The Variation of Substituent Resonance Effects with Electron Demand

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The Hammett substituent constants for a number of substituents have been resolved into constant inductive (σ_I) and variable resonance (σ_R) contributions. Variations in σ_R have been interpreted in terms of changes in the demand for π electrons made on substituents and an empirical scale of ' electron demand ' has been set up. The relationship has been tested using reactivity data, and its applications discussed.

In recent years there has been a number of attempts to resolve the electronic effects of substituents in aromatic systems into independent inductive and resonance contributions.[1-3] The most successful of these approaches has been the dual substituent parameter (DSP) treatment of Ehrenson, Brownlee, and Taft,[3] who assume that resonance and inductive effects are totally independent and who use a modified form [equation (1)] of the Hammett equation, in which the terms P and P_0 refer to the property of interest expressed in energy

$$P - P_o = \rho_I\sigma_I + \rho_R\sigma_R \qquad (1)$$

units—usually log K (or k) and log K_o (or k_o). The validity of such a separation was tested by Ehrenson, Brownlee, and Taft, using equation (1), on a large body of data. The results were considered to justify the assumption that σ_I was dependent solely on the nature of the substituent, but to show that σ_R varied in a non-linear fashion according to the demands made on the substituent. Such variation is to be expected because the ability of a substituent to donate or accept π electrons cannot be limitless. Ehrenson *et al.* chose to overcome this difficulty by offering a number of σ_R scales (σ_R^o, $\sigma_{R(BA)}$, σ_R^+ and $\sigma_{R(A)}^-$) and suggested that the scale most suitable for the system under study be selected, the choice being the one which gave the best statistical correlation. In their study, ρ_I^{meta} and ρ_I^{para} were assumed to be independent; data involving *meta*-substituents were treated separately from data for *para*-substituents. Superficially this is advantageous because the equation can be applied to systems in which the susceptibility of the measured property to inductive and resonance effects is very different—perhaps even in opposition—but it does introduce the serious problem of deciding whether the results of such correlations are meaningful. Discrepancies which really arise because σ_R is not permitted values between or beyond a few fixed points are minimised by changes in the values of ρ_R and ρ_I. The result is serious enough if ρ_R alone is varied, but when ρ_I is adjusted as well it is hard to justify the claim that the electronic effect has been resolved into inductive and resonance contributions. The problem is likely to be most serious for reactions of the σ_R^+ type since the difference between the actual σ_R and σ_R^+ may be quite large. In view of this the results obtained from the DSP treatment in cases where ρ_I is substantially different from ρ_R must be treated with caution.

It seemed to us that these difficulties inherent in the DSP treatment might be overcome by discarding the assumption of a limited range of discrete values for σ_R and allowing it to be a continuous function of the π electron demand on the substituent. This paper describes the derivation of this function—the relationship between σ_R and electron demand—and examines the utility of the approach to the analysis of substituent effects.

DISCUSSION

The concept of ' electron demand ' made on a substituent is most conveniently considered by looking at the effect on the substituent of the total aromatic system plus attached groups and reaction site. This is the reverse of the normal viewpoint, in which the effect of the substituted aryl group on the reaction site is considered, but it confers several advantages. There need be no distinction between effects operating from the *meta*- or *para*-positions, or between aromatic and aliphatic systems. The reaction or equilibrium studied, or the spectroscopic measurement made, becomes simply the probe that measures the extent of π electron demand on the substituent (the term ' electron demand ' will be used to include situations in which the substituent accepts π electrons, where demand may be considered to be numerically negative). The extent to which a substituent donates or attracts π electrons will depend on the strength of this demand.

In setting up our scale of electron demand we have made two key assumptions. The first is that the relationship between σ_R and electron demand is independent of the source of the demand. The second is that this relationship is of the same mathematical form for all substituents. Both are reasonable if the π interaction between the substituent and the rest of the molecule is always of the same type; the second may be questioned in some circumstances—for example when *d* orbitals are involved—but such cases arise infrequently. The first assumption allows us to define the relationship between σ_R and electron demand for one situation and apply it to all others and, for no other reason than the amount of data available, we chose to attempt to define the relationship using the benzenoid system and the Hammett equation.

