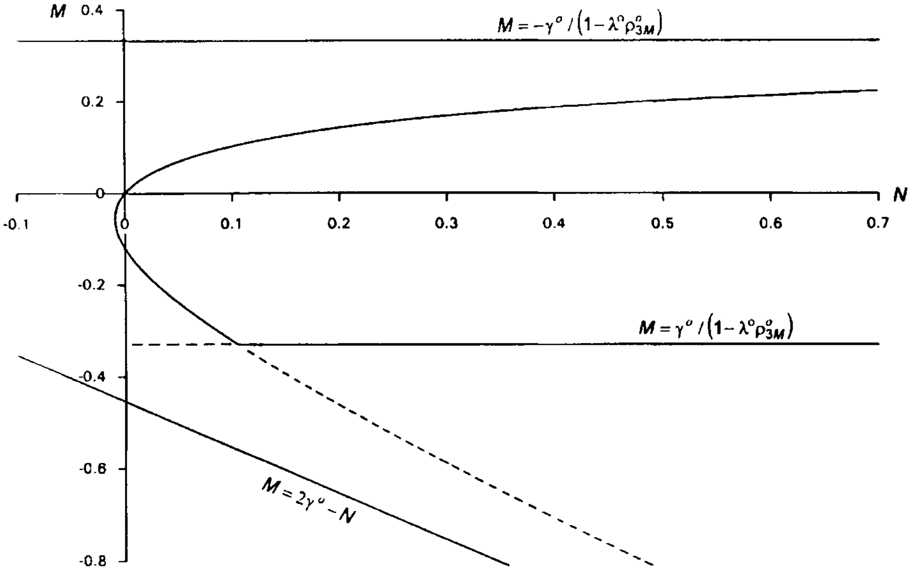

Figure 4. Schematic representation of M and N contributions to σ^0 constants. Hyperbolic equation (16) and its asymptotes for normal substituents and equation (15) for special substituents with $\rho^0_{3M} = 1/3$

and λ values in the small interval 1·13–1·17 have been reported[9–12] for the ionization of benzoic acid derivatives in aqueous and non-aqueous solvents. In our opinion, the virtue of Exner's analysis of the *meta–para* problem has been to recognize that the decisive feature for classifying a given substituent is the presence or absence of a lone electron pair in its first atom. Exner's insight is confirmed by our hyperbolic analysis of the unified σ^0-scale. Fitting experiments reported in the Appendix show that substituents —SO_2NH_2, —SO_2CH_3 and —NO_2 are best grouped together with other normal, carbon-family substituents rather than with special, heteroatom-family substituents.

Least rectangles fitting of (unweighted) σ^0_{n} values from Table 1 to equation (19) yields

$$\sigma^0_{4\mathrm{n}} = -0{\cdot}02 + 1{\cdot}18\sigma^0_{3\mathrm{n}} \qquad (r = 0{\cdot}993) \qquad (20)$$

a result within the approximation of Exner's equation. Although our hyperbolic model asymptote λ^0 and slope λ from equation (19) are intended to measure the same physico-chemical quantity [see equation (14)], the consequences of their numerically different values are opposite. The single, smaller than unity λ^0 value common to normal and special substituents means that non-mesomeric effects are slightly better transmitted to the reaction centre from the *meta* than the *para* position, in accordance with chemical intuition. Also, $\lambda^0 = 0{\cdot}960$ is in excellent agreement with Ehrenson's estimates[25] 0·936 and 0·966 of the same quantity for σ^0 reactivities by using a non-linear procedure,and with the evidence presented by Hoefnagel *et al.*[26] for the *meta*/*para* ratio of the inductive (or non-mesomeric) effect. Performing Exner's analysis with σ^0_{n} values led to equation (20) and thus to the opposite conclusion. Therefore, it cannot be reconciled with our hyperbolic model. On the other hand, a parameter λ should in general be a function of the skeletal structure of a given benzene compound. This is contrary to Taft's assumption[20,27,28] of the inductive effect being transmitted equally from *meta*- and from *para*-positions in all reaction series of benzene derivatives.

Parameter γ^0

The hyperbolic model asymptotic value γ^0 is a parameter with a simple physical definition. Referring to Figure 1, γ^0 can be defined as the non-zero σ^0_4 value to which corresponds an infinitely large σ^0_4/σ^0_3 ratio and thus a zero-valued σ^0_3 substituent constant. Therefore, γ^0 is expressed in sigma units. Since this is the first time that parameter γ^0 has been defined, a detailed analysis of this quantity is appropriate. The choice of conjugate rectangular hyperbolae to construct our model was based on the empirical evidence illustrated in Figure 1. Consequently, common γ^0 values for normal and special substituents were assumed. Now it can be shown that if Taft's dual equations (10) and (11) with identical transmission coefficients are to be applied to normal and special substituents, then $\gamma^0_{\mathrm{n}} = \gamma^0_{\mathrm{s}}$ as we have assumed. This assumption also leads to equal upper and lower limiting values for the M-effect. As shown in Figure 4, the lower limit is the constant value M_{s} given by equation (15) and the upper limit is the asymptotic value $M_{\mathrm{n}} = -M_{\mathrm{s}}$. This finding is clearly in agreement with the expected behaviour of the M-effect in systems insulated in relation to through-resonance effects.

