The Interpretation of Quantitative Linear Correlations. Substituent Effects on the Properties of Naphthalene and its Derivatives

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A recently proposed theoretical model for quantitative linear correlation analysis, which involves a major modification to the physical interpretation usually given to each of the parameters in the dual substituent parameter expression $\rho_I(\sigma_I + \lambda\sigma_R)$, is tested by application to substituent effects on the properties of naphthalene and its derivatives. The model is shown to be capable of accounting for the variation in precision of quantitative linear correlations among substituent effects on the four properties for which adequate experimental data are available, and of interpreting in a self-consistent way the variations in the values of ρ_I and λ as the nature of the property and the disposition of the substituent site and the probe site are changed. In these respects it appears to be superior to other models in current use. It is concluded that the novel interpretations of ρ_I and λ, and hence of σ_I and σ_R, provided by the model are strongly supported by the results of the present study.

THE effects of a set of structural perturbations (*e.g.* substituent effects) on either a pair of properties of a given molecular system, or on a given property of a pair of molecular systems, are often very simply correlated with a high degree of precision. For example, equation (1) often holds well when δP represents changes in values of properties, σ_I and σ_R † are characteristic parameters for substituent-induced perturbations and ρ and λ are coefficients.[1] The usefulness of linear correlation analyses

$$\frac{\delta P_1}{\delta P_2} = \frac{\rho_{I1}(\sigma_I + \lambda_1\sigma_R)}{\rho_{I2}(\sigma_I + \lambda_2\sigma_R')} \qquad (1)$$

in elucidating electronic structure and reaction mechanisms depends on the validity and the sophistication of the interpretations given to the parameters. We are concerned with the possibility of designing more useful theoretical models than those currently available. In previous publications on this topic [2-5] we have proposed a novel model which seems to have the capability, not found in popular models, of correctly predicting the circumstances required for equation (1) to be obeyed with high precision in its general form, and the additional circumstances required for it to be obeyed with σ_R' the same as σ_R, and λ_2 equal in value to λ_1 (*i.e.* the circumstances required for $\delta P_1/\delta P_2$ to be independent of the nature of the substituent). A particularly interesting feature of this model is that it involves a major modification to the physical interpretation usually given to each of the substituent parameters σ_I and σ_R, and hence to each of the coefficients ρ_I and λ.

Here we report on the application of our model to the analysis of substituent effects on the four properties of naphthalene and its derivatives for which adequate experimental data are available. We first predict the variations in the *precision* of the quantitative linear correlations with the disposition of the substituent site and the probe site, and secondly we interpret in terms of electronic effects the variations in the values of the coefficients ρ_I and λ as the disposition of sites and the nature of the property are changed. This application provides a particularly severe test of our model because the number of distinguishable dispositions of substituent site and probe site in which the two sites are not adjacent to one another, eleven, is so large for naphthalene derivatives: for benzene derivatives the corresponding number is only two. The results should be of extra interest since an attempt by Wells, Ehrenson, and Taft [6] to interpret the variations in the values of ρ_I and of λ for naphthalene derivatives *in terms of familiar theoretical concepts* left many problems unresolved.

Before presenting and discussing the results of our test, we will outline our theory and discuss contemporary concepts in substituent effect analysis, including the general interpretation of σ_I, σ_R, ρ_I, and λ, in terms of it.

The Theoretical Model for Electronic Effects.—The basic postulate in our model for quantitative linear correlations is that *perfect* correlations exist only when (i) the change in value of each property is directly proportional to some linear combination of the changes in electron population at the probe site and at the sites immediately adjacent to it, and (ii) the changes in electron populations significantly involve only a certain set of electronic effects, namely, the polarisation and charge-transfer (PCT) effects. We now briefly specify what these PCT effects are: full details have been given elsewhere.[2]

The PCT electronic effects of structural perturbations of a molecular system are considered to originate in the immediate vicinity of the source site and to be transmitted to the vicinity of the probe site *via* interactions between small *sub-systems* of the molecular system. The first step in calculating these electronic effects in a particular molecular system is to divide that system into a set of sub-systems (a typical sub-system is a vinylene group): the recipe for doing this is given later in this section, after we have described the nature of the interactions between sub-systems.

The interactions between sub-systems are of two kinds, namely, *coulombic* and *non-coulombic*. The coulombic interactions arise out of charges and dipoles within the isolated sub-systems. The non-coulombic interactions arise out of overlap between orbitals of one sub-system and orbitals of adjacent sub-systems. The non-

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† There are four scales of σ_R values. In general each σ_R and σ_R' might be any one of the four.

coulombic interactions are of two kinds, namely, *charge-transfer*, which arises out of overlap between filled orbitals of one sub-system and vacant orbitals of another and is stabilising, and *overlap-repulsion*, which arises out of overlap between filled orbitals of one sub-system and filled orbitals of another and is destabilising. Each sub-system may in principle undergo *self-polarisation* in order to increase any stabilising effect, or to decrease any destabilising effect, of the coulombic and non-coulombic interactions. The self-polarisation involves the perturbation of the orbitals of the sub-system through mixing with other orbital functions. Thus, for example, a vinylene sub-system would polarise if the π-bonding orbital was mixed with a π-antibonding orbital function, and the π-antibonding orbital was mixed with a π-bonding function. The self-polarisation of a sub-system is in itself a destabilising process and hence it will be allowed in practice only if it leads to an increase in the net stabilising effect of the interactions with other sub-systems that is greater than the destabilising effect of the polarisation.

