

On the Analysis of Substituent Effects. Part 1. Hammett and Related Plots

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The overall pattern of significant deviations from straight lines through the origin in Hammett-like plots is shown to be remarkably simple when the choice of standard substituent constants is based on ^{13}C substituents chemical shifts at the β site in ring-substituted styrenes. This simplicity is explained in terms of a novel theoretical analysis of substituent effects. It could also be explained in terms of field and resonance substituent effects if the concept that the resonance effect supplements the field effect was replaced with the concept that the resonance effect modifies the field effect by an amount that can vary but only up to a maximum. The concept of through-resonance could be retained but some effects currently attributed to through-resonance would have to be reattributed to a field-modifying major rearrangement of electronic structure within the benzene ring. From our analysis, the ratio of values of the resonance parameter for corresponding *meta* and *para* substituents is not even approximately independent of the nature of the substituent, which indicates a serious flaw in commonly used dual substituent parameter expressions.

It is well established¹ that the quantitative effects of substituents on the values of various physical and chemical properties of derivatives of benzene and other unsaturated hydrocarbons (δP) cannot be expressed accurately in terms of a single scale of substituent constants. Thus equation (1) will not hold

$$\delta\text{P} = \rho\sigma_{\text{standard}} \quad (1)$$

universally whatever the choice of σ_{standard} . In this paper we shall show that the overall pattern of significant deviations from straight lines through the origin in δP versus σ_{standard} plots is particularly simple, and easy to interpret in electronic terms, when the choice of σ_{standard} is a scale based on the ^{13}C substituent chemical shifts (s.c.s.) at the β site in *meta*- and *para*-ring-substituted styrenes. Our reasons for choosing this particular scale, which we label σ_{ST} , will be explained.

The theory of equation (1) to hold universally is usually explained² in terms of there being at least two independent kinds of substituent effect, such as a field/inductive effect and a resonance effect. The total substituent effect is usually considered to be expressible in terms of a field constant whose value does not vary with the nature of the rest of the molecule to which the substituent is bonded, and a resonance parameter whose value is considered by most, although not by all,³ to vary significantly with the nature of the rest of the molecule to which the substituent is bonded. The mixture of field and resonance effects on different properties is expected to be different even in the same functional group. Figure 1 shows a plot of the σ^+ substituent constants⁴ against σ_{ST} . The σ^+ constants are based on $\log k$ for reactions involving the formation of conjugated cations. The resonance demand on conjugated π -donors is expected to be very much greater in the activated states of the appropriate reaction complexes than in the ground state of styrene. However the plot shows that for a set of common π -donors the points lie almost perfectly on a straight line through the origin, irrespective of the nature of the donor and of whether it is in the conjugated *para*-position or the non-conjugated *meta*-position relative to the probe site. Clearly there is something wrong with the usual method of analysis of substituent effects.

Figure 2 shows plots against σ_{ST} of the commonly used σ , σ^0 , and σ sets of standard substituent constants.^{4,5} The pattern of deviations from linearity is qualitatively similar in the three cases. We have found that these scales and many other sets of δP can be expressed quantitatively by equation (2) with the same

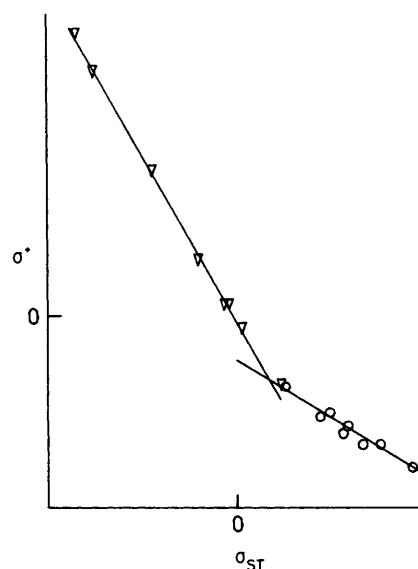


Figure 1. A plot of σ^+ against σ_{ST} . In this and subsequent figures: (a) σ_{ST} is the $^{13}\text{C}_\beta$ s.c.s. in ring-substituted styrenes⁹ expressed in units of 5 p.p.m.; (b) the symbols ∇ and \circ refer to substituents which are π -donors and π -acceptors respectively; (c) except where indicated both *meta* and *para* substituents are included; (d) the lines have no statistical significance: they are for guidance in detecting qualitative patterns

$$\delta\text{P} = \rho[\sigma_{\text{ST}} - \lambda(\sigma_{\text{ST}} - \sigma_1)] \quad (2)$$

values of ρ and of λ for *meta* and *para* substituents. The values of λ invariably lie between zero and unity (e.g. 0 for σ^+ , 0.25 for σ , 0.45 for σ^0 , and 1 for σ_1).