It follows from this analysis that the parameter γ^0 is a measure of the largest possible M-effect by a substituent in the reference system for the sigma-zero scale. It has the same sign as the M-effect of special substituents. The physico-chemical significance of the quantity γ^0 should became clearer when γ-values are obtained for a variety of chemical processes involving different benzene derivatives. Nonetheless, it can be anticipated that the ratio γ/γ^0 gives the sensitivity to mesomeric effects of a given system in relation to the standard reaction.

Separation of M and N effects

As shown in Figure 4, a resolution of mesomeric (M) and non-mesomeric (N) contributions to σ^0 constants arises from combining Taft's equations for dual electronic effects with our hyperbolic *meta–para* interrelationship. M and N values are, however, dependent on the transmission coefficient ρ^0_{3M}, which corresponds to Taft's parameter α and whose fixing needs some sort of scaling. In spite of this limitation, some conclusions can be drawn. One is that the constant M_{s} value given by equation (15) can explain the finding by Hoefnagel and Wepster[17]that 'the most important and intriguing generalization is that, in contradiction with listed σ^0_{R} values, simple first-row substituents have essentially identical $\sigma^{\mathrm{n}}_{\mathrm{R}}$ values of about −0·35.' If this value is used for M_{s}, then from equation (15) $\rho^0_{3M} = 0.37$, which, although far from its maximum value, is a reasonable result in view of equation (18). Wells[29] reviewed the various α values in the literature and opined that for insulated reaction series α should have its maximum value. In accordance with our analysis this equals $1/2\lambda^0$ or 0·52. We note further that Taft and Lewis[27] found α to be 0·50 for their σ^0 scale while using $\lambda^0 = 1$. Another conclusion is concerned with the proposal by Pollet and Van Poucke,[30] who, based on Exner's analysis,[9] suggested using the difference $\sigma^0_{4\mathrm{s}} - \lambda^0\sigma^0_{3\mathrm{s}}$ as a measure of mesomeric effects in special substituents. Exner and Lakomý,[31] while supporting this proposal, add that 'with increasing positive inductive effect the negative mesomeric effect diminishes and in the limiting case is equal to zero.' Since it follows from equations (8) and (15) that

$$\sigma^0_{4\mathrm{s}} - \lambda^0\sigma^0_{3\mathrm{s}} = (1 - \lambda^0\rho^0_{3M})M_{\mathrm{s}}$$

this difference is indeed directly related to M_{s}, although we use a numerical value for λ^0 different from Exner's. However, contrary to Exner and Lakomý's expectation,[31] equation (15) predicts a non-variable negative mesomeric effect in special substituents.

Next we discuss Exner's contention[1,3,9,10,32] that mesomeric effects are negligible in normal substituents with the possible exception[1,10,11] of carbonyl substituents. This much criticized[4,13-15] consequence of equation (19) is dismissed by our analysis of the *meta–para* interrelationship. Inspection of Figure 3 reveals that the hyperbolic model introduces a slight curvature in Exner's straight line. However, this modification is enough to make provision for a non-negligible mesomeric effect in normal substituents. In fact, equation (9) can be rewritten as

$$\sigma^0_{4n} - \lambda^0\sigma^0_{3n} = -\gamma^0/(1 - 2\gamma^0/\sigma^0_{4n}) \tag{21}$$

On the other hand, combining equations (10) and (11) with equation (14) yields

$$\sigma^0_4 - \lambda^0\sigma^0_3 = (1 - \lambda^0\sigma^0_{3M})M \tag{22}$$

Now it follows from equations (21) and (22) that

$$M_n = -\gamma^0/(1 - \lambda^0\sigma^0_{3M})(1 - 2\gamma^0/\sigma^0_{4n}) \tag{23}$$

It is true that if $M_n = 0$ for all normal substituents then equation (22) would reduce to Exner's equation. However, this would imply $\gamma^0 = 0$, as can be seen from equation (21). In contrast, given our estimates for the parameters appearing in equation (23), with increasing positive σ^0_{4n} values the positive mesomeric effect increases and in the limiting case is equal to $-M_s$. An equivalent conclusion can be drawn from equation (16).

