

**X-ray Crystal Structure Analysis of 14.** Suitable crystals of 14 formed from ethyl acetate-hexane mixtures with space group symmetry of *P1* and cell constants of  $a = 9.699$  (2) Å,  $b = 12.688$  (4) Å,  $c = 8.122$  (3) Å,  $\alpha = 96.41$  (3)°,  $\beta = 110.88$  (2)°, and  $\gamma = 77.74$  (2)° for  $Z = 2$  and a calculated density of 1.353 g/cm<sup>3</sup>. Of the 2503 reflections measured with an automatic four-circle diffractometer equipped with Cu radiation, 2138 were observed ( $I \geq 3\sigma I$ ). The function  $\sum \omega(|F_o| - |F_c|)^2$  was minimized to give an unweighted residual of 0.057. Tables IV, V, and VI containing the final fractional coordinates, temperature parameters, bond distances, and bond angles are available as supplementary material.

**Acknowledgment.** We thank Drs. S. Danishefsky, G. Hartman, and D. Claremon for helpful discussions held during the course of this work. We are indebted to John Moreau for microanalytical combustion analysis, J. Murphy

for selected NMR spectra, and M. Banker for typing the manuscript. Dr. S. Pitzemberger carried out the NMR studies on 9 and 13.

**Registry No.** 1, 96557-29-8; 2, 98014-99-4; 3, 98015-09-9; 4, 98015-00-0; 5, 96575-49-4; 6, 98015-10-2; 7, 98015-17-9; 8, 98015-01-1; 9, 98015-03-3; 12, 98015-06-6; 13, 98015-04-4; 14, 98015-11-3; 16, 98015-02-2; 17, 98015-05-5; 18, 98015-12-4; 19, 98015-18-0; 20, 7507-86-0; 21, 98015-08-8; 22, 610-93-5; 23, 77619-93-3; 24, 98015-13-5; 25, 98015-16-8; ethylene glycol, 98015-07-7; methyl acetoacetate, 105-45-3; methyl 3-aminocrotonate, 14205-39-1; 2-[1,3-dithian-2-yl]-5-nitrobenzyl alcohol, 98015-14-6; 2-[1,3-dithian-2-yl]-5-nitrobenzaldehyde, 98015-15-7.

**Supplementary Material Available:** Tables of the atomic positional and thermal parameters, bond distances, and bond angles for 14 and 16 (10 pages). Ordering information is given on any current masthead page.

## A Comparison of Single- and Dual-Parameter Equations in the Correlation of Carbon-13 Shifts in Substituted Styrenes

Carl D. Slater\*

*Department of Physical Sciences, Northern Kentucky University, Highland Heights, Kentucky 41076*

Charles N. Robinson,\* Russell Bies, David W. Bryan, Kimun Chang, Andy W. Hill, William H. Moore, Jr., Teresa G. Otey, Mary L. Poppelreiter, John R. Reisser, Gregory E. Stablein, Vayden P. Waddy, III, William O. Wilkinson, and William A. Wray

*Department of Chemistry, Memphis State University, Memphis, Tennessee 38152*

Received February 21, 1985

<sup>13</sup>C chemical shifts of  $\beta$ -carbon atoms in 17 series of substituted styrenes have been used to establish  $\sigma^{13}$  substituent constants for nine para and seven meta substituents. The  $\sigma^{13}$  values are similar to  $\sigma^+$  values for electron-donating substituents, but are somewhat elevated for the cyano and nitro groups in both meta and para positions. Despite this, the use of mixed constants,  $\sigma^+$  for electron donors and  $\sigma^-$  for electron withdrawers, does not enhance the correlations. In dual substituent parameter (DSP) treatments, Swain's field and resonance parameters,  $F$  and  $R$ , give very slightly better correlations than do Taft's parameters,  $\sigma_1$  and any one of the four standard  $\sigma_R$  scales. The Swain and Taft approaches agree closely on the relative amounts of electron supply and demand through resonance and field effects. The  $\sigma^{13}$  scale based on  $\beta$ -carbon shifts fails completely to correlate the shifts of the  $\alpha$ -carbon atoms. In this case, Swain's parameters are clearly superior to any combination of the Taft sets. These results suggest that, at least for the 289 compounds comprising the data set reported here, the use of multiple resonance scales in DSP treatments is perhaps unjustified.

The number of observations that <sup>13</sup>C chemical shifts in various series of substituted benzenes correlate well with Hammett-type substituent constants is sufficient to suggest that the use of shift data can provide a convenient way to determine such constants.<sup>1-8</sup> Despite this, attempted correlations of shifts of the carbons in an aromatic ring are sometimes unsatisfactory,<sup>9</sup> perhaps because of substituent anisotropies that are not handled by the usual substituent constants. Consequently, attention has been directed toward substituted styrenes,<sup>3-5,8,10-17</sup> in which the side-chain

carbons are far enough removed from the substituents to minimize anisotropic effects yet electrical effects can still be reliably transmitted to them by virtue of extended conjugation. In these series, the chemical shifts of  $\alpha$ -carbon atoms typically show a very narrow range and a "reverse" correlation that is interpretable in terms of substituent-induced charge alternation throughout the carbon skeleton.<sup>14</sup> Those of the  $\beta$ -carbons, however, usually show a fairly wide range and an excellent correlation of expected

(1) Dhami, K. S.; Stothers, J. B. *Can. J. Chem.* **1967**, *45*, 233-238. This article contains leading references to earlier work.

(2) Bromilow, J.; Brownlee, R. T. C. *Tetrahedron Lett.*, **1975**, 2113-2114.

(3) Posner, T. B.; Hall, D. C. *J. Chem. Soc., Perkin Trans. 2* **1976**, 729-732.

(4) Happer, D. A. R. *Aust. J. Chem.* **1976**, *29*, 2607-2614.

(5) Cornelis, A.; Lambert, S.; Laszlo, P. *J. Org. Chem.* **1977**, *42*, 381-382.

(6) Ray, G. J.; Kurland, R. J.; Colter, A. J. *Tetrahedron* **1971**, *27*, 735-752.

(7) Robinson, C. N.; Irving, C. C. *J. Heterocyclic Chem.* **1979**, *16*, 921-923.

