noic acid and the 5-bromopentanoic acid, respectively, the relative rate being 38.5.

From the recently determined rate constant for 5-bromopentanoic acid[1] ($1.88\ s^{-1}$), the rate constant for 5-bromo-3,3-dimethylpentanoic acid was calculated as $72.4\ s^{-1}$.

Registry No.—**1**, 22791-80-6; **2**, 69120-94-1; **3**, 69120-95-2; **4**, 69120-96-3; **5**, 69120-97-4; 5-bromo-3,3-dimethylpentanoic acid, 69120-98-5.

References and Notes

(1) Part 11: L. Mandolini, *J. Am. Chem. Soc.*, **100**, 550 (1978).

(2) A preliminary account of this work was presented by G. Illuminati at the Euchem Conference on Stereochemistry, Bürgenstock, April 30–May 5, 1978.

(3) (a) G. Illuminati, L. Mandolini, and B. Masci, *J. Am. Chem. Soc.*, **99**, 6308 (1977); (b) C. Galli, G. Illuminati, L. Mandolini, and P. Tamborra, *ibid.*, **99**, 2591 (1977).

(4) L. Mandolini, B. Masci, and S. Roelens, *J. Org. Chem.*, **42**, 3733 (1977), and unpublished results.

(5) B. Capon and S. P. McManus, "Neighboring Group Participation", Vol. 1, Plenum Press, New York, 1976.

(6) N. L. Allinger and V. Zalkow, *J. Org. Chem.*, **25**, 701 (1960).

(7) T. C. Bruice and U. K. Pandit, *J. Am. Chem. Soc.*, **82**, 5858 (1960).

(8) (a) S. Milstein and L. A. Cohen, *Proc. Natl. Acad. Sci. U.S.A.*, **67**, 1143 (1970); (b) R. T. Borchardt and L. A. Cohen, *J. Am. Chem. Soc.*, **94**, 9175 (1972), and previous papers of the series.

(9) (a) J. Dale, *J. Chem. Soc.*, 93 (1963), and previous papers of the series; (b) G. Borgen and J. Dale, *Acta Chem. Scand.*, **26**, 159 (1972).

(10) S. L. Björnstad and G. Borgen, *Acta Chem. Scand.*, **29**, 13 (1975).

(11) G. Borgen and J. Dale, *Acta Chem. Scand.*, **26**, 952 (1972).

(12) E. S. Huyser, "Methods in Free-Radical Chemistry", Vol. 3, Marcel Dekker, New York, 1972.

(13) (a) F. L. M. Pattison, J. B. Stothers, and R. G. Woolford, *J. Am. Chem. Soc.*, **78**, 2255 (1956); (b) R. G. Woolford, *Can. J. Chem.*, **40**, 1846 (1962); (c) R. G. Woolford, W. Arbic, and A. Rosser, *Can. J. Chem.*, **42**, 1788 (1964).

(14) O. H. Wheeler and E. E. Granell de Rodriguez, *J. Org. Chem.*, **29**, 1227 (1964).

(15) H. E. O'Neal and S. W. Benson, *J. Chem. Eng. Data*, **15**, 266 (1970).

(16) (a) E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, 1962, Chapter 7; (b) J. Sicher, *Prog. Stereochem.*, **3**, 202 (1962).

(17) J. Dale, *Angew. Chem., Int. Ed. Engl.*, **5**, 1000 (1966).

(18) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, 1963, pp 119 and 120.

(19) L. P. Hammett, "Physical Organic Chemistry", 2nd ed., McGraw-Hill, New York, 1970, pp 117–119.

(20) (a) W. P. Jencks, "Catalysis in Chemistry and Enzymology", McGraw-Hill, New York, 1969; (b) M. I. Page and W. P. Jencks, *Proc. Natl. Acad. Sci. U.S.A.*, **68**, 1678 (1971).

(21) C. Danforth, A. W. Nicholson, J. C. James, and G. M. Loudon, *J. Am. Chem. Soc.*, **98**, 4275 (1976).

(22) G. Borgen, *Acta Chem. Scand.*, **27**, 1840 (1973).

(23) C. Galli and L. Mandolini, *Gazz. Chim. Ital.*, **105**, 367 (1975).

(24) C. Galli, G. Illuminati, and L. Mandolini, *J. Am. Chem. Soc.*, **95**, 8374 (1973).

