On the Interpretation of Linear Correlations between Nuclear Magnetic Resonance Substituent Chemical Shifts and Substituent Reactivity Parameters in Benzene Derivatives

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The currently poorly-understood relationships between n.m.r. substituent chemical shift (s.c.s) data and substituent reactivity parameters are reconsidered within the framework of a substantially modified version of the usual general theory for structure–property relationships, that has recently been proposed. Predictions concerning the circumstances under which quantitative linear correlations of two kinds should or should not occur are confirmed for compounds which are formally substituted benzenes. It is concluded that the theory merits consideration in the theoretical treatment of any case of a structure–property or an interproperty relationship. The implications for the use of n.m.r. s.c.s. data to obtain structural information about molecular systems are briefly discussed.

IN many cases observed n.m.r. s.c.s. data correlate well with a linear combination of a *pair* of substituent reactivity parameters, and in some cases they also correlate well with a *single* substituent reactivity parameter.[1] For example, the generalised † linear correlations [equations (1) and (2)] often hold when δP_1 is taken to

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† In the general case δP refers to the change in value of a molecular property P due to a structural perturbation; κ and λ are constants for a given set of perturbations, with values depending on the natures of the Ps. The various Ps may refer to the same property of different molecular systems, different properties of the same molecular system, or different properties of different molecular systems.

[1] R. B. Mallion, in 'Nuclear Magnetic Resonance,' ed. R. K. Harris, Chem. Soc. Specialist Periodical Report, 1975, vol. 4, p. 1, gives some recent references.

represent n.m.r. s.c.s., δP_2 is taken to represent a Hammett substituent constant σ,* and δP_3 and δP_4 are taken to represent either pairs of Taft substituent constants, σ_I and σ_R,* or pairs of Swain and Lupton substituent constants, $\mathscr{F}$ and $\mathscr{R}$. Both the substituent reactivity

$$\delta P_1 = \kappa \delta P_2 \tag{1}$$

$$\delta P_1 = \kappa(\delta P_3 + \lambda \delta P_4) \tag{2}$$

parameters and the s.c.s. data have been interpreted by several groups of workers, notably those led by Dewar, Taft, Reynolds, and Phillips, as measures of combinations of direct through-space field effects, various σ- and π-inductive effects, resonance effects, and various solvent effects. However, no one has been able to predict correctly the circumstances under which either correlation equation does and does not hold.

Dewar, Golden, and Harris [2] have convincingly argued that quantitative linear correlations between n.m.r. s.c.s. and substituent reactivity parameters ought not to occur if direct through-space field effects on the molecular properties concerned are of comparable importance to indirect through-bond electronic effects. The widespread occurrence of empirical quantitative linear correlations implies that these types of effect are not of comparable importance except in special circumstances. However, the theory of substituent effects used by Dewar *et al.*[2] postulates that direct field effects *are* usually of comparable importance to indirect electronic effects.

Fukunaga and Taft [3] have quoted several observations which lead them to conclude that polar substituent effects on fluorine n.m.r. s.c.s. data are largely carried internally by π-bond frameworks and any direct through-space transmission is relatively minor. Dayal, Ehrenson, and Taft,[4] and also Reynolds and his co-workers [5,6] have argued in favour of the existence of a type of π-inductive effect on chemical shifts, which is not directly related to the resonance effect. (In the theory of substituent effects used by Dewar *et al.*[2] there is a type of π-inductive effect which *is* directly related to the resonance effect.) This approach provides a basis for interpreting *dual-term* linear correlations [equation (2)], but leads to the conclusion that *single-term* correlations [equation (1)] are unlikely. Its usefulness is also limited in that it does not involve a device for predicting anything about the values of λ or of κ.