(8) Reynolds, W. F.; Gomes, A.; Maron, A.; MacIntyre, D. W.; Tanin, A.; Hamer, G. K.; Peat, I. R. *Can. J. Chem.* **1983**, *61*, 2376-2384.

(9) Briggs, J. M.; Randall, E. W. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1789-1791.

(10) Hamer, G. K.; Peat, I. R.; Reynolds, W. F. *Can. J. Chem.* **1973**, *51*, 897-915.

(11) Happer, D. A. R.; McKerrow, S. M.; Wilkinson, A. L. *Aust. J. Chem.* **1977**, *30*, 1715-1725.

(12) Krabbenhoft, H. O. *J. Org. Chem.* **1978**, *43*, 1830-1832.

(13) Bromilow, J.; Brownlee, R. T. C. *J. Org. Chem.* **1979**, *44*, 1261-1263.

(14) Robinson, C. N.; Slater, C. D.; Covington, J. S.; Chang, C. R.; Dewey, L. S.; Franceschini, J. M.; Norris, D. W.; Rodman, L.; Smith, V. I.; Stablein, G. E.; Fritzsche, J. L.; Hamilton, L.; Irving, C. C.; Morris, J. M.; Ward, F. E. *J. Magn. Res.* **1980**, *41*, 293-301.

(15) Cornelis, A.; Lambert, S.; Laszlo, P.; Schaus, P. *J. Org. Chem.* **1981**, *46*, 2130-2134.

(16) Craik, D. J.; Brownlee, R. T. C.; Sadek, M. *J. Org. Chem.* **1982**, *47*, 657-661.

(17) Reynolds, W. F.; Gomes, A.; Maron, A.; MacIntyre, D. W.; Maunder, R. G.; Tanin, A.; Wong, H.; Hamer, G. K.; Peat, I. R. *Can. J. Chem.* **1983**, *61*, 2367-2375.

slope. Nonetheless, debate centers on whether a single<sup>5,15</sup> or dual<sup>10,16,17</sup> parameter form should be used for the correlations and on which set of substituent constants should be employed in which approach. The arguments are complicated by the fact that the best empirical correlation may be the most objectionable to some on theoretical grounds. Craik and Brownlee have recently reviewed the work on styrenes.<sup>18</sup>

In an early paper, Hamer, Peat, and Reynolds<sup>10</sup> argued that the dual substituent parameter approach is required for satisfactory analysis of <sup>13</sup>C spectra of substituted styrenes, and this contention has been supported recently by Craik, Brownlee, and Sadek.<sup>16</sup> Subsequently, Reynolds and co-workers<sup>8,17</sup> have shown by factor analysis and target testing that Taft's  $\sigma_1$  and  $\sigma_R^0$  parameters<sup>19</sup> provide excellent correlations for these systems. In fact, these authors used their styrene data to refine  $\sigma_1$  and  $\sigma_R^0$  values. Following the suggestion of Reynolds,<sup>20</sup> who attempted to show that  $\sigma_1$  correlates field effects exclusively, they redesignated  $\sigma_1$  as  $\sigma_F$  and reported values for  $\sigma_F$  and  $\sigma_R^0$  that were thought to represent a complete separation of field and resonance effects. As a result of a long-standing concern that resonance effects may vary depending upon electron demand,<sup>21-23</sup> Reynolds and Topsom<sup>22</sup> and Reynolds et al.<sup>21</sup> continue to recommend that resonance scales for intermediate demands be set up based on interpolation between  $\sigma_R^0$  and  $\sigma_R^+$  or  $\sigma_R^-$ . This general approach has led to proposals of three-parameter equations<sup>24-26</sup> and of more complex expressions involving two parameters.<sup>27-29</sup> At present, there seems to be no generally accepted way to apply this approach. Craik and Brownlee, in their review,<sup>18</sup> state that it is the usual practice to perform four separate correlations, each with a different resonance scale, and then select the one that yields the best fit of the experimental data. Although this procedure may afford good correlations, it is certainly open to criticism on predictive grounds.

An alternative dual-parameter treatment that has not yet been fully explored with styrenes is that of Swain and Lupton.<sup>30</sup> These authors felt that regardless of electron demand, correlation of substituent effects should be possible by some combination of universally applicable field and resonance parameters. Recently, Swain, Unger, Rosenquist, and Swain<sup>31</sup> have presented an extensive set of refined parameters toward this end. This treatment has been criticized both from the standpoint of theory<sup>22,23</sup> and because the field parameter was felt to be lacking in correlative ability.<sup>32</sup> Despite this, Swain<sup>33</sup> considers that the

evidence cited as vitiating his approach is less compelling than alleged.

Treatments of styrene shifts by means of a single substituent parameter have also been described. Cornelis, Lambert, and Laszlo<sup>5</sup> found excellent correlations for the  $\beta$ -carbon atoms in one series with the  $\sigma^+$  values of Okamoto and Brown. They suggested, in fact, that  $\sigma^+$  values could be obtained this way. In response to criticism by Bromilow and Brownlee,<sup>13</sup> the authors then showed that, at least in four series, the single substituent parameter treatment gave better correlations than did dual substituent parameter approaches, although a theoretical interpretation was not offered. In contrast, Krabbenhoft's work with  $\beta,\beta$ -dichlorostyrenes suggested that electron-withdrawing groups can produce shifts that are best correlated by the use of  $\sigma^-$  values.<sup>12</sup> This was interpreted to mean that the resonance effect produced by either type of substituent makes the principal contribution to total electron density variation in a given series and that correlations may require "mixed" substituent constants.

In our own previous work,<sup>14</sup> we utilized 12 series of para-substituted styrenes to assess further the  $\sigma^+$  correlations of Laszlo et al. Chemical shifts of the  $\beta$ -carbon atoms were used to derive a substituent constant scale referred to as  $\sigma^{13}$ . The  $\sigma^{13}$  values for electron donors corresponded quite closely to  $\sigma^+$  values, but those for electron-withdrawing groups deviated from accepted  $\sigma$  ( $\sigma^+$ ) values. Of the 12 series employed, unfortunately only 3 included the cyano substituent. Accordingly, the statistical significance of the  $\sigma^{13}$  value found for this group was suspect, and it was not possible to evaluate fully the use of mixed constants, as suggested by Krabbenhoft. However, it was noted that the use of  $\sigma^-$  for the nitro group and  $\sigma^+$  for the others did not lead to generally improved correlations. Consequently, it was felt that  $\sigma^{13}$  values would be better predictors in NMR correlative work than would any other single or mixed substituent scale. Dual-parameter correlations were not attempted.