(25) S. F. Birch, V. E. Gripp, D. T. McAllan, and W. S. Natham, *J. Chem. Soc.*,

(26) W. S. Greaves, R. P. Linstead, B. R. Shephard, S. L. S. Thomas, and B. C. L. Weedow, *J. Chem. Soc.*, 3326 (1950).

(27) C. Galli and L. Mandolini, *Org. Synth.*, in press.

Investigating the σ^+ Resonance Scale Using C-13 Nuclear Magnetic Resonance Shifts. Graphical Representation of the Dual Substituent Parameter Equation[1]

John Bromilow and Robert T. C. Brownlee*

Department of Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia

Received June 19, 1978

The advantages of using the dual substituent parameter (DSP) method in preference to the single parameter σ^+ scale for the analysis of C-13 substituent chemical shift data are discussed. A graphical representation of the DSP equation is presented. This makes possible a fast, qualitative DSP analysis and indicates the best substituents to use for a good linear free energy correlation.

The σ^+ set of substituent parameters is used to describe the effects of substituents in electron deficient systems where enhanced effects for π donors are observed. The σ^+ scale was originally derived by Brown and Okomoto[2] from the solvolysis of para-substituted cumyl chlorides and has since been used to study mechanisms involving electron deficient transition states and intermediates.[3] σ^+ values for strong donors, such as NMe_2 and NH_2, have not been determined accurately in many of these systems because of the extremely short reaction times involved. Accurate measurements for NMe_2 and NH_2 are critical for a good linear free energy correlation because they have large absolute σ^+ values and ensure a wide substituent range. Recently, attempts have been made to generate new σ^+ constants from C-13 substituent chemical shifts (SCS).[4-6] C-13 chemical shifts give precise values for all substituents, provided that concentration and solvent effects are minimized, and they are relatively easy to measure. Despite these advantages we caution against the direct estimation of σ^+ parameters from SCS data.

It has been shown that spectral, and especially NMR substituent effect, data should be analyzed using a two-parameter equation.[7] The dual substituent parameter (DSP) equation (eq 1) separates substituent effects into inductive ($\rho_I\sigma_I$) and resonance ($\rho_R\sigma_R$) components[3a] and uses one of four different resonance scales ($\sigma_R = \sigma_R^-, \sigma_R^0, \sigma_R^{BA}$, or σ_R^+), depending on the electron demand at the reaction or measuring site.[3b] The resonance to inductive blend ($\lambda = \rho_R/\rho_I$) varies markedly both for different systems and for different measuring sites within the same system.[3,8] To analyze the diverse range in data with a single parameter equation which has a fixed λ would require many different σ scales.

$$\delta = \rho_I\sigma_I + \rho_R\sigma_R \qquad (1)$$

Substituent effect data are usually fitted to eq 1 by a standard computer least-squares analysis, and a detailed description of the use of the DSP method is given in ref 3. Additional insight into the DSP method may be gained from a graphical representation where the effective substituent constant, $\bar{\sigma}$, is determined for different resonance to inductive blends. This may be achieved by rearranging eq 1 into eq 2,

$$\delta = (\rho_I^2 + \rho_R^2)^{1/2}(\sigma_I \cos\theta + \sigma_R \sin\theta) \qquad (2)$$

where the effective ρ and σ values are separated.[9] In Figure 1, the effective σ constant, $\sigma_I \cos\theta + \sigma_R^0 \sin\theta$ (using σ constants from ref 3b), is plotted as a function of θ, which represents all of the possible combinations and proportions of σ_I and σ_R ($\tan\theta = \rho_R/\rho_I = \lambda$). Since the signs of $\cos\theta$ and $\sin\theta$ vary with θ, so does the sign of the contribution from σ_I and σ_R^0. Between 0 and 90° the contributions from σ_I and σ_R^0 are

0022-3263/79/1944-1261$01.00/0

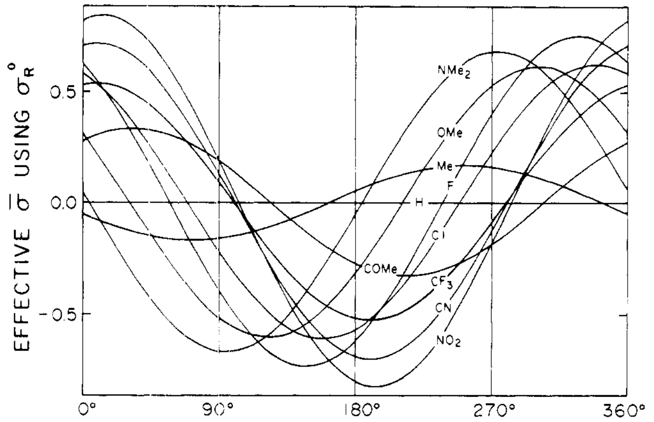


Figure 1. Plot of effective σ constants ($\bar{\sigma} = \sigma_I \cos\theta + \sigma_R{}^0 \sin\theta$) for varying resonance to inductive blends ($\tan\theta = \rho_R/\rho_I = \lambda$) using the $\sigma_R{}^0$ scale.

