The Interpretation of Quantitative Linear Correlations. Studies on the Substituent Shell Concept

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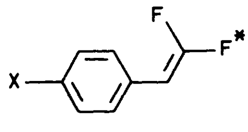
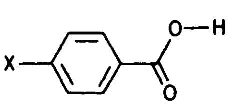
The substituent shell concept is that in series of compounds XGY with a common class of group G, the effects of changing X on various properties of Y ought to be linearly related to one another irrespective of the nature of the property or the nature of Y. The concept is examined both empirically and theoretically. It is concluded that substituent shell behaviour is very common even when G is unsaturated. This result is not compatible with theories of electronic effects in which polar effects are complemented by an independent resonance effect, but it is shown to be in accord with a theory in which coulombic field effects and charge-transfer effects are modified by a non-coulombic polarisation effect, so that they tend to become directly proportional to one another as the distance from X increases. The meanings of field, inductive, and resonance effects are discussed in terms of the new theory.

WHEN the effects of changing X on the ^{19}F substituent chemical shift in (1) are plotted against the corresponding effects on the O–H stretching frequency in (2), the result is a very good straight line: for X = OMe, Me, F, Cl, CF_3, CN, and NO_2, the correlation coefficient (r) is 0.994, and the value of the standard deviation/root mean square goodness of fit parameter (f) is 0.095. This result is in accord with the substituent shell concept as described by Wold and Sjöström.[1] The concept is conveniently summarised by equation (1) which, for compounds XGY, describes the effects of changing X on appropriate properties, Q, of Y. In the equation, P is a function of X and G but not of Y and Q, c is a function of Y and G but not of X and Q, and a is a function of Y, G, and Q, but not of X. Thus, for a given G, any two sets of δ_XQ when plotted against one another ought to give a straight line which, however, need not pass through the point for X = H: the natures of Y and Q do not need to be the same for both sets of δ_XQ. The fragment XG is called the ' substituent shell,' and straight lines are expected whenever two sets of δ_XQ are plotted against one another for compounds with common substituent shells.



(1)



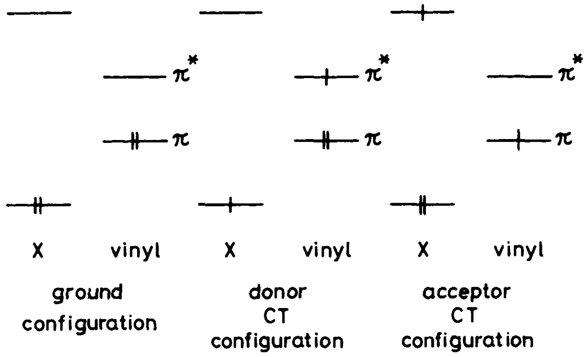
(2)

$$\delta_XQ = a\,(P - c) \qquad (1)$$

The inclusion of c in equation (1) allows for the possibility[2] that there may be two somewhat different structures for G, one of which is the more stable in compounds XGH or HGY, and the other of which is the more stable in compounds XGY (X, Y $\neq$ H). If there was only one structure for a particular G in both sets of compounds, c would be zero in that case.

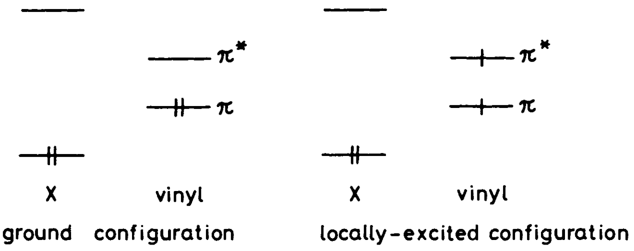
In this work we shall show that substituent shell behaviour is very common in practice. This result has important implications for theories of electronic effects. For reasons discussed below, it is incompatible with theories in which there are two or more independent electronic effects, for example, polar effects complemented by an independent resonance effect. It requires either that there is only one significant electronic effect, or that there are two or more interdependent effects. We shall show that it is in accord with a theory in which coulombic field effects and charge-transfer effects are modified by a non-coulombic polarisation effect so that they tend to become directly proportional to one another as the distance from X increases. We call the latter theory the ' Polarisation and Charge-transfer Modified Coulombic Field (PCT–MCF) Theory.' We next describe that theory and show that it leads to the expectation of substituent shell behaviour in certain conditions which are commonly met in practice.

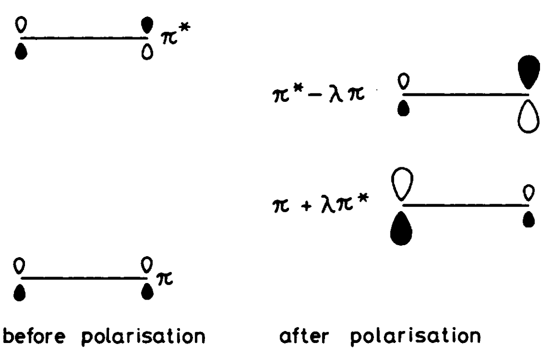
The PCT–MCF Theory of Substituent Effects.—This theory is a development of the previously reported[2-4] PCT theory of substituent effects. It will be described through consideration of various aspects of substituent effects on π-electron populations in molecules. The extension to effects on σ-electron populations is straightforward.