Any structural change within a sub-system should in principle affect the interactions of that sub-system with its neighbours. Thus the replacement of one sub-system in a molecule by another of different nature (*i.e.* the introduction of or the replacement of a substituent group) may result in one or more of the following effects: (i) a self-polarisation of the neighbouring sub-system in order to create or to increase stabilising coulombic interactions (hereafter called coulombic self-polarisation), (ii) a self-polarisation of the neighbouring sub-system in order either to increase charge-transfer interactions or to decrease overlap-repulsion interactions (hereafter called non-coulombic self-polarisation), and (iii) a *net* transfer of electronic charge between the substituent and the neighbouring sub-system. These *three* effects of a substituent on its neighbouring sub-system are illustrated in Figure 1. The coulombic field exerted by the charges and dipoles within the substituent also affects the energies of the orbitals within the neighbouring sub-system. The *four* effects we have just described are called *direct* substituent effects.

Since the electronic structure of the sub-system adjacent to the substituent group has been changed by the introduction of the substituent, the interactions between *that* sub-system and *its* neighbouring sub-system(s) should in principle also be affected by the introduction of the substituent and so on through the whole molecular system: these effects are called *transmitted* substituent effects. It should be noted that *each* type of effect *transmitted* by a given sub-system depends on *all* types of effect *exerted* on that sub-system. Thus our theoretical model does not involve the assumption, commonly made in other models, that there are two or more types of electronic effect each of which is transmitted *independently* of the others.

In order to keep the transmission mechanism reasonably simple, all interactions involving non-adjacent sub-systems are neglected in our treatment. Even so, the calculation of substituent-induced changes in PCT electron population is complicated *in the general case.* However, the calculation becomes much easier in cases where non-coulombic self-polarisation effects involving many of the sub-systems happen to be zero, and fortunately it appears from the results of previous[4] applications of our model that non-coulombic self-polarisation effects *are* usually zero when the sub-systems involved are hydrocarbon groups of similar nature to one another. Thus the calculation is quite easy for substituent effects on naphthalene when non-coulombic self-polarisation effects involving neighbouring sub-systems in the naphthyl moiety are taken to be zero, as we shall demonstrate below.

The sub-systems in any molecular system are chosen so that they each contain a set of orbitals, called the *principal orbitals*, which are analogous to the π-orbitals of ethylene. Thus in hexatrienes (Figure 2a) the sub-systems are three vinylene units; in styrenes (Figure 2b) they are two semiphenylene units plus a vinylene unit; in propanes (Figure 2c) they are three methylene units; and in naphthalenes (Figure 2d) they are two semiphenylene units plus two vinylene units. The principal orbitals of a semiphenylene unit are the allylic π-orbitals: they can be transformed into the π-orbitals of ethylene by reducing the C–C–C bond angle to zero. The principal orbitals of a methylene unit are one of the two orbitals which give C–H bonding character, and one of the two orbitals which give C–H antibonding character.

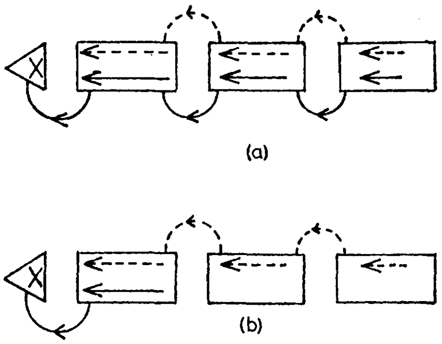

FIGURE 1 A schematic representation of the direct and the transmitted electronic effects of a substituent X. The boxes represent molecular sub-systems and the arrows represent electron displacements due to self-polarisation or charge-transfer. The broken lines represent *coulombic* self-polarisation effects, or charge-transfer effects brought about by the influence of the coulombic field of one sub-system on the energies of the orbitals of its neighbouring sub-system. The solid lines represent *non-coulombic* self-polarisation effects or associated charge-transfer effects. The lengths of the lines indicate qualitatively the magnitudes of the effects. The transmitted effects are illustrated for (a) the general case, and (b) the case in which the degree of non-coulombic self-polarisation and associated charge-transfer involving other sub-systems are not affected by the substituent sub-system

It should be noted that all four types of PCT effect can in principle be generated in and transmitted through *saturated* as well as *unsaturated* hydrocarbon derivatives. This contrasts with the common assumption that some types of perturbation (*e.g.* mesomeric) can be transmitted only through unsaturated molecular systems or sub-systems.

The model does not neglect altogether interactions involving orbitals other than the principal ones. Thus, for example, that component of charge-transfer between a substituent sub-system and a planar hydrocarbon sub-system, which involves only σ-orbitals, is considered to be a major source of coulombic perturbation for the principal orbitals. Also, the polarisation of the principal orbitals in a sub-system is considered to be a major source of perturbation for the other orbitals in the same sub-system. However, the transmission of electronic disturbances through more than one or two bonds is assumed to require the involvement of the principal orbitals if significant effects are to be observed.

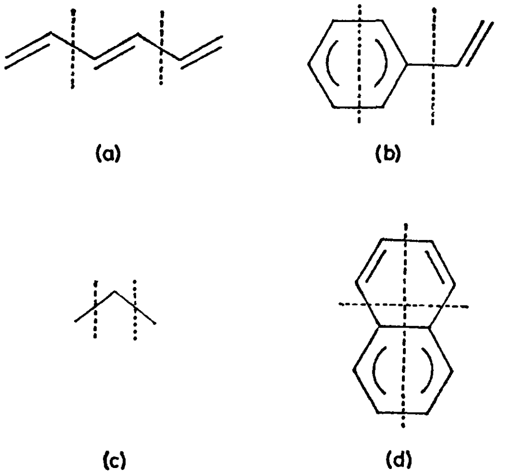

FIGURE 2 The sub-systems in some hydrocarbons. The broken lines divide the sub-systems