There is good evidence⁶ that the value of σ_1 is a quite accurate measure of the field effect of a substituent in the absence of overlap between the substituent and the rest of the molecule to which it is attached. Thus we can reasonably regard the deviations in the plot of σ_1 against σ_{ST} as being due to such π -overlap effects. However the $\lambda(\sigma_{\text{ST}} - \sigma_1)$ term cannot be regarded as a measure of the variation of an independent resonance effect because of the way in which the value of λ varies with the nature of the property and with the nature and the position of the functional group. We shall suggest modifications

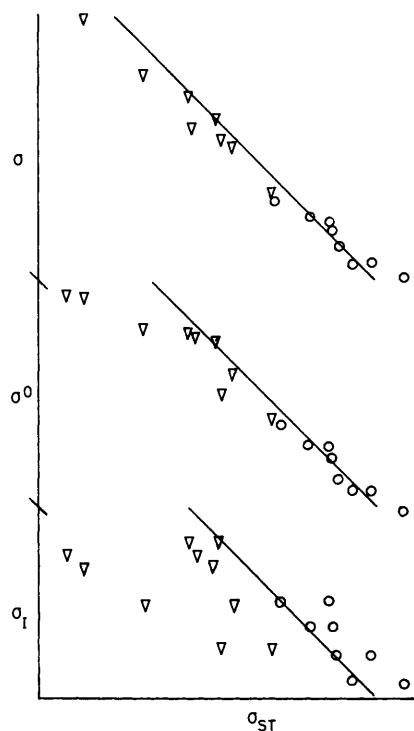


Figure 2. Plots of σ , σ^0 , and σ_1 against σ_{ST} . See footnotes to Figure 1

to the field and resonance analysis after proposing a novel theoretical analysis which is compatible with the experimental observations mentioned above.

Theory

Some Necessary Conditions for a Quantitative Linear Correlation.—In any field model of substituent effects there are certain conditions which are necessary, although not sufficient, for quantitative linear correlations to be widely observed. First, the magnitude of the field in the vicinity of the probe site must be directly proportional to a single substituent constant. As a consequence, at these sites the substituent effect on the π -electron density will be directly proportional to the substituent effect on the σ -electron density. Secondly, the magnitude of the field at the probe site must be sufficiently small that second- and higher-order terms in the perturbation theory expansion⁷ of the electronic wavefunction are negligible. In this case substituent effects on both electron densities and electronic energies will be directly proportional to the substituent constant.⁸ Thirdly, the effect of every substituent in the set must be described relative to the same zeroth-order electronic wavefunction. (It is conceivable that the electronic wavefunction of, for example, the ring in a monosubstituted benzene will be better described by a perturbed form of a virtual electronic wavefunction of unsubstituted benzene than by a perturbed form of the real electronic wavefunction.) If the above conditions were closely approached in the system used to define the standard substituent constants, a failure to meet any one of the conditions in any other system would stand out clearly in the plot of δP against $\sigma_{standard}$. We shall present evidence below that the ^{13}C s.c.s. at the β site in *meta* and *para* ring-substituted styrenes,⁹ the basis of our σ_{ST} scale, provides a good system for defining the standard substituent constants for all *meta*- and *para*-substituted derivatives of benzene.

