

that these frequencies will change only slightly in going to $(\text{CH}_3\text{BeCH}_3)_n$. In the 200–1000- cm^{-1} Raman region in Figure 2, it can be seen that only a band near 930 cm^{-1} fits these expectations, and accordingly it is assigned as the B_g mode. This high value, compared to $(\text{CH}_3)_6\text{Al}_2$, is not unreasonable in view of the much lighter mass for the Be atom. Moreover, an infrared counterpart for the B_u mode occurs in the same frequency region. It should be noted however that these B_g and B_u assignments yield a slight upward shift in frequency on deuteration ($B_g = 937 \rightarrow 945$, $B_u = 924 \rightarrow 942 \text{ cm}^{-1}$). This behavior suggests that these frequencies may involve repulsive mixing with the BH_{2t} twisting and deformation modes which drop below 900 cm^{-1} on BH_4 deuteration. A similar effect has been observed for the asymmetric BeC stretch in monomeric CH_3BeCH_3 in going to CD_3BeCD_3 (1081 \rightarrow 1150 cm^{-1}).¹⁶

The Be...Be stretch would be of A_g symmetry and hence should have high Raman intensity but no nearby infrared counterpart. The $(\text{CH}_3\text{BeBH}_4)_2$ feature at 357 cm^{-1} satisfies this requirement and also gives an H/D ratio of 1.08, the same as that calculated for a $(\text{BH}_4\text{Be}) \cdots (\text{BeBH}_4)$ point mass model. For dimethylberyllium this frequency is significantly higher (455 cm^{-1}) whereas the BeC stretches are actually lower. This implies that the electron density has shifted somewhat from the bridge bonds into the middle of the Be...Be region in $(\text{CH}_3\text{BeCH}_3)_n$. The lowest frequency skeletal mode should be the out-of-plane BeC_2Be bend and the far infrared band at 120 cm^{-1} seems a logical choice since no other feature was observed down to 33 cm^{-1} . The assignments of the remaining skeletal modes are uncertain but are not unreasonable.

Summary

From vapor density measurements, methylberyllium borohydride has been shown to be largely dimeric in the vapor phase even at low pressures. The infrared spectra of the

vapor and solid phases are quite similar, indicating that there is no significant structural change on condensation. The infrared and Raman spectra of the solid contain all of the major features of the spectra of $(\text{CH}_3\text{BeCH}_3)_n$, a polymer known to involve methyl bridges. The BH stretching and bending frequencies further establish the presence of double hydrogen bridges between the Be and B atoms, and thus a C_{2h} model with double hydrogen and methyl bridges is favored. The spectra are satisfactorily assigned in terms of this model and the BeH_2BH_2 and CH_3 group vibrations are compared with similar molecules.

Acknowledgment. The authors wish to thank Dr. Thomas Cook for providing the samples used in this work. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

References and Notes

- (1) A. Almenningen, G. Gundersen, and A. Haaland, *Acta Chem. Scand.*, **22**, 328 (1968).
- (2) D. A. Coe, J. W. Nibler, T. H. Cook, D. Drew, and G. L. Morgan, *J. Chem. Phys.*, in press.
- (3) G. Gundersen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, **59**, 3777 (1973).
- (4) J. W. Nibler, *J. Am. Chem. Soc.*, **94**, 3349 (1972).
- (5) V. Plato and K. Hedberg, *Inorg. Chem.*, **10**, 590 (1971).
- (6) D. S. Marynick and W. N. Lipscomb, *J. Am. Chem. Soc.*, **93**, 2322 (1971).
- (7) J. W. Nibler, D. F. Shriver, and T. H. Cook, *J. Chem. Phys.*, **54**, 5257 (1971).
- (8) J. W. Nibler and T. H. Cook, *J. Chem. Phys.*, **58**, 1596 (1973).
- (9) E. R. Bernstein, W. C. Hamilton, T. A. Keiderling, S. J. LaPlaca, S. J. Lippard, and J. J. Mayerlie, *Inorg. Chem.*, **11**, 3009 (1972).
- (10) T. H. Cook and G. L. Morgan, *J. Am. Chem. Soc.*, **92**, 6487 (1970).
- (11) A. Shaw and R. Rundle, *Acta Crystallogr.*, **4**, 348 (1951).
- (12) A. Almenningen, S. Halvorsen, and A. Haaland, *Acta Chem. Scand.*, **25**, 1937 (1971).
- (13) T. Ogawa, *Spectrochim. Acta*, **24**, 15 (1968).
- (14) G. Goubeau and K. Walter, *Z. Anorg. Allg. Chem.*, **322**, 58 (1963).
- (15) T. Shimanouchi, *J. Phys. Chem. Ref. Data*, **3**, 269 (1974).
- (16) R. A. Kovar and G. L. Morgan, *Inorg. Chem.*, **8**, 1099 (1969).