Qualitative Aspects of Substituent Effects on π-Electron Populations.—(a) *The effects of* X *on the vinyl group in* $XCH{=}CH_2$. Two kinds of effect are distinguished, namely, the charge-transfer effect and the polarisation effect. The charge-transfer effect is the result of mixing together the ground electronic configuration and charge-transfer configurations.[5] It is always stabilising.

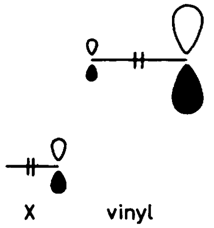
The polarisation effect is the result of mixing the ground electronic configuration with the locally excited configuration.* It is in itself destabilising, but it should occur when it leads to more favourable interactions between the vinyl π-system and the rest of the molecule. These interactions are of two kinds, (i) coulombic and (ii) non-coulombic.





(i) Coulombic interactions. The introduction of X should create a coulombic field which is different in strength at the two carbon atoms in the vinyl group, and should therefore favour the flow of π-electrons.

(ii) Non-coulombic interactions. Non-coulombic interactions are those involving overlap between the π-orbitals of the vinyl group and orbitals of X. They are of two kinds, namely, overlap-repulsion and charge-transfer. Overlap-repulsion is the effect of two filled orbitals overlapping one another. It is always destabilising. It would be smaller, and hence less destabilising, if the filled vinyl orbital was polarised such that the amplitude at the carbon atom adjacent to X was reduced. Charge-transfer is the effect of a filled orbital overlapping with a vacant orbital and is always stabilising. Donor charge-transfer would be larger, and hence more stabilising, if the vinyl group was polarised such that the amplitude of the vacant orbital was increased at the carbon atom adjacent to X. Acceptor charge-transfer would be larger if the vinyl group was polarised such that the amplitude of the filled orbital was increased at the carbon atom adjacent to X.

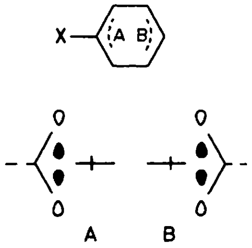


(b) *The effect of* X *on the terminal vinyl group in* $XCH=CH-CH=CH_2$. In the absence of any π-orbital overlap, the coulombic field effect of X on the polarisation of the terminal vinyl group ought to be attenuated because of the polarisation of the intervening vinylene group. The consequences of including the π-orbital overlap should be as follows.

There would be no net charge-transfer between the vinylene group and the vinyl group if neither π-system was polarised, since charge-transfer in either direction would be equally likely. However, any polarisation of the groups would lead to a proportional amount of net charge-transfer. Furthermore, both vinylene and vinyl groups would further polarise in order to optimise this charge-transfer. Thus the polarisation of the terminal vinyl group by X would be enhanced by a non-coulombic effect.

The effect of orbital overlap between X and the vinylene group would be to modify the polarisation of that group. This additional polarisation would in turn modify the polarisation of the terminal vinyl group.

Clearly, coulombic and non-coulombic interactions are interdependent, and we could not reasonably analyse the total substituent effect into separate coulombic and non-coulombic effects. One consequence is that we would not expect the total π-electron population of the terminal vinyl group to be directly proportional to the amount of charge-transfer between X and the intervening vinylene group.



(c) *The effect of* X *on the phenyl group in* XC_6H_5. The phenyl group is conveniently regarded as a semi-phenylene group A attached to a semi-phenyl group B. Groups A and B each possess a filled π-bonding orbital and a vacant π-antibonding orbital. In this respect they resemble the vinylene and vinyl groups in $XCH=CH-CH=CH_2$. However, each group also possesses a half-filled non-bonding orbital. These non-bonding orbitals cannot be polarised by X since they cannot by symmetry mix with the corresponding bonding and antibonding orbitals.

In benzene, charge-transfer in which group A was the donor and group B the acceptor would be equal in weight to charge-transfer in which group B was the donor and group A the acceptor. Hence there would be no net charge-transfer. The introduction of X would lift the degeneracy of the two non-bonding orbitals because of

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* This mixing of configurations and the reasons for it have been described in detail by Murrell.[5]

the difference in the strength of the associated coulombic field at the appropriate sites in the two orbitals. Hence there would then be a net charge-transfer involving these orbitals.

TABLE 1

The separate polarisation and charge-transfer effects on the π-electron populations[a] in monosubstituted benzenes

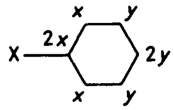
Substituent	Polarisation				Charge-transfer			
X	*i*	*o*	*m*	*p*	*i*	*o*	*m*	*p*
NO_2(orthogonal)	+80	−19	−6	−30	0	0	0	0
NH_2(planar)	−96	+68	−37	+36	+39	+20	+11	+21
NH_2(pyramidal)	−75	+55	−31	+28	+31	+16	+8	+16
OH	−58	+52	−33	+21	+33	+17	+9	+18
OMe	−52	+46	−30	+20	+34	+17	+9	+18
Me	−31	+17	−7	+11	+3	+1	+1	+1
F	−19	+29	−22	+7	+26	+13	+7	+14
$CH=CH_2$	−2	+3	−2	+1	−2	−1	0	−1
C≡CH	+26	−8	0	−9	−2	−1	0	−1
COMe	+29	−14	+6	−11	−9	−5	−2	−5
CHO	+30	−14	+5	−12	−10	−5	−3	−6
CF_3	+38	−12	0	−14	−4	−2	−1	−2
CN	+64	−21	+1	−24	−7	−4	−2	−4
NO_2	+100	−37	+6	−37	−10	−5	−3	−6

[a] The unit of population change is 10^{-3} electrons. A positive sign indicates an increase in population.