We now propose that σ_{ST} is a measure of the field effect of a substituent, fully modified by the effects of π -overlap between

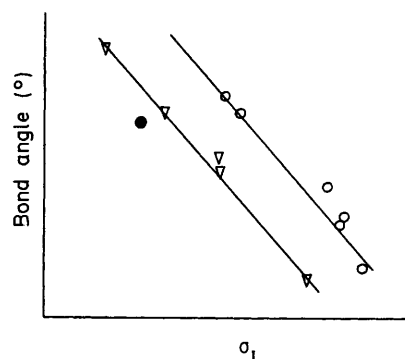


Figure 3. A plot of *ortho* ring bond angles in monosubstituted benzenes against σ_1 . See footnotes to Figure 1. The symbol ● represents unsubstituted benzene

the substituent and the rest of the molecule. The justification for the proposal is made in the next two sections. The $\lambda(\sigma_{ST} - \sigma_1)$ term in equation (2) then describes the extent to which the modification of the field effect is incomplete. When the value of λ is zero or unity for any one property there is no reason for it to be different for any other property, but otherwise the value of λ may vary with the nature of the property even with the same functional group.

The pK_a values⁴ of benzoic acids (the basis of the σ scale) and of phenylacetic acids (one basis of the σ^0 scale) show clear evidence of incomplete modification of the substituent field effect. If either of these data sets had been chosen for $\sigma_{standard}$ the qualitative similarity of so many plots of δP against σ_{ST} would not have been so apparent. Also the plot of σ^+ against $\sigma_{standard}$ would not have shown the excellent straight line through the origin for *meta* and *para* π -donors: the points for the *para* π -donors would have lain above the best straight line through the points for all *meta* substituents, providing apparently enhanced values of the π -overlap parameter in σ^+ . Thus the particular choice of $\sigma_{standard}$ is critical in optimising the simplicity of the overall pattern of deviations from a straight line through the origin in Hammett-like plots.

In terms of our modified field model the parameter that divides the substituents into two sets in the σ^+ versus σ_{ST} plot is the value of the field as modified by π -overlap, rather than π -donor or π -acceptor character. We shall label the substituents A or R depending on the strength of the modified field they cause at the probe site, A if the field is more electron-attracting than the critical value, otherwise R. It is possible that certain substituents may be A in the *meta*-position and R in the *para*-position or *vice-versa*.

The two-line pattern of the σ^+ versus σ_{ST} plot is also found in the plot of the $^{13}C_{\beta}$ s.c.s. of β -dicyanostyrenes¹⁰ against those of the parent styrenes. For R substituents the slope is approximately two, as expected for a more π -accepting functional group, but for A substituents it is only approximately two-thirds. The change in slope and intercept in going from R to A substituents may reasonably be attributed to a change in the zeroth-order wavefunction of the benzene ring. The change would in itself cost energy, but by reducing the effects of substituent fields which oppose the energetically favourable charge-transfer between the ring and the functional group there would be a net saving for the stronger of these substituent fields. There is other evidence that marked changes in the zeroth-order wavefunction of benzene occur with different classes of substituent; a plot of *ortho* ring bond angles in monosubstituted benzenes¹¹ against σ_1 (Figure 3) shows two separate lines, one for π -donors and one for π -acceptors, neither of which passes through the points for unsubstituted benzene. In our interpret-

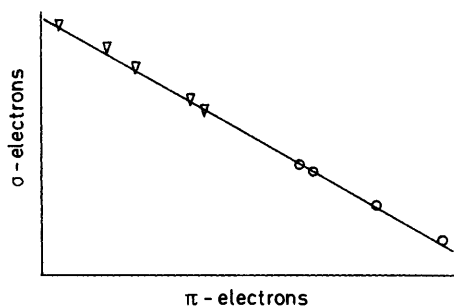


Figure 4. A plot of σ^- against π^- electron populations at the C_β atom in 4-substituted styrenes. See footnotes to Figure 1