The Determination of σ_R *Values*.—The usual approach to calculating σ_{para} values using the original, one-substituent parameter version of the Hammett equation, is to calculate ρ for the reaction based on the *meta* substituents and then to assume that $\rho_{para} = \rho_{meta}$. That σ_{meta} is independent of the nature of the reacting side-chain to within normal error limits is generally accepted; that $\rho_{para} = \rho_{meta}$ is arguable. There is some evidence to suggest that $\rho_I(para)/\rho_I(meta) \sim 1.12$ [4] and therefore some support for assuming a similar value for ρ_{para}/ρ_{meta}. However, in calculating σ_R values in this paper it has been assumed that $\rho_{meta} = \rho_{para}$; any resulting systematic deviations in σ_R will be taken care of by the empirical nature of the calculations. The substituent constant derived will be unresolved ($\sigma_I + \sigma_R$), from which σ_R is obtained by subtracting the value of σ_I.

The choice of suitable σ_I values presents some difficulty. Most of the data used in setting up the scale of electron demand (see later) are based on spectroscopic measurements in carbon tetrachloride, deuteriochloroform or dimethyl sulphoxide, whereas most of the σ_I values available have been derived from kinetic or equilibrium measurements in weakly protic solvents such as water, alcohols, or mixed aqueous–organic systems. Recent work has shown that good Hammett correlations for *meta*-substituents in non-polar solvents may require σ constants significantly different from normal; the discrepancies appear too high to arise from resonance effects operating from the *meta*-position.[5] This suggests that literature values of σ_I may not necessarily apply in non-polar solvents, and for this reason we have compiled a list of σ_I values by comparing the literature values for protic media with the data of Taft and his co-workers on ^{19}F chemical shifts in *meta*-fluorobenzenes [6] and with the σ_{meta} values reported in ref. 5. The ^{19}F chemical shift values for Me, Ph, OPh, Br, and F substituents show little solvent dependence and an excellent correlation with literature σ_I values. The OMe group ($\sigma_{I(H_2O)} = 0.27$) gave an acceptable correlation, but a value of 0.24 was better for non-aqueous systems; this is consistent with the lower value of σ_{meta} for this substituent observed in CCl_4 and Me_2SO. For the important NMe_2 substituent the ^{19}F data suggest that in CCl_4 a value of 0.12 would be suitable, but as there is no way of estimating the figure for dimethyl sulphoxide the literature value of 0.06 has been used. No reliable σ_I for the OAc substituent exists in the literature, but the ^{19}F data support a value of 0.29 in carbon tetrachloride. Taft does not report data for the Cl and I substituents but in view of the solvent independence of the values for Br and F the literature σ_I values should apply satisfactorily in non-polar solvents. The ^{19}F chemical shift data for the CN and NO_2 groups do not correlate well with σ_I, even in solvents such as methanol, and the deviations are in the opposite direction to that suggested by their σ_{meta} values. On the basis of the σ_{meta} data for Me_2SO and CCl_4 solvents, the literature values of +0.56 and +0.65 have been retained for these substituents for dimethyl sulphoxide and +0.64 and +0.74 used for carbon tetrachloride. Table 1 lists the σ_I values used in this work; it is unfortunate but unavoidable that no series exists by which their validity can be tested.