A Semiempirical Theory of Substituent-Induced ^{13}C Chemical Shifts in π Systems¹

D. J. Sardella

Contribution from the Department of Chemistry, Boston College, Chestnut Hill, Massachusetts 02167. Received March 19, 1975

Abstract: A general semiempirical theory of ^{13}C chemical shifts induced by substituents in hydrocarbon π systems is outlined. Beginning with the assumption that the shifts reflect substituent-induced electron density redistributions, it is shown that substituent chemical shifts in any π system can be calculated using a two-parameter equation, analogous to a linear free-energy equation, involving an atom-atom polarizability, obtained from Hückel molecular orbital calculations, and an empirically determined substituent parameter. Predictions of the theory are tested against available experimental data for four representative substituents: methyl, methoxyl, chloro, and cyano.

The earliest systematic studies of ^{13}C chemical shifts revealed cumulative effects of substituents to be remarkably additive.² Empirical additivity schemes abound in the literature and are frequently employed for shift assignments. Their major shortcomings are that each substituent requires one parameter for each unique carbon in the monosubstituted molecule, and that parameters are not transferable between different molecular systems. Thus, the wealth of tabulated data for benzene derivatives might be expected to

be applicable to systems such as styrenes, less useful for naphthalenes, and virtually useless for acyclic π systems or nonbenzenoid ring systems, such as azulenes. As Table I illustrates, even for closely related molecular systems, substituent-induced chemical shifts (SCS) can vary widely. The observed variability in the empirical parameters for any single type of carbon position (for instance, three bonds removed from the site of attachment of the substituent) suggests that SCS are governed by both the nature of the

Table I. Methyl-Induced Substituent Chemical Shifts in Various π Systems^a

Molecule	Carbon position ^b			
	1	2	3	4
<i>trans</i> -1,3-Pentadiene ^c	-16.1	+8.3	-0.2	+2.8
Toluene ^d	-9.2	-0.7	+0.1	+4.7
2-Methylstyrene ^e	-7.6	+2.7, -0.7	0.0, -0.7	+1.7
3-Methylstyrene ^e	-9.5	-0.3, -2.2	-0.1, -0.5	+4.2
4-Methylstyrene ^e	-11.5	-1.0	-1.0	-0.4
4-Methylbiphenyl ^f	-9.6	-0.1	+0.2	+2.9
1-Methylnaphthalene ^g	-6.3	-0.8, +0.8	-0.1, +0.3	-1.5
2-Methylnaphthalene ^g	-8.8	-1.0, -2.3	-0.2, -0.5	+1.7

^a SCS are defined as the shift of a carbon in the substituted system minus the shift of the same carbon in the parent π system. ^b 1 = directly attached to methyl; 2 = one carbon removed; 3 = two carbons removed; 4 = three carbons removed. ^c O. Kajimoto and T. Fueno, *Tetrahedron Lett.*, 3329 (1972). ^d W. B. Smith and D. L. Deavenport, *J. Magn. Reson.*, 7, 364 (1972). ^e K. S. Dhami and J. B. Stothers, *Can. J. Chem.*, 43, 510 (1965). ^f E. M. Schulman, K. A. Christensen, D. M. Grant, and C. Walling, *J. Org. Chem.*, 39, 2686 (1974). ^g N. K. Wilson and J. B. Stothers, *J. Magn. Reson.*, 15, 31 (1974).

substituent group and the electronic structure of the π system being perturbed by that group. Any general approach to the understanding and prediction of SCS must take explicit account of both factors.