Finally in this section, we compare our PCT electronic effects with the seven types of electronic effect listed by Topsom in a recent compilation.[7] The π_F, π_{orb}, and R effects in Topsom's list *together* correspond to our PCT electronic effects transmitted through the principal orbitals. The π_σ and σ_π effects correspond to PCT effects which arise out of the involvement of orbitals other than the principal ones. Since PCT electronic effects are generated in and transmitted through saturated as well as unsaturated molecular systems, analogues of the π_F, π_{orb}, R, π_σ, and σ_π effects should also be found in saturated systems. The F and I_σ effects mentioned by Topsom correspond to *non-PCT* electronic effects. It is our contention that, except at sites close to the substituent, non-PCT electronic effects are negligibly small compared with PCT electronic effects in both unsaturated and saturated molecular systems.[3]

The relationship between, on the one hand parameters which are measures of the individual PCT electronic effects, and on the other hand σ_I and σ_R, will be considered later, after we have discussed how PCT electronic effects provide a basis for quantitative linear correlations involving two substituent parameters.

The Application of the Theoretical Model to the Prediction and the Interpretation of Quantitative Linear Correlations.—Empirically, the effects of substituents on the electron populations, as calculated by *ab initio* MO methods, at various sites i within a molecular system (δq_i), can in many cases * be described with quantitative accuracy in terms of just two characteristic substituent parameters, **F** and **S**, as in equation (2).[2] Where the *ab initio* electron populations are not significantly different from the PCT electron populations our model gives precise physical significance to **F** and to **S**. **F** represents the degree of self-polarisation of the molecular sub-system adjacent to the substituent (called the *base* sub-system) required to optimise the stabilising effects of the coulombic fields originating in the substituent itself and in the bond between the substituent and the base sub-system. **S** represents the degree of self-polarisation of the base sub-system required to optimise the stabilising effects of the charge-transfer interactions between the substituent and the base sub-system: this non-coulombic self-polarisation is accompanied by a near-proportionate amount of net charge-transfer.

$$\delta q_i = f_i(\mathbf{F} + g_i\mathbf{S}) \qquad (2)$$

The value of the coefficient g_i in equation (2) reflects the *relative* sensitivity of the electron population at the probe site to the coulombic and the non-coulombic self-polarisations of the base sub-system. The value of the coefficient f_i reflects the *absolute* sensitivity of the electron population at the probe site to the coulombic self-polarisation of the base sub-system.

The effects of substituents on the value of each of various properties P can also be expressed in terms of **F** and **S**, as in equation (3), provided that δP is directly proportional to some blend of δq_i and δq_j where i is the probe site and j is any site adjacent to it. The values of the coefficients f_i and g_i in *this* equation then reflect not only the sensitivity of the electron populations at site i to the self-polarisation of the base sub-system, but also the relative importance of the electron populations at sites i and j in contributing to δP_i.

$$\delta P_i = f_i(\mathbf{F} + g_i\mathbf{S}) \qquad (3)$$

The *details* of the self-polarisation of the base sub-system per unit value of **F** or **S** depend on the *nature* of the base sub-system. The choice of the nature of the base sub-system and the details of the self-polarisation used to *define* unit values of **F** and **S** is a matter of convenience. In the present work we have in fact used a method of evaluating **F** and **S** from *ab initio* π-electron populations in monosubstituted benzenes, which has been described elsewhere.[2] The absolute values of the coefficients f_i and g_i depend on the choice of definition of **F** and **S**. In order to reach conclusions which are independent of this choice we shall concern ourselves in this work only with the way in which g values and the ratio of f values vary with the nature of the property

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* The exceptions are substituents which do not give rise to marked *net* charge-transfer, *e.g.* methyl, ammonio, and certain halogeno groups.

and with the disposition of the substituent site and the probe site.

Some general features of the behaviour of g that arise out of our model and are used below are as follows: (i) the values of g for changes in electron population ought not to depend on the position of the site for sites in the third and more remote sub-systems relative to the base sub-system, provided that the sub-systems are linked in a *chain* and that the nature of the substituent does not affect the degrees of self-polarisation required to optimise the non-coulombic interactions between the sub-systems; (ii) the values of g for changes in any property that is linearly related to any one or more of those changes in electron population ought not to depend on the position of the probe site for a given position of the substituent site; and (iii) the values of g should be fixed only by the natures of the base and second sub-systems and by the site(s) of attachment of the third sub-system to the second and the second sub-system to the base. (This implies that any change in the nature or the structure of the third or any of the subsequent sub-systems would not in itself affect the g value.)

In terms of the *substituent shell* concept recently discussed by Wold and Sjöström,[8] the regions of constant g value for substituent effects on any particular property may be said to lie *outside* the substituent shell for that property, and conversely the regions of variable g value may be said to lie *inside* the substituent shell. Outside the substituent shell the value of $\mathbf{F} + g\mathbf{S}$ for any substituent is obviously constant and therefore could be replaced by a single substituent parameter in equation (**3**), whereas inside the substituent shell the value of $\mathbf{F} + g\mathbf{S}$ varies with the probe site and could not be replaced by a single parameter. The value of g, and hence of the single substituent parameter, should be characteristic of the nature and the structure of the *inside* of the substituent shell, but should not depend on the nature or the structure of the *outside* of the substituent shell.

The location of the *boundary* of a substituent shell would change if the degree of self-polarisation required to optimise the non-coulombic interactions involving any of the sub-systems lying inside the shell did, or could be made to, depend in any way on the nature of the substituent. This particular phenomenon cannot be studied with the available data on naphthalene derivatives and therefore we will not consider it in detail here. However, we mention it because it is involved in the general interpretation of the differences between the various σ_R scales which we shall consider in the next section.