Phillips and his co-workers [7,8] have suggested that the Hammett substituent constants, σ, are measures of electronic effects transmitted through π-bonds by all mechanisms, and that Taft's substituent constant, σ_I, is a measure of electronic effects transmitted through space or through σ-bonds. Hence, equation (2) should apply when δP_3 and δP_4 represent, respectively, σ and σ_I. The existence of single-term correlations in certain cases would not be a surprise within the context of this treatment, but there is still no device in the treatment for predicting the values of λ or of κ. Dawson and Reynolds [6] have questioned the validity of the arguments of Mitchell and Phillips.[8]

The ability to predict the conditions necessary for the existence of simple quantitative linear correlations between changes in the values of different molecular properties that accompany a given structural perturbation provides a low-hurdle test for any general theory of the relationship between molecular structure and molecular properties. The failures to interpret the empirical relationships between n.m.r. s.c.s data and substituent reactivity parameters might well be indicative of serious weaknesses within the theories used.

We have proposed elsewhere [9,10] a version of the general theory of structure–property relationships which was designed to form a suitable basis for interpreting inter-property correlations. It differs from the commonly used versions of the theory in three important respects. First, coulombic and non-coulombic disturbances within a molecular system are *not* transmitted through bonds independently of one another. (The theory of substituent effects used by Dewar *et al.*[2] does involve a *degree* of interdependence.) Secondly, the relative importance of direct through-space field transmission to indirect through-bond transmission is very much less. Thirdly, no formal distinction is made between π-electronic and σ-electronic disturbances. The new version of the theory also involves *concepts* which are not used in other versions. The traditional concept of resonance is replaced, and the traditional concept of induction is modified, by the concept of charge transfer and the novel concept of the overlap field (see below). The theory requires that certain structural features (see below) must be present within a molecular system in order for equation (2) to hold. The introduction of a further structural constraint permits equation (2) to be reduced to equation (1). In the present work the relationship between n.m.r. s.c.s. and substituent reactivity parameters is considered within the context of this new theoretical framework. The main aim is to test whether or not the predictions concerning the structural requirements for equations (1) and (2) to hold in the general case are confirmed in this specific case.

Theory and Predictions.—The new version of the theory and the predictions concerning the circumstances

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* The symbol σ (σ_R) is used here to represent any Hammett (Taft resonance) substituent parameter. The symbol σ^{BA} ($\sigma_R{}^{BA}$) is used to represent the parameter appropriate to the dissociation of benzoic acids in water at 25 °C.

[2] M. J. S. Dewar, R. Golden, and J. M. Harris, *J. Amer. Chem. Soc.*, 1971, **93**, 4187.

[3] J. Fukunaga and R. W. Taft, *J. Amer. Chem. Soc.*, 1975, **97**, 1612.

[4] S. K. Dayal, S. Ehrenson, and R. W. Taft, *J. Amer. Chem. Soc.*, 1972, **94**, 9113.

[5] G. K. Hamer, I. R. Peat, and W. F. Reynolds, *Canad. J. Chem.*, 1973, **51**, 897, 915.

[6] D. A. Dawson and W. F. Reynolds, *Canad. J. Chem.*, 1975, **53**, 373.

[7] I. R. Ager, L. Phillips, and S. J. Roberts, *J.C.S. Perkin II*, 1972, 1988.

[8] P. J. Mitchell and L. Phillips, *J.C.S. Perkin II*, 1974, 109.

[9] M. Godfrey, *J.C.S. Perkin II*, 1975, 1016.

[10] M. Godfrey, *Adv. Linear Free Energy Relationships*, in the press.

under which quantitative linear correlations should and should not occur in the general case are reported in detail elsewhere.[9,10] Here we merely *quote* the material in those references that is essential for an appreciation of the matters considered in the present work.

The theory is concerned specifically with the effects of structural changes (*e.g.* the introduction of substituent groups) within a molecular system consisting of substrate molecule and, where appropriate, reagent, solvent, and catalyst molecules too. Each molecular system is formally divided into a ' source ' region of electronic disturbances, a ' detector ' region of electronic disturbances, and a ' core ' region. The core region may be subdivided into unit groups, each belonging to the set shown in Figure 1. Interactions between any of the moieties are of three kinds, namely, coulombic field, charge transfer, and overlap field. The coulombic field falls off with distance from the source region. *In the present theory* it is considered, for reasons of operational simplicity, to be zero except in the region of the core unit group which is immediately adjacent to the source region. Charge transfer is the familiar stabilising interaction which results from the overlap between *occupied* (unoccupied) orbitals of one moiety and *unoccupied* (occupied) orbitals of the other.[11] The overlap field is a novel concept. It represents the consequences of opposing drives within a molecular system to *maximise* charge transfer and to *minimise* repulsive interactions which involve overlap between *occupied* orbitals of one moiety and *occupied* orbitals of the other moiety.[11] The overlap field differs from the coulombic field in that, by postulate, it falls to zero beyond the atom of the core which is immediately adjacent to the source region.