This paper describes a simple, semiempirical theory of substituent-induced ¹³C chemical shifts in π systems. Beginning with the assumption that the observed SCS reflect substituent-induced electron redistribution, and employing first-order perturbation theory applied to simple Hückel molecular orbitals to evaluate the changes in electron density, I have been able to establish that the ¹³C SCS for any position in a π system is given by the product of a single, substituent-specific parameter and an atom-atom polarizability.

The Model

The basic assumption of the model is that attachment of a substituent to a molecular π system polarizes it, producing a redistribution of electron density which is reflected in the induced chemical shifts.

The effect of substitution on the electron distribution within a π system can be described in terms of perturbational molecular orbital theory.³ Assuming the substituent not to interact conjugatively with the π system, its primary effect will be to alter the effective electronegativity of the carbon to which it is bonded. In simple Hückel molecular orbital theory, this electronegativity change can be accommodated by variation of the Coulomb integral of the relevant carbon.

If an attached substituent produces a change, $\Delta\alpha_i$, in the Coulomb integral of C_i , the first-order correction to the electron density at any other carbon, C_j , in the π system is given by

$$\Delta q_j = 4\Delta\alpha_i\pi_{ij} \quad (1)$$

with π_{ij} , the atom-atom polarizability, being defined by

$$\sum_{\mu}^{\text{occ}} \sum_{\nu}^{\text{unocc}} \frac{a_{i\mu}a_{i\nu}a_{j\mu}a_{j\nu}}{E_{\mu} - E_{\nu}} \quad (2)$$

where the a 's are coefficients of atomic orbitals in occupied (μ) and unoccupied (ν) molecular orbitals of energies E_{μ} and E_{ν} , respectively.³ Since it is generally agreed that ¹³C chemical shifts are proportional to total electron densities at carbon, except when bond polarization effects and the presence of low-lying energy states are important,⁴ the expression for a substituent-induced chemical shift becomes

$$\Delta\delta_{c_j} = \kappa\Delta\alpha_i\pi_{ij} \quad (3)$$

leading to the predictions that: (1) for a given position in a π system (π_{ij} fixed), SCS will exhibit a linear correlation with substituent parameters which measure their π -polarizing effects; (2) for a given substituent ($\Delta\alpha_i$ fixed), a plot of $\Delta\delta_j$ for all carbons vs. π_{ij} will be linear; (3) since the atom-atom polarizabilities sum to zero in any molecule, the SCS should also sum to zero. Moreover, if substituents can be assumed to exert independent perturbations of the π system, then in the case of multiple substitution, the net SCS will be

$$\Delta\delta_{c_j}(\text{net}) = \kappa \sum_i \Delta\alpha_i\pi_{ij} = \sum_i \Delta\delta_{c_j}(i) \quad (4)$$

leading to the further expectations that (4) SCS will be additive and (5) electron densities will also exhibit additivity relations.

It remains now to demonstrate the validity of these predictions for a variety of substituents, to examine the range of applicability of this approach, and to determine its limitations.

Tests of the Model's Predictions

The validity of this admittedly oversimplified model can be ascertained by testing each of its five predictions against data taken from the literature.

Additivity of ¹³C SCS. Of the five predictions, that concerned with the additivity of ¹³C SCS is firmly supported by an impressive array of data for a wide range of molecular π systems⁵ among which are substituted benzenes, anilines, styrenes, anisoles, benzaldehydes, acetophenones, furans, pyrroles, nitrobenzenes, and naphthalenes. In general, ¹³C chemical shifts of polysubstituted systems can be predicted, using empirical additivity relations, to within 2 ppm and often much better. Significant deviations from additivity occur primarily in cases of steric crowding, where carbons bound to ortho substituents exhibit anomalous high-field shifts of about 3–4 ppm. A limited amount of data for methyl-substituted naphthalenes indicates *peri* substituents to deviate still further from additivity,⁵ⁿ as expected.⁶

Correlation of SCS with Substituent Parameters. According to eq 3, for any single π system where the relation between substituted and observed carbon is fixed (e.g., carbon para to a substituent), there will exist a linear correlation between the SCS and some parameter which measures the ability of a substituent to interact with the π system. Indeed, a variety of studies, dating back to the earliest systematic investigations of SCS, revealed good correlations of SCS with Hammett's σ and other substituent parameters.⁷ Significantly, Schulman et al. have recently performed a multiple regression analysis of SCS in 4-substituted biphenyls using the Dewar-Grisdale substituent parameters^{7e} and found mesomeric effects to be dominant, a conclusion consistent with our initial assumption that π -system polarization, rather than conjugation, is primarily responsible for the induced shifts.