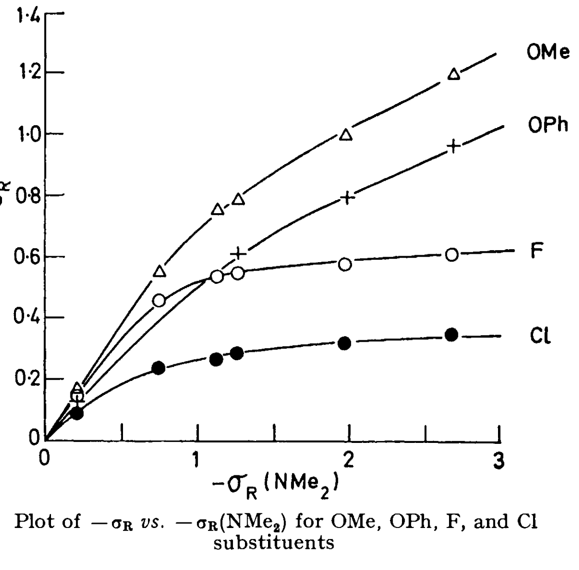
TABLE 1

Values [a] of σ_I used in the resolution of substituent constants

Substituent:	NMe_2	OH	OMe	OPh	F	Cl	Br	I	Me	OAc	CN	NO_2	Ac	CO_2R
$\sigma_I(CCl_4)$	0.12		0.24	0.38	0.50	0.46	0.44	0.39	−0.04	0.29	0.64	0.74	0.18 [d]	
$\sigma_I(Me_2SO)$	0.06	0.12 [b]	0.24	0.38	0.50	0.46	0.44	0.39	−0.04	0.29 [c]	0.56	0.65		
$\sigma_I(H_2O)$	0.06	0.29 [b]	0.27	0.38	0.50	0.46	0.44	0.39	−0.04	0.29 [c]	0.56	0.65	0.28	0.30

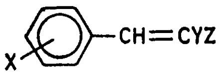
[a] Derived as described in the text. [b] An estimate based on a comparison of σ_{meta} for the OH and OMe groups. [c] The value of σ_I is assumed to be solvent independent (see Discussion). [d] An estimate based on Taft's ^{19}F work.[5] Unreliable (*cf.* NO_2 and CN).

Constructing a Scale of Electron Demand.—We have assumed that σ_R is a continuous function of electron demand from $\sigma_R = 0$ (no demand) asymptotically approaching $\sigma_R = \sigma_R^{\infty}$ with increasing demand. As a preliminary electron demand scale we used σ_R for the NMe_2 group, on the grounds that such a powerful electron donor will show approximately linear variation in σ_R with electron demand over the normal range of reactivities. (The most powerful common +R group, O^-, we rejected because its behaviour is strongly solvent dependent). No common −R substituent is sufficiently powerful to be suitable as a preliminary measure of electron demand and for this reason we limited our initial study to +R substituents. Figure 1 shows σ_R values for a selection of +R groups plotted against $\sigma_R(NMe_2)$ for six systems; this family of curves could be used to estimate σ_R for any substituent in an analogous system provided σ_R for one substituent is known. In practice it would be more useful to fit the data to a suitable mathematical function. If this can be done successfully for enough systems it justifies the assumption that the relationship between σ_R and demand is in-



Plot of $-\sigma_R$ *vs.* $-\sigma_R(NMe_2)$ for OMe, OPh, F, and Cl substituents dependent of the source of the demand, and it also makes the method more generally useful.

We chose to adopt $\delta^{13}C_\beta$ for the styrene series (I; Y = Z = H) as that in which the substituent X experiences unit electron demand, because the ^{13}C n.m.r. chemical shifts at C_β in these series constitute the most precise data set available to include the NMe_2 group.[7,8] (For a few substituents these chemical shifts are not available and other data were used.) Trial curve-fitting showed a logarithmic relationship between σ_R and electron demand to be the most satisfactory.



(I)

$$\varepsilon_+ = \log[1 - (\sigma_R/\sigma_R{}^{\infty})]/\log[1 - (\sigma_R{}^H/\sigma_R{}^{\infty})] \qquad (2)$$

$$\sigma_R = \sigma_R{}^{\infty}\left[1 - \left(\frac{\sigma_R - \sigma_R{}^H}{\sigma_R{}^{\infty}}\right)^{\varepsilon_+}\right] \qquad (3)$$