To permit a more complete evaluation of the various treatments possible, we have selected 17 series of substituted styrenes and used them to assess  $\sigma^{13}$  constants for 16 para and meta substituents. These include *p*-phenyl, which was not utilized in our previous study, *p*-cyano, and seven meta substituents, as well as the seven para substituents used in all the previously reported series. Accordingly, we now report the results for the 16 substituents in 7 new series and an elaboration of 10 previously reported series to include all 16 substituents. Including the parent, unsubstituted compounds, 289 substances are reported in this data set.

## Compounds

The styrenes employed were synthesized as previously described.<sup>14</sup> Substituted benzaldehydes, **1**, were condensed with appropriate compounds, **2**, containing an active methylene group to give the correspondingly substituted styrenes, **3-21**. Series **3-14** with para substituents **a-i** were reported in the previous study, although substituent **h** was included only in series **4, 7, and 8**. The present analyses are based on all substituents **a-ii** and all series except **5 and 14**, were not extended to include the additional substituents. (See Scheme I.) Spectra were obtained by means of a Varian CFT-20 spectrometer. Samples consisted of 0.5 g of the compound dissolved in 1.5 mL of CDCl<sub>3</sub> with Me<sub>4</sub>Si added as an internal standard. In a few cases of lower solubility, undissolved compound was fil-

(18) Craik, D. J.; Brownlee, R. T. C. *Prog. Phys. Org. Chem.* **1983**, *14*, 1-73.

(19) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1-80.

(20) Reynolds, W. F. *Prog. Phys. Org. Chem.* **1983**, *14*, 165-203.

(21) Reynolds, W. F.; Dais, P.; MacIntyre, D. W.; Topsom, R. D.; Marriott, S.; von Nagy-Felsobuki, E.; Taft, R. W. *J. Am. Chem. Soc.* **1983**, *105*, 378-384.

(22) Reynolds, W. F.; Topsom, R. D. *J. Org. Chem.* **1984**, *49*, 1989-1992.

(23) Hofnagel, A. J.; Oosterbeek, W.; Wepster, B. M. *J. Org. Chem.* **1984**, *49*, 1993-1997.

(24) Van Bekkum, H.; Verkade, P. E.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1959**, *78*, 815-850.

(25) Weeks, G.; Horak, V. *J. Org. Chem.* **1980**, *45*, 2068-2071.

(26) Yukawa, Y.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 971-981.

(27) O'Brien, M.; More O'Ferrall, R. A. *J. Chem. Soc., Perkin Trans.* **2** **1978**, 1045-1053.

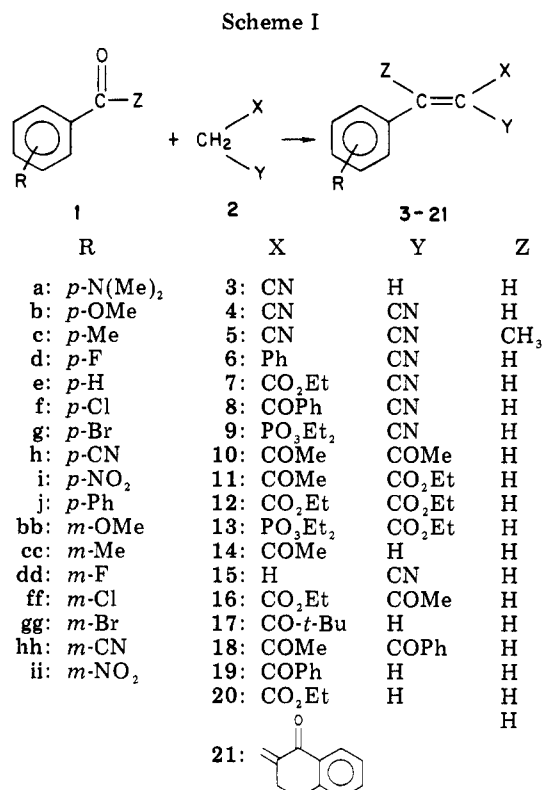
(28) Happer, D. A. R.; Wright, G. J. *J. Chem. Soc., Perkin Trans.* **2** **1979**, 694-698.

(29) Bromilow, J.; Brownlee, R. T. C.; Craik, D. J.; Sadek, M.; Taft, R. W. *J. Org. Chem.* **1980**, *45*, 2429-2438.

(30) Swain, C. G.; Lupton, E. C., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 4328-4337.

(31) Swain, C. G.; Unger, S. H.; Rosenquist, N. R.; Swain, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 492-502.

(32) Charton, M. *J. Org. Chem.* **1984**, *49*, 1997-2001.



tered off before the Me<sub>4</sub>Si was added. Concentration effects have been shown to be negligible for compounds of this type.<sup>3</sup> Chemical shifts are reported as ppm downfield from Me<sub>4</sub>Si. Assignments were made based on a combination of predicted chemical shift, peak height, and/or off-resonance decoupling.<sup>34</sup> Absorptions due to side-chain carbons were assigned in a straightforward manner, although distinguishments among ring carbons were sometimes more difficult. Chemical shifts for the β-carbon atom in all 17 series are summarized in Table S-I. Those for the α-carbon atoms of the para-substituted series are collected in Table S-II.

### Statistical Methods

The coefficient of determination,  $R^2$ , or the derived correlation coefficient, usually denoted as  $r$  for correlations involving a single variable and  $R$  for those utilizing multiple variables, have been the most common assessments of goodness-of-fit. Other measures have been introduced in an effort to spread the values of the indicator, which has been felt to be desirable in those instances where a high degree of correlation exists. For example, Ehrenson, Brownlee, and Taft<sup>19</sup> recommended the use of the  $f$  statistic and Ehrenson<sup>35</sup> has presented a detailed justification. This statistic has been applied in several publications.<sup>13,15,16,18,36</sup> Nonetheless, the relationship between  $f^2$  and  $R^2$  merits comment.