Finally we point out that the value of f should in general be variable both inside and outside the substituent shell, with a tendency to fall off exponentially with increasing remoteness of the probe site from the substiuent site, but with additional variations at the different sites within each particular sub-system.

The General Interpretations of σ_I, σ_R, ρ, *and* λ.—Each of the parameters in equation (**3**) can be expressed precisely in terms of the parameters involved in the dual substituent parameter expression $\rho_{Ii}(\sigma_I + \lambda_i\sigma_R)$ and *vice versa*. Hence our model also gives precise physical significance to each of the parameters involved in that expression. *Our* physical interpretation of the parameters in that expression differs quite a lot from the interpretations usually given.

Empirically, σ_I and σ_R^- may be expressed quantitatively in terms of **F** and **S**, as in equations (4), and *vice versa*, as in equations (5). Particularly interesting features here are that σ_I values are not directly proportional to **F** values, and that the appropriate σ_R scale is based on anilinium ion dissociation and not on benzoic acid dissociation.

$$\sigma_I = -0.20(\mathbf{F} + 0.7\mathbf{S}) \qquad \sigma_R^- = -0.04(\mathbf{F} + 4.2\mathbf{S}) \quad (4)$$

$$\mathbf{F} = -1.0(6\sigma_I - 5\sigma_R^-) \qquad \mathbf{S} = -1.4(5\sigma_R^- - \sigma_I) \quad (5)$$

The values of σ_I depend on the values of the non-coulombic effects involved in **S**, as well as on the coulombic effects involved in **F**. Since σ_I is evaluated from empirical data on derivatives of saturated hydrocarbons, this result will be surprising to those who believe that non-coulombic effects operate only in unsaturated hydrocarbon derivatives. The question of whether σ_I or **F** is the better measure of coulombic effects needs to be resolved. Reynolds has pointed out to us [9] that values of **F**, but not of σ_I, are nearly directly proportional to *ab initio* MO calculated values of Σq_σ, the total substituent-induced change in electron populations for hydrogen 1s and carbon σ orbitals, in substituted *styrenes* [10,*] (see Figure 3). In other words **F**, but not σ_I, appears to be dominated by a measure of what is commonly considered to be the major source of the I_σ effect, and is considered by us to be the major source of the coulombic PCT effect.

The only σ_R scale which can be expressed quantitatively in terms of **S** and **F** values for *all* substituents is the one based on anilinium ion dissociation. The σ_R scale based on benzoic acid dissociation, σ_R^{BA}, cannot be so expressed for substituents which are strong electron acceptors (*e.g.* NO_2 and CN groups). Since the values of **S** and **F** were obtained from calculated electron populations in monosubstituted benzenes, the concept of *through conjugation* which is commonly used in explaining the differences between the two σ_R scales is called into question. In a previous publication [5] we have proposed and discussed a novel alternative concept, namely, that there are two markedly different possible electronic structures for the ground state of a phenylene system which are energetically fairly similar, and that which one of these structures is actually found in a particular substituted benzene depends on the nature of the substituent(s). If the introduction of a particular substituent changes the order of relative energies of the two possible structures, it is said to effect a *structure switch.* Each of the other σ_R scales can be obtained from σ_R^- by

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[*] *ab initio* MO calculated values of Σq_σ in substituted *benzenes* [11] are almost identical with those in substituted styrenes for corresponding substituents.

changing the values of the coefficients in equations (4) for all substituents in the set, and/or by adjusting the values of **S** and, especially, of **F** for the strong electron accepting substituents in order to allow for the effects of the structure switch within the phenylene group. Equations (6) give the relationships between the σ_R scales and the adjusted **F** and **S** scales.

$$\begin{aligned}\sigma_R{}^{BA} &= -0.04(\mathbf{F}^* + 4.2\mathbf{S}^*)\\ \sigma_R{}^{0} &= -0.06(\mathbf{F}^* + 2.7\mathbf{S}^*)\\ \sigma_R{}^{+} &= -0.20(\mathbf{F}^* + 2.1\mathbf{S}^*)\end{aligned} \qquad (6)$$

In terms of the usual interpretation of $\sigma_R{}^0$, this scale ought to be directly proportional to the net π-electron charge-transfer, Σq_π, between the substituent and the ring in monosubstituted benzenes, and hence it ought to be directly proportional to the **S** scale. Clearly, this is not in accord with the relationship given by equation (6). Ford, Katritzky, and Topsom[12] have found that Σq_π in substituted *ethylenes* is directly proportional to $\sigma_R{}^0 - 0.32\ \sigma_I$, in excellent agreement with the expectation based on equations (6) that Σq_π should be directly proportional to $\sigma_R{}^0 - 0.30\ \sigma_I$. In apparent contrast, Hehre, Taft, and Topsom[13] has shown that Σq_π in substituted *benzenes* gives a very good correlation with $\sigma_R{}^0$ alone, but their data set is dominated by the effects of substituent groups with small values of **F***.

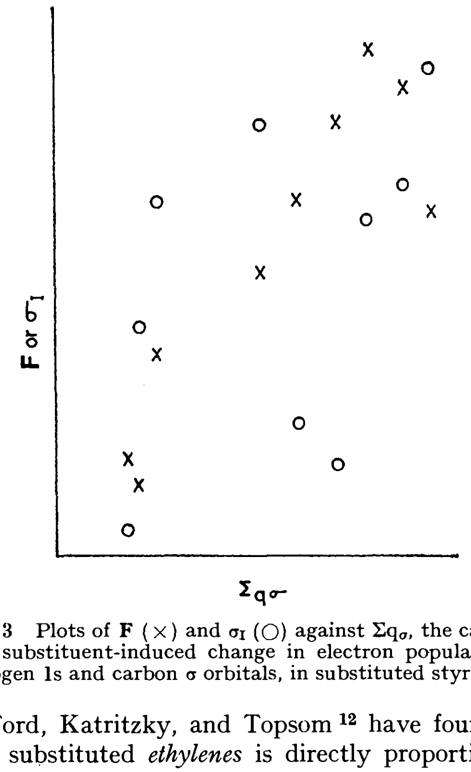

FIGURE 3 Plots of **F** (×) and σ_I (○) against Σq_σ, the calculated total substituent-induced change in electron populations for hydrogen 1s and carbon σ orbitals, in substituted styrenes

Equations (5) can be used to obtain values of **F** and **S** from measured values of σ_I and $\sigma_R{}^-$ for substituents for which the standard method referred to in the previous section has not been applied, but where such substituent groups do not give rise to marked net charge-transfer effects on hydrocarbons the values of **F** and **S** obtained will not have their normal physical significance.