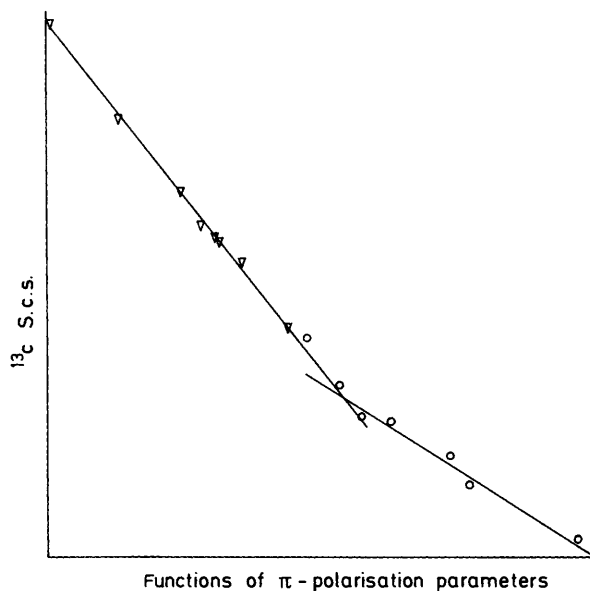


Figure 5. The ^{13}C s.c.s. at the C_β atom in 3- and 4-substituted styrenes against simple functions (see text) of parameters for π -polarisation of the ring in monosubstituted benzenes. See footnotes to Figure 1

ation the sudden change in slope and intercept in the plot of σ^+ against σ_{ST} signifies a change in the mechanism of the reactions on which the σ^+ scale is based, not in the vicinity of the reaction site but within the benzene ring. This point will be developed in Part 2.¹²

There is evidence of enhanced resonance effects (or significant direct substituent to functional group charge-transfer effects) at the probe site in some plots. The points for some *para*, but not *meta*, substituents (SiMe_3 , SMe , Cl , and Br) which do not have a first-row atom bonded to the ring lie above each guide line in the σ^+ plot. Also the points for *para* π -acceptors lie below the guide line of a plot of the σ^- scale⁴ against $\sigma_{\text{ST}} - \lambda(\sigma_{\text{ST}} - \sigma_1)$ with $\lambda = 0.3$.

$^{13}\text{C}_\beta$ S.C.S. in Styrenes as the Basis for Standard Substituent Constants.—The effects of substituents on calculated π -electron and σ -electron populations at the C_β atom in 4-substituted styrenes¹³ are almost directly proportional to one another, as can be seen in Figure 4. Also the magnitude of the effect (< 0.03 electrons) is small for all common substituents. Figure 5 shows that the $^{13}\text{C}_\beta$ s.c.s. in both 3- and 4-substituted styrenes linearly correlate with simple functions of the π -polarisation of the ring in monosubstituted benzenes (see below), except that there is a

Table 1. Values of σ_1 , σ_{ST} , and $\sigma_{\text{R,ST}}$ for some common substituents

Substituent	σ_1^4	σ_{ST}^a		$\sigma_{\text{R,ST}}^b$	
		<i>meta</i>	<i>para</i>	<i>meta</i>	<i>para</i>
NMe_2	+0.06	-0.16	-0.85	-0.22	-0.91
NH_2	+0.12	-0.08	-0.76	-0.20	-0.88
OMe	+0.32	+0.03	-0.44	-0.29	-0.76
SMe	+0.25	+0.13	-0.11	-0.12	-0.36
Me	-0.01	-0.05	-0.20	-0.04	-0.19
SiMe_3	-0.13	-0.02	+0.05	+0.11	+0.18
F	+0.54	+0.24	-0.03	-0.30	-0.57
Cl	+0.50	+0.32	+0.15	-0.18	-0.35
Br	+0.49	+0.34	+0.18	-0.15	-0.31
COMe	+0.29	+0.28	+0.54	-0.01	+0.25
CO_2Me	+0.32	+0.26	+0.50	-0.06	+0.18
CF_3	+0.43	+0.44	+0.56	+0.01	+0.13
CN	+0.58	+0.59	+0.77	+0.01	+0.19
NO_2	+0.72	+0.67	+0.94	-0.05	+0.22

^a σ_{ST} is the $^{13}\text{C}_\beta$ s.c.s. in ring-substituted styrenes⁹ expressed in units of 5 p.p.m. ^b $\sigma_{\text{R,ST}} \equiv \sigma_{\text{ST}} - \sigma_1$.