Correlation of SCS with Atom-Atom Polarizabilities. Perhaps the most stringent test of this model is verification of the assertion that, for a given substituent at position i in any molecular π system, the SCS of carbon atom j will be directly proportional to the atom-atom polarizability, π_{ij} , for this requires that one single parameter per substituent suffice to describe the induced shifts of all carbons in the π systems, and that this same parameter ($\kappa\Delta\alpha$ in eq 3) be transferrable between different π systems. Experimental verification of this prediction would permit a simultaneous simplification and generalization of existent approaches to the calculation of substituent-induced ¹³C chemical shifts.

Table II. ^{13}C SCS in Methyl-Substituted π Systems^a

Molecule	Carbon no.	π_{ij}	$\Delta\delta_c$	
			Obsd	Calcd
<i>trans</i> -1,3-Pentadiene ^b	1	-0.626	-16.1	-14.8
	2	+0.402	+8.3	+7.9
	3	-0.009	-0.2	-1.2
	4	+0.268	+2.8	+4.9
2-Methylstyrene ^c	1	+0.130	+2.7	+1.9
	2	-0.430	-7.6	-10.5
	3	+0.165	-0.7	+2.7
	4	-0.016	-0.0	-1.3
	5	+0.096	+1.7	+1.1
	6	-0.004	-0.7	-1.1
1-Methylnaphthalene ^d	α	-0.016	+0.3	-1.3
	β	+0.075	-1.4	+0.7
	1	-0.495	-6.3	-11.9
	2	+0.213	-0.8	+3.7
	3	-0.018	+0.3	-1.4
	4	+0.139	+1.6	+2.1
	5	+0.023	-0.6	-0.5
	6	-0.006	+0.3	-1.1
	7	+0.032	+0.2	-0.3
	8	+0.027	+3.80-	
	9	+0.089	+0.8	+1.0
	10	-0.004	-0.2	-1.1

^a In the interests of brevity, this table contains only a representative sampling of data. The full table will appear in the microfilm addition. ^b O. Kajimoto and T. Fueno, *Tetrahedron Lett.*, 3329 (1972). ^c Reference 5f. ^d Reference 5n.

Table III. ^{13}C SCS in Alkoxy-Substituted Systems^a

Molecule	Carbon no.	π_{ij}	$\Delta\delta_c$	
			Obsd	Calcd
<i>trans</i> -1-Ethoxy-1,3-butadiene ^b	1	-0.626	-36.2	-39.3
	2	+0.402	+24.1	+23.7
	3	-0.009	+1.3	-1.5
	4	+0.268	+7.6	+15.5
Anisole ^c	1	-0.398	-32.4	-25.3
	2	+0.157	+14.4	+8.7
	3	-0.009	-1.0	-1.5
	4	+0.102	+7.9	+5.3
1-Methoxynaphthalene ^d	1	-0.495	-28.4	-31.3
	2	+0.213	+21.5	+12.1
	3	-0.018	-0.9	-2.0
	4	+0.139	+7.0	+7.6
	5	+0.023	-0.3	+0.5
	6	-0.006	-1.3	-1.3
	7	+0.032	+0.1	+1.0
	8	+0.027	+5.0	+0.7
	9	+0.089	+6.8	+4.5
	10	-0.004	-2.3	-1.2

^a In the interests of brevity, this table contains only a representative sampling of data. The full table will appear in the microfilm addition. ^b O. Kajimoto and T. Fueno, *Tetrahedron Lett.*, 3329 (1972). ^c W. B. Smith and D. L. Deavenport, *J. Magn. Reson.*, 7, 364 (1972). ^d Reference 5n.

The validity of the prediction has been established for four representative substituents: methyl, methoxyl, chloro, and cyano. In each case, data for simple systems (typically a substituted benzene and either a butadiene or a 4-substituted styrene) were used to demonstrate the linear relation between SCS ($\Delta\delta_c$) and polarizability (π_{ij})⁸ and the resulting least-squares-fitted equation employed to predict SCS for the compounds in the tables.