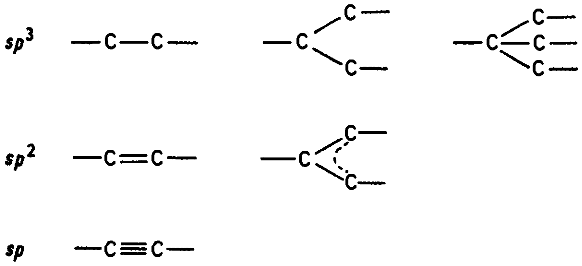

FIGURE 1 Set of hydrocarbon core unit groups (carbon skeletons)

Both the coulombic field and the overlap field generated by an electronic disturbance cause a polarisation of the electrons in the neighbouring core unit group. They also modify the transfer of electrons between that core unit group and its immediate neighbours. The resulting changes in the electronic structure of the first core unit group become a source of electronic disturbance for the second core unit group, and so on throughout the molecular system. It should be noted that the transmission of coulombic (non-coulombic) disturbances arising in the source region depends on the creation of non-coulombic (coulombic) disturbances in the core region. In this sense the transmission of coulombic and non-coulombic disturbances are interdependent. The creation of overlap fields *between* submolecular groups are expected to be opposed by drives *within* the individual groups to optimise internal bonding. Consequently, it is possible that the interactions between *certain* pairs of groups in molecular systems will not be directly subject to the effects of a non-zero overlap field when *certain* structural perturbations are made. Any region of a molecular system that is *free* from the direct effects of any non-zero overlap fields will be called a DOF-free region.

The significance of a DOF-free region is that changes in the electron density at every atom within such a region ought to be proportional to the same fixed combination of coulombic field, charge transfer, and overlap field parameters that are characteristic of the nature of the initial structural change, *i.e.* they ought to be effectively proportional to a *single* parameter that is characteristic of the nature of the initial structural change. The changes in the *potential energy* of the interaction between the source region and a detector region that lies within a DOF-free region ought to be proportional to the same single structural parameter under certain commonly met conditions.* It follows that, under these conditions, *single-term linear correlations ought to exist even between different types of molecular property, when the detector sites are within a common DOF-free region.* The *absolute* value of any particular molecular property ought to depend on the spatial relationship between the detector group and the adjacent core unit group, but for a given spatial relationship, the absolute value of any particular molecular property ought to fall off with increasing number of core unit groups between the source group and the detector group, at a rate which depends only on the nature of the core unit group.

DOF-free regions are normally expected to cover the third and subsequent core unit groups (with respect to the source region) both in fully conjugated hydrocarbon cores and in fully saturated hydrocarbon cores. Thus, for example, in most *para*-substituted styrenes, the vinylene group but not the phenylene group is expected to lie within a region that is DOF-free with respect to the substituent effect.

The insertion or substitution into a DOF-free region of a group which allows overlap fields to be induced between itself and its neighbours ought to affect the magnitude of the effects of other structural perturbations on the molecular properties. The individual groups within the resulting new DOF region cannot be assocatied with a characteristic attenuation factor, and the value of the attenuation factor for the entire new DOF region ought not to be similar to (it could be either smaller or larger than) the product of the values of the attenuation factors for the individual unit groups when they were in a DOF-free region. If the insertion still leaves a small

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* The conditions are (*a*) that there is direct proportionality between the abilities of the structural changes to induce *and to respond to* disturbances elsewhere in the molecular system, and (*b*) that the source and the detector groups are attached to sites that would be electronically indistinguishable in the undisturbed core.

[11] L. Salem, *J. Amer. Chem. Soc.*, 1968, **90**, 543.

