thiosulfate react at both electron-deficient sites to varying degrees and afford mixtures of redox and C-substitution products. Aliphatic thiols and disulfides react slightly at the nitrenium ion. There was no evidence for electron transfer to form a radical intermediate.

Experimental Section

Weighed samples of 10 μmol (2.5 mg) of analytically pure 3-acetoxyxanthine hydrochloride[15] were dissolved in 5 mL of 0.1 M NaH_2PO_4 buffer containing 0.01 M (5 equiv) of the desired nucleophile. Reactions were allowed to proceed in the dark at ambient temperature for 24 h, most of the solvent was removed under reduced pressure, and the solutions were chromatographed over 9 × 150 mm columns containing Dowex 50 (H^+) resin. H_2O eluted uric acid, 8-thiouric acid, 8-nitroxanthine, 8-(phenylthio)xanthine, and **2** while 0.1 or 1 N HCl eluted **6**. Products were identifiable both by their position of elution from the column and by comparison of UV spectral values in acid and base to those of authentic samples or to reported values. Yields were determined from the optical density of measured elution volumes and known ϵ values: 8-nitroxanthine (pH 1), λ_{max} 360 nm (ϵ 10600);[59] 3-hydroxyxanthine (**2**; (pH 2–4), λ_{max} 272 nm (ϵ 10000);[60] 8-thiouric acid (pH 2), λ_{max} 303 nm (ϵ 18200);[61] xanthine (**6**; pH 0), λ_{max} 260 nm (ϵ 9200).[15] OD values were determined with a Unicam SP800A recording spectrophotometer. Values in Table I are the average of two or more determinations when standard deviations are indicated. Assignment of structure of 8-(phenylthio)xanthine is based on the similarity of the UV spectra of the product in acid (λ_{max} 288 nm and, in base, 297 nm) to those of 8-(methylthio)-xanthine: λ_{max} (pH 1) 218 nm (ϵ 12400), 289 (15800); λ_{max} (pH 12) 252 (7000), 292 (12800). Since the λ_{max} and ϵ values of 8-ethoxy-[62] and 8-phenoxyxanthine[62] are reasonably close, the extinction of 8-(methylthio)xanthine was used to estimate the yield of 8-(thiophenoxy)xanthine in Table I. The yield of triiodide (70%) was determined spectrophotometrically at 352 nm (ϵ 26500).[14]

Acknowledgment. We are very much indebted to Dr. Roger Sealy of the National Biochemical ESR Center for his time and effort in performing the ESR experiments and thank Dr. George Bosworth Brown for his support and interest in this work.

Registry No. **1**·HCl, 64761-25-7; **2**, 13479-29-3; **4** (Nu = OH), 69-93-2; **4** (Nu = SH), 2476-54-2; **4** (Nu = SC_6H_5), 80106-08-7; **4** (Nu = NO_2), 80106-09-8; **6**, 69-89-6; I^-, 20461-54-5; $H_2NCSeNH_2$, 630-10-4; H_2NCSNH_2, 62-56-6; $C_5H_4N_4S$, 50-44-2; CH_3CSNH_2, 62-55-5; $EtOCS_2^-$, 28563-38-4; CH_3COS^-, 29632-72-2; CS_3^{2-}, 15644-49-2; HSe^-, 16661-43-1; HS^-, 15035-72-0; $HSCH_2CHNHAcCO_2^-$, 41079-67-8; C_6H_5SH, 108-98-5; $(CH_3)_3CSH$, 75-66-1; $(CH_3S)_2$, 624-92-0; $S_2O_3^{2-}$, 14383-50-7; CN^-, 57-12-5; HSO_3^-, 15181-46-1; NO_2^-, 14797-65-0; BH_4^-, 16971-29-2; $S_2O_4^{2-}$, 14844-07-6; $S_2O_6^{2-}$, 14781-81-8.

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(59) J. W. Jones and R. K. Robins, *J. Am. Chem. Soc.*, **82**, 3773 (1960).
(60) U. Wölcke and G. B. Brown, *J. Org. Chem.*, **34**, 978 (1969).
(61) T. L. Loo, M. E. Michael, A. J. Garceau, and J. C. Reid, *J. Am. Chem. Soc.*, **81**, 3039 (1959).
(62) G. Stöhrer and G. B. Brown, *Biochemistry*, **15**, 2772 (1976).