The most extensive data are available for methyl-substituted systems. Substituent-induced shifts in *trans*-1,3-pen-

tadiene and toluene correlate well with atom-atom polarizabilities and obey the relation

$$\Delta\delta_c = 22.08\pi_{ij} - 0.98 \quad (5)$$

with a correlation coefficient of 0.963. Substituent-induced shifts calculated using this equation were compared with experimental data for *trans*-1,3-pentadiene, toluene, 2-, 3-, 4-, and α -methylstyrenes, 4-methylbiphenyl, and 1- and 2-methylnaphthalenes, a total of 66 unique SCS covering a range of 24 ppm, and representative data are given in Table II. The average deviation for all 66 SCS is 1.8 ppm. Significant deviations (i.e., greater than twice the average deviation) between calculated and experimental shifts are confined primarily to carbon atoms in sterically congested sites (C-1, C- α , and C- β of α -methylstyrene) or involved in peri interactions (such as C-1, C-2, and C-8 of 1-methylnaphthalene). These are precisely the places where empirical additivity relations break down. Since this model employs a one-parameter fit, the good agreement is gratifying.

We have shown previously¹ for alkoxy substitution that the relationship between $\Delta\delta_c$ and π_{ij} is linear. Data for *trans*-1-ethoxy-1,3-butadiene and anisole are described by the relation

$$\Delta\delta_c = 61.35\pi_{ij} - 0.92 \quad (6)$$

(correlation coefficient = 0.973). As with methyl substitution, we have calculated SCS for a variety of molecules: *trans*-1-ethoxy-1,3-butadiene, anisole, 4-methoxystyrene, 4-methoxybiphenyl, and 1- and 2-methoxynaphthalene (42 unique SCS), and some data are summarized in Table III. Here, the SCS cover a range of 60 ppm and the average deviation is 2.7 ppm, or less than 5% of the range. Large deviations occur in the methoxynaphthalenes, where protonated carbons ortho to methoxyl are 9 ppm more shielded than expected. Smaller deviations (ca. 5-6 ppm) occur in corresponding positions in other π systems as well. Substituted carbons in anisole, 4-methoxystyrene, and 4-methoxybiphenyl show deviations to lower field of similar magnitude, which may be attributable to σ -inductive effects. The largest deviation, 12.6 ppm, is observed for C-4 in 4-methoxybiphenyl, and is difficult to explain, even granting the operation of σ -inductive deshielding. However, its SCS is itself anomalous (-13.5 ppm, compared to -33 ± 2 ppm for the other five molecular systems), suggesting the reported ^{13}C shift to be erroneous.

Chlorine, typifying a deactivating, ortho,para-directing substituent, may both polarize and conjugate with π systems to which it is bound. A plot of $\Delta\delta_c$ vs. π_{ij} for chlorobenzene and 4-chlorostyrene gives a straight line described by the equation

$$\Delta\delta_c = 13.74\pi_{ij} - 1.45 \quad (7)$$

with a correlation coefficient of 0.917. In Table IV, some SCS for chlorobenzene, 4-chlorostyrene, 3-chlorostyrene, and 4-chlorobiphenyl, calculated using this relation, are compared with experimental values. The average deviation for 26 ^{13}C SCS is 1.1 ppm, out of a total range of 12.4 ppm. Significant deviations occur for C-6 and C- α of 3-chlorostyrene and C-1' of 4-chlorobiphenyl.