Finally, a theoretical interpretation is in order. Considering (i) the unified σ^0-scale is referred to a model system in which through-resonance between substituents and the reactive centre is inoperative, (ii) there is an appreciable *M*-effect in polar substituents even from the *meta* position and (iii) for attaining the maximum *M*-effect the presence of an electron pair in an atom next to the benzene ring in the *para* position suffices, we are led to the apparently startling interpretation that the *M*-effect appearing in Taft's equations (10) and (11) is most probably the polarization of benzene π-bonds resulting from interaction with substituents. The concept of non-classical or π-inductive effect is due to Everard and Sutton,[33] and we observe that Dewar and co-workers theory[34-36] of substituent effects 'book-keeps' jointly mesomeric interactions and π-inductive effects. However, we cannot forget that Exner[1,9,10] considers the π-inductive effect as a non-mesomeric effect which he invokes to justify a slope λ in equation (19) larger than unity. Setting aside the semantics involved, we continue to be at variance with Exner because this is not just a matter of different book-keeping. In fact, our criterion for distinguishing *M* from *N* effects was their different range of variation. In short, for *M*-effects we understand those electronic effects in which π-electrons participate that are bounded by upper and lower limits and that are not proportional to other, *N*-effects. In contrast, Exner's analysis implies a problematic proportionality between the π-inductive effect and other polar and field effects, or identical transmission coefficients. Lastly, it should be emphasized that our interpretation of *M*- and *N*-effects follows closely Taft's proposed separation between resonance (*R*) and inductive (*I*) effects. Since the π-inductive effect can be regarded as arising from mesomeric interactions, it is a resonance polar effect as defined by Taft and Lewis.[27] Such a term should then be included in the *R* values, not in the *I* values.[27,28]

CONCLUSIONS

An analysis of the unified σ^0-scale[8] with the aim of unravelling the *meta–para* interrelationship in benzene derivatives has led to the following conclusions. By a shifting from the conventional plot of σ^0_4 vs σ^0_3 to the representation of σ^0_4 vs σ^0_4/σ^0_3 (Figure 1), two groups of substituents are differentiated according to the presence or absence of a lone electron pair in the substituent atom attached to the benzene ring. Substituents belonging to these groups are called special or normal, respectively. To model this interrelationship, conjugate rectangular hyperbolae were fitted to the data by using a non-linear least rectangles procedure. Because of algebraic constraints, only the asymptotic values (designated by λ^0 and γ^0) were found to be theoretically important. Although necessitating two different equations (one for each group of substituents), single-valued parameters λ^0 and γ^0 suffice to describe the whole data.

Taft's dual substituent parameter treatment is employed to interpret our results. Two independent mechanisms for transmitting electronic effects are considered and freely designated as mesomeric (*M*) and non-mesomeric (*N*). It is shown that parameter λ^0 is equal to the *para/meta* ratio of transmission coefficients for the *N*-effect, and that the new parameter γ^0 is directly proportional to limiting values for the *M*-effect. On the basis of $\lambda^0 = 0{\cdot}96$, a new upper boundary value equal to 0·52 is found for the *meta/para* ratio (Taft's symbol α) of transmission coefficients for the *M*-effect [equation (18)].

In the representation of *para* vs *meta* σ^0 constants for normal substituents, our hyperbolic model introduces a slight curvature in relation to Exner's straight line (Figure 3). As a consequence, a λ^0 value smaller than unity and a non-zero *M*-effect in normal substituents were found, in contradiction with Exner's analysis[1,9,10,32] of these problems. The origin of this disagreement is ascribed to opposite views concerning the role of the π-inductive effect. In accordance with Dewar and co-workers' analysis,[34-36] we have concluded that the π-inductive effect is indistinguishable from other mesomeric interactions that are bound by small limiting values. On the other hand, Exner has associated the π-inductive effect with field and other inductive effects.

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APPENDIX

Non-linear fitting procedure

Luus and Jaakola[19] proposed a simple optimization method for solving non-linear programming problems. It is based on a direct search procedure utilizing pseudorandom numbers over a region whose size is reduced after each iteration. In our least rectangles problem, initial estimates for the fitting parameters were suggested by Figure 1. The number of iteractions was made equal to 100 and in each iteration 100 trials were performed. The searching interval began at 0·2 for all parameters and the reduction factor was 0·05. A constraint was introduced to avoid a combination of parameter values leading to a negative rectangle area. The Luus–Jaakola method was programmed in Turbo-Pascal version 5·0 and executed on a PC-compatible computer, model 486, 33 MHz. For each fitting experiment, a good convergence was obtained in less than 5 s of execution time, not including the printout of results.

Classifying substitutents —SO_2NH_2, —SO_2CH_3 and —NO_2

The unified σ^0-scale[8] includes three substituents whose first atom is a heterotatom without a lone electron pair.

Table A1. Fitting by three-parameter hyperbola of —SO_2NH_2, —SO_2CH_3 and —NO_2 as a normal or as a special substituent

	dS^a	
Substituent	Normal	Special
—SO_2NH_2	754	1116
—SO_2CH_3	251	3261
—NO_2	<1	11896

[a] Increase in the sum of rectangle areas ($S = \Sigma_i w_i R_i$) over the best fit for the other 23 substituents in Table 1.

The remaining data for 13 normal and 10 special substituents were taken as the basic set. Then the data for each of the substituents —SO_2NH_2, —SO_2CH_3 and —NO_2, considered alternatively as a normal or as a special substituent, were added once to the basic set. Table A1 reports the resulting increase in the sum of weighted least rectangle areas over the basic set. In all cases studied, these substituents are better described as normal substituents.