Transmission of Substituent Effects via Molecular Lines of Force: Defense of the DSP Method and an Illustration of Its Use in Explaining π Polarization

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This paper disputes the conclusions of a recent report by Laszlo and co-workers[33] regarding the applicability of the dual substituent parameter (DSP) method to studies of substituent effects on ^{13}C chemical shifts. We show that the ρ_I and ρ_R transmission coefficients obtained from DSP analyses of ^{13}C shifts in side chains of styrene derivatives provide useful mechanistic information. Trends in chemical shifts for a number of C=O or C≡N probe groups are discussed and interpreted in terms of the π-polarization mechanism. The concept that π-polarization effects may be partially transmitted via "molecular lines of force" is introduced and compared with the classical through-space transmission mode of polarization effects. The interrelationship between this concept and that of extended polarization is discussed.

^{13}C NMR chemical shifts have been used extensively as monitors of molecular structure and electron distribution. In particular, the use of substituent chemical shifts (SCS) to monitor the transmission of electronic effects in rigid molecular frameworks has been a fruitful area of research for many years.[1-10] Studies have been made of the transmission of substituent effects both within aromatic rings[1,3,5,9,11-14] and in (often unsaturated) side chains attached to those substituted aromatic systems.[15-29]

The most successful analyses of substituent effects on chemical shifts have used Hammett-type[30] treatments. The dual substituent parameter (DSP)[31] extension of the Hammett approach has proven particularly useful. In this method, the observed ^{13}C SCS (δ^c) values are correlated

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† La Trobe University.

(1) For a review see: Shorter, J. In "Correlation Analysis in Chemistry: Recent Advances"; Shorter, J., Chapman, N. B., Eds., Plenum: New York, 1978; Chapter 4.
(2) (a) Levy, G. C.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley-Interscience: New York, 1972; Chapter 4. (b) Strothers, J. B. "C-13 NMR Spectroscopy"; Academic Press: New York, 1972; Chapter 6.
(3) Bromilow, J.; Brownlee, R. T. C.; Taft, R. W.; Topsom, R. D. *J. Am. Chem. Soc.* **1976**, *98*, 2020.
(4) Reynolds, W. F.; McClelland, R. A. *Can. J. Chem.* **1977**, *55*, 536.
(5) Hehre, W. J.; Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1976**, *12*, 159.
(6) Happer, D. A. R.; McKerrow, S. M.; Wilkinson, A. L. *Aust. J. Chem.* **1977**, *30*, 1715.
(7) Posner, T. B.; Hall, C. D. *J. Chem. Soc., Perkin Trans. 2* **1976**, 729.

0022-3263/82/1947-0657$01.25/0

with a linear combination of the inductive and resonance substituent constants σ_I and σ_R by using eq 1.

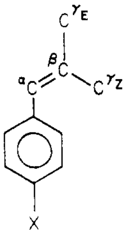
$$\delta^c = \rho_I\sigma_I + \rho_R\sigma_R \qquad (1)$$

The derived ρ_I and ρ_R values give a direct measure of the relative transmission of inductive and resonance effects. The advantages of this approach have been discussed fully elsewhere.[31,32] It suffices to say here that the DSP method represents a *general* approach for the correlation of substituent effects over a large range of different data sets. (Of course, due regard must be made for certain limitations, namely, the minimization of steric or solvent-related effects. For this reason, NMR studies of substituent effects should be carried out in dilute solutions of an inert solvent.) The generality arises because of the independence of the ρ_I and ρ_R transmission coefficients. Since inductive and resonance effects are transmitted by different mechanisms,[31] their relative importance may change from one system to another. This feature cannot be accommodated in a single-parameter approach.