(d) *The effect of* X *on the vinyl group in* XC_6H_4–$CH=CH_2$. The effect of X should depend on whether or not there is a change in the π-electron population in the non-bonding orbital at the atom to which the vinyl group is attached. When the vinyl group is *para* to X there is no such change, and hence the effect of X ought to be qualitatively similar to the effect of X on the terminal vinyl group in a polyene chain molecule. However, when the vinyl group is *meta* to X there is such a change, and hence there ought to be an additional contribution to the total effect of X. This additional contribution should depend on the strength of the coulombic field emanating from X, with little modification.

(e) *The polarisation of* X. Just as a phenyl group or a vinyl group may polarise in order to make interactions with X more favourable, a polyatomic X group may itself polarise, or reorientate, in order to make these interactions even more favourable. For example, in arenecarbaldehydes, the carbon of the carbonyl group might possibly optimise overlap with the aryl group rather than with the carbonyl oxygen. It could be that a particular X group will so polarise only in certain compounds, depending on whether or not this polarisation would cost more energy than would be regained from the more favourable interactions with the vinyl or the phenyl group. It is also possible that certain groups may, in certain compounds, change internal polarisation so that instead of maximising donor charge-transfer with the phenyl group or the vinyl group, they will minimise overlap-repulsion.

Quantitative Aspects of Substituent Effects on Electron Populations.—(a) *The analysis of the effect of* X *in* XC_6H_5. The effects of X on the π-electron population and its distribution in the phenyl group have been determined by *ab initio* MO calculations by Hehre *et al.*[6] In the conformation of nitrobenzene in which the nitro-group is at right angles to the phenyl group, there is no net charge-transfer. Hence, by PCT–MCF theory, the π-electron distribution in the phenyl group must be due to the polarisation effect alone. The effect at the *ipso*- and *para*-positions is the result of mixing only the bonding and the antibonding semi-phenylene and semi-phenyl group orbitals. The ratio of the polarisation effects at these sites should be the same for all X groups. Hence only one variable is required to express the polarisation effect of any X group at these sites. The net π-electron population transferred between any group X and the phenyl group is given directly by the MO calculation. The distribution of this excess or deficiency of electron population must be as shown. Since the sum of *x* and *y* is known, only one variable is required to express the charge-transfer effect of any X at each of the ring sites. Thus, at the *ipso*- and *para*-sites only two variables are required to express the total PCT effect, one polarisation variable, and one charge-transfer variable. Consequently the polarisation and charge-transfer contributions at these sites can be separated by solving two simultaneous equations.



The charge-transfer contributions at the *ortho*- and *meta*-sites are respectively one-half of the contributions at the *ipso*- and *para*-sites. The polarisation contributions at the *ortho*- and *meta*-sites can be obtained by subtracting the charge-transfer contributions from the total effects. The results of analysing the effects of many common X groups are listed in Table 1.

(b) *Scales of polarisation and charge-transfer effects*. The quantitative polarisation effects of X at the *ipso*-site in benzene derivatives provide a suitable basis for a scale of *P* effects appropriate for *p*-phenylene derivatives. In order to make the magnitudes of the effects of the same order as those described by the Hammett σ_p scale, we have chosen a charge of one-tenth of one electron to be our unit. This scale will be labelled the P_A scale.

The quantitative polarisation effects of X at the *ortho*-site provide a suitable basis for a scale of *P* effects which allows for the additional polarisation effects expected with *meta*-phenylene derivatives. This scale will be labelled the P_B scale. The P_B scale involves the effect measured by the P_A scale as well as the additional effect: $P_A + 2.0P_B$ would be an appropriate scale for the additional effect alone.

TABLE 2

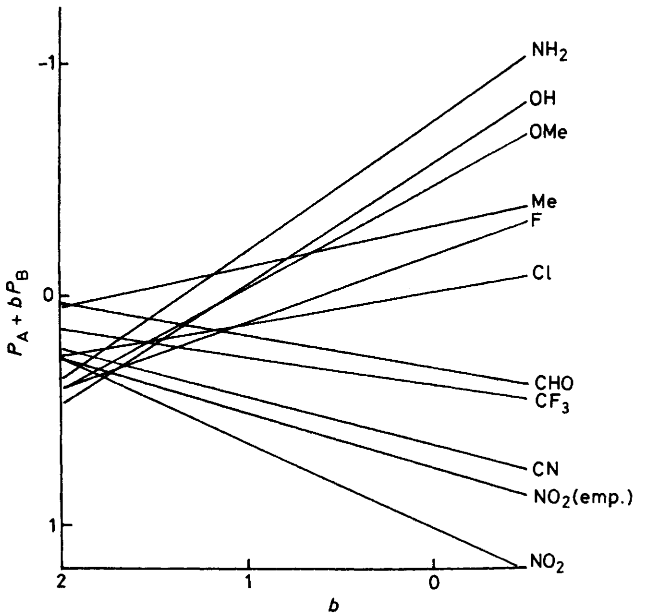
PCT–MCF scales of substituent effects [a]