The relationship between ρ and λ on the one hand, and f and g on the other hand, can be found through substituting in equation (3) for **F** and **S** in terms of σ_I and σ_R. The precise relationship depends on the choice of σ_R scale. The relationships shown in equations (7) correspond respectively to the $\sigma_R{}^-$ and $\sigma_R{}^{BA}$, $\sigma_R{}^0$, and $\sigma_R{}^+$ scales.

$$\begin{aligned}\rho_{Ii} &= f_i(1.4g_i - 6) & \lambda_i &= (5 - 7g_i)/(1.4g_i - 6)\\ \rho_{Ii} &= f_i(3g_i - 8)/1.2 & \lambda_i &= (7 - 10g_i)/(3g_i - 8)\\ \rho_{Ii} &= f_i(10g_i - 21)/2.8 & \lambda_i &= (7 - 10g_i)/(10g_i - 21)\end{aligned} \qquad (7)$$

Since ρ is a rather complex function of f and g, and λ is a rather complex function of g, the physical interpretations of ρ and λ values in terms of our model are likely to be unreasonably complex in the general case, although simple qualitative interpretations might well be possible in certain cases. It seems to us more sensible to convert ρ and λ values to f and g values using equations (8), which are rearranged forms of equations (7). The details of the physical interpretations of f and g values for the properties of naphthalene and its derivatives are set out in the next section. It will be assumed that the interpretations of f and g values obtained *via* equations (8) are not significantly affected by the *composition* of the set of substituents involved in determining the values of ρ_i and λ.

$$\begin{aligned}f_i &= -\rho_{Ii}(0.2\lambda_i + 1)/5 & g_i &= (6\lambda_i + 5)/(1.4\lambda_i + 7)\\ f_i &= -\rho_{Ii}(0.3\lambda_i + 1)/5 & g_i &= (8\lambda_i + 7)/(3\lambda_i + 10)\\ f_i &= -\rho_{Ii}(\lambda_i + 1)/5 & g_i &= 7(3\lambda_i + 1)/10(\lambda_i + 1)\end{aligned} \qquad (8)$$

The Application of the Theory to Substituent Effects on the Properties of Naphthalene and its Derivatives.—We now report the results of applying our model to the determination of δq_i values, and to the interpretation of the empirical data, in naphthalene derivatives. The precise problem was to obtain values of g_i and ratios of values of f_i for the δq_i and for each set of the δP_i, and then to interpret the variations of the g values and the ratios of f values for the δP with the nature of the measured property and with the disposition of probe site and substituent site, in terms of the variations of the g values and the ratios of the f values for the δq with the disposition of the sites. The method of labelling the probe sites is that suggested by Wells, Ehrenson, and Taft,[6] and now in common use: the labels are shown in Figure 4.

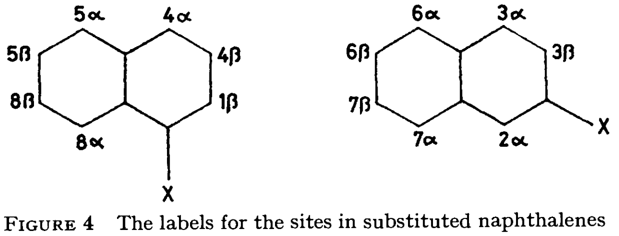

FIGURE 4 The labels for the sites in substituted naphthalenes

It should be noted that in the α-substituted molecules, but not in the β-substituted molecules, there ought to be a significant direct coulombic interaction between the substituent and a hydrocarbon sub-system which is not immediately adjacent to it. Since this electronic effect does not belong to the PCT set, it should provide a potential source of deviation from obedience to equation (3) in the former set of molecules which is not present in the latter set.

It is convenient to consider quantities relating to the primary ring of a substituted naphthalene, *i.e.* the ring containing the substituent, after considering quantities relating to the secondary ring.

Secondary ring. (a) *The calculation of* f$_i$ *and* g$_i$ *values for* δq. In a β-substituted molecule the δq_i due to the substituent should, according to our model, be a combination of the δq_i in the side-chains of *meta*- and *para*-butadienyl derivatives of the corresponding substituted benzene, as in equation (9). The labels of the sites in these side-chains are given in Figure 5. Note that a given site *i* in the naphthalene molecule and the corresponding sites in the butadienyl-benzenes all have different labels, *e.g.* 6β in naphthalene corresponds to 2α in *m*-butadienyl-substituted benzene and to 1β in *p*-butadienyl-substituted benzene.