In a recent examination of a number of styrene derivations, Laszlo and co-workers[33] reached the conclusion that "There is no systematic significant superiority, in general, of a dual substituent parameter (DSP) treatment with respect to the simpler single substituent parameter (MSP) treatment". That report has prompted us to present this reply. First, we point out that Laszlo's data *do not* indicate any weakness or redundancy of the DSP method. In fact, as we will show below, some of the data in Laszlo's paper can be used to indicate the strength of the DSP method. Second, Laszlo's paper provides a convenient summary of data which enable us to show the power of the DSP method in explaining new features of a very important mechanism for the transmission of polar substituent effects, i.e., π polarization. Experimental evidence supporting this mechanism has been provided by many groups,[36-44] including ours[14,23,25] and those of Reynolds.[4,24,34,35,42] We have also recently presented a theoretical model of this effect.[40]

Discussion

Laszlo and co-workers[33] examined both single and dual parameter correlations for side-chain ^{13}C chemical shifts in compounds containing the general structural unit 1. Of particular interest were correlations for the γ_E and γ_Z carbons which differ only in their orientation with respect to the substituent X.



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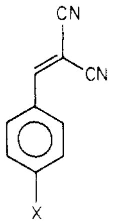
The specific series examined were as follows.



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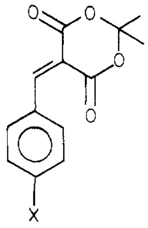

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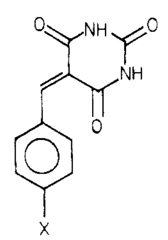

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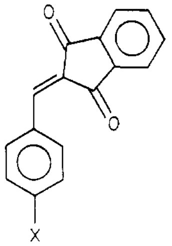

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Using two statistical criteria to adjudge the significance of each correlation, they concluded[33] that "We failed to find an overwhelming, or merely a clear-cut, advantage for the multiple parameter correlations". However, our current examination of the data in their Table II[33] reveals that in *every* correlation listed (29 in all) the DSP method yields fits statistically equal to or *better than* those of a single parameter treatment. Although in many cases the statistical fits for the two methods are similar, it should be remembered that the series examined constitute a specific situation in which the DSP method is not expected to yield *much* better fits. This is because the relative transmissions of inductive and resonance effects to the sites examined are fairly similar (i.e., $\lambda = \rho_R/\rho_I$ varies only from approximately 0.5 to 1.5). It is precisely in this range of λ values that the difference between dual and single parameter treatments is less pronounced. However, there are many

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

(9) Ewing, D. F. *Org. Magn. Reson.* **1979**, *12*, 499.

(10) Ewing, D. F. In "Correlation Analysis in Chemistry: Recent Advances"; Shorter, J., Chapman, N. B., Eds.; Plenum: New York, 1978; Chapter 8.

(11) Bromilow, J.; Brownlee, R. T. C.; Lopez, V. O.; Taft, R. W. *J. Org. Chem.* **1979**, *44*, 4766.

(12) Bromilow, J. Ph.D. Thesis, La Trobe University, 1977.

(13) Lynch, B. M. *Can. J. Chem.* **1977**, *55*, 541.

(14) Bromilow, J.; Brownlee, R. T. C.; Craik, D. J.; Sadek, M.; Taft, R. W. *J. Org. Chem.* **1980**, *45*, 2429.

(15) Schulman, E. M.; Christensen, K. A.; Grant, D. M.; Walling, C. *J. Org. Chem.* **1974**, *39*, 2686.

(16) Schaeffer, C. D., Jr.; Zuckerman, J. J.; Yoder, C. D. *J. Organomet. Chem.* **1974**, *80*, 29.

(17) Robinson, C. N.; Irving, C. C. *J. Heterocycl. Chem.* **1979**, *16*, 921.

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

(19) Yoshimi, Y.; Takabayashi, T.; Yamada, F. *Org. Magn. Reson.* **1980**, *13*, 94.

(20) Takai, H.; So, K.; Sasaki, Y. *Chem. Pharm. Bull.* **1978**, *26*, 1303.

(21) Reynolds, W. F.; Gibb, V. G.; Plavac, N. *Can. J. Chem.* **1980**, *44*, 839.

(22) Happer, D. A. R.; Wright, G. J. *J. Chem. Soc., Perkin Trans. 2* **1979**, 694.