Representing electron demand by ε_+ (for π electron flow towards the side chain), equation (2) satisfies the conditions $\sigma_R = 0$ at $\varepsilon_+ = 0$, $\sigma_R = \sigma_R{}^H$ at $\varepsilon_+ = 1$ and $\sigma_R \longrightarrow \sigma_R{}^{\infty}$ at $\varepsilon_+ \longrightarrow \infty$. [Equation (3) is the more convenient form for calculating σ_R values.] An initial ε_+ scale derived from the expression $\varepsilon_+ = \sigma_R(NMe_2)/\sigma_R{}^H$ gave curves that were not strictly logarithmic. These curves were constrained to logarithmic form and a mean ε_+ scale derived from this. Table 2 gives the 'best-fit' values of $\sigma_R{}^H$ and $\sigma_R{}^{\infty}$ for each data set; Table 3 shows the excellent agreement between experimental values for σ_R and the values obtained from equation (2), and the best-fit ε_+ values for each system. The only serious

TABLE 2

Calculated values of $\sigma_R{}^H$ and $\sigma_R{}^{\infty}$ for +R substituents

Substituent	$\sigma_R{}^H$	$\sigma_R{}^{\infty}$
NMe_2	−1.13	−12
OH	−0.84	−1.58
OMe	−0.75	−1.24
OPh	−0.57	−1.02
F	−0.53	−0.61
Cl	−0.28	−0.35
Br	−0.23	−0.31
I	−0.17	−0.31
OAc	−0.20	−0.38
Me	−0.19	−0.33

TABLE 3

Experimental values of σ_R used to evaluate[a] $\sigma_R{}^H$ and $\sigma_R{}^{\infty}$, and calculated σ_R and ε_+ values from equation (2)

		NMe_2	OH	OMe	OPh	F	Cl	Br	I	OAc	Me
Reaction (1)	$-\sigma_R$(expt.)	2.68	1.49	1.20	0.97	0.61	0.35	0.31	0.29	0.36	0.32
$\varepsilon_+ = 3.7$	$-\sigma_R$(calc.)	3.68	1.48	1.20	0.97	0.61	0.35	0.31	0.29	0.36	0.32
Reaction (2)	$-\sigma_R$(expt.)	1.97	1.16	1.00	0.80	0.58	0.32	0.27	0.26	0.30	0.26
$\varepsilon_+ = 1.8$	$-\sigma_R$(calc.)	1.97	1.18	1.01	0.79	0.59	0.33	0.28	0.24	0.33	0.26
Reaction (3)[b]	$-\sigma_R$(expt.)	1.26		0.79	0.61	0.55	0.29	0.25	0.18	0.22	0.23
$\varepsilon_+ = 1.12$	$-\sigma_R$(calc.)	1.26		0.80	0.61	0.55	0.29	0.24	0.18	0.22	0.20
Reaction (4)	$-\sigma_R$(expt.)	1.13		0.76		0.54[c]	0.27	0.22	0.15		0.19
$\varepsilon_+ = 1.00$	$-\sigma_R$(calc.)	1.13		0.75		0.53	0.28	0.23	0.19		0.19
Reaction (5)	$-\sigma_R$(expt.)	0.75		0.55		0.46	0.24	0.20			0.12
$\varepsilon_+ = 0.66$	$-\sigma_R$(calc.)	0.76		0.57		0.45	0.23	0.18			0.14
Reaction (6)	$-\sigma_R$(expt.)		0.17	0.15		0.16	0.09	0.05		0.03	0.03
$\varepsilon_+ = 0.15$	$-\sigma_R$(calc.)		0.17	0.16		0.16	0.08	0.05		0.04	0.04

[a] The data used in the evaluation are based on the following reaction series: Reaction (1) $\delta^{13}C_\beta$ for β,β-dicyanostyrenes in Me_2SO. Reaction (2) $\delta^{13}C_\beta$ for β-nitrostyrenes in Me_2SO. Reaction (3) $\delta^{13}C_\beta$ for stilbenes in $CDCl_3$. Reaction (4) $\delta^{13}C_\beta$ for styrenes in CCl_4. Reaction (5) $\delta^{13}C_\beta$ for β,β-dimethylstyrenes in CCl_4. Reaction (6) mean σ_{meta} values based on reactions 1—5. [b] Unpublished data. It has been assumed that $\sigma_I(CDCl_3) = \sigma_I(CCl_4)$. [c] The data reported[8] by Reynolds and his co-workers for this substituent are in error. This value is based on a re-measurement ($\delta^{13}C_\beta = 113.01$ p.p.m.).