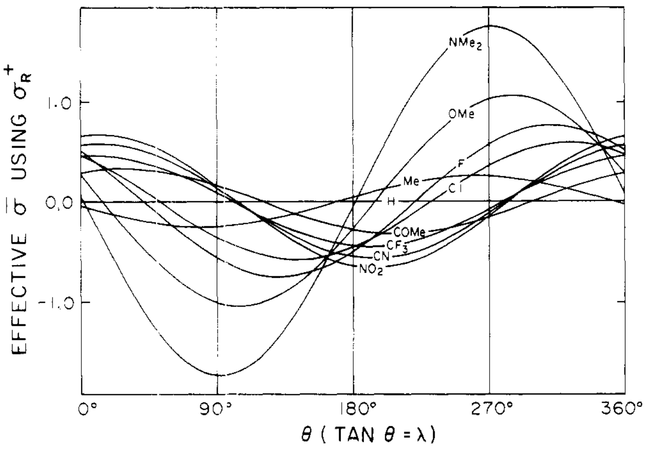


Figure 2. Plot of effective σ constants ($\bar{\sigma} = \sigma_I \cos\theta + \sigma_R{}^+ \sin\theta$) for varying resonance to inductive blends ($\tan\theta = \rho_R/\rho_I = \lambda$) using the $\sigma_R{}^+$ scale.

both positive, between 90 and 180° the contribution from σ_I is negative and $\sigma_R{}^0$ positive, between 180 and 270° both are negative, and between 270 and 360° the contribution from σ_I is positive and $\sigma_R{}^0$ negative. Within each of these sections the proportion of σ_I to $\sigma_R{}^0$ is varied: for example, at 0°, $\bar{\sigma} = 1.0\sigma_I + 0.0\sigma_R{}^0$; at 45°, $\bar{\sigma} = 0.7\sigma_I + 0.7\sigma_R{}^0$; and at 90°, $\bar{\sigma} = 0.0\sigma_I + 1.0\sigma_R{}^0$. Using this graph it is possible to analyze substituent data "by eye" by noting the substituent order of the data and finding the appropriate region of the graph that corresponds to that order.

The DSP equation gives well-defined ρ_I and ρ_R values only when a comprehensive "basis set" of substituents[3] is used to provide the data. The substituent set is chosen to provide the greatest separation of inductive and resonance components. This is achieved by choosing substituents with the greatest nonlinear σ_I/σ_R relationship.[3] For a good correlation it is also necessary to choose substituents which will provide the widest distribution of data points. Figure 1 shows that there are regions of the graph, in particular when θ = 135°, where the standard set is inadequate. We recommend that a carbonyl-containing substituent be included, making the basis set the following: two strong donors (NMe_2, NH_2, or OMe); two halogens (not both Cl and Br); Me and H; one acceptor (NO_2, CN, or CF_3); and one carbonyl acceptor (COMe or COOR). Much of the spectral data appearing in the literature can not be analyzed properly due to the lack of appropriate substituents.

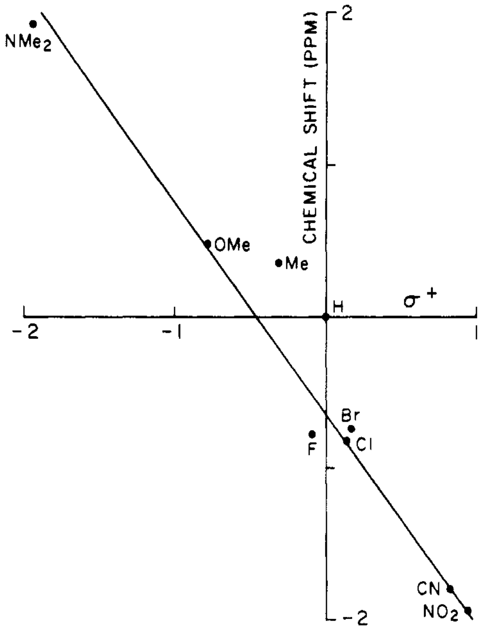


Figure 3. Plot of CN C-13 SCS of *p*-benzonitriles (λ = 0.42) vs. "σ^+" taken from ref 6.