(23) Brownlee, R. T. C.; Butt, G.; Chan, M. P.; Topsom, R. D. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1486.

(24) Reynolds, W. F.; Peat, I. R.; Freedman, M. H.; Lyerla, J. R., Jr. *Can. J. Chem.* **1973**, *51*, 1857.

(25) Bromilow, J.; Brownlee, R. T. C.; Craik, D. J.; Fiske, P. R.; Rowe, J. E.; Sadek, M. *J. Chem. Soc., Perkin Trans. 2* **1981**, 753.

(26) Taskinen, E.; Tuominen, L. *Finn. Chem. Lett.* **1978**, 240.

(27) Membrey, F.; Doucet, J. P. *J. Chem. Phys. Phys.-Chim. Biol.* **1976**, *73*, 1024.

(28) Krabbenhoft, H. O. *J. Org. Chem.* **1978**, *43*, 1830.

(29) Exner, O.; Kalfus, K. *Collect. Czech. Chem. Commun.* **1976**, *41*, 569.

(30) Hammett, L. P. "Physical Organic Chemistry"; McGraw-Hill: New York, 1970.

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

(32) Bromilow, J.; Brownlee, R. T. C. *J. Org. Chem.* **1979**, *44*, 1261.

(33) Cornelis, A.; Lambert, S.; Laszlo, P.; Schaus, P. *J. Org. Chem.* **1981**, *46*, 2130.

(34) Reynolds, W. F. *Tetrahedron Lett.* **1977**, 675.

(35) Reynolds, W. F.; Hamer, G. K. *J. Am. Chem. Soc.* **1976**, *98*, 7296.

(36) Ewing, D. F.; Sotheeswaren, S.; Toyne, K. J. *Tetrahedron Lett.* **1977**, 2041.

(37) Ewing, D. F.; Toyne, K. J. *J. Chem. Soc., Perkin Trans. 2* **1979**, 243.

(38) (a) Shapiro, M. J. *J. Org. Chem.* **1978**, *43*, 3769. (b) *Ibid.* **1976**, *41*, 3197.

(39) Shapiro, M. J. *Tetrahedron* **1977**, *33*, 1091.

(40) Brownlee, R. T. C.; Craik, D. J. *J. Chem. Soc., Perkin Trans. 2* **1981**, 760.

(41) Topsom, R. D. *Prog. Phys. Org. Chem.* **1976**, *12*, 1.

(42) Reynolds, W. F. *Prog. Phys. Org. Chem.*, in press.

(43) Butt, G.; Topsom, R. D. *Spectrochim. Acta, Part A* **1980**, *36A*, 811. Butt, G. M.Sc. Thesis, La Trobe University, 1981.

(44) Private communication with G. Butt and R. D. Topsom.

Table I. DSP Analyses[a] of SCS Values in Series 2-7

series	γ *E* carbon					γ *Z* carbon				
	ρ_I	ρ_R	λ	SD	*f*	ρ_I	ρ_R	λ	SD	*f*
2	−1.1	1.1	1.01	0.13	0.13	−1.1	−1.3	1.15	0.21	0.20
3[b,f]	−1.5	−1.2	0.80	0.13	0.14	−1.4	−1.1	0.76	0.12	0.14
4[b,e]	−1.0	−0.8	0.77	0.02	0.05	−0.5	−0.7	1.34	0.04	0.09
5[b]	−1.1	−1.0	0.87	0.09	0.12	−0.3	−0.7	2.35	0.06	0.12
6[c]	−1.2	−1.1	0.88	0.05	0.07					
7[d]						−1.5	−1.0	0.69	0.05	0.06

[a] DSP correlations are normally done by using σ_I and one of σ_R^-, σ_R^0, σ_R^{BA} or σ_R^+. The above correlations used the σ_R^+ scale. Correlations were done by using our DSP program and data from the indicated source. [b] Reference 33. [c] Reference 43. [d] Reference 44. [e] Reference 17. [f] General conclusions only can be derived from these correlations because of the limited substituent sets used to determine some of theses equations; e.g., series 3 contains no acceptors, and the data for the OMe substituent was anomalous and had to be excluded. The ρ_I and ρ_R values are accurate to ±0.1.

other situations involving more extreme λ values that clearly require a dual parameter treatment.[25]

We emphasize that the failure to note a significant difference between the DSP and single parameter treatments for a near-unity λ situation should not be construed as evidence that the DSP method is generally redundant. The single parameter equation is a particular case of the general DSP equation. Where a correlation is precise with a single parameter equation, a DSP equation will make no improvement to the fit. However, if a correlation with a single parameter equation is poor, then there may be a number of reasons for the bad fit. These may include the need to use a DSP equation, as well as poorly defined data.