Substituent	P_A	P_B	CT	F^O	S^O
Theoretical values					
NH_2(planar)	−0.96	+0.68	+0.39	+1.20	−2.16
NH_2(pyramidal)	−0.75	+0.55	+0.31	+1.05	−1.80
OH	−0.58	+0.52	+0.33	+1.38	−1.96
OMe	−0.52	+0.46	+0.34	+1.20	−1.72
Me	−0.31	+0.17	+0.03	+0.09	−0.40
F	−0.19	+0.29	+0.26	+1.17	−1.36
COMe	+0.29	−0.14	−0.09	+0.03	+0.26
CHO	+0.30	−0.14	−0.10	+0.06	+0.24
CF_3	+0.38	−0.12	−0.04	+0.42	−0.04
CN	+0.64	−0.21	−0.07	+0.66	−0.02
NO_2	+1.00	−0.37	−0.10	+0.78	+0.22
Empirical values					
NO_2	+0.74 [b]	−0.24 [c]		+0.78	−0.04
Cl	+0.03 [b]	+0.11 [c]		+0.75	−0.72
Br	+0.03 [d]	+0.10 [d]		+06.9	−0.66

[a] Definitions of P_A, P_B, CT, F^O, and S^O are given in the text. [b] From ^{19}F s.c.s. in ββ-difluorostyrenes (see Table 6). [c] From σ_m (see Table 6). [d] From relative effects of Br and Cl on rates of nucleophilic substitution reactions of polyhalogenoaromatic compounds, *cf.* M. Godfrey, *J. Chem. Res.* (*S*), 1978, 480.

The quantitative charge-transfer effects at the *ipso*-site are used to determine a CT scale. The P_A, P_B, and CT scales are shown in Table 2, and the Figure shows how the absolute and the relative values of $P_A + bP_B$ vary with the value of the weighting factor *b*.

(c) *Correlations involving* X *effects on the phenyl group in benzene derivatives and the vinyl group in styrene derivatives.* The effects of X on the electron populations and their distribution in the styryl group have been determined by *ab initio* MO calculations by Reynolds *et al.*[7] The effects on the π-electrons of the vinyl group may be analysed into separate polarisation and charge-transfer components as follows: the *sum* of the effects of X on the total π-electron populations at the two carbon atoms is twice the charge-transfer effect at either atom, and the corresponding *difference* is twice the polarisation effect. The results of the analysis for several common X groups are given in Table 3.



Plot of $P_A + bP_B$ *versus b*

The polarisation and the charge-transfer effects of X on the vinyl group have been separately plotted against the P_A scale. In each case an excellent straight line was obtained (*r* 0.999, *f* 0.06: *r* 0.998, *f* 0.07) which missed the point for X = H. The charge-transfer effect on the vinyl group has also been plotted against the CT scale. This time the correlation was rather poor (*r* 0.935, *f* 0.38). We conclude that in the styrene derivatives the polarisation of the phenylene group is a major influence in determining both the π-polarisation and the π-charge-transfer perturbations of the vinyl group.

(d) *Correlations involving* X *effects on the phenyl group in benzene derivatives and various groups in molecules located near methane derivatives.** The effects of substituents in methane on the π-electron population and its distribution in a nearby ethylene molecule have also been calculated by Reynolds *et al.*[7] The PCT analysis of the results indicates polarisation effects only. These correlate well with $P_A + 1.35P_B$ (*r* 0.988, *f* 0.11). Brownlee and Craik[8] have examined the effects of substituents in methane on the π-electron populations in a formaldehyde molecule at various separations of the pair of molecules. The polarisation effects again correlate well with $P_A + 1.35P_B$, and they fall off in magnitude with increasing separation of the pairs of molecules. In the same paper the substituent effects in the carbonyl groups

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* For example, (3) and (4).

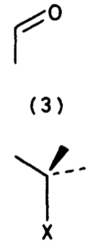
TABLE 3

The separate polarisation and charge-transfer effects on the π-electron populations[a] in the vinyl group in 4-substituted styrenes

Substituent	NH_2[b]	NH_2[c]	OH	Me	F	CHO	CF_3	CN	NO_2
Polarisation	+16	+11	+8	+4	+2	−7	−8	−15	−21
Charge-transfer	+7	+5	+4	+2	+2	−3	−3	−5	−7

[a] The unit of population change is 10^{-3} electrons. A positive sign indicates an increase in population at the β carbon atom. [b] Planar. [c] Pyramidal.

were compared in the pairs of molecules (3) and (4), in which the relative locations of the C–X and the C=O bonds were identical.