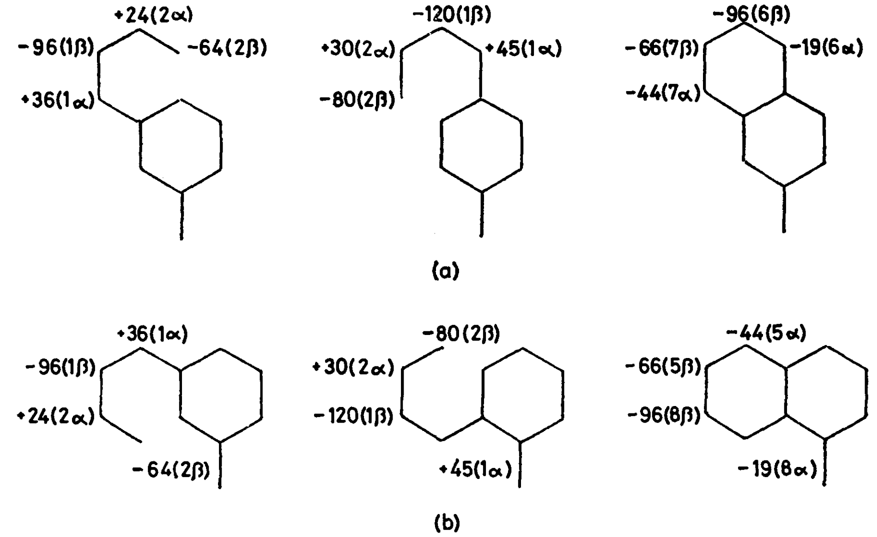

FIGURE 5 The calculated values of δq_i for a hypothetical substituent for which the value of $\mathbf{F} + g\mathbf{S}$ is unity, used in the determination of values of f_i and g_i in (a) β-naphthalenes, and (b) α-naphthalenes. The labels of the sites *i* are given in parentheses

$$\delta q_{i,\beta\text{-naph.}} = \delta q_{i,m\text{-butabenz.}} + \delta q_{i,p\text{-butabenz.}} \qquad (9)$$

It is clear from equation (2) that the values of $f_{i,\beta\text{-naph.}}$ must be equal to those of $\delta q_{i,\beta\text{-naph.}}$ for a hypothetical substituent for which the value of $\mathbf{F} + g\mathbf{S}$ is unity (*i.e.* **F** is unity and **S** is zero). Therefore in order to calculate $f_{i,\beta\text{-naph.}}$ we had only to apply equation (9) to the values of δq_i for the effects of the hypothetical substituent on the butadienylbenzenes. The latter were obtained by the following method.

(i) The 1 site in the *meta*-isomer was given a net charge of +36 units. The change in electron population at *one* site in *one* isomer could be given *any* convenient value since we were interested in the calculation only of the ratios of values of δq_i.

(ii) the 1α site in the *para*-butadienyl-substituted benzene was given 5/4 times this value (*i.e.* 45 units): the ratio is that of f_p/f_m obtained from **F**,**S** analyses, by equation (3), of ΔG data on the dissociation of substituted anilinium ions in aqueous solution.[14] This data set was chosen to calculate f_p/f_m because there is some evidence[3] that the degree of non-coulombic self-polarisation within the $-C_6H_4CH_2-$ group is not affected markedly either by the nature of the ring substituent or by the proton transfer. (Because of doubts about the chosen value of f_p/f_m we later repeated the calculations using other values. We comment on the differences in the final section.)

(iii) Each of the 1β sites was given minus 8/3 times the value for the corresponding 1α site: the ratio is that obtained from the results of an MO calculation of δq_α and δq_β in styrene.[10]

(iv) Each of the 2 sites, α and β, was given 2/3 times the value for the corresponding 1 site: the ratio is that obtained from the results of MO calculations of $\delta q_n/\delta q_{n-1}$ in polyvinylenes.[15]

The values of $g_{i,\beta\text{-naph.}}$ were calculated by means of equation (10), which was generated by applying equation (2) to expand each term in equation (9). The required values of f_i for the butadienylbenzenes are equal to the corresponding δq_i values for the hypothetical substituent. The required values of g_i for the butadienylbenzenes, 0.85 for *meta* and 1.35 for *para*, were obtained from the **F**,**S** analyses of the ΔG data on anilinium ions mentioned above.

$$f_{i,\beta\text{-naph.}}(\mathbf{F} + g_{i,\beta\text{-naph.}}\mathbf{S}) = f_{i,m\text{-butabenz.}}(\mathbf{F} + g_{m\text{-butabenz.}}\mathbf{S}) + f_{i,p\text{-butabenz.}}(\mathbf{F} + g_{p\text{-butabenz.}}\mathbf{S}) \qquad (10)$$

In an α-substituted naphthalene the δq_i caused by the substituent should be a combination of the δq_i in the side-chains of *meta*- and *ortho*-butadienyl derivatives of the corresponding substituted benzene. The method we used for obtaining values of $f_{i,\alpha\text{-naph.}}$ and $g_{i,\alpha\text{-naph.}}$ corresponded to the one we used with the β-substituted naphthalenes except in one respect. The values of f_o/f_m and of g_o for the butadienyl-benzenes could not be obtained from ΔG data on anilinium ions because of large proximity effects. The way in which we modified the method to overcome this problem will be described later after we have discussed the interpretation of the experimental data on the β-substituted compounds.