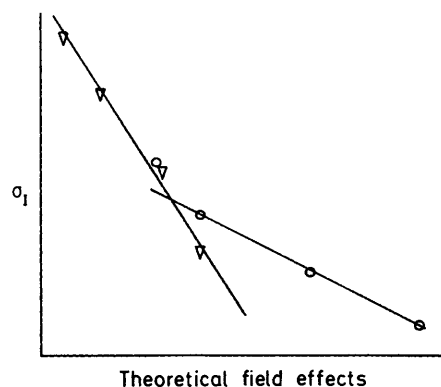


Figure 6. A plot of σ_1 against theoretical field effects¹² in the absence of π -overlap in monosubstituted benzenes. See footnotes to Figure 1

significant difference in both slope and intercept for strong π -acceptors. Figure 6 shows that strong π -acceptors deviate in the same sense from otherwise straight line plots of σ_1 , a good experimental measure of substituent field effects in the absence of π -overlap,⁶ against theoretical calculations¹³ of such field effects in monosubstituted benzenes. The case for regarding $^{13}\text{C}_\beta$ s.c.s. as an experimental measure of a field effect fully modified by π -overlap effects is as good as the case for regarding pK_a of bicyclo[2.2.2]octanecarboxylic acids as an experimental measure of a field effect in the absence of π -overlap.

The values of the σ_{ST} constants are expressed in units of 5 p.p.m. This unit was chosen to bring the values of σ_{ST} for weak π -acceptors in the *meta*-position near to equality with the corresponding values of σ_1 . The values of σ_{ST} for some common substituents are listed in Table 1.

The Electronic Significance of Values of σ_{ST} .—Figure 5 shows that the values of σ_{ST} linearly correlate with simple functions of the π -polarisation of the ring in monosubstituted benzenes. The π -electron distribution in monosubstituted benzenes may be analysed to give the very simple expression shown in Figure 7. The first term describes charge-transfer between the ring and the substituent X. When the value of T^0 is positive, for example, this charge comes from an orbital formally localised in the region of the *ipso* and *ortho* carbon atoms; the localised π -orbitals of the ring are shown in Figure 8. It is partly replaced by charge from

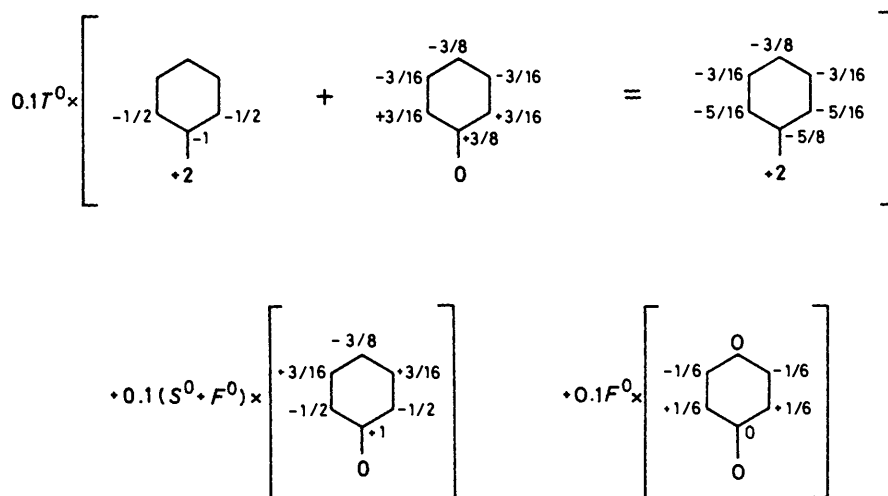
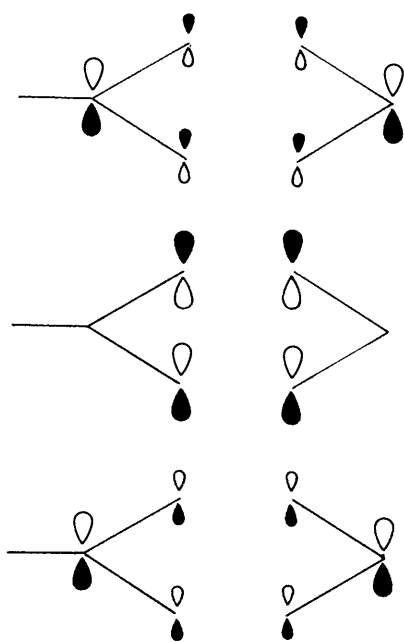


Figure 7. An analysis of π -electron redistributions in monosubstituted benzenes in terms of theoretical substituent parameters