The defining equation for  $R^2$  can be rewritten as eq 1,

$$\frac{\sum(P_i - \hat{P}_i)^2 / \sum(P_i - \bar{P})^2}{\sum(P_i - \bar{P})^2} = 1 - R^2 \quad (1)$$

$$f = (\sum(P_i - \hat{P}_i)^2 / n)^{1/2} / (\sum P_i^2 / n)^{1/2} \quad (2)$$

in which  $P_i$  represents the observed value of the property,  $\bar{P}$  is the mean value of the observations, and  $\hat{P}$  is the

predicted value for each observation based on the least-squares treatment.<sup>37</sup> The  $f$  statistic is defined according to Ehrenson in eq 2.<sup>35</sup> The use of a zero-intercept correlating equation would require the replacement of the  $P_i$  term in the denominator by  $P_i - P_H$ , in which  $P_H$  is the observed value for the parent, unsubstituted compound to be used as a reference. Similar substitutions into the numerator would leave this part of the expression unchanged due to cancellation of two  $P_H$  terms. By making the substitutions and squaring, we obtain eq 3. Cornelis,

$$f^2 = \frac{\sum(P_i - \hat{P}_i)^2}{\sum(P_i - P_H)^2} \quad (3)$$

Lambert, Laszlo, and Schaus<sup>15</sup> have pointed out that  $f$ , as it would be applied in eq 2 to the analysis of substituent-induced chemical shifts, depends upon the choice of an origin for the chemical shift scale and upon the location of the range of measurement with respect to a predetermined zero. To circumvent this, they normalized their SCS values by referring them to the unsubstituted system through the application of eq 3. By comparing eq 1 and 3, however, we note that  $f^2$  approaches  $1 - R^2$  as  $\bar{P}$  approaches  $P_H$ . In the data presented in this report,  $\bar{P}$  never differed from  $P_H$  by more than  $\pm 2\%$  and with the para series agreement was usually much closer. This correspondence can be expected in any data set that includes a reasonable number of both electron-withdrawing and electron-donating substituents. Consequently, the  $f$  statistic does not appear to offer any information not contained in  $R^2$ . As Ehrenson has pointed out, all proposed indices of goodness-of-fit ultimately refer to residuals minimized by linear or linearized least-squares procedures.<sup>35</sup> Thus, in our view, the introduction of new indices should be discouraged. Accordingly, we have opted to include the measurement for the unsubstituted compound as a single data point in each series and to utilize a more conventional statistical comparison than  $f$  values.

Analyses were done with the REG procedure incorporated in the statistical analysis system package available from the SAS Institute.<sup>38</sup> The  $\bar{R}^2$  values reported herein are coefficients of determination that have been adjusted for the degrees of freedom for error.  $\bar{R}^2$  is calculated according to eq 4.<sup>39</sup> We note that as residuals become

$$\bar{R}^2 = 1 - (1 - R^2)(n - 1) / dfe \quad (4)$$

progressively smaller,  $R^2$  approaches unity less rapidly than does its square root, the correlation coefficient. Similarly, the correction for degrees of freedom tends to retard the approach of  $\bar{R}^2$  to unity. The use of  $R^2$  and  $R$  as a standard for goodness-of-fit has been criticized as favoring those correlations that contain fewest data points.<sup>40</sup> This criticism applies less to  $\bar{R}^2$ .

### $\sigma^{13}$ Substituent Constants

The  $\sigma^{13}$  scale was defined according to eq 5, in which  $\delta_X$

$$\sigma_X^{13} = a(\delta_X - \delta_H) \quad (5)$$

and  $\delta_H$  represent the chemical shifts of the β-carbon atoms in the substituted and unsubstituted compounds, respectively, and  $a$  is a scaling factor introduced to set the value for the *p*-dimethylamino group to  $-1.75$ .<sup>14</sup> This scaling ensures that the  $\sigma^{13}$  values will be in the same range as

(33) Swain, C. G. *J. Org. Chem.* 1984, 49, 2005-2010.

(34) Levy, G. C.; Lichter, R. L.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance", 2nd ed.; Wiley-Interscience: New York, 1980.

(35) Ehrenson, S. *J. Org. Chem.* 1979, 44, 1793-1797.

(36) Bromilow, J.; Brownlee, R. T. C.; Topsom, R. D.; Taft, R. W. *J. Am. Chem. Soc.* 1976, 98, 2020-2022.

(37) McClave, J. T.; Dietrich, F. H., Jr. "Statistics"; Dellen Publishing Co.: San Francisco, 1979; p 503.

(38) SAS Institute Inc., Box 8000, Cary, NC 27511.

(39) "SAS User's Guide: Statistics"; SAS Institute Inc.: Cary, NC, 1982; p 69.

(40) Wold, S.; Sjöström, M. in "Correlation Analysis in Chemistry"; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; Chapter 1.

Table I. Substituent Constants<sup>a</sup>

| substituent                  | $\sigma$ | $\sigma^+$ | $\sigma^-$ | $\sigma^{13}$ |
|------------------------------|----------|------------|------------|---------------|
| <i>p</i> -N(Me) <sub>2</sub> | -0.83    | -1.7       | -0.83      | -1.75         |
| <i>p</i> -OMe                | -0.27    | -0.78      | -0.27      | -0.74 ± 0.03  |
| <i>p</i> -Me                 | -0.17    | -0.31      | -0.17      | -0.30 ± 0.03  |
| <i>p</i> -Ph                 | -0.01    | -0.18      | -0.01      | -0.10 ± 0.03  |
| <i>p</i> -F                  | 0.06     | -0.07      | 0.06       | -0.05 ± 0.02  |
| H                            | 0.00     | 0.00       | 0.00       | 0.00          |
| <i>p</i> -Cl                 | 0.23     | 0.11       | 0.23       | 0.13 ± 0.05   |
| <i>p</i> -Br                 | 0.23     | 0.15       | 0.23       | 0.15 ± 0.05   |
| <i>p</i> -CN                 | 0.66     | 0.66       | 0.90       | 0.85 ± 0.15   |
| <i>p</i> -NO <sub>2</sub>    | 0.78     | 0.78       | 1.24       | 1.01 ± 0.19   |
| <i>m</i> -Me                 | -0.07    | -0.07      | -0.07      | -0.07 ± 0.01  |
| <i>m</i> -OMe                | 0.12     | 0.12       | 0.12       | 0.05 ± 0.03   |
| <i>m</i> -F                  | 0.34     | 0.34       | 0.34       | 0.35 ± 0.05   |
| <i>m</i> -Cl                 | 0.37     | 0.37       | 0.37       | 0.36 ± 0.05   |
| <i>m</i> -Br                 | 0.39     | 0.39       | 0.39       | 0.36 ± 0.06   |
| <i>m</i> -CN                 | 0.56     | 0.56       | 0.56       | 0.69 ± 0.10   |
| <i>m</i> -NO <sub>2</sub>    | 0.71     | 0.71       | 0.71       | 0.79 ± 0.12   |