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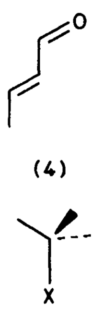

(4)

The results of the PCT analyses of these data are given in Table 4. They show that the polarisation of the carbonyl group is twice as great in (4) as in (3), and that the effect on charge-transfer between the vinyl group and the carbonyl group in (4) is very nearly directly proportional to the polarisation effect. The ease of transmission of polarisation and, especially, of charge-transfer increases as the amount of molecular material between X and Y increases. In (4) there is a small net charge-transfer between the two molecules. The effect of X on the amount of this charge-transfer correlates with $P_A - 1.0P_B$ rather than with $P_A + 1.35P_B$. This indicates that the effect of the methyl group on the interaction between X and the carbonyl system must involve more than polarisation of the π-system of the methyl group. If the effect of X on the methyl group was a pure coulombic field effect, the polarisation of the carbonyl group in (3) ought to correlate with $P_A + 2.0P_B$ rather than with $P_A + 1.35P_B$. Hence the involvement of a significant non-coulombic interaction between X and the methyl group is indicated. Polarisation of the σ-system is an obvious candidate for the additional effect of the methyl group on the interaction between X and the carbonyl system.

The Extension of the PCT–MCF Theory to include Effects on σ-Electron Populations. In the absence of an intervening group the coulombic field emanating from any X ought to polarise the π-system and the σ-system of Y to directly proportional extents. In the presence of G, but in the absence of any orbital overlap between G and X or Y, the field felt at Y should be reduced as a consequence of the total polarisation of G. Since, under these conditions, the π and the σ components of the polarisation of G induced by any X must be directly proportional to one another, the π and the σ components of the polarisation of Y should remain proportional to one another. G should act as a simple dielectric. On introducing orbital overlap between G and Y, both groups should undergo additional polarisation in order to optimise charge-transfer between them. The amount of the additional polarisation of Y ought to depend on the amount of the existing polarisation of G, and hence on the magnitude of the field emanating from X. The π and the σ components of the polarisation induced by any X should remain proportional to one another, but the constant of proportionality should change depending on the relative amounts of π and σ orbital overlap. The introduction of orbital overlap between G and Y should reduce the apparent dielectric constant of G, possibly to a value of less than unity.

Under the conditions specified so far, the substituent shell concept should be absolutely valid, with a common scale of *P* values for all G groups. The introduction of orbital overlap between G and X should, however, complicate the situation. G should undergo additional polarisation in order to maximise charge-transfer with X. Furthermore, the π and the σ components of this non-

TABLE 4

The separate polarisation and charge-transfer effects on the π-electron populations[a] in compounds (3) and (4)

	Compound (3)	Compound (4)				
	carbonyl[b]	carbonyl		vinylene		total
Substituent	*P*	*P*	CT	*P*	CT	CT
NH_2(planar)	0.0	−0.05	+0.05	+0.80	+0.40	+0.45
NH_2(pyramidal)	−0.4	−0.75	−0.25	−0.75	+0.45	+0.20
OH	−0.9	−1.75	−0.65	−2.95	+0.85	+0.20
F	−1.4	−2.75	−1.05	−5.25	+1.15	+0.10
Me	+0.1	+0.35	+0.15	+1.05	−0.05	+0.10
CF_3	−1.5	−2.85	−1.05	−5.55	+0.85	−0.20
CN	−2.4	−4.80	−1.80	−9.70	+1.40	−0.40
NO_2	−3.3	−6.65	−2.45	−13.00	+1.90	−0.55

[a] The unit of population change is 10^{-3} electrons. A positive sign indicates an increase in population at the oxygen atom or at the β carbon atom. [b] There is no charge-transfer effect.

coulombic polarisation induced by any X need not have the same constant of proportionality as with the corresponding coulombic polarisations. As a consequence, the π and the σ components of the total polarisation of G need not be directly proportional to one another. As the total electronic perturbation induced by X travels across G, coulombic interactions between adjacent sub-groups within G should tend to produce π–σ proportionality, but the corresponding non-coulombic interactions in both π and σ systems should favour the extension of non-proportionality.

The *ab initio* MO calculations on 4-substituted styrenes[7] mentioned above give substituent effects on σ- as well as on π-electron populations. The pattern of substituent effects on the σ-electron population at the carbon atom adjacent to X is quite different from the corresponding pattern of effects on the π-electron population. However, at the other end of the molecule there are excellent linear correlations between the effects on the σ- and the π-electron populations.

There are two other interesting features of the π–σ correlations. First, the correlation is less good at the α-carbon atom of the vinyl group than at either of the adjacent carbon atoms. Secondly, although the *sum* of the effects at the two terminal hydrogen atoms correlates well with the effects at the β-carbon atom of the vinyl group, the corresponding *difference* of these effects does not. The first feature is readily interpreted as a consequence of the fact mentioned above that π-charge-transfer between X and the phenylene group does not directly affect π-charge-transfer between the phenylene group and the vinyl group, whereas it must influence the displacement of σ-electrons between the *para*-carbon atom of the phenylene group and the α-carbon atom of the vinyl group. The second feature suggests to us that the modified coulombic field *parallel* to the C=C bond of the vinyl group is not directly proportional to the modified coulombic field *perpendicular* to the bond and in the plane of the vinyl group. Such non-proportionality would be a further consequence of the non-proportionality of substituent effects on the σ-electron and the π-electron populations at the α-carbon atom of the vinyl group. Our interpretation of this feature will be discussed below.