TABLE 4

Comparison of calculated σ_R values with those derived from σ scales based on reactivity data[a]

		NMe_2	OH	OMe	OPh	F	Cl	Br	I	OAc	Me
$\sigma_R{}^+$ (ref. 10)[a]	$-\sigma_R$(expt.)	1.76	1.21	1.05	0.88	0.57	0.35	0.29	0.24	0.37[b]	0.27
$\varepsilon_+ = 2.0$	$-\sigma_R$(calc.)	2.15	1.23	1.05	0.82	0.60	0.34	0.29	0.25	0.30	0.27
σ_R (ref. 9)[a]	$-\sigma_R$(expt.)	0.89[c]	0.66	0.54	0.70[d]	0.44	0.23	0.21	0.12[e]	0.13[f]	0.13
$\varepsilon_+ = 0.67$	$-\sigma_R$(calc.)	0.77	0.63	0.57	0.44	0.45	0.23	0.19	0.13	0.15	0.14
$\sigma_R{}^n$ (ref. 11)[a]	$-\sigma_R$(expt.)	0.30	0.41	0.36	0.29	0.32	0.17	0.14	0.08		0.06
$\varepsilon_+ = 0.38$	$-\sigma_R$(calc.)	0.44	0.40	0.37	0.29	0.33	0.16	0.13	0.08	0.09	0.09
σ_R(*meta*) (ref. 9)[a]	$-\sigma_R$(expt.)	0.21	0.17	0.15	0.13	0.16	0.09	0.05	0.04		0.03
$\varepsilon_+ = 0.15$	$-\sigma_R$(calc.)	0.18	0.17	0.16	0.12	0.16	0.08	0.06	0.04	0.04	0.04
$\sigma_R{}^+$ (ref. 3)[a]	$-\sigma_R$(expt.)	1.75		1.02	0.87	0.57	0.36	0.30	0.25		0.27
$\varepsilon_+ = 2.0$	$-\sigma_R$(calc.)	2.15	1.23	1.05	0.82	0.60	0.34	0.29	0.25	0.30	0.27
$\sigma_{R(BA)}$ (ref. 3)[a]	$-\sigma_R$(expt.)	0.83		0.61	0.58	0.45	0.23	0.19	0.16		0.11
$\varepsilon_+ = 0.73$	$-\sigma_R$(calc.)	0.84	0.67	0.61	0.46	0.47	0.24	0.20	0.14	0.16	0.14
$\sigma_R{}^o$ (ref. 3)[a,g]	$-\sigma_R$(expt.)	0.52		0.45	0.34	0.34	0.23	0.19	0.16		0.11
$\varepsilon_+ = 0.45$	$-\sigma_R$(calc.)	0.52	0.46	0.42	0.31	0.37	0.18	0.14	0.09	0.11	0.10

[a] The σ scales used as a source of σ_R values were the σ^+ scale of H. C. Brown,[10] the σ scale of McDaniel and Brown,[9] the σ^n scale of Hoefnagel and Wepster,[11] and the $\sigma_R{}^+$, $\sigma_{R(BA)}$ and $\sigma_R{}^o$ scales of Ehrenson, Brownlee, and Taft.[3] [b] P. B. D. de la Mare, personal communication; based on the solvolysis of *p*-acetoxyphenyldimethylcarbinyl chloride in 90% aqueous acetone. [c] Based on a pK_a with no correction for zwitterion. Hoefnagel and Wepster[11] suggest that $\sigma = -0.7$ ($\sigma_R = -0.76$) would be a better value. [d] Comparison with the methoxy-value suggests that this value is in serious error in spite of the reported reliability of the pK_a (±0.02). [e] R. A. Robinson and K. P. Ang, *J. Chem. Soc.*, 1959, 2314. [f] Reference 13, O. Oxner and J. Lakomy, *Coll. Czech. Chem. Comm.*, 1970, **35**, 1371. [g] The authors claim that for the Cl, Br, I, and Me substituents $\sigma_R{}^o$ is not statistically different from $\sigma_{R(BA)}$.