<sup>a</sup>  $\sigma$ ,  $\sigma^+$ , and  $\sigma^-$  values were taken from ref 41.

other types of  $\sigma$  constants and that the calculated values from each reaction series are similarly scaled. The  $\sigma^{13}$  value resulting from this definition was calculated for each substituent in all series of compounds, and the mean values are collected in Table I. For comparison,  $\sigma$ ,  $\sigma^+$ , and  $\sigma^-$  values are also shown.<sup>41</sup> Alternative approaches in which the  $\sigma^{13}$  scale was developed by anchoring the value for the *p*-nitro group to either  $\sigma$  or  $\sigma^-$ , or by anchoring the value for the *p*-dimethylamino group to its  $\sigma$  value, resulted in  $\sigma^{13}$  values for all other substituents that agree less well with any other scale and show larger standard deviations.

A comparison of the  $\sigma^{13}$  values for para substituents with the previously reported ones is interesting. The incorporation of the new series into the analysis results in essentially no change in the value for electron donors and halogens, although in several instances the standard deviations are very slightly improved. To the contrary, the value for the *p*-nitro group is changed from 0.94 to 1.01, and the standard deviation is now somewhat larger than previously found. Similarly, the value for the *p*-cyano group, formerly based on only three series, is changed from 0.68 to 0.85. The *p*-cyano value now more nearly matches  $\sigma^-$  than  $\sigma$ , but that for the *p*-nitro group is virtually the mean of  $\sigma^-$  and  $\sigma$ .

The  $\sigma^{13}$  values established for meta substituents are also given in Table I. These values were developed using the same scaling procedure employed with para substituents; i.e., in a given series the  $\sigma$  value established from the shifts of the *p*-dimethylamino and the unsubstituted compounds was also used to calculate  $\sigma^{13}$  values for meta substituents. As anticipated, they agree quite closely with the standard  $\sigma$  values, but, again, those for the nitro and cyano groups are slightly elevated.

### Correlations

A number of different correlative methods were tried. The single- and dual-parameter treatments were based on eq 6–8. Equation 6 represents the standard, single-parameter Hammett equation, while eq 7 and 8 refer to the

$$\delta_X = \rho\sigma_X + h \quad (6)$$

$$\delta_X = \rho_I\sigma_I + \rho_R\sigma_R + \delta_0 \quad (7)$$

$$\delta_X = fF + rR + h \quad (8)$$

parameter Hammett equation, while eq 7 and 8 refer to the

Table II. Correlation Summary for  $\beta$ -Carbon Atom<sup>a</sup>

| type of parameter <sup>b</sup> |                  | type of substituent |                 |
|--------------------------------|------------------|---------------------|-----------------|
| $F_X$                          | $R_X$            | para                | meta            |
|                                | $\sigma^{13}$    | 0.9955 (0.9882)     | 0.9976 (0.9932) |
|                                | $\sigma_I$       | 0.8165 (0.7770)     | 0.9165 (0.8770) |
| $\sigma_F$                     | $\sigma_R^0$     | 0.9330 (0.8974)     | 0.9796 (0.9708) |
| $\sigma_I$                     | $\sigma_R^0$     | 0.9300 (0.8929)     | 0.9815 (0.9705) |
| $\sigma_I$                     | $\sigma_{R(BA)}$ | 0.9548 (0.9218)     | 0.9915 (0.9787) |
| $\sigma_I$                     | $\sigma_R^+$     | 0.9915 (0.9837)     | 0.9825 (0.9670) |
| $\sigma_I$                     | $\sigma_R^\pm$   | 0.9865 (0.9699)     | 0.9942 (0.9864) |
| $F$                            | $R$              | 0.9931 (0.9821)     | 0.9906 (0.9815) |

<sup>a</sup> The values given are the mean adjusted coefficients of determination,  $\bar{R}^2$ , for all 17 series studied. The values in parentheses are those for the poorest correlation of the 17. <sup>b</sup>  $\sigma^{13}$  values are those reported in this study.  $\sigma_I$ ,  $\sigma_{R(BA)}$ ,  $\sigma_R^+$ , and  $\sigma_R^\pm$  values were those of Ehrenson, Taft, and Brownlee, taken from ref 19.  $\sigma_R^\pm$  used the  $\sigma_R^-$  values for cyano and nitro groups and  $\sigma_R^+$  for all others.  $\sigma_F$  and  $\sigma_R^0$  values were those of Reynolds et al.<sup>8</sup> Because these authors did not report a  $\sigma_R^0$  value for the phenyl group, analyses using  $\sigma_R^0$  did not include this substituent.  $F$  and  $R$  values are those of Swain, Unger, Rosenquist, and Swain.<sup>31</sup>

Taft and Swain dual-parameter approaches, respectively. For each of the 17 series, meta- and para-substituted compounds were analyzed separately. The unsubstituted, parent compound was included in all series. Consequently, each para series was comprised of 10 compounds and each meta series had 8. The correlations for para and meta substituents in each series are given in Tables S-III and S-IV, respectively, and are summarized in Table II. The columns headed  $F_X$  and  $R_X$  contain the type of field or inductive and resonance parameter employed in each case. The  $\sigma_R^\pm$  parameter given for one of the Taft treatments used Taft's  $\sigma_R^-$  values for the cyano and nitro substituents and his  $\sigma_R^+$  values for all others.<sup>19</sup> The adjusted coefficients of determination,  $\bar{R}^2$ , shown in the table are the average for all 17 data sets. The  $\bar{R}^2$  for the poorest correlation in each set is given in parentheses.