The Conditions required for Substituent Shell Behaviour to be observed in Practice.—In terms of the PCT-MCF theory of substituent effects, two conditions are necessary for substituent-shell behaviour to be observed when two sets of δ_XQ in compounds XGY are compared. First, each δ_XQ must, to a very good approximation, be directly proportional to the modified coulombic field felt at Y in a particular direction. Secondly, the effects of changing X on the coulombic fields felt at Y in the two cases must be linearly related to one another. We expect on theoretical grounds that the second condition will be closely approached when X and Y are in both cases separated by a long G group. The practical usefulness of the substituent shell concept depends on whether or not the second condition is closely approached for common substituents when the G group is quite short, or when there are two different G groups that are similar in nature only in the region that is close to X. We have examined numerous data sets in order to assess the practical value of the concept.

We have found that, except when the range of δ_XQ values is very small, δ_XQ can be expressed empirically by equation (2) for all or many of the following substituents: NH_2 (planar), NH_2 (pyramidal), OH, OMe, Me, F, Cl,* CHO, COMe, CF_3, CN, and NO_2.* This finding does not in itself imply that charge-transfer effects of X are always modified, since the CT scale is well reproduced (r 0.995, f 0.10) by 0.45 ($P_A + 2.90P_B - 0.12$).

$$\delta_XQ = a\,(P_A + bP_B - c) \qquad (2)$$

Two sets of δ_XQ which obey equation (2) must give a straight line when plotted against one another if the value of b is the same. Substituent shell behaviour will appear to be the more common the more the value of b can differ before the two sets of δ_XQ fail to correlate to an acceptable degree (say $f \leqslant 0.10$). We have found that the choice of substituents to be included in the data sets is important in this context. A plot of $P_A + bP_B$ against b (Figure) shows that several common substituent groups have very similar values of $P_A + bP_B$ (0.28 ± 0.05) at certain values of b (*ca.* 1.8). This means that, provided neither value of b is close to 1.8, we should expect two sets of δ_XQ involving only these substituents to show substituent shell behaviour even when the two values of b are quite dissimilar. In Table 5 we report the results of comparing $P_A + b_1P_B$ with $P_A + b_2P_B$ for several values of b_1 and b_2 for a typical set of common substituent groups.

TABLE 5

Statistical data for plots of $P_A + b_1P_B$ against $P_A + b_2P_B$ [a]

b_1	b_2	r	f
−0.5	0.0	0.999	0.05
0.3	0.0	0.999	0.05
0.5	0.0	0.996	0.10
0.8	1.0	0.995	0.10
0.9	1.0	0.998	0.05
1.1	1.0	0.997	0.07
1.2	1.0	0.987	0.15
1.25	1.35	0.991	0.10
1.30	1.35	0.997	0.05
1.40	1.35	0.996	0.06
1.45	1.35	0.985	0.12

[a] The substituents involved were NH_2(pyramidal), OH, OMe, F, Me, Cl, COMe, CHO, CF_3, CN, NO_2.

The Extent to which Substituent Shell Behaviour is observed in Practice.—In order to investigate whether or not substituent shell behaviour is common in practice, we evaluated b for a varied selection of sets of δ_XQ by comparing empirical and theoretical values of a quantity which is very sensitive to the value of b, namely (Q_{Me} —

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* The values of P_A and P_B for these substituents were obtained empirically from values of δ_XQ in cases in which equation (2) was well obeyed by all other available substituents in the set. They are listed at the bottom of Table 2.

$Q_{\text{OMe or OH}})/(Q_{\text{F, Cl, or Br}} - Q_{\text{Me}})$. That quantity involves a substituent, the methyl group, for which the value of $P_A + 1.8P_B$ is not close to 0.28. The values of *b* we obtained are reported in Table 6.