The cyano group is a substituent which may affect ^{13}C chemical shifts by π -electron polarization, resonance interaction, and (or) diamagnetic anisotropy effects. We reported previously¹ that a plot of $\Delta\delta_c$ vs. π_{ij} for *trans*-1-cyano-1,3-butadiene and benzonitrile is linear and is described by the equation

$$\Delta\delta_c = -32.23\pi_{ij} + 0.08 \quad (8)$$

(correlation coefficient = 0.976). Although few data are

Table IV. ^{13}C SCS in Chlorine-Substituted π Systems^a

Molecule	Carbon no.	π_{ij}	$\Delta\delta_c$	
			Obsd	Calcd
Chlorobenzene ^b	1	-0.398	-6.6	-6.9
	2	+0.157	-0.4	+0.7
	3	-0.009	-1.3	-1.6
	4	+0.102	+2.1	0.0
4-Chlorostyrene ^c	1	+0.087	-0.2	-0.3
	2	-0.016	-1.1	-1.7
	3	+0.152	-1.1	+0.6
	4	-0.415	-8.2	-7.2
	α	-0.009	0.0	-1.6
	β	+0.065	-1.6	-0.6
3-Chlorostyrene ^c	1	-0.007	-1.4	-1.5
	2	+0.165	+1.1	+0.8
	3	-0.396	-6.7	-6.9
	4	+0.152	-0.6	+0.6
	5	-0.010	-1.3	-1.6
	6	+0.096	+3.3	-0.1
	α	+0.001	+2.1	-1.4
	β	-0.002	-1.8	-1.5

^a In the interests of brevity, this table contains only a representative sampling of data. The full table will appear in the microfilm addition.
^b W. B. Smith and D. L. Deavenport, *J. Magn. Reson.*, **7**, 364 (1972).
^c Reference 5f.

Table V. ^{13}C SCS in Cyano-Substituted Systems

Molecule	Carbon no.	π_{ij}	$\Delta\delta_c$	
			Obsd	Calcd
<i>trans</i> -1-Cyano-1,3-butadiene ^a	1	-0.626	+17.8	+20.3
	2	+0.402	-12.5	-12.9
	3	-0.009	+4.2	+0.4
	4	+0.233	-10.6	-7.4
Benzonitrile ^b	1	-0.398	+15.4	+12.9
	2	+0.157	-3.9	-5.0
	3	-0.009	-0.8	+0.4
	4	+0.102	-4.2	-3.2
4-Cyanobiphenyl ^c	1	+0.090	-5.2	-2.8
	2	-0.015	-0.8	+0.6
	3	+0.153	-3.8	-4.9
	4	-0.411	+18.4	+13.3
	1'	-0.006	+2.1	+0.3
	2'	+0.018	-0.3	-0.5
	3'	0.000	-0.3	+0.1
	4'	+0.016	-1.4	-0.4

^a O. Kajimoto and T. Fueno, *Tetrahedron Lett.*, 3329 (1972). ^b W. B. Smith and D. L. Deavenport, *J. Magn. Reson.*, **7**, 364 (1972). ^c Reference 7e.

available to test the applicability of this relation to other systems, comparison of calculated and observed SCS (Table V) reveals an average deviation of 1.8 ppm over a 30-ppm range. Again, this amounts to less than 7% of the full range of SCS.

SCS in a Molecule Sum to Zero. The fourth prediction, that the sum of all SCS in a molecule will be zero, is a direct consequence of the fact that atom-atom polarizabilities sum to zero. Physically, this is reasonable, since the model postulates SCS induction to stem from substituent-induced electron redistribution. Since no net gain or loss of electrons occurs, the sum of induced shifts must be zero. The data in Tables II-V were used to test this prediction. Clearly, as shown in Table VI, this is approximately true for methoxyl and cyano substitution, but not for methyl and chlorine, suggesting some other factor besides electron-density redistribution to be operative in these cases.

Additivity of Electron Densities. If, as the model postulates, substituents act primarily by polarizing the π -electron

Table VI. Sums of SCS for Four Substituents

Molecule	ΣSCS
A. Methyl Substitution	
<i>trans</i> -1,3-Pentadiene	-5.2
Toluene	-5.1
2-Methylstyrene	-5.7
3-Methylstyrene	-7.6
4-Methylstyrene	-17.5
4-Methylbiphenyl	-5.1
1-Methylnaphthalene	-0.9
2-Methylnaphthalene	-7.5
α -Methylstyrene	-9.6
B. Methoxyl Substitution	
<i>trans</i> -1-Ethoxyl-1,3-butadiene	-3.2
Anisole	+2.3
4-Methoxystyrene	+1.5
4-Methoxybiphenyl	-22.7
1-Methoxynaphthalene	-2.8
2-Methoxynaphthalene	-4.0
C. Chlorine Substitution	
Chlorobenzene	-6.2
4-Chlorostyrene	-14.4
3-Chlorostyrene	-5.3
4-Chlorobiphenyl	-6.5
D. Cyano Substitution	
<i>trans</i> -1-Cyano-1,3-butadiene	-1.1
Benzonitrile	+1.8
4-Cyanobiphenyl	+3.5