TABLE 1

The values of $f_i/f_{6\beta}$ and of gi for substituent effects on various properties of naphthalene and its derivatives (to the nearest 0.05)

	6β		7β		7α		6α		8β		5β	
Property	f	g	f	g	f	g	f	g	f	g	f	g
q calculated [a] A [b]	1.00	1.45	0.70	0.65	0.45	1.75	0.20	−0.35	1.00	1.05	0.70	0.80
B [c]	1.00	1.45	0.50	0.55	0.50	1.65	0.10	−1.85	0.80	1.05	0.55	0.80
^{13}C substituent chemical shift [d]	1.00	1.45	0.45	0.80	0.40	1.70	0.00		0.80	1.10	0.40	0.80
log k: detritiation [e]	1.00	1.35	0.45	0.75	0.50	1.15	0.40	0.65	0.75	1.00	0.55	0.75
^{19}F substituent chemical shift [f]	1.00	1.35	0.50	0.95	0.45	1.20	0.30	1.05	0.90	1.00	0.45	1.00
pK_a: naphthoic acids [g]	1.00	1.20	0.90	1.05	0.80	1.20	0.90	1.10	0.65	1.30	0.95	1.05

[a] See text for method. [b] Using $f_p/f_m = 5/4$. [c] Using $f_p/f_m = 6/4$. [d] Ref. 16. [e] C. Eaborn and A. Fischer, *J. Chem. Soc.* (*B*), 1969, 152. [f] Ref. 17. [g] P. R. Wells and W. Adcock, *Austral. J. Chem.*, 1965, **18**, 1368.

(b) *The interpretation of the experimental data for β-substituted compounds.* The values of $f_i/f_{6\beta}$, and of g_i, for the δq_i as calculated above, and for the four measured properties are set out in Table 1. In the case of the measured properties, the values of f_i and g_i were obtained by applying equations (8) to convert values of ρ_{Ii} and λ_i previously obtained by other workers from σ_I, σ_R analyses of the experimental data. The patterns of calculated $f_i/f_{6\beta}$ and g_i values for the various properties are shown in Figure 6. The measurable property most likely, among the four, to reflect the δq_i pattern is ^{13}C substituent chemical shift. There is an obvious similarity for both $f_i/f_{6\beta}$ and g_i values, although unfortunately no meaningful value of g_i could be obtained for the chemical shifts at the 6α position because the corresponding value of f is close to zero.

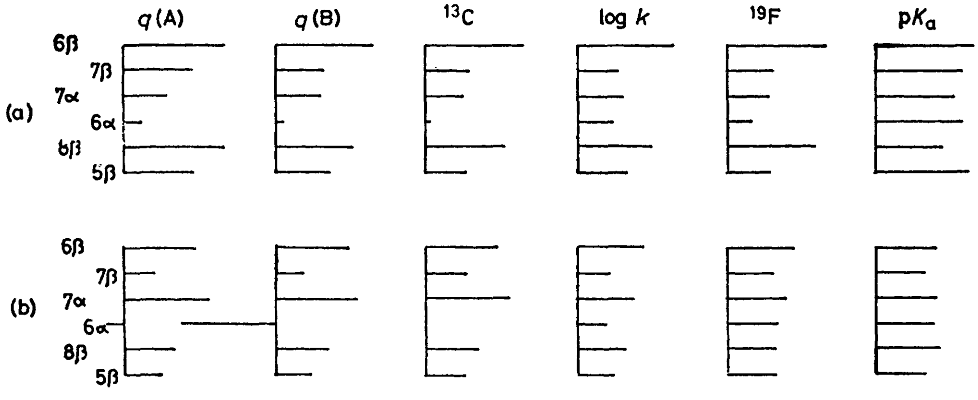

FIGURE 6 The patterns of the values of (a) $f_i/f_{6\beta}$, and (b) g_i, for the properties listed in Table 1

With properties for which the δP values are related to the δq values at *more* than one site, the spread of values of f and g ought to be smaller. Thus on inspecting Table 1 and Figure 6 it would appear that δq_j, where j represents sites adjacent to the probe site, has a very important influence on the acidity of naphthoic acids in aqueous ethanol since the values of f and g are close together. In the cases of ^{19}F substituent chemical shifts and the rates of detritiation there are signs of a smaller influence. The mechanistic significance of the relative influences of δq_j and δq_i on chemical properties detected at site i will be discussed in detail elsewhere. The point to be taken here is simply that the pattern of the experimental data can be interpreted self-consistently in terms of the behaviour of δq_j and δq_i.

There will inevitably be some contributions to the observed substituent effects which do not themselves obey the dual substituent parameter equations. If our theory is valid, these contributions should tend to become relatively less important in a series of δP values as the value of f (or ρ_I) increases, and hence the *precision of fit* of observed δP values should tend to increase as the value of f (or ρ_I) increases. The values of the standard deviation/root mean square (S.D./R.M.S.) precision of fit parameter for the n.m.r. chemical shifts data, based on σ_I, σ_R^0 analyses, are given in Table 2: they behave as predicted by us. The precision of fit to the dual substituent parameter equation is in general almost always better with chemical data than with n.m.r. chemical shift data.[6] For the data on the pK_a values of naphthoic acids we have found that the values of S.D./R.M.S. are below 0.1, the level of excellent correlation, for all except the 7β set, and even there it is only 0.14. Each of the data sets on the detritiation reaction usually contains only two or three members and therefore no meaningful precision of fit can be determined.

(c) *The calculation of* f_i *and* g_i *values for* δq *in α-substituted molecules.* The method of calculation described in sub-section (a) was modified with respect to the ways in which the required values of g_o and f_σ/f_m for the butadienyl-benzenes were estimated. In order to appreciate the reasons behind the ways of selecting these values it is necessary to be aware that the 8β, 6β, 5β, and 7β sites in naphthalenes correspond to 1β sites in *ortho*, *para*, *meta*, and *meta* again, isomers, respectively, of butadienyl-benzene. The value of g_o was taken to be the same as the value of g (1.00) at the 8β site for the ^{19}F substituent chemical shifts, because the value of g at the 6β site for the same property is the same as the value of g_p. The value of f_o/f_m was taken to be the same as that of f_p/f_m (5/4) because the values of $f_{8\beta}/f_{6\beta}$ and of $f_{5\beta}/f_{7\beta}$ are both very close to unity for the ^{19}F substituent chemical shifts.