TABLE 6

The values of *b* from applying equation (2) to various sets of $\delta_X Q$

$\delta_X Q$ set	*b*	Ref.
1a Sets involving X attached to a saturated carbon atom: $b = 1.35 \pm 0.10$		
Reynolds *et al.*, T_F scale	1.35	7
Taft σ^* scale	1.30	*a*
pK_a of 4-X-BCO-1-carboxylic acids [b] (aq. ethanol)	1.30	*c*
pK_a of 4-X-quinuclidinium ions (aq.)	1.35	*d*
pK_a of acetic acids (aq.)	1.25	*e*
pK_a of 4-X-BCO-2-ene-1-carboxylic acids	1.25	*c*
^{13}C of 4-X-1-phenylBCO ($DCCl_3$): 1′ site	1.35	*f*
^{13}C of X-$(CH_2)_2$-phenyl: 1′ site	1.35	*g*
1b Sets involving X attached to a saturated carbon atom: $b \neq 1.35 \pm 0.10$		
pK_a of 4-X-dibenzo-2,5-diene-1-carboxylic acids	1.05	*c*
^{19}F of 4-X-fluorophenylBCO (DMF): *p*-fluoro	1.20	*f*
m-fluoro	1.20	*f*
o-fluoro	1.45	*f*
^{13}C of 4-X-1-phenylBCO ($DCCl_3$): 4′ site	1.10	*f*
3′ site	1.00	*f*
2′ site	1.95	*f*
^{13}C of X-$(CH_2)_2$-phenyl: 4′ site	1.10	*g*
^{13}C of X-$(CH_2)_3$-phenyl: 4′ site	0.95	*g*
1′ site	1.10	*g*
2a Sets involving X attached to a *m*-phenylene group: $b = 1.0 \pm 0.10$		
pK_a of benzoic acids (aq.): σ_m	1.10	*h*
pK_a of phenylacetic acids (aq. ethanol)	1.00	*i*
pK_a of anilinium ions (aq.)	1.10	*j*
pK_a of benzenethiols	0.95	*k*
ΔH° benzoic acid to benzoate (gas)	0.95	*l*
ΔH° phenol to phenolate (gas)	1.00	*l*
ΔS° phenol to phenolate (gas)	0.90	*m*
log *k* for solvolysis of $ArCMe_2Cl$: $\sigma^+{}_m$	0.95	*n*
i.r. CN band in benzonitriles	0.95	*o*
^{13}C of ArCOMe: carbonyl site	0.90	*p*
^{13}C of ArOCOMe: carbonyl site	1.00	*p*
^{19}F of 3-X-4′-F-biphenyl	1.00	*q*
2b Sets involving X attached to a *m*-phenylene group: $b \neq 1.0 \pm 0.10$		
pK_a of anilinium ions (methanol)	0.80	*r*
ΔE for X-anilinium + benzene $\longrightarrow$ X-benzene + anilinium	0.80	*s*
^{13}C of benzonitrile: CN site	0.85	*t*
pK_a of phenols (aq.)	1.25	*m*
ΔE for X-phenolate + benzene $\longrightarrow$ X-benzene + phenolate	1.20	*s*
^{19}F of fluorobenzenes	1.25	*u*
3a Sets involving X attached to a *p*-phenylene group: $b = 0 \pm 0.5$		
pK_a of benzoic acids (aq.): σ_p	0.4	*h*
pK_a of anilinium ions (aq.): σ_p^-	0.4	*j*
ΔE for X-phenolate + benzene $\longrightarrow$ X-benzene + phenolate	0.1	*s*
log *k* for solvolysis of $ArCMe_2Cl$: σ_p^+	0.0	*n*
i.r. CN band in benzonitriles	0.2	*o*
i.r. OH band in benzoic acids	0.3	*v*
^{13}C of phenylacetylene at the β-carbon site	0.0	*w*
^{13}C of styrene at the β-carbon site	0.2	14
^{13}C of $ArSCH{=}CH_2$: α-carbon site	−0.1	*x*
β-carbon site	−0.2	*x*
^{13}C of ArOCOMe: carbonyl site	0.3	*p*
^{19}F of 4-X-4′-F-*trans*-stilbenes (DMF)	0.2	*y*
^{19}F of $ArCH{=}CF_2$: *trans*-fluorine site	−0.1	*z*
3b Sets involving X attached to a *p*-phenylene group: $b \neq 0 \pm 0.5$		
pK_a of phenols (aq.)	0.9	*m*
pK_a of benzenethiols	0.8	*k*
pK_a of phenylacetic acids (aq. ethanol)	0.8	*i*
ΔH° benzoic acid to benzoate (gas)	0.8	*l*
^{13}C of phenylacetylenes at the α-carbon site	0.8	*w*
^{13}C of ArCOMe: carbonyl site	1.35	*p*

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We found that when X is bonded to a saturated carbon atom, the value of *b* is usually 1.35 ± 0.10. Exceptions were found in cases where effects of π polarisation and charge-transfer, mentioned above in the analysis of the MO calculations on compound (4), might reasonably be expected to be important. When X is bonded to an unsaturated carbon atom, the value of *b* often lies in the range 0 ± 0.5. In *meta*-phenylene derivatives, however, the value of *b* is usually 1.0 ± 0.1: we attribute this high value to the effects of the coulombic field on π-charge-transfer involving the non-bonding orbitals of the two semiphenylene groups. In compounds which are simultaneously *m*- and *p*-phenylene derivatives, such as 2-X-naphthalenes, the value of *b* ought to vary with the disposition of Y relative to X.[3] In *p*-phenylene derivatives, the value of *b* ought to be significantly different from zero when the effects of the displacement of σ-electrons in the bond between the phenylene ring and the side-chain which contains Y are important. Thus, for example, ^{13}C s.c.s. for atoms directly bonded to the phenylene ring invariably have values of *b* well above zero. The insertion of another atom or group between the phenylene group and the α-carbon atom often brings *b* to within the range 0 ± 0.5.

In a few data sets involving *p*-phenylene derivatives, for example σ^- and σ^+, there are departures from substituent shell behaviour which can reasonably be attributed to the effects of certain X groups or Y groups changing their usual internal polarisation or their usual behaviour with respect to G. When the Y group changes, the plot of $\delta_X Q$ against $P_A + bP_B$ ought either to change slope abruptly at a particular point or to curve somewhat, as with σ^+. Where an X group changes, the point for that group ought to deviate from the straight line through the points for well behaved X groups, as with σ^-.