DOF-free region between the inserted group and the substituent, it ought not to affect the scale of structural parameters appropriate to the original DOF-free region. However, if the insertion converts the whole DOF-free region into a DOF region, the scale of structural parameters ought to become inappropriate, and single-term linear correlations should not be expected either between the same property of different molecular systems or between different properties of the same molecular system.

The insertion of saturated hydrocarbon groups into unsaturated hydrocarbon cores and that of unsaturated hydrocarbon groups into saturated hydrocarbon cores are important examples of cases in which DOF-free regions are expected to be converted into DOF regions.

In favourable circumstances DOF-free regions can be converted into DOF regions simply by changing a substituent group. For example, in unsubstituted phenylene the resistance to the creation of an overlap field between the two C_3 π-systems has been postulated to be sufficiently large to prevent it from happening. The introduction of a substituent group which stabilises an electron-rich environment by more than a critical amount ought to allow the overlap field to be generated, thereby distorting the electronic and geometric structures of the hydrocarbon. Consequently, *certain* electrophilic substituents in *certain* benzene derivatives might well not obey correlations that are *usually* operative for substituent effects in benzene derivatives. The effects of this type of geometric distortion are not considered in other versions of the general theory of structure–property relationships.

The theory has been made quantitative for the special case in which the structural changes are substitutions. For substituent groups, the coulombic field, the overlap field, and the net charge transfer parameters, labelled **F**, **S**, and **T** respectively, have been evaluated by applying the theoretical treatment of structural perturbations to the analysis of substituent effects on calculated π-electron populations in monosubstituted benzenes. The values of **F** and **S** for easily polarisable groups, *e.g.* the nitro-group, depend on the conformation of the substituted benzene molecule.

When the ratio **T** : **S** is taken to be unity * the theoretical equation for substituent effects on molecular properties can be written in the form of equation (3): the parameters f and s each reflect both coulombic and non-coulombic disturbances in the molecular system. The plot of $\delta P/f$ against s/f (Figure 2) generates the theoretically possible patterns of substituent effects and provides the basis for a graphical evaluation of s/f from experimental measures of δP. Equation (3) provides the theoretical connection between all δPs that are linearly related to substituent-induced changes in electronic structure.

$$\delta P = f\mathbf{F} + s\mathbf{S};\ \delta P/f = \mathbf{F} + (s/f)\mathbf{S} \qquad (3)$$

Interpretation of the Substituent Reactivity Parameters.— The various substituent parameters mentioned in the introduction have previously [9,10] been interpreted in terms of equation (3). The interpretation assumes that each parameter represents a measure of some linear combination of the theoretical substituent parameters **F** and **S**, after allowance has been made, in appropriate cases, for the effects of geometric distortion of the molecular core. The specific equations for each parameter are equations (4). The values of the correlation coefficients

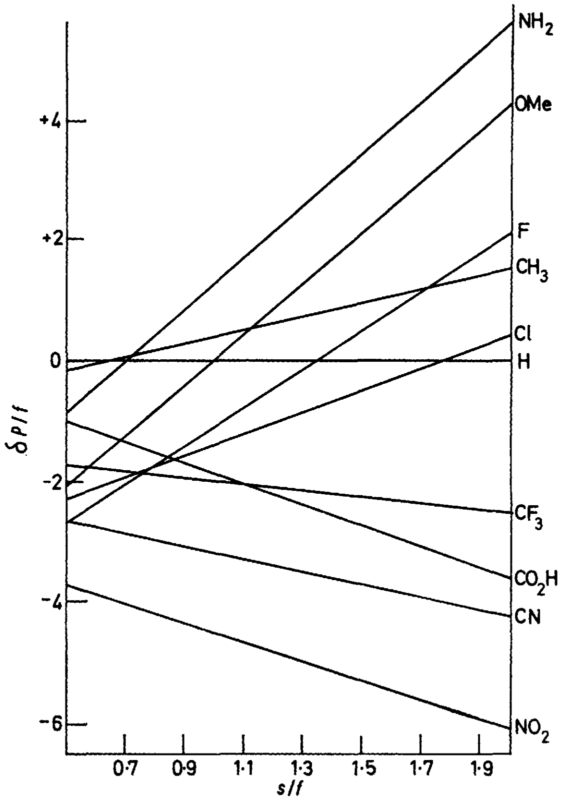

FIGURE 2 Variation with the value of s/f in the pattern of the effects of some common substituent groups