Moreover, even in those cases where the statistical fits (e.g., correlation coefficients (*r*) or "*f*" values[31]) using the two types of treatment are similar, the *DSP method provides important additional information not obtainable from a single parameter treatment*, *viz*., the relative magnitudes of the ρ_I and ρ_R values. For example, in a single parameter treatment, only one ρ value (transmission coefficient) is obtained, and it is not possible to assess relative contributions from the various modes of transmission of substituent effects. The DSP method readily allows one to determine differential changes in polar (ρ_I) and resonance (ρ_R) effects.

Laszlo[33] noted that there was a change in the ratio $(\rho_I)_E/(\rho_I)_Z$ for the series 2–5 while the ratio $(\rho_R)_E/(\rho_R)_Z$ remained close to unity in all series. The latter fact was assumed to indicate that the geometries, or conformer populations of 2–5 were all similar. We propose here an alternative explanation of the constant $(\rho_R)_E/(\rho_R)_Z$ ratios. Our explanation is based on the fact that differences in geometry affect the ratios of the ρ_R values (for either the *E* or the *Z* carbon) for different series and not the ratio of the ρ_R values for the *E* and *Z* carbons in the same series.

For a given angle of twist between the ring and side chain there will be associated a certain ρ_R value, which, because resonance effects are largely geometry (*within the side chain*) independent, should be equal for the *E* and *Z* carbons. This can be seen from the data in Table I for series 2–5. These data were obtained by using the original formulation of the DSP equation[31] and not that version including an intercept as used by Laszlo.[33,45] For a given series, the ρ_R values for the *E* and *Z* carbons are indeed similar. However, series 2 and 3 have slightly larger ρ_R values (especially for the *Z* carbon) than series 4 and 5, indicating a reduced transmission of resonance effects in the latter compounds, most likely due to an increased angle of twist between the ring and side chain.[46] We stress that this is only a qualitative explanation, as the limited range of substituents used in the DSP analysis precludes a more definite conclusion. In addition, not all of the studies were carried out in the same solvent.

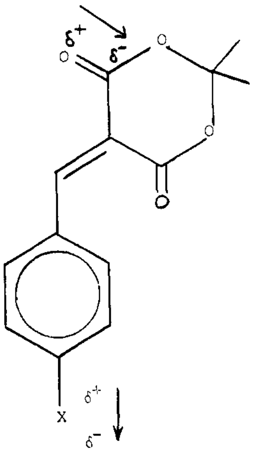

Figure 1. π polarization induced by an electron-withdrawing substituent.

On the other hand, the ρ_I values for the *E* and *Z* carbons in a given series are not necessarily expected to be identical. A referee has suggested that steric effects might contribute to the ^{13}C shifts of the *Z* carbon. If this is so, then they appear to affect mainly the polar component of the shifts and not the resonance component. Nevertheless, the dominant mechanism determining the polar component of the shifts is π polarization of the unsaturated side chain. Thus, the most important thing to note about the ρ_I values at the γ-position is that they are *negative*. This is indicative of a reverse substituent effect, where donors induce downfield shifts and acceptors upfield ones. The π-polarization mechanism accounts for this trend in terms of substituent-induced polarization of the carbonyl groups in 3–5 or the cyano groups in 2 as shown in Figure 1.