We conclude that substituent shell behaviour is commonly observed in practice among $\delta_X Q$ data sets in compounds XGY when, for all members of the series concerned, the group G belongs to the same class. Where X is bonded to a carbon atom, there are three classes of G, namely, methylene derivative, *m*-phenylene derivative, and *p*-phenylene–vinylene derivative. Departures from substituent shell behaviour are observed in all three classes, but this non-ideal behaviour can be rationalised in terms of the PCT–MCF theory.

DISCUSSION

We have shown that, in practice, substituent shell behaviour, although by no means universal, is very common. We have also shown that this result is in accord with the PCT–MCF theory of electronic effects described in this paper. We shall now discuss the implications for theories involving independent electronic effects.

The σ_I and $\sigma_R{}^0$ scales of substituent effects can each be well expressed by equation (2). Therefore equation (2) may be transformed into (3), and those data sets which obey equation (2) should also obey (3) with comparable precision. The problem with the σ_I–$\sigma_R{}^0$ analysis is to explain why b' should be constant in those cases in which b was found to be constant. If σ_I and $\sigma_R{}^0$ are regarded as measures of a polar substituent effect and an independent resonance substituent effect respectively, the value of b' is expected to vary with the natures of Y and Q even when the nature of G is fixed. This is because the relative contributions of the two effects on the electrons at the various sites within any Y group should vary from site to site.

$$\delta_X Q = a'\,(\sigma_I + b'\sigma_R{}^0 - c') \qquad (3)$$

The fact that b in equation (2), or b' in equation (3), sometimes varies with the nature of G, Y, or Q, implies that there must be two distinct types of significant electronic effect. However, the fact that b, or b', is so often independent of the nature of Y or Q implies that these two types of electronic effect are not transmitted independently of one another. Thus, for example, it is not legitimate to follow the common practice of regarding σ_I as a universal scale for local coulombic field effects, and $\sigma_R{}^0$ as a universal scale for charge-transfer effects, at all sites in all molecules. The precise physical significance of the individual terms in σ_I and in $\sigma_R{}^0$ in the expansion of equation (3) must vary with the location of the probe site(s) and with the nature of the molecule.

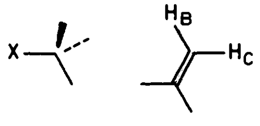
A disadvantage of equation (2) is that each of the parameters P_A and P_B represents a *blend* of substituent electronic effects. P_A represents a 1 : 1 blend of coulombic field strength and non-coulombic polarisation power, and $P_A + 2P_B$ represents almost pure coulombic field strength (see above). We have used these two relationships to define,* by equations (4), approximate scales F^0, for coulombic field strength, and S^0, for non-coulombic polarisation power. The values of F^0 and S^0 for some common substituent groups are given in Table 2. The F^0 scale qualitatively resembles certain scales of group electronegativity.[9–12] The S^0 scale resembles the $\sigma_R{}^0$ scale, suggesting that $\sigma_R{}^0$ measures non-coulombic polarisation. The very small negative values of S^0 for certain weak electron-accepting substituents (*e.g.* CF_3 and CN) probably arise out of the approximate nature of the expressions for F^0 and S^0. These groups are so weak as electron acceptors that any gain in charge-transfer energy arising out of non-coulombic polarisation would probably be smaller than the loss in energy involved in that polarisation. Therefore the true non-coulombic polarisation power of these substituents is probably zero, leaving the true coulombic field strength as P_A.

$$F^0 + S^0 = P_A;\ F^0 = 3(P_A + 2P_B);\quad S^0 = -2(P_A + 3P_B) \qquad (4)$$

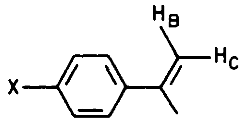
Combining equations (2) and (4) gives equation (5) as the expression for $\delta_X Q$ in terms of F^0 and S^0. The value of f represents the sensitivity of Q to the modified coulombic field at the probe site, and the value of g represents the extent to which the non-coulombic power modifies the coulombic field.

$$\delta_X Q = f\,(F^0 + gS^0 - h) \qquad (5)$$

The value of g for the σ_I scale is *ca.* 0.6. This result indicates that non-coulombic polarisation may markedly modify the coulombic field at Y, of a substituent X, even when the intervening group G is a saturated hydrocarbon. This conclusion conflicts with the commonly held view that σ_I represents a pure coulombic field effect. Reynolds *et al.*[7] have found what, at first sight, seems a good piece of evidence in support of this common view. From the results of *ab initio* MO calculations on compounds (5) and (6), they found that the effects of substituents on the differences in σ-electron population at the vinyl hydrogen atoms H_C and H_B, $\delta_X \Delta q_H$, in the two compounds, are directly proportional to one another. However, the



(5)



(6)

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* The **F** and **S** scales in the original version of PCT theory are defined somewhat differently.

results of CNDO/2 calculations by Hamer *et al.*[13] show that the pattern of $\delta_H \Delta q_X$ in compound (6) changes markedly when the substituted phenyl group is rotated through 90°. The latter result indicates that the component of the coulombic field perpendicular to the C=C bond in (6) must depend on orbital-overlap interactions between the substituted phenyl group and the vinyl group.

Finally, the phenomenon of non-coulombic polarisation also plays a critical role in determining the structures of transition states, in a recently reported theoretical model for predicting when and how the selectivity of reagents with respect to substrates ought to vary with their reactivity.[4]

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