Localised π orbitals

Figure 8. Localised π -orbitals of the benzene ring

an orbital formally localised in the region of the *meta* and *para* carbon atoms. The second term describes the contributions to the polarisation of the ring which arise out of the mixing of the π -orbitals that have non-zero amplitude at the *ipso* and *para* carbon atoms. The third term describes the contribution to the polarisation of the ring which arises out of charge-transfer between the localised π -orbitals which have zero amplitude at the *ipso* and *para* carbon atoms. The parameter F^0 represents the polarising power of X in the absence of π -overlap between the orbitals of X and the orbitals of the ring. The parameter S^0 represents the additional polarising power of X in the presence of such overlap. The latter polarisation optimises the extent of π charge-transfer or π overlap repulsion. The *meta-para* π -bonds are polarised less than the *ipso-ortho* π -bonds. The fall-off

Table 2. Values of the theoretical substituent parameters T^0 , F^0 , and S^0 for some common substituents^a

Substituent	T^0	F^0	S^0
NH ₂	-0.48	+1.05	-1.80
OMe	-0.52	+1.20	-1.72
Me	-0.04	+0.09	-0.40
F	-0.40	+1.17	-1.36
COMe	+0.14	+0.03	+0.26
CF ₃	+0.06	+0.42	-0.04
CN	+0.11	+0.66	-0.02
NO ₂	+0.16	+0.78	+0.22

^a The symbols are defined in the text.

factors for charge-transfer (*meta/para* to *ipso/ortho* compared with *ipso/ortho* to X) and for polarisation (*meta-para* compared with *ipso-ortho*) were determined empirically. Their values were identical (3/8) suggesting a direct connection between the degree of polarisation of a group and the degree of charge-transfer involving that group. The factor of 0.1 in the expression was introduced to make the values of the substituent parameters T^0 , F^0 , and S^0 (Table 2) the same order of magnitude as the σ substituent constants.

The functions of the re-polarisation parameters F^0 and S^0 that are involved in Figure 5 are $[(F^0 + h) + S^0]$ for *para* ring substituents and $\frac{1}{2}[(F^0 + h) + S^0] + b(F^0 + h)$ for *meta* ring substituents; b and h are constants with empirically determined values of one-sixth and 0.16 respectively. The correlation shown in Figure 5 indicates that the polarisation of the vinyl group in styrene by any *para* ring substituent is linearly related to the polarisation of the ring in benzene due to mixing of the π -orbitals that have non-zero amplitude at the *ipso* and *para* carbon atoms, and is independent of the polarisation of the ring in benzene due to mixing of the other orbitals. This clearly demonstrates that substituent-induced polarisation of the vinyl group occurs overwhelmingly *via* a through-bond mechanism. Theoretically, the polarisation of the vinyl group in styrene by any *meta* ring substituent should depend on contributions to the polarisation of the ring due to mixing of all π -orbitals because no π -orbital has a node at the *meta* carbon atom. Hence the dependence of the polarisation of the vinyl group on the value of F^0 relative to the dependence on S^0 should be greater in the *meta*-styrenes than in the *para*-styrenes. Using polarisation and

charge-transfer theory,¹⁴ we calculate the absolute dependence on the value of S^0 to be only one-half as great in the *meta*-styrenes as in the *para*-styrenes (this factor reflects the smaller amplitude at the *meta*-site relative to the *para*-site of the π -orbitals that do not have a node at the *para*-site). Thus, since the polarisation of the vinyl group is $a[(F^0 + 0.16) + S^0]$ for *para* ring substituents (a is a constant of proportionality), it should be $\frac{1}{2}a[(F^0 + 0.16) + S^0] + ab(F^0 + 0.16)$ for *meta* ring substituents. The non-zero value of h may reasonably be attributed to the effects of a change in the zeroth-order wavefunction of benzene when any substituent is introduced.