$$\sigma_I = A(\mathbf{F} + a\mathbf{S});\ \sigma_R = B(\mathbf{F} + b\mathbf{S});\ \sigma = C(\mathbf{F} + c\mathbf{S});$$
$$\mathscr{F} = A'(\mathbf{F} + a'\mathbf{S});\ \mathscr{R} = B'(\mathbf{F} + b'\mathbf{S}) \qquad (4)$$

(A,a, *etc.*) were obtained empirically, ignoring ill-fitting data on compounds in which geometric distortion of the core was considered to be a strong possibility. The results are reproduced in Table 1.

It has been suggested [9,10] that the σ^{BA} and σ^- scales are appropriate for application to reactions occuring in the DOF-free regions of benzene derivatives. The difference between these two scales was attributed to the effects of geometric distortion of the core where the former but not the latter scale applies. For substituent groups that do not cause geometric distortion of the core, any difference in the dependence of the transmission of coulombic and non-coulombic perturbations that arises from either the introduction of DOF into benzene derivatives or the replacement of the

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* This simplication is empirically justified as a good approximation for many common substituent groups.

phenylene group by other core groups ought to be accommodated by taking linear combinations of *any* non-equivalent (*i.e.* differing in the value of at least one of the parameters f and s) pair of the empirical substituent parameters. When substituent groups that do cause geometric distortions of the core are included, experimental data should correlate better with one particular pair of the substituent parameters than with the others.

TABLE 1

Substituent constant(s) [a]	Correlation coeff. Label	Correlation coeff. Value	Correlation coeff. Label	Correlation coeff. Value
σ_I	A	−0.20	a	0.70
σ_R^{BA}, σ_R^- [b]	B	−0.04	b	4.2
σ_R^+	B	−0.20	b	2.1
σ_R^0	B	−0.06	b	2.7
σ_m^{BA}, σ_m^-, σ_m^0	C	−0.22	c	0.85
σ_p^{BA}, σ_p^- [b]	C	−0.24	c	1.30
σ_p^+	C	−0.40	c	1.40
σ_p^0	C	−0.26	c	1.15
$\sigma^*(YCH_2) - \sigma^*(HCH_2)$	C	−0.50	c	0.70
$\mathscr{F}$	A′	−0.33 [c] −0.20 [d]	a′	0.70
$\mathscr{R}$	B′	−0.04	b′	4.0

[a] No common substituent groups deviate from the σ_R^-, σ_m, σ_m^-, σ_m^0, or σ_p^- scales. The values for the Taft and the Hammett constants are based on experimental data cited by S. Ehrenson, R. T. C. Brownlee, and R. W. Taft (*Progr. Phys. Org. Chem.*, 1973, **10**, 1). [b] Based on experimental data for the dissociation of *anilinium ions* in water. [c] Based on values given by C. G. Swain and E. C. Lupton (*J. Amer. Chem. Soc.*, 1968, **90**, 4328). [d] Based on values given by C. Hansch, A. Leo, S. H. Unger, K. H. Kim, D. Nikaitani, and E. J. Lien (*J. Medicin. Chem.*, 1973, **16**, 1207).

Interpretations of the N.m.r. S.c.s. Data and of the Correlations with Substituent Reactivity Parameters.—In the present work ^{13}C and ^{19}F s.c.s. data for a number of compounds (see Tables 2—4) which are formally monosubstituted or *para*- or *meta*-disubstituted benzenes were tested graphically for obedience to the theoretical equation (3). The fit was invariably satisfactory, provided that the possible effects of geometric distortion by strongly electrophilic substituents were taken into account. The only clear exceptions to the rule involved cases in which the detector was closer to the substituent than the *meta*-carbon atom, that is the only cases in which in terms of the considered theoretical model, direct field interactions ought to be of comparable importance to indirect through-bond interactions. (Hence, the decision made at the design stage of the theory to disregard long-range direct field effects appears to be justified.)