Several conclusions can be drawn from this table. For both meta and para substituents, the  $\sigma^{13}$  scale appears to afford the best correlations, but other treatments may be very nearly as good. Of the dual parameter approaches for para substituents, both Swain's  $F$  and  $R$  and Taft's  $\sigma_I$  and  $\sigma_R^+$  parameters give excellent correlations. For meta substituents, Swain's parameters again give excellent results, but of the Taft treatments, the  $\sigma_I$  and  $\sigma_{R(BA)}$  as well as  $\sigma_I$  and  $\sigma_R^\pm$  sets give excellent correlations that are superior to those afforded by the other Taft sets. It should be noted that  $\sigma_I$  and  $\sigma_R^0$ , along with the revised  $\sigma_F$  and  $\sigma_R^0$ , give poorer correlations. This contrasts with the previous reports of Reynolds and his co-workers.<sup>8,10,17</sup> Parenthetically, it should be mentioned for those accustomed to standard correlation coefficients that the worst-case correlation among the seven cited above ( $\bar{R}^2 = 0.9787$ ) shows a multiple correlation coefficient,  $R$ , of 0.9924. Accordingly, on the basis of correlative ability alone, there is little reason to designate any of the three general approaches with either meta or para substituents as being clearly superior when applied to the fairly extensive data reported here.

### Comparison of Treatments

Contrary to the findings of Cornelis, Lambert, Laszlo, and Schaus<sup>15</sup> and in accord with those of Craik, Brownlee, and Sadek,<sup>16</sup> the single-parameter treatment of our data does not provide correlations significantly superior to those of the dual-parameter treatments. Interestingly, this is so even if the single parameter is a very carefully selected one that is based solely on the data to be analyzed. The differences in goodness-of-fit found here would clearly not justify the promulgation of the new set of substituent

(41) (a) Fuchs, R.; Lewis, E. S. In "Techniques of Chemistry", 3rd ed.; Weissberger, A., Ed.; Wiley-Interscience: New York, 1974; Part I Vol 6, p 777–824. (b) Exner, O. In "Correlation Analysis in Chemistry"; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; Chapter 10.

**Table III. Correlation of  $\sigma^{13}$  with Dual Substituent Parameter Sets according to Eq 9<sup>a</sup>**

| substituent type | $\lambda$ | $F_X$      | $\delta$ | $R_X$            | $c$    | $\bar{R}^2$ | $\lambda/\delta$ |
|------------------|-----------|------------|----------|------------------|--------|-------------|------------------|
| para             | 0.485     | $F$        | 0.548    | $R$              | -0.043 | 0.9956      | 0.885            |
|                  | 1.266     | $\sigma_I$ | 1.966    | $\sigma_{R(BA)}$ | -0.063 | 0.9595      | 0.664            |
|                  | 1.313     | $\sigma_I$ | 2.990    | $\sigma_{R^+}$   | 0.008  | 0.9339      | 0.439            |
|                  | 1.117     | $\sigma_I$ | 1.119    | $\sigma_{R^+}$   | 0.023  | 0.9931      | 0.998            |
|                  | 0.880     | $\sigma_I$ | 1.036    | $\sigma_{R^\pm}$ | 0.014  | 0.9905      | 0.848            |
| meta             | 0.660     | $F$        | 0.176    | $R$              | 0.001  | 0.9919      | 3.41             |
|                  | 1.034     | $\sigma_I$ | 0.452    | $\sigma_{R(BA)}$ | -0.007 | 0.9931      | 2.29             |
|                  | 1.040     | $\sigma_I$ | 0.683    | $\sigma_{R^0}$   | 0.012  | 0.9838      | 1.52             |
|                  | 1.022     | $\sigma_I$ | 0.303    | $\sigma_{R^+}$   | 0.008  | 0.9839      | 3.37             |
|                  | 1.135     | $\sigma_F$ | 0.539    | $\sigma_{R^0}$   | -0.017 | 0.9812      | 2.11             |
|                  | 0.957     | $\sigma_I$ | 0.263    | $\sigma_{R^\pm}$ | 0.005  | 0.9960      | 3.64             |

<sup>a</sup> Column headings are explained in the text. Substituent constants were taken from the sources described in Table II.

constants needed to make the single-parameter treatment correlatively competitive. Nonetheless, the  $\sigma^{13}$  scale devised as the best single-parameter treatment can perhaps be used advantageously. Although neither the parameter sets nor the detailed form of the correlating equations are agreed upon, both the Taft and Swain schools of thought urge the separation of electronic effects into field and resonance contributions. Accordingly, it is of interest to examine correlations between  $\sigma^{13}$  values and those of other scales that offer such a separation of effects. This can be done by utilizing eq 9, in which  $F_X$  and  $R_X$  are the field or inductive and resonance parameters. The results of these correlations are given in Table III. Not surprisingly, since the  $\sigma^{13}$  set arose from the measurements reported here, those treatments that best correlate the raw data also

$$\sigma_X^{13} = \lambda F_X + \delta R_X + c \quad (9)$$

best correlate the derived  $\sigma^{13}$  values.

Specifically, for the data on para substituents, Swain's parameters and Taft's  $\sigma_I$  and either  $\sigma_{R^+}$  or  $\sigma_{R^\pm}$  all showed very excellent correlations. The separate assumptions involved in the derivation of Swain's and Taft's parameters and the vigor with which Swain's set has been objected to led to the expectation that they would be largely uncorrelated. Despite this, the  $\lambda/\delta$  ratios in Table III show that the different sets all predict virtually identical field and resonance contributions. With Taft's parameters  $\sigma_I$  and  $\sigma_{R^+}$  give a very slightly better correlation than do  $\sigma_I$  and  $\sigma_{R^\pm}$ , but both sets give a  $\lambda/\delta$  ratio very close to that of the Swain set (0.885). All three ratios are interpretable as meaning that electron supply by substituents requires resonance and field effects in nearly equal proportions, with the resonance effect being only slightly larger (53%).