The interesting thing to note is that the observed direction of polarization of the *Z* carbonyl group is similar to that of the *E* carbonyl group even though these two C=O probes have almost opposite orientations with respect to the C–X dipole. This observation provides evidence that the π-polarization mechanism is transmitted significantly *vis "molecular lines of force"* (MLF). This effect has been mentioned previously only in passing.[41] We define a MLF pathway as a (not necessarily linear) low-

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(45) The advantages of using the DSP method without an intercept have been discussed in detail elsewhere.[31] In summary, we prefer our version because (1) it has fewer degrees of freedom and few substituent measurements are required and (2) the basis set of substituents necessary to independently define ρ_I and ρ_R is easier to satisfy.

(46) This is confirmed by noting that the ρ_R values at Cβ in the latter two series are smaller than those in series 2 and 3. Our DSP analysis of the Cβ SCS values gave the following pairs of ρ_I and ρ_R values respectively. Series 2, 6.5, 6.0; series 3, 4.8, 6.7; series 4, 4.6, 5.2; series 5, 3.8, 3.6.

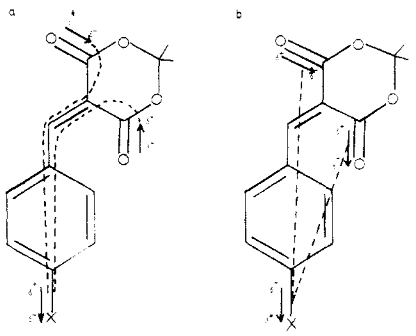
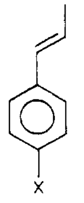


Figure 2. (a) MLF π polarization. (b) Direct π polarization.

resistance pathway between a substituent dipole and a probe site via which polarization effects may be transmitted. Specifically, the intervening π orbitals of the molecule often provide a more suitable dielectric pathway for the transmission of polarization effects than does the direct through-space pathway. In this sense, the MLF concept represents an extension of existing ideas. For example, Taft and co-workers[47] have shown how the polar component of ^{19}F SCS values is determined by the nature of the intervening π system in series of the form X–Ph–G–Ph–F, where G is a bridging group between two para-substituted phenyl rings. However, the MLF concept is more general, and in addition to the lines of force being directed via the π orbitals, nonlinear through-space pathways are also possible. These arise because the electron distribution of a molecule generates electric field lines, and polarization effects may then be transmitted along these lines. We use the term "molecular lines of force" because it is the nature of the molecular framework which determines the polarization pathway.

Figure 2a shows the expected polarization of the probe groups resulting from a MLF transmission pathway. Each C═O probe group is influenced by a polarizing field which approaches from near C-β. In a classical electrostatic (field) effect the interaction is transmitted in a straight line and is proportional to the inverse cube of the distance between the substituent dipole and probe site. Figure 2b shows this pathway.

Both MLF and direct through-space transmission pathways will contribute to the total observed π-polarization. The reduced ρ_I values for the *Z* carbon compared with the *E* carbon arise because at the former site the two transmission pathways oppose each other, whereas for the latter carbon they reinforce one another. That the overall ρ_I value is negative for the *Z* carbon shows that the MLF pathway is dominant. Measured ^{13}C chemical shifts are infrared intensities in cinnamonitriles also support this conclusion. DSP analyses of these data yield similar ρ_I values for the trans (**6**)[43] and cis (**7**)[44] series. On the other hand, IR frequencies, which appear to reflect the local C≡N bond order, show opposite polar substituent effects in the two series.[44]



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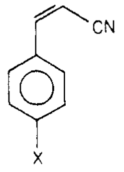

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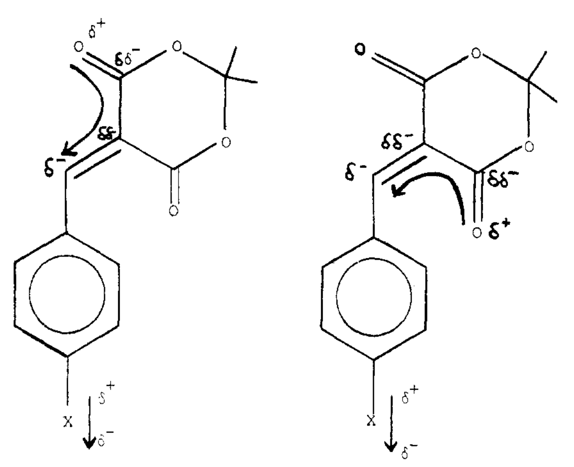
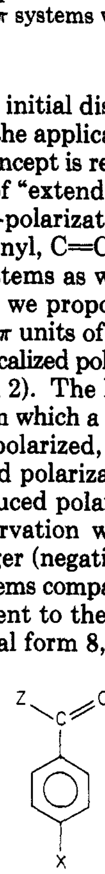