TABLE 2

S.D./R.M.S. values [a] for n.m.r. substituent chemical shifts

Position [b]	Property ^{13}C [c]	 ^{19}F [d]
6β	0.06	0.11
8β	0.15	0.24
5β	0.18	0.33
7β	0.16	0.14
7α	0.40	0.17
8α	*e*	*e*
5α	0.80	0.42
6α	0.78	0.28

[a] σ_I, σ_R^0 Analyses. [b] Listed in order of decreasing f value for q calculated. [c] Ref. 16. [d] Ref. 17. [e] Very poor correlation.

(d) *The interpretation of the experimental data for α-substituted compounds.* Because of the proximity of the secondary ring to the substituent, already mentioned, the precision of fit at any site ought to be poorer than for the corresponding site in the β-substituted compounds, so that, for example, the precision at 8β ought to be less than at 6β. This prediction is confirmed by the S.D./R.M.S. values for the observed ^{13}C and ^{19}F substituent chemical shifts (see Table 2). Nevertheless, we found that when the values of $f_i/f_{6\beta}$, and of g_i, for the various properties at the 8β and the 5β sites were considered alongside those for the sites in the β-substituted compounds (see Table 1 and Figure 6), they fell into the places expected on the basis of our theoretical treatment except in the case of the pK_a values of the 8β naphthoic acids.*

Primary ring. In terms of our model the δq_i in the primary ring of a β-substituted naphthalene ought to be as in the corresponding substituted benzene. Consequently it is expected that the values of a property measured at the 3α site in β-substituted naphthalene derivatives will be similar to the values of the same property measured at the *meta* site in benzene derivatives. In the case of α-substituted molecules the effects of direct coulombic interaction between the substituent and the secondary ring should be a source of difference between values of properties measured at corresponding sites in naphthalene and benzene derivatives (4α corresponds to *para* and 4β corresponds to *meta*). These effects would be similar to those exerted by a second substituent (X′) in a benzene derivative, located *ortho* to the first substituent (X). Since substituents usually affect the electron populations at the *para* site more than at the *meta* site, the influence of X′ relative to that of X, should be smaller at the site *para* to X than at the site *meta* to X and *para* to X′. Therefore the precision of fit to valid linear correlation equations should be poorer for 4β data than for 4α data. The precision of fit for the 4β data should also be poorer than for the data relating to that site in β-substituted naphthalene derivatives which corresponds to the *meta* site in benzene derivatives, *i.e.* the 3α site.

Experimentally [16,17] the precision of fit of both ^{13}C and ^{19}F substituent chemical shifts to the σ_I, σ_R correlation equation for the 4β data (S.D./R.M.S. *ca.* 0.5) is much worse than for the 3α (S.D./R.M.S. *ca.* 0.2) and 4α (S.D./R.M.S. *ca.* 0.1) data. The values of the chemical shifts even at the 4α and 3α sites are not in general as close as predicted to those at corresponding sites in benzene derivatives. However, this result does not greatly surprise us, since in previous applications of our model to aromatic systems [4] it was found that the direct relationship between substituent chemical shifts and δq_i broke down in the primary ring, although the dual substituent parameter correlation equations were obeyed quite well. The values of substituent effects on the *acidity of carboxylic acids* (in aqueous ethanol) are very similar for corresponding sites in naphthalene and benzene derivatives.[6]

Conclusions.—The results reported here indicate that our theoretical model gives a satisfactory account of the dominant factors contributing to the existence of quantitative linear correlations among observed substituent effects on properties of naphthalene and its derivatives. These dominant factors are certain precisely defined electronic ones, namely, the coulombic and the non-coulombic self-polarisation and charge-transfer (PCT) effects described above. Where these PCT electronic effects are small, or where other electronic effects are expected to be important, the precision of fit of experimental data to the dual substituent parameter equation, $\delta P_i = \rho_{Ii}(\sigma_I + \lambda_i\sigma_R)$, is found to be poorer than otherwise. Furthermore, the patterns of the variation in values of the substituent coefficients, ρ_I and λ, with the disposition of substituent site and probe site for each of the properties considered, can be satisfactorily interpreted in terms of the calculated values of the PCT electronic effects. The interpretation is simpler when ρ_I and λ are expressed in terms of the coefficients, f and g, of parameters **F** and **S** which are respectively measures of the coulombic and the non-coulombic self-polarisation

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* The discrepancy might be due to structural differences in the naphthalene skeleton in these compounds compared to the others.

of a standard molecular sub-system induced by substituents.

In the calculations reported above, no attempt was made to adjust the values of the variables involved in order to improve the quality of agreement between the predicted and the empirical patterns of the values of f and g. However, we have found that it is possible to make the patterns for the calculated substituent PCT electronic effects match even more closely the patterns for the observed ^{13}C substituent chemical shifts simply by increasing the value of f_p/f_m used in the calculations from 5/4 to 6/4 (set B in Table 1 and Figure 6).

Our theory can account for the fact that the values of g, and hence of λ, *are not constant* for the observable effects of either α or β substituents measured in any region of the naphthalene molecular system for any of the properties considered. This finding is significant because in other studies [2,4] our theory has been shown to account for the fact that there are regions of other molecular systems in which the values of g *are constant* for such properties.

The assumptions involved in the interpretation of the σ_I and σ_R substituent parameters in terms of the PCT electronic effects are not *directly* examined in the present work. However, our successes in interpreting the ρ_I and λ parameters provide good indirect evidence for the validity of these assumptions, and support our view that the physical significance usually attached to each of the σ_I and σ_R parameters is not correct.

Finally, the success of our treatment of naphthalene and its derivatives gives grounds for hoping that the treatment can be extended to any large hydrocarbon and its derivatives.

[9/176 *Received, 5th February,* 1979]

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