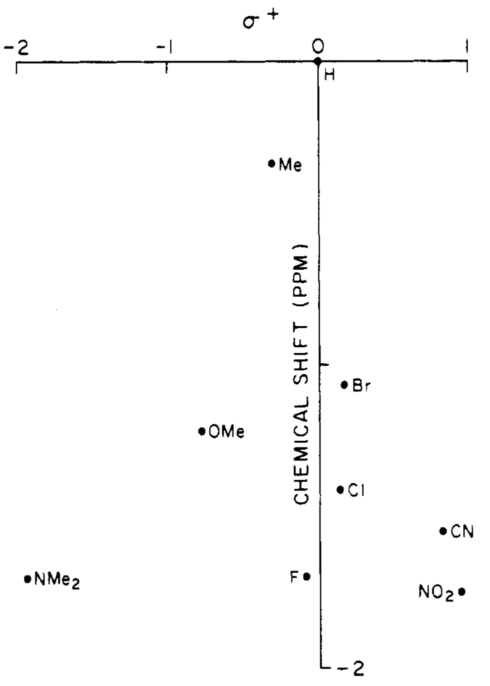
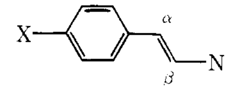


Figure 4. Plot of C=O C-13 SCS of *p*-acetophenones (λ = −0.3) vs. "σ^+" taken from ref 6.

For electron deficient systems, the $\sigma_R{}^+$ scale is used in the DSP equation;[3] this is represented graphically in Figure 2. The main difference between this and Figure 1 is the enhanced σ_R values required for strong π-donor substituents.

The advantages of using the DSP equation and its graphical representation can best be illustrated by examining substituent data in the recent literature. When the β position of styrene (1) is substituted with a π-accepting group (NO_2 or di-CN), an electron deficient center is created. The side chain conjugates strongly with para substituents on the benzene ring, making C-13 SCS's at the β site a good measure of enhanced resonance parameters.[4-6] Table I contains DSP



1

Table I. DSP Analyses of the C-13 SCS's of the β-Carbon Atom of Para-Substituted Styrenes

series	resonance scale	ρ_I	ρ_R	$\lambda = \rho_R/\rho_I$	f = SD/rms	n	ref
Brown and Okomoto	σ_R^+	4.6	4.7	1.0	0.08	12	2
p-XPhCH=CHNO$_2$	σ_R^+	3.7	3.4	0.9	0.04	10	6, 10
p-XPhCH=C(CN)$_2$	σ_R^+	5.4	6.7	1.2	0.08	8	4, 5
p-XPhCH=CHCOPh	σ_R^{BA}	4.4	6.0	1.4	0.12	8	11
m-XPhCH=CHNO$_2$	σ_R^{BA}	3.2	0.8	0.3	0.06	6	10

Table II. DSP Analyses of the C-13 SCS's of the α-Carbon Atom of Para-Substituted Styrenes

series	resonance scale	ρ_I	ρ_R	f = SD/rms	n	ref
p-XPhCH=CHNO$_2$	σ_R^+	−3.6	−1.1	0.11	10	6, 10
p-XPhCH=C(CN)$_2$	σ_R^+	−3.0	1.1	0.27	8	4, 5
p-XPhCH=CHCOPh	σ_R^{BA}	−4.0	−1.7	0.06	8	11

analyses of Brown's original data and some β-substituted styrene series having an acceptable range of para substituents. The DSP correlations are good and result in ρ_I and ρ_R values which are not identical.

Correlating chemical shift data in the styrene series with σ^+ is the same as comparing the effective $\bar{\sigma}$ values at two different θ positions in Figure 2. The comparison is reasonable for the NO$_2$ and di-CN styrene SCS data because their σ values are similar; however, any suggested modifications to the original σ^+ constants from the SCS data may be due to the slight changes in λ and not necessarily due to the improved technique.

As λ ($= \tan \theta$) varies further from +1.0, specific substituents show larger deviations, making the σ^+ scale redundant. The C-13 SCS of the nitrile carbon in para-substituted benzonitriles is a good example. This carbon SCS correlates best with the DSP σ_R^+ scale with a λ of +0.42 ($f = 0.09$).[8] If this data is compared with σ^+, the line of general fit deviates markedly from the origin (Figure 3). This is essentially the same as comparing the data for $\theta = 45°$ (σ^+; $\lambda = 1.0$) with those of $\theta = 23°$ ($\lambda = 0.42$) in Figure 2. In this particular case, the direction of change of $\bar{\sigma}$ for the H and Me substituents differs from that of the other substituents and hence H and Me show the greatest deviation in Figure 3. It is predicted that COMe and COOR would also show large deviations.