Figure 3. Possible "extended polarization" modes in which a polar substituent X can redistribute charge in an extended π system. Other extended polarization modes may also occur; e.g., the ring and side-chain π systems will be polarized together as an extended unit.[40]

We believe that our initial discussion of the MLF concept here will lead to the application of this idea to many future studies. The concept is related to but distinct from our previous studies of "extended polarization",[25] where we showed that the π-polarization effect can be applied not only to single phenyl, C═C, or C═O π systems but also to conjugated systems as well. For example, in the current systems (**2**–**7**) we propose that extended polarization of two or more π units of the side chain (Figure 3) occurs in addition to localized polarization of the individual π units (Figures 1 and 2). The MLF concept strictly defines the direction from which a π system (either localized or extended) will be polarized, whereas the concepts of localized and extended polarization relate to the nature and extent of the induced polarization.

An important observation which confirms extended polarization is the larger (negative) ρ_I values seen in conjugated side-chain systems compared with those containing a single π bond adjacent to the benzene ring.

In systems of general form **8**, a ρ_I value of −2.7 is generally measured for the α-carbon,[18] irrespective of the nature of the *Z* group.[25] In other systems, for example, styrene analogues containing conjugative β groups, extended polarization of the side chain is possible[48] (Figure 3), and larger ρ_I values are observed for C-α; e.g., in series **2**–**7** the ρ_I values for C-α range between −3.1 and −4.5. Note that here C-α is the carbon atom in the vinyl group adjacent to the benzene ring and that in parent styrene derivatives, where there is no β substituent and no extended polarization, a ρ_I value of only −2.4 is observed,[42]



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(47) Fukunaga, J.; Taft, R. W. *J. Am. Chem. Soc.*, **1975**, *97*, 1612. Dayal, S. K.; Taft, R. W. *Ibid.* **1973**, *95*, 5595. Dayal, S. K.; Ehrenson, S.; Taft, R. W. *Ibid.* **1972**, *94*, 9113.

(48) It should be noted that to obtain this type of extended polarization it is necessary to attach an unsaturated group to the β-position of the π system adjacent to the benzene ring. This can be done in styrene derivatives but not in systems like **8** where the β site is an oxygen atom. This explains why even conjugated Z groups do not affect the ρ_I value of −2.7 in carbonyl systems.

Table II. ^{13}C Chemical Shifts (ppm)[a] of the C-α Carbon in Benzylidene Malononitriles

X	Posner and Hall[7]	Laszlo et al.[33]	this work[b]	Robinson et al.[49]
NMe_2	158.4	158.04	158.01	158.0
OMe	159.1	158.91	158.79	159.0
F		158.44	158.23	158.4
Cl	159.7	158.07		158.2
Br	159.4		158.38	158.4
Me	160.3		159.69	159.8
H	160.8	159.85	159.86	160.1
CN	159.0	156.50	157.31	157.3
NO_2	158.7	157.55	156.77	156.8
solvent	acetone	$CDCl_3$	$CDCl_3$	$CDCl_3$
concn (w/v), %	~5	~25[c]	3	~30

[a] Relative to Me_4Si. [b] Shifts are accurate to ±0.05 ppm and were measured on a FX-200 spectrometer operating at 50.10 MHz. [c] The concentrations used were not specified directly in this study but are assumed to be similar to those of the preliminary study.[8]

similar to that observed in carbonyl systems.[25]

Finally, we note that Laszlo and co-workers do not obtain a good DSP correlation for the C-α position of series 2 (benzylidene malononitriles). In other studies[25] we have measured extensive series of ^{13}C spectra for structurally related compounds and found that when the data are measured with precision, at low concentration, the DSP correlations for the C-α position of a conjugating side chain are of good quality and consistently show a negative polar substituent effect. We note that ^{13}C spectra for substituted benzylidene malononitriles have been measured by three groups (Laszlo et al.,[33] Posner and Hall,[7] and Robinson et al.[49]) and that the SCS values derived differ somewhat. We have therefore carefully remeasured ^{13}C SCS values for a series of these compounds.