For those cases in which equation (3) was obeyed, either with or without allowance for deviations due to geometric distortions, the empirical values of s/f and of f are listed in Tables 2—4. The cases are grouped so as to bring out the presence or the absence at the detector site of anticipated DOF effects of substituent groups, and also the effects of solvent polarity changes. In the cases which are expected to be essentially free from DOF effects, the values of s/f lie in the range 1.30 ± 0.15 for formally *para*-disubstituted compounds (except when the monitored atom is bonded to the *para*-carbon atom of the ring), and in the range 0.85 ± 0.10 for formally *meta*-disubstituted compounds. These values are to be compared with 1.30 for σ_p^{BA} and 0.85 for σ_m^{BA}, the substituent parameters previously suggested to be appropriate for reactions occurring in a DOF-free region (see above).

TABLE 2

Results of analyses by equation (3) of s.c.s. data on three types of benzene derivative

Compd. (Posn. of detector)	f (^{13}C)	f (^{19}F)	s/f (^{13}C)	s/f (^{19}F)	Data ref. ^{13}C	Data ref. ^{19}F
(A) *para*-Disubstituted benzene type						
4-*trans*-Stilbene (4′)		0.55		1.30		7
(3′)		0.30		1.20		7
4-Biphenyl (4′)	0.48	0.77 [a]	1.35	1.30	*b*	12
(3′)	0.11		1.20		*b*	
(2′)	0.24		1.45		*b*	
(1′)	−0.74		0.90		*b*	
4-Phenylacetylene (β) [c]	1.0		1.30		6	
4-Styrene (β) [c]	1.3		1.40		5	
(α) [c]	−0.65		0.75		5	
β-Naphthalene (6)	1.4	2.2 [a]	1.40	1.40	*d*	*e*
(B) *meta*-Disubstituted benzene type						
3-Biphenyl (4′)		0.5		0.9		*f*
β-Naphthalene (7)	1.0	1.6 [a]	0.75	0.75	*d*	*e*
(C) Monosubstituted benzene type						
1-Benzene (4) [c]	1.2	1.9 [a]	2.60	2.60	*g*	*h*
(4) [i]	0.9	1.4 [a]	2.60	2.60		
α-Naphthalene (4)	1.2	1.9 [a]	2.60	2.85	*d*	*e*
1-Benzene (3) [c]	0.5	2.0 [j]	0.60	0.90	*g*	*h*
(3) [i]	0.2	0.8 [j]	−2.70	−2.70		
α-Naphthalene (3)		2.0		0.95		*e*

[a] $f(^{19}F)/f(^{13}C) = 1.6$. [b] In acetone; E. M. Schulman, K. A. Christensen, D. M. Grant, and C. Walling, *J. Org. Chem.*, 1974, **39**, 2686. [c] Calculated π-electron densities are given in the data reference. [d] In chloroform; P. R. Wells, D. P. Arnold, and D. Doddrell, *J.C.S. Perkin II*, 1974, 1745. [e] In acetone or dimethylformamide; W. Adcock and M. J. S. Dewar, *J. Amer. Chem. Soc.*, 1967, **89**, 379; W. Adcock, P. D. Betless, and S. Q. A. Rizvi, *Austral. J. Chem.*, 1970, **23**, 1921. [f] In benzene; M. J. S. Dewar and A. P. Marchand, *J. Amer. Chem. Soc.*, 1966, **88**, 3318. [g] In carbon tetrachloride; G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Amer. Chem. Soc.*, 1972, **94**, 3089. [h] In carbon tetrachloride; ref. 16. [i] Corrected for deviation from direct proportionality to π-electron-density (see text). [j] $f(^{19}F)/f(^{13}C) = 4.0$.

The introduction of DOF effects by inserting groups into a molecular system usually has a definite effect on the *s*/*f* values. The values of *s*/*f* in those cases in which the detector is in a region that *ought* not to be DOF-free, are *quite* different from the DOF-free values.