discrepancy in Table 3 is the difference between the experimental and calculated $\sigma_R(NMe_2)$ values for the β,β-dicyanostyrene series. Of all the compounds for which data are available, *p*-dimethylamino-β,β-dicyanostyrene will show the greatest resonance interaction between the substituent and side-chain. The extent of this electron transfer may be so great that the nature of the side-chain is changed and its electron-withdrawing power diminished, so that our assumption that ε_+ is independent of the nature of the substituent has broken down in this instance.

We tested our approach by deriving ε_+ and σ_R values for the most reliable extensive data sets in the literature. These are the σ values of McDaniel and Brown for the ionisation of benzoic acids,[9] the σ^+ values of Brown and Okamoto,[10] the σ^n values of Hoefnagel and Wepster,[11] and the σ^o values of Yukawa *et al.*[1] The $\sigma_{R(BA)}$, σ_R^o, and σ_R^+ values [3] of Ehrenson, Brownlee, and Taft were also used since although these are based on reaction series for which $\lambda \neq 1$, the DSP relationship should be sufficiently general to handle situations for which $\lambda = 1$. The results (Table 4) show that agreement between σ_R values calculated by our method and values derived from the literature is generally good; obvious discrepancies (*e.g.* for NMe_2 and OPh) can be accounted for in terms of the limited and scattered data for these groups.

The success of this approach for +R groups suggested to us that σ_R^H and σ_R^∞ values might be derived from reactivity data for substituents for which suitable n.m.r. data were not available—in particular —R substituents. Parameters for these, calculated mainly from literature reactivity data, are listed in Table 5. The ε_- scale for π electron-withdrawing groups was placed on the same scale as the ε_+ scale by constraining it to pass through the point $\sigma_R = \sigma_R^n$ at $\varepsilon_- = 0.38$; it was pleasing to find that with reasonable values for σ_R^∞ the curve also passes through $\sigma_R = \sigma_R(meta)$ at $\varepsilon_- = 0.15$. The σ_R^H and σ_R^∞ values for —R substituents (Table 5) are less reliable than those for +R substituents (Table 2) and they could not be tested; they have been calculated from the most reliable data available and no reactions for which results have been reported require σ_R values between σ_R^n and σ_R^∞. However, comparison of the calculated and experimental values in Table 5 gives an indication of the goodness of fit.

TABLE 5

σ_R Values for —R substituents

	NO_2	CH_3CO	CN	CO_2R
σ_R^H	0.28	0.41	0.25	0.29
σ_R^∞	0.55	0.54	0.40	0.41
σ_R^- (A) [a]	0.55	0.54	0.40	0.41
σ_R^- (P) [b]	0.55	0.54	0.30 [h]	0.32 [h]
σ_R (styrenes) [c]	0.39	0.47	0.27	
$\varepsilon_- = 1.7$	0.39	0.49	0.32	
σ_R (nitrostyrenes) [d]	0.28		0.25	
$\varepsilon_- = 1.0$	0.28		0.25	
σ_R (dicyanostyrenes) [e]	0.20		0.20	
$\varepsilon_- = 0.65$	0.20		0.19	
$\sigma_{R\,(BA)}$ [f]	0.13	0.22	0.14	0.16
$\varepsilon_- = 0.38$	0.13	0.23	0.12	0.15
σ_R (*meta*) [g]	0.06	0.10	0.00	0.07
$\varepsilon_- = 0.1$	0.06	0.10	0.06	0.07

[a] Based on pK_a values of anilinium ions in H_2O at 25 °C. [b] Based on pK_a values of phenols in H_2O at 25 °C. [c] Reaction (4), Table 3. [d] Reaction (2), Table 3. [e] Reaction (1), Table 3. [f] Calculated from σ scale of McDaniel and Brown.[9] [g] Reference 9. The σ_R value for the cyano-substituent is unreliable. [h] The reason for these deviations is unknown but some type of saturation effect may be involved.