An examination of Table II reveals that for the three independent sets of data measured in the same solvent ($CDCl_3$) there is agreement (within experimental error) between our data and that of Robinson et al.[49] However, the data of Laszlo and co-workers[33] for the NO_2 and CN substituents differ from the other two sets by more than the maximum expected experimental error of ±0.2 ppm. Since these are the only two electron-accepting substituents included in the DSP analyses, errors in their SCS values markedly affect the correlations.

DSP analysis of our data gives a good correlation (eq 2)

$$\delta^{c} = -4.1\sigma_{I} - 0.7\sigma_{R}^{-} \quad \mathrm{SD} = 0.19 \quad f = 0.11 \qquad (2)$$

provided that the SCS for the NMe_2 substituent is excluded. The observed SCS value for the NMe_2 substituent differs from that predicted from eq 2 by about 8 times the standard deviation, and we have checked that it is not a concentration effect by measuring the shift at a concentration of less than 1% w/v. We suggest that the two highly electron-deficient nitrile groups induce a large through-conjugation effect, hence modifying the electronic properties of this substituent (and hence its SCS value). Similar suggestions have been made by other authors.[22] This conclusion is also implicit in Laszlo's study.[33]

In conclusion, we reemphasize the following points. (1) While in *some* situations there might be no significant improvement in fits obtained by the DSP method compared with single parameter treatments, this is not so in the general case. (2) The ρ_I and ρ_R values obtained from a DSP analysis are extremely useful in assigning mechanistic significance to proposed pathways for the transmission of substituent effects. (3) The SCS data for the two carbonyl groups in **3–5** provide evidence that π-polarization effects may be transmitted (partially) via molecular lines of force.

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Registry No. 2 (X = NMe_2), 2826-28-0; 2 (X = OMe), 2826-26-8; 2 (X = F), 2826-22-4; 2 (X = Br), 2826-24-6; 2 (X = Me), 2826-25-7; 2 (X = H), 2700-22-3; 2 (X = CN), 36937-92-5; 2 (X = NO_2), 2700-23-4.

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(49) Robinson, C. N.; Slater, C. D.; Covington, J. S.; Chang, C. R.; Dewey, L. S.; Franceschini, J. M.; Fritzsche, J. L.; Hamilton, J. E.; Irving, C. C.; Morris, J. M.; Norris, D. W.; Rodman, L. E.; Smith, V. I.; Stablein, G. E.; Ward, F. C. *J. Magn. Reson.* **1980**, *41*, 293.

Carbon-13 Nuclear Magnetic Resonance Spectra of 7-Heterotetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptanes. Annelation Effects of Aziridine, Oxirane, and Thiirane Rings. Unusual γ and δ Substituent Effects

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The ^{13}C NMR spectra of 7-heterotetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptanes and of the 7-methyl- and 7-phenyltetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptanes have been measured, and the three-membered-ring annelation effects were determined. The unusual deshielding found for the C-3 resonance in a cyclopropane-annelated cyclopentane derivative (bicyclo[3.1.0]hexane derivative) in the chair conformation carries an even stronger effect in the analogous aziridine-, oxirane-, and thiirane-annelated systems. Substituents in the 7-position of tetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptanes exert unprecedented long-range effects. Literature data of dehydroadamantanes, dehydronoradamantane, [3.3.1]- and [3.1.1]propellanes containing bicyclo[3.1.0]hexane systems are summarized and discussed from the viewpoint of cyclopropane annelation.

In a ^{13}C NMR spectroscopic investigation of the two tricyclo[3.2.1.0^{2,4}]octenes **42** and **44**, Tori et al.[1] discovered two cyclopropane annelation effects, which are observed intramolecularly in tetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptane (1) in

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