TABLE 3

Results of analyses by equation (3) of ^{19}F s.c.s. data [a] on bridged biphenyls (in CCl_4)

Bridging group	*f*/*f*(biphenyl)	*s*/*f*
CHPh	0.45	1.10
HC=N	0.55	1.25
N=CH	0.55	1.25
CH=CH	0.60	1.25
N=N	0.80	1.30
O	1.00	1.30
S	1.20	1.35

[a] Ref. 12.

TABLE 4

Results of analyses by equation (3) of solvent polarity effects on ^{19}F s.c.s.

Compound	$\Delta^{DMF}_{CCl_4}(s) = \Delta^{DMF}_{CCl_4}(f)$ [a]	Data ref.
p-Subst. benzenes	+0.4	16
4-Subst. 4′-fluorobiphenyls	−0.2	12

[a] $\Delta^{DMF}_{CCl_4}$ (*s* or *f*) represents the change in the value of *s* or *f* on changing the solvent from carbon tetrachloride to dimethyl formamide.

These results are fully in accord with our predictions concerning linear correlations between different molecular properties in the general case, except for the results when the monitored atom is bonded to the *para*-carbon atom of the ring (see below). The success of the new theoretical treatment and the failures of the traditional theoretical treatments in the particular example considered here indicate to us that the differences between the basic theories mentioned in the introduction merit consideration in the theoretical treatment of any case of a structure–property or an interproperty relationship.

Solvent-transmitted Substituent Effects.—On applying equation (3) to measures of solvent shifts on s.c.s. data[12] the values of *s*/*f* were found to be approximately *unity* for any pair of solvents of markedly different polarity. It was also discovered that geometric distortions do not necessarily cause deviations from obedience to equation (3) for solvent effects, nor do they have marked effects on the values of *f*. These results are consistent with the transmission of substituent effects mainly *via* overlap-dependent interactions involving the α atom of the molecular core and an atom of a solvent molecule.

This type of solvent-transmitted electronic effect should not modify substituent effects on *chemical behaviour*, within the limits of validity of Hepler's[13] direct relationship between free energy changes and internal enthalpy changes [equation (5)]. Since, in general,

$$\delta\Delta G \propto \delta\Delta H_{\text{Internal}} \qquad (5)$$

solvent-transmitted effects on s.c.s. data do not have the same *s*/*f* values as bond-transmitted effects, and also do not reflect geometric distortions, equations (1) and (2) for n.m.r.–reactivity correlations ought to be less well fitted in polar solvents than in non-polar solvents. Examples of this predicted result have been reported.[14] If Hepler's treatment of substituent effects on chemical behaviour is valid, there ought to be a definite correlation between this type of solvent-transmitted effect on s.c.s. and the net *entropy* changes in a chemical reaction. We have indeed found such a correlation in the case of entropy changes for benzoic acids in water.[15]

Our treatment of solvent-transmitted substituent effects provides a ready explanation of the fact that the effect on the ^{19}F resonance of twisting the nitro-group in 1-fluoro-4-nitrobenzene through 90° is virtually independent of solvent polarity.[16] The observation implies that the *sum* of the theoretical substituent parameters **F** and **S** for the nitro-group must be the same in the two conformations. This is precisely the result obtained in our treatment of substituent effects on calculated π-electron population distributions in the planar and orthogonal conformations of nitrobenzene.[9,10]

Other interpretations of solvent-transmitted substituent effects have been proposed. Brownlee *et al.*[16] have concluded that π-electron delocalisation between the substituent and the benzene ring *must be* unimportant and that consequently σ-bond polarisation *must be* the predominant factor. Since our treatment is capable of interpreting the same experimental data that Brownlee *et al.* considered, we obviously cannot agree with their conclusion. Nevertheless we do agree with them that the experimental data rule out solvent-induced π-polarisation as the *major* contributor to the total solvent effect in the general case.