cloud, and if in addition their effects are small, independent, perturbations, it follows that

$$\Delta q_j^{\text{total}} = \sum_i 4\Delta\alpha_i\pi_{ij} = \sum_i \Delta q_j(i) \quad (9)$$

i.e., electron densities should also obey additivity relations. Jones and Partington,^{5m} in a study of substituted nitrobenzenes, found the ^{13}C shifts to correlate with total electron densities derived from CNDO calculations. Furthermore, they were able to derive from the calculations a set of electron density substituent parameters which permitted calculation of electron densities in polysubstituted nitrobenzenes in excellent agreement with those obtained directly from CNDO calculations.

Discussion

The most significant result of this study is the demonstration that chemical shifts induced by any substituent in any π system can be calculated using a simple two-parameter equation of the type

$$\Delta\delta_{c_j} = K_i\pi_{ij} \quad (10)$$

involving a single, substituent-specific parameter, K_i (analogous to Hammett, or other, substituent parameters), and a position-specific parameter, π_{ij} (analogous to reaction constants in linear free-energy equations), with a reliability approaching that of the much less flexible empirical additivity schemes. Not unexpectedly, the method does not apply in cases where steric crowding or sterically induced nonplanarity are important. The generally good agreement between calculated and observed SCS implies the underlying assumptions to be reasonable, although the failure of SCS in any given molecule to sum to zero (as in the cases of methyl and chloro substituents) indicates other factors to contribute to the shift induction mechanism. The lack of any significant deviations in the cyano-substituted series seems to suggest that magnetic anisotropy effects are unimportant, although no firm conclusions can be drawn from the limited data at hand.

Table VII. Comparison of K Values with Substituent Parameters Derived from Linear Free-Energy Relations

Substituent	K	σ_p	\mathcal{F}	\mathcal{R}	F'	M'
C≡N	-32.2	+0.660	0.847	0.184	+1.00	+1.60
Cl	+13.7	+0.227	0.690	-0.161	+0.63	-0.91
CH ₃	+22.1	-0.268	0.413	-0.500	-0.14	-1.00
CH ₃ O	+61.4	-0.170	-0.052	-0.141	+0.13	-3.36

Since the parameters K_i describe the ability of a substituent to perturb the electronic structure of a π system, it is of interest to attempt to relate them to more classical substituent parameters derived from chemical equilibrium studies. Table VII lists the K values for the four substituents studied here, along with Hammett σ constants,⁹ Dewar and Grisdale's F' and M' parameters,¹⁰ and Swain and Lupton's \mathcal{F} and \mathcal{R} values.¹¹ No obvious relation obtains between K and σ , or F' . However, K correlates extremely well with M' , the parameter which describes the combined π inductive and mesomeric effects of the substituents. A least-squares fit gave the relation

$$K = -18.9M' - 1.1 \quad (11)$$

(correlation coefficient = 0.997) and Table VIII contains a comparison of calculated and observed K values. The good agreement suggests that inclusion of other effects, such as field effects, will not significantly improve results, and this in turn appears to provide empirical support for the assumption that polarization of the π cloud is the dominant shift-inducing mechanism. Indeed, a recent study of SCS in 4-substituted biphenyls^{7c} led to the conclusion that the SCS could be correlated well by the equation

$$\Delta\delta_c = 0.48AF' - 19.85BM' + 1.05CM_F \quad (12)$$

where A , B , and C are geometric factors, in agreement with one of the conclusions of this study.