The data on the meta series, also in Table III, again suggest that the treatments are equivalent. Interestingly, in these cases  $\sigma_I$  and  $\sigma_{R^\pm}$  are definitely superior to  $\sigma_I$  and  $\sigma_{R^+}$ , although  $\sigma_I$  and  $\sigma_{R(BA)}$  give an excellent correlation also. Once again, the  $\lambda/\delta$  ratios from Swain's parameter set and Taft's  $\sigma_I$  and  $\sigma_{R^\pm}$  are nearly identical (3.41 vs. 3.64). This means that from the meta position, the substituent effect is composed of approximately 77% field and 23% resonance contributions. In fact, the  $\sigma_{R(BA)}$  correlation indicates very similar contributions, viz., 70% field and 30% resonance.

Because of the similarities in these results, it was of interest to compare parameter sets directly. For the para substituents employed in this study, regression of  $\sigma_{R^\pm}$  on  $R$  gave an  $\bar{R}^2$  of 0.9591. If only the values for the meta substituents were used, i.e., if the dimethylamino and phenyl groups were excluded, regression of  $\sigma_{R^\pm}$  on  $R$  gave an  $\bar{R}^2$  of 0.9573. Thus, it appears that the Taft  $\sigma_{R^\pm}$  scale

**Table IV.  $\bar{R}^2$  Values for Correlations of Chemical Shifts of  $\alpha$ -Carbons of Para-Substituted Styrenes with Various Substituent Constants<sup>a</sup>**

| series | correlation   |         |                             |                             |                           |                           |
|--------|---------------|---------|-----------------------------|-----------------------------|---------------------------|---------------------------|
|        | $\sigma^{13}$ | $F + R$ | $\sigma_I + \sigma_{R(BA)}$ | $\sigma_I + \sigma_{R^\pm}$ | $\sigma_I + \sigma_{R^0}$ | $\sigma_I + \sigma_{R^+}$ |
| 3      | 0.6017        | 0.9867  | 0.9767                      | 0.9660                      | 0.9767                    | 0.9516                    |
| 4      | 0.0386        | 0.8927  | 0.7095                      | 0.7257                      | 0.6860                    | 0.7462                    |
| 6      | 0.6514        | 0.9915  | 0.9855                      | 0.9709                      | 0.9800                    | 0.9572                    |
| 7      | 0.4751        | 0.9667  | 0.9371                      | 0.9214                      | 0.9386                    | 0.9061                    |
| 8      | 0.6438        | 0.9784  | 0.9743                      | 0.9594                      | 0.9700                    | 0.9395                    |
| 9      | 0.5187        | 0.9684  | 0.9456                      | 0.9295                      | 0.9439                    | 0.9108                    |
| 10     | 0.8067        | 0.9821  | 0.9573                      | 0.9635                      | 0.9822                    | 0.9605                    |
| 11     | 0.8148        | 0.9279  | 0.9236                      | 0.9263                      | 0.9862                    | 0.9144                    |
| 12     | 0.7232        | 0.9936  | 0.9869                      | 0.9814                      | 0.9879                    | 0.9718                    |
| 13     | 0.7928        | 0.9450  | 0.9115                      | 0.9374                      | 0.8931                    | 0.9557                    |
| 15     | 0.4840        | 0.9808  | 0.9584                      | 0.9477                      | 0.9628                    | 0.9377                    |
| 16     | 0.7211        | 0.9840  | 0.9734                      | 0.9723                      | 0.9839                    | 0.9732                    |
| 17     | 0.7686        | 0.9930  | 0.9896                      | 0.9831                      | 0.9873                    | 0.9692                    |
| 18     | 0.7943        | 0.9943  | 0.9897                      | 0.9874                      | 0.9893                    | 0.9760                    |
| 19     | 0.7953        | 0.9965  | 0.9877                      | 0.9865                      | 0.9881                    | 0.9791                    |
| 20     | 0.7077        | 0.9947  | 0.9898                      | 0.9840                      | 0.9893                    | 0.9724                    |
| 21     | 0.8411        | 0.9974  | 0.9891                      | 0.9923                      | 0.9786                    | 0.9874                    |
| mean   | 0.6576        | 0.9749  | 0.9521                      | 0.9491                      | 0.9491                    | 0.9417                    |

<sup>a</sup> Substituent constants were taken from the sources described in Table II.

and the Swain  $R$  scale are actually very similar.

On the other hand, for all substituents employed, regression of  $\sigma_I$  on  $F$  gave an  $\bar{R}^2$  of only 0.8427, whereas for meta substituents only, the corresponding value was 0.9845. Again, it seems that  $\sigma_I$  and  $F$  are also strongly correlated for most common substituents. Unfortunately, it is not possible to comment on the correctness of either scale based on the substituent set employed and the analysis of SCS for only the  $\beta$ -carbon atoms.

#### Correlations for $\alpha$ -Carbon Atoms

The fact that substituents show a "reverse" correlation at the  $\alpha$ -carbon atom offers interesting possibilities. As mentioned, the range of substituent effects at this site is considerably diminished as compared to that at the  $\beta$ -carbon. In the 17 series studied here, the spread of SCS values at the  $\alpha$ -carbon was typically <3 ppm, while that at the  $\beta$ -carbon was ~7-15 ppm. The narrowness of the range of values, the proximity of the  $\alpha$ -carbon to the benzene ring and its associated anisotropic effects, and a preliminary analysis of previous work<sup>14</sup> elicited the expectation that the  $\alpha$ -carbon data would not correlate with substituent constants as well as those for  $\beta$ -carbons. Despite this, the "reverse" effect suggested that perhaps a different substituent scale would be needed for whatever correlation could be found. Consequently, we analyzed the  $\alpha$ -carbon data for para substituents according to the various treatments. The results are collected in Table IV.

This table shows that  $\sigma^{13}$  values based on  $\beta$ -carbon correlations are totally inadequate when applied to  $\alpha$ -carbon shift data. All of the Taft treatments give distinctly poorer results than does that of Swain. The mean  $\lambda/\delta$  ratio from the Swain treatment is 3.982, neglecting that for series 4 which was out of line by a factor of 10. Accordingly, the  $\alpha$ -carbon site requires electron removal, 80% of which is accomplished inductively. This different mix of resonance and inductive requirements causes the  $\sigma^{13}$  constants to correlate poorly, since these were predicated on nearly equal contributions. The diminished significance of resonance effects at the  $\alpha$ -carbons in para-substituted styrenes seems a logical extension of the known diminution of such effects at the meta positions as compared to those at the ortho and para positions in substituted benzenes. Further, although Craik and Brownlee<sup>18</sup> have discussed effects at the  $\alpha$ -carbons in terms of  $\pi$ -polarization operating

through "molecular lines of force", the simple recognition<sup>14</sup> of the alternate charge relay effect described by Pople and Gordon<sup>42</sup> seems adequate to account for gross effects at both  $\alpha$ - and  $\beta$ -carbon atoms.