When inductive and resonance effects oppose each other, as for the carbonyl SCS of para-substituted acetophenones ($\lambda = -0.30$; $\theta = 163°$),[8] even greater deviations are experienced (Figure 4). Attempts to correlate this type of data using σ^+, or any other substituent parameter scale, would provide no useful information. The DSP equation gives a good correlation ($\delta = -2.6\sigma_I + 0.8\sigma_R^+$; $f = 0.15$), and from the results a mechanism for the transmission of the inductive effect may be proposed. Such a correlation can be made qualitatively from Figure 2, and in addition it is possible to predict the substituents required for an even distribution of data.

The chalcone series is included in Table I to illustrate how a change in the β substituent may result in a DSP correlation requiring a different resonance scale. The m-nitrostyrene analysis is included to emphasize that C-13 meta-substituent effects are independent of the para effects and that both should not be included in the same correlation.

The DSP method also allows analysis of the α-carbon SCS on the styrene series. Substituent effects at this position are generally not examined because they give poor correlations with single-parameter equations. The DSP analyses in Table II show good correlations, with nearly constant inductive contributions for all of the series. Resonance effects are small and variable, a result of the narrow range in chemical shifts. For the dinitrile series, the poor correlation may be due to the concentration used. For this type of correlation, where the total range in chemical shifts is small and where strongly interactive groups are involved, concentration effects only become negligible at extremely low concentrations (<3% w/v).[8]

Acknowledgment. We wish to thank Professor R. W. Taft for helpful discussions.

Registry No.—p-N,N-Dimethylaminobenzonitrile, 1197-19-9; p-methoxybenzonitrile, 874-90-8; p-methylbenzonitrile, 104-85-8; benzonitrile, 100-47-0; p-bromobenzonitrile, 623-00-7; p-fluorobenzonitrile, 1194-02-1; p-chlorobenzonitrile, 623-03-0; p-cyanobenzonitrile, 935-16-0; p-nitrobenzonitrile, 619-72-7; acetophenone, 98-86-2; p-methylacetophenone, 122-00-9; p-bromoacetophenone, 99-90-1; p-methoxyacetophenone, 100-06-1; p-chloroacetophenone, 99-91-2; p-cyanoacetophenone, 1443-80-7; p-fluoroacetophenone, 403-42-9; p-N,N-dimethylaminoacetophenone, 2124-31-4; p-nitroacetophenone, 100-19-6.

References and Notes

(1) Taken from the Ph.D. Thesis of J. Bromilow, La Trobe University, July, 1977.

(2) H. C. Brown and Y. Okomoto, *J. Am. Chem. Soc.*, **80,** 4979 (1958).

(3) (a) P. R. Wells, S. Ehrenson, and R. W. Taft, *Prog. Phys. Org. Chem.*, **6,** 147 (1968); (b) S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *ibid.*, **10,** 1 (1973).

(4) T. B. Posner and C. D. Hall, *J. Chem. Soc., Perkin Trans. 2,* 729 (1976).

(5) A. Cornelis, S. Lambert, and P. Laszlo, *J. Org. Chem.*, **42,** 381 (1977).

(6) D. A. R. Happer, *Aust. J. Chem.*, **29,** 2607 (1976).

(7) R. T. C. Brownlee and R. D. Topsom, *Tetrahedron Lett.*, 5187 (1972).

(8) J. Bromilow, R. T. C. Brownlee, and D. J. Craik, *Aust. J. Chem.*, **30,** 351 (1977).

(9) Blended $\bar{\sigma}$ values have been reported in ref 3a. A referee has pointed out that a graphical representation related to the one described in this paper could be obtained by plotting the original σ blends, $\bar{\sigma} = (\sigma_I + \lambda\sigma_R^0)/(1 + |\lambda|)$, against $\lambda/(1 + |\lambda|)$.

(10) D. A. R. Happer, S. M. McKerrow, and A. L. Wilkinson, *Aust. J. Chem.*, **30,** 1715 (1977).

(11) E. Solaniova, S. Toma, and S. Gronowitz, *Org. Magn. Reson.*, **8,** 439 (1976).