Application of S.c.s. Data to obtain Structural Information.—We have seen that the new interpretation of the n.m.r. s.c.s. data presented here permits the use of such data to reveal certain structural information about molecular systems in a form that should be immediately useful for predicting chemical behaviour and other kinds of physical behaviour. This information was obtained without knowledge of the *details* of the relationships between changes in molecular properties and changes in the electronic structures of molecular systems. Of course, even more structural information could be obtained if some knowledge of these details *were* available from either theoretical or empirical studies. The new theoretical description of electronic structural perturbations provides a new conceptual framework within which to search empirically for additional relationships between n.m.r. s.c.s. data and changes in electronic structure. We have already seen this to advantage in the indication of the possible role of overlap-dependent interactions between solute and solvent in interpreting observed solvent polarity effects. We now briefly

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[12] S. K. Dayal and R. W. Taft, *J. Amer. Chem. Soc.*, 1973, **95**, 5595.

[13] L. G. Hepler, *J. Amer. Chem. Soc.*, 1963, **85**, 3089.

[14] W. Adcock, J. Alste, S. Q. A. Rizvi, and M. Aurangzeb, *J. Amer. Chem. Soc.*, 1976, **98**, 1701.

[15] Experimental data taken from T. Matsui, H. C. Ko, and L. G. Hepler, *Canad. J. Chem.*, 1974, **52**, 2906.

[16] R. T. C. Brownlee, S. K. Dayal, J. L. Lyle, and R. W. Taft, *J. Amer. Chem. Soc.*, 1972, **94**, 7208.

report two other hypothetical relationships which have a sufficient measure of empirical support to be worthy of further investigation.

Maciel[17] has stated that it seems likely that simple relationships between ^{13}C shieldings and local electronic distributions obtain within the restricted scopes of special structural situations. We now hypothesise that in unsaturated molecular systems ^{13}C s.c.s. data are effectively good direct measures of changes in π-electron populations at the monitored atoms *except* when those atoms lie inside, or immediately adjacent to, a region that is subject to direct overlap field effects of the substituent. The constant of proportionality obtained by applying this hypothesis to the data in Tables 2—4 is *ca.* 160 p.p.m. per electron, which is the value obtained by Spiesecke and Schneider[18] through comparing chemical shifts in cyclopentadienide ion, benzene, tropylium ion, and cyclooctatetraene dianion. The observed deviations from the direct quantitative relationship, at the *para*-carbon atom in each compound, and at *each* carbon atom that is bonded to the *para*-carbon atom are, at least to a good approximation, *identical* with one another at about one-third of the shift predicted for the *para*-carbon atom itself. This deviation accounts for the one exception to the general rule concerning s.c.s. data in DOF-free regions, that was mentioned above.

We have found that although the empirical f values for ^{19}F s.c.s. data are generally proportional to the empirical f values for ^{13}C s.c.s. data at the carbon atom to which the fluorine atom is bonded, the constant of proportionality differs considerably according to whether that carbon atom is the first or the second member of its core unit group relative to the source site (see Table 2). The difference should correspond to an increase of *ca.* 0.4 in the value of s/f for ^{19}F shifts as compared with corresponding ^{13}C shifts monitored at the *meta*-carbon atom relative to the substituent: an increase of *ca.* 0.3 was found empirically. We have also found that ^{14}N and ^{15}N s.c.s. data in substituted nitrobenzenes[19] show no significant dependence on bond-transmitted substituent effects. (The observed substituent effects fit the pattern predicted for solvent-transmitted effects.) These findings on fluorine and nitrogen s.c.s. data suggested to us the hypothesis that the magnitudes of fluorine and nitrogen chemical shifts depend predominantly on changes in the overlap field between the detector group and the neighbouring core and solvent groups. If this hypothesis is correct, reagent-induced changes in the overlap field between a functional group and the neighbouring core and solvent groups ought to be readily detectable by n.m.r. s.c.s. There is *qualitative* evidence for the validity of this conclusion. The values of s/f obtained by applying equation (3) to observed substituent effects on the pK_a of phenol in water[20] indicate that the changes on dissociation in the overlap-dependent interactions between the core and the functional group, which in this case is electronically very similar to a fluorine atom, are very different in *meta*- and *para*-isomers. Furthermore, the s/f values for substituent effects on the pK_a of benzoic acid in water[15] indicate that the changes on dissociation in the overlap-dependent interaction between the core group and the functional group, which in this case is electronically very similar to a nitro-group, are negligibly small.

[5/939 *Received*, 19*th May*, 1975]

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