Conclusion

The success of this simple model in reproducing the observed SCS in a variety of π systems perturbed by methyl, methoxyl, chloro, and cyano substituents demonstrates, in principle, that, in general, SCS can be calculated by a two-parameter equation of the form

$$\Delta\delta_c = K\pi_{ij}$$

analogous to a linear free-energy relation, in which polarizabilities are theoretically calculated and the K 's are determined empirically. Moreover, if, as preliminary results indicate, the K 's are expressible as linear combinations of sub-

Table VIII. Comparison of Observed and Calculated K Values

Substituent	M'	K	
		Obsd	Calcd ^a
C≡N	+1.60	-32.2	-31.4
Cl	-0.91	+13.7	+16.1
CH ₃	-1.00	+22.1	+17.8
CH ₃ O	-3.36	+61.4	+62.4

^a Calculated using eq 11.

stituent parameters, such as Dewar's field (F or F') and mesomeric (M or M') parameters, it may be that this approach may be generalized still further to permit calculation of SCS in any π system for any substituent for which F' and M' values are available, without any prior NMR data whatsoever.

Supplementary Material Available: ¹³C substituent chemical shifts in methyl-, alkoxy-, and chlorine-substituted π systems (6 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) A preliminary account has been published: D. J. Sardella, *J. Am. Chem. Soc.*, **95**, 3809 (1973).
- (2) For a review, cf. J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, Chapters 3, 5, and 7.
- (3) M. J. S. Dewar, "Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969, Chapter 6 and references therein.
- (4) (a) J. E. Bloor and E. L. Breen, *J. Phys. Chem.*, **72**, 716 (1968); (b) T. Tokuhiro and G. Fraenkel, *J. Am. Chem. Soc.*, **91**, 5005 (1969).
- (5) (a) P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1846 (1961); (b) *J. Chem. Phys.*, **38**, 1406, 1415, 1432 (1963); (c) G. B. Savitsky, *J. Phys. Chem.*, **67**, 2723 (1963); (d) C. P. Nash and G. E. Maciel, *ibid.*, **68**, 832 (1964); (e) G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.*, **42**, 2427 (1965); (f) K. S. Dhama and J. B. Stothers, *Can. J. Chem.*, **43**, 479, 498, 510 (1965); (g) K. S. Dhama and J. B. Stothers, *ibid.*, **44**, 2855 (1966); (h) *ibid.*, **45**, 233 (1967); (i) G. E. Maciel and R. V. James, *J. Am. Chem. Soc.*, **86**, 3892 (1964); (j) T. F. Page, *Mol. Phys.*, **13**, 523 (1967); (k) F. W. Wehrli, J. W. de Haan, A. I. M. Keulemans, O. Exner, and W. Simm, *Helv. Chim. Acta*, **52**, 103 (1969); (l) T. F. Page, T. Alger, and D. M. Grant, *J. Am. Chem. Soc.*, **87**, 5333 (1965); (m) R. G. Jones and P. Partington, *J. Chem. Soc., Faraday Trans 2*, **68**, 2087 (1972); (n) N. K. Wilson and J. B. Stothers, *J. Magn. Reson.*, **15**, 31 (1974); (o) D. Doddrell and P. R. Wells, *J. Chem. Soc., Perkin Trans 2*, 1333 (1973); (p) P. R. Wells, D. P. Arnold, and D. Doddrell, *ibid.*, 1745 (1974).
- (6) D. M. Grant and B. V. Cheney, *J. Am. Chem. Soc.*, **89**, 5315 (1967).
- (7) (a) Cf. ref 2 for a summary of early work; (b) O. A. Gansow, W. M. Beckenbaugh, and R. L. Sass, *Tetrahedron*, **28**, 2691 (1972); (c) T. Okuyama and T. Fueno, *Bull. Chem. Soc. Jpn.*, **47**, 1263 (1974); (d) O. Kajimoto, M. Kobayashi, and T. Fueno, *ibid.*, **46**, 1422 (1973); (e) E. M. Schulman, K. A. Christensen, D. M. Grant, and C. Walling, *J. Org. Chem.*, **39**, 2686 (1974).
- (8) Polarizabilities are taken from: C. A. Coulson and A. Streitwieser, "Dictionary of π -Electron Calculations", W. H. Freeman, San Francisco, Calif., 1965.
- (9) L. P. Hammett, "Physical Organic Chemistry", 2nd ed, McGraw-Hill, New York, N.Y., 1969, Chapter 11.
- (10) M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3548 (1962).
- (11) C. G. Swain and E. C. Lupton, *J. Am. Chem. Soc.*, **90**, 4328 (1968).