### Conclusions

The findings reported here are based on an extensive set of substituents that exceeds the requirements for a minimal set to test correlative ability.<sup>19,22</sup> Although a set of substituent constants similar to  $\sigma^+$  values can be devised to give the best correlations with SCS at the  $\beta$ -carbon atom, these constants fail completely when applied to SCS data at the  $\alpha$ -carbon. The DSP approach is therefore mandated. A comparison of currently existing parameters for DSP treatments showed that both the Taft and Swain approaches gave very good results for the  $\beta$ -carbon data. In fact, for the substituents employed, Taft's  $\sigma_{R^{\pm}}$  scale ( $\sigma_{R^+}$  for electron donors and  $\sigma_{R^-}$  for electron withdrawers)

correlates reasonably well with Swain's  $R$  values. The correlation between  $\sigma_I$  and  $F$  is unsatisfactory if the dimethylamino and phenyl groups are included, but excellent if they are excluded. Swain's parameters are definitely superior for the  $\alpha$ -carbon data, where electronic effects are largely (80%) inductive. These results suggest that multiple resonance scales may be unnecessary and, possibly, that the Swain and Taft parameter sets would give nearly identical results if  $\sigma_I$  and  $F$  were more nearly parallel. The discrepancy seems to be in the  $\sigma_I$  value for either the dimethylamino or phenyl group, or both.

**Acknowledgment.** C.D.S. thanks Profs. F. H. Dietrich, Jr., and J. E. McKenney for helpful discussions.

**Supplementary Material Available:** Tables giving the chemical shifts for  $\beta$ -carbon atoms (S-I) in all series and for  $\alpha$ -carbon atoms (S-II) in the para-substituted series, and adjusted correlation coefficients,  $\bar{R}^2$ , for correlations of shifts for  $\beta$ -carbon atoms in each para-substituted series (S-III) and meta-substituted series (S-IV) with various DSP treatments (4 pages). Ordering information is given on any current masthead page.

(42) Pople, J. A.; Gordon, M. J. *Am. Chem. Soc.* 1967, 89, 4253-4261.

## Micellar Effects on the Reaction of (Arylsulfonyl)alkyl Arenesulfonates with Hydroxide Ion. 2.<sup>1</sup> The Absence of Substrate Orientational Effects in a Series of Sulfonates of Different Hydrophobicities

Frank M. Witte and Jan B. F. N. Engberts\*

Department of Organic Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

Received February 21, 1985

Second-order rate constants for nucleophilic attack of hydroxide ion at the sulfonate sulfur atom of a series of sulfonates  $R_1SO_2CH_2OSO_2R_2$  (1a-g) in the presence of CTAB micelles (at 50 °C) have been analyzed in terms of the pseudophase ion-exchange (PPIE) model. It is shown that the catalysis by the micelles is caused by the increased reactant concentrations in the micellar reaction volume. Large variations in the hydrophobicities of the substituents  $R_1$  and  $R_2$  (alkylaryl, alkyl) had only a minor influence on the rate constant for reaction in the micellar pseudophase ( $k_m$ ). The same conclusion holds if the rate constants  $k_m$  are corrected for the different propensities of the sulfonates to respond to changes in the polarity of the reaction medium as expressed in the dielectric constant. Therefore there is no evidence that the depth of penetration and/or the orientation of the sulfonates 1a-g bound to the cetyltrimethylammonium bromide micelles is significantly affected by the hydrophobicities of  $R_1$  and  $R_2$ . These findings are reconcilable with recent views concerning the morphology of micelles.

The rates of a large variety of chemical reactions in aqueous solution are influenced by the presence of micelles.<sup>2</sup> The magnitude of the catalysis (or inhibition) depends crucially on the efficiency of micellar incorporation of the reactant(s) and on the effect of the specific microenvironment at the micellar binding sites, usually located at the micellar surface. In the case of bimolecular reactions, two reactants should bind to the micelle. This may lead to locally increased reactant concentrations and concomitant increased reactivity even if the rate constant in the micellar pseudophase is decreased relative to that

in aqueous solution. Among the various kinetic treatments advanced for the analysis of catalysis by ionic micelles of bimolecular reactions involving a neutral reactant and hydrophilic reactant counterions, the pseudophase ion-exchange (PPIE) model<sup>3</sup> is one of the most successful approaches. But a quantitative analysis of the micellar rate effects is still hampered by several problems including the question of the constancy of counterion binding<sup>4</sup> and the choice of the volume element for reaction in the micellar pseudophase.<sup>5</sup> Mechanistically, the development of a clear picture of micellar catalytic effects hinges also on the availability of a realistic model for the morphology of ionic micelles. Although one should recognize the

(1) Part 1: van de Langkruis, G. B.; Engberts, J. B. F. N. *J. Org. Chem.* 1984, 49, 4152.

(2) (a) Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems"; Academic Press: New York, 1975. (b) Fendler, J. H. "Membrane Mimetic Chemistry"; Wiley-Interscience: New York, 1982; Chapter 12. (c) Sudhölter, E. J. R.; van de Langkruis, G. B.; Engberts, J. B. F. N. *Recl. Trav. Chim. Pays-Bas* 1980, 99, 73. (d) Bunton, C. A. *Catal. Rev. Sci. Eng.* 1979, 20, 1. (e) Mittal, K. L.; Lindman, B., Eds. "Surfactants in Solution"; Plenum Press: New York, 1984; Vol. 1.

(3) Romsted, L. S. In "Micellization, Solubilization, and Microemulsions"; Mittal, K. L., Ed.; Plenum Press: New York, 1977; Vol. 2, p 509.

(4) Compare, for example: Sudhölter, E. J. R.; Engberts, J. B. F. N. *J. Phys. Chem.* 1979, 83, 1854.

(5) Bunton, C. A.; Carrasco, M.; Huang, S. K.; Paik, C. H.; Romsted, L. S. *J. Am. Chem. Soc.* 1978, 100, 5420.