The results presented so far gave us confidence that the parameters ε_+ and ε_- are a satisfactory measure of π-electron demand at the site generating the demand. In the following section the application of these parameters is considered.

The Variable Resonance Parameter Equation.—Equation (3) may be written as a dual substituent parameter equation with three unknowns ρ_I, ρ_R, and ε [equation (4)].

$$P_i - P_o = \rho_I\sigma_I + \rho_R\sigma_R^\infty\left[1 - \left(\frac{\sigma_R^\infty - \sigma_R^H}{\sigma_R^\infty}\right)^\varepsilon\right] \quad (4)$$

We refer to this as the Variable Resonance Parameter (VRP) equation, which allows calculation of the π electron demand ε_+ and ε_-. With a suitable body of reliable data equation (4) can be used with a non-linear regression computer programme to evaluate ρ_I, ρ_R, and ε, and the ε values so obtained provide a single-parameter estimate of electron demand. In the DSP treatment, demand must be judged in terms of both λ (= ρ_I/ρ_R) for the system and the type of σ_R required to obtain a correlation. The need for a multiple regression analysis can be avoided if some simplifying assumptions are made. The data in Table 4 suggest that the assumption $\rho_I \sim \rho_R$ may well hold for all reactivity data in benzenoid systems; if ρ can be evaluated independently then a table of ε *vs.* σ_R generated at intervals of 0.01 in ε allows rapid evaluation of the best-fit ε value. The independent evaluation of ρ requires either that $\rho_{meta} = \rho_{para}$ or that ρ is the same for +R and —R substituents. In many situations both are good approximations, particularly for simple reactions of benzene derivatives, and they provide a useful cross-check. The resulting approximate values for ρ can be used to give improved values by iteration if required. In cases where ρ_I and ρ_R are significantly different and independent evaluation of either is not possible, equation (4) must be evaluated by regression analysis or the DSP equation employed.

Reactions of simple benzenoid systems will fall into a small number of classes distinguished by the magnitude of their ε_+ and ε_- values. Of the systems in which substituent and reaction site are *meta*, most will have $\varepsilon_+ = \varepsilon_- = 0.15$; when a third group is present which can interact directly with the substituent (*e.g.* in the ionisation of 3-X-naphthols [12] and naphthylamines [13]) this may no longer be true. Reactions usually described as σ^o or σ^n type will have $\varepsilon_+ = \varepsilon_- = 0.38$. Reactions for which $\varepsilon_+ = 0.38$, $\varepsilon_- > 0.38$, will be those usually referred to as σ^- or partial σ^-, and those with $\varepsilon_+ > 0.38$, $\varepsilon_- = 0.38$ will cover the spectrum σ^n to σ^+ and beyond, including the reactions of the benzoic acids and their derivatives. Reactions for which neither ε_+ nor ε_- have values of 0.15 or 0.38 will be rare in benzenoid systems but will include pK_a values of 4-X-pyridinium ions, ^{13}C

n.m.r. chemical shifts of 4-X-styrenes and all reactions of non-benzenoid compounds.

TABLE 6

Comparison of experimental and calculated pK_a values for the ionisation of 4-substituted pyridinium ions in water at 25 °C

Substituent	pK_a(expt)[a]	pK_a(DSP)[b]	pK_a(VRP)[c]
H	5.21	5.21	5.21
NMe_2	9.59[d]	9.60	8.57
OMe	6.58	6.57	6.59
Cl	3.83	3.83	3.84
Br	3.75	3.77	3.73
I	4.01[e]	3.89	4.55
Me	6.03	6.09	6.09
CO_2R	3.49	3.30	3.47
Ac	3.51	3.35	3.53
CN	1.86	2.00	1.85
NO_2	1.39	1.94	1.37

[a] Data are those of Fischer, Galloway, and Vaughan[14] unless otherwise noted. [b] Calculated from the equation $pK_a^X = pK_a^H - 5.104\ \sigma_I - 2.081\ \sigma_R^+$. [c] For +R substituents $\rho = 5.5$, $\varepsilon_+ = 0.58$; for −R substituents $\rho = 6.0$, $\varepsilon_- = 0$. [d] Measured by F. Cruege, G. Girault, S. Coustal, J. Lascombe, and P. Rumpf, *Bull. Soc. Chim. France*, 1970, 3889. [e] Unpublished result of E. Spinner at 20 °C.