The degree of π charge-transfer between the ring and the vinyl group in 4-styrenes is directly proportional to the degree of π -polarisation of the ring arising out of the orbitals without nodes at the substituted atoms. Hence π -delocalisation effects appear to be strongly coupled to π -inductive effects. Both σ - and π -polarisation of the vinyl group in the styrenes are linearly related to the polarisation of the ring. Hence σ -inductive effects appear to be strongly coupled to π -inductive effects. This coupling might well be responsible for the failure of values of our F^0 parameter (which describes the extent of π -polarisation of the ring arising out of the orbitals with nodes at the substituted atom) to be directly proportional to values of the σ_I parameter (which describes the extent of π -polarisation of a vinyl group in the absence of π -conjugation between the substituent and the vinyl group). Empirically $F^0 + h \approx 1.2$ ($\sigma_I - 0.5S^0$). Thus it appears that F^0 represents a field effect modified by effects of π -overlap and change in zeroth-order electronic structure, and not a pure field effect.¹⁵ Since σ_{ST} values for both *para* and *meta* ring substituents and σ_I values can all be well expressed linearly in terms of $F^0 + h$ and S^0 , then through equation (2) δP can also be well expressed linearly in terms of these two substituent parameters. The value of the S^0 parameter appears truly to represent the extent of the modifying effect on π -overlap on the field of the substituent. In view of the strong coupling of π charge-transfer and π -polarisation, it is not surprising that the values of S^0 also qualitatively reflect the extent of π charge-transfer from the substituent to the ring.

To summarise, σ_{ST} can reasonably be interpreted as a blend of field/ σ -inductive, π -inductive (I_π and π_{orb}), and π -delocalisation effects² of substituents at the probe site. The individual effects are strongly coupled and it is not reasonable to interpret σ_{ST} as a sum of independent individual effects.

Discussion

The Field and Resonance Analysis of Substituent Effects.—The analysis of substituent effects into independent field/ σ -inductive and resonance effects has played a major role in structural and mechanistic organic chemistry for over half a century. It is therefore of interest to discover what modifications to this system of analysis are necessary in order to formulate an explanation of the simplicity in the overall pattern of the δP versus σ_{ST} plots. With the aid of the identities (3), equation (2) may be recast into equation (4).

$$\sigma_{ST} \equiv \sigma_I + (\sigma_{ST} - \sigma_I); \quad \sigma_{R,ST} \equiv \sigma_{ST} - \sigma_I \quad (3)$$

$$\delta P = \rho[\sigma_I + (1 - \lambda)\sigma_{R,ST}] \quad (4)$$

The values of $\sigma_{R,ST}$ for some common substituents are listed in Table 1. It should be noticed that they are different for corresponding *para* and *meta* substituents. The *para* values correlate quite well with the amount of charge-transfer between the ring and the substituent, and the *meta* values are near zero for Me and for most common π -acceptors. These results are in

accord with the resonance concept. However the *meta* values are not very close to zero for common π -donors.

The value of λ is identical for *para* and *meta* substituents. It should vary with the nature of the property in most cases, but not when it is zero or unity. These restrictions on the behaviour of λ are not compatible with the traditional method of analysis. It seems necessary to replace the concept that the resonance effect supplements the field effect with the concept that the resonance effect modifies the field effect by an amount that can vary but only up to a maximum (corresponding to λ equals zero).

The variation in the value of ρ with the class of substituent at a critical value of the resonance-modified field (RMF) has no analogue in traditional theory. It appears that when the magnitude of the RMF opposing the flow of electrons out of the ring through the *meta* or *para* site reaches a critical level, the electronic structure of the ring abruptly rearranges so as to reduce the sensitivity of the electron outflow to the magnitude of the RMF.

The concept of through-resonance could be retained without change. However some effects currently attributed to through-resonance would have to be reattributed to the ring-structure rearrangement.

We conclude that the only major conceptual problem in our modified field and resonance analysis is with the non-zero values of $\sigma_{R,ST}$ for *meta* substituents. The non-zero resonance effect for *meta* substituents is also a problem in traditional schemes of field and resonance analysis. The common method of dealing with it is to assume that the ratio of values of the resonance parameter for corresponding *meta* and *para* substituents is independent of the nature of the substituent. However it is obvious from the values of $\sigma_{R,ST}$ in Table 1, that in reality this ratio varies greatly with the nature of the substituent. Consequently there is a serious flaw in the dual substituent parameter analyses of Ehrenson, Brownlee, and Taft⁵ and of Swain and Lupton.³

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