The assessment of electron demand in terms of the VRP parameters ε_+ and ε_- can give additional insight into the nature of the system under study. For example, a DSP analysis[3] of the pK_a values of 4-X-pyridinium ions (water at 25 C°)[14] assigned the system as σ^+ type, $\rho_I = 5.153$, $\rho_R = 2.688$, $f = 0.06$. Other workers[14] have described the same data as σ_{BA} for +R substituents and σ_I for −R groups. The results of our VRP analysis (Table 6) support the second view; for +R substituents $\rho = 5.5$ and $\varepsilon_+ = 0.58$, and for −R substituents $\rho = 6.0$ and $\varepsilon_- = 0$. The low value for ε_- can be accounted for by assuming that −R substituents almost completely suppress the resonance form which places a positive charge on the aza-nitrogen in both the protonated and unprotonated derivative. We believe that the difference of almost one pK unit between the experimental value for the p-NMe_2 derivative and our calculated value arises from the saturation effect already noted for $\delta^{13}C_\beta$ for p-dimethylamino-β,β-dicyanostyrene.

Conclusion.—The ε_+ and ε_- parameters of the VRP treatment provide a convenient measure of electron demand which allows ready comparison between systems. Where the property being measured is sensitive to the resonance effect of both +R and −R substituents, application of the DSP treatment may result in the effect passing unnoticed as a rather poor correlation. The VRP approach, which treats +R and −R substituents independently, deals with this situation well but for each type of substituent the data must cover a more restricted range with a consequent loss of precision in derived parameters. The VRP equation does not easily accommodate situations where ρ_I is clearly different from ρ_R; the DSP treatment on the other hand will give misleading λ values in situations where no one of its σ_R scales is satisfactory. At the present time suitable data are not available to allow us to apply the VRP treatment to non-benzenoid systems. Preliminary studies we have done suggest that in such systems ρ values for +R and −R substituents differ, but the range of substituents available is too limited for us to be confident of the results. Satisfactory study of any such system will require data for the +R groups OMe, Me, F, Cl, and Br, with NMe_2 if possible; for −R substituents $^-NO_2$, ^-CN, and ^-Ac would constitute the minimum set. Others should be included as their σ_R^H and σ_R^∞ values are evaluated.

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REFERENCES

[1] Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Japan*, 1959, **32**, 971.

[2] C. G. Swain and E. C. Lupton, *J. Amer. Chem. Soc.*, 1968, **90**, 4328.

[3] S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Progr. Phys. Org. Chem.*, 1973, 10.

[4] O. Exner, *Coll. Czech. Chem. Comm.*, 1966, **31**, 65.

[5] D. A. R. Happer, S. M. McKerrow, and A. L. Wilkinson, *Austral. J. Chem.*, 1977, **30**, 1715.

[6] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, 1963, **85**, 709.

[7] D. A. R. Happer, *Austral. J. Chem.*, 1976, **29**, 2607.

[8] G. K. Hamer, I. R. Peat, and W. F. Reynolds, *Canad. J. Chem.*, 1973, **51**, 897.

[9] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

[10] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

[11] A. J. Hoefnagel and B. M. Wepster, *J. Amer. Chem. Soc.*, 1973, **95**, 5357.

[12] A. Bryson and R. W. Matthews, *Austral. J. Chem.*, 1963, **16**, 401.

[13] A. Bryson, *J. Amer. Chem. Soc.*, 1960, **82**, 4862.

[14] A. Fischer, W. J. Galloway, and J. Vaughan, *J. Chem. Soc.*, 1964, 3591.