(HFIP–H_2O) vs. −2.60 (HFIP–PDT) on the high end of the reactivity scale. This is not surprising if reactivity is controlled predominantly by the solvent's ionizing power term, Y_{OTs}, as these solvents have similar Y_{OTs} values. What is surprising, however, is the good correlation of all substrates even though in solvents of moderate nucleophilicity and ionizing power (e.g., aqueous alcohols) they represent k_s, k_c, and k_Δ types.[1a] For example, because the nucleophilicity of HFIP–PDT is 3 orders of magnitude greater than that of HFIP–H_2O (N_{OTs} = −1.02 and −4.27, respectively), one would expect the k_s substrates to react faster in HFIP–PDT. It thus appears that, unlike MeOTs, the model k_s substrate used to define the N values, solvent nucleophilicity may be kinetically unimportant for the secondary substrates in these highly electrophilic solvents. However, we cannot rule out the contribution of steric effects on solvent nucleophilicity.[10c,21]

In summary, we have studied various HFIP–PDT compositions, finding that thiols indeed are highly nucleophilic solvents. However, with their poor electrophilicity, solvolytic rates in pure thiols are very low. By mixing them with an electrophilic cosolvent like HFIP, high reaction rates may be obtained. Using the Bentley–Schleyer method of determining solvent ionizing power and nucleophilicity, the HFIP–PDT mixtures were characterized. The low nucleophilicity of HFIP–H_2O and the nonlinearity of our N_{OTs} vs. molar composition plot was attributed to hydrogen bonding to the more nucleophilic oxygen or sulfur atom by the electrophilic cosolvent (or by either solvent in HFIP–H_2O). Secondary substrates, in both 95/5 HFIP–PDT (mol/mol) and 97/3 HFIP–H_2O (w/w), are suggested to react by k_c or k_Δ mechanisms. As more of the nucleophilic cosolvent is added (i.e., either PDT or H_2O, respectively), other evidence would suggest that the normally k_s substrates should become k_s in these binary mixtures.

Experimental Section

Chemicals. Methyl tosylate, obtained commercially (Eastman and Aldrich), was recrystallized. All other tosylates and brosylates were prepared by the standard pyridine method[22] and purified by repeated recrystallization at −70 °C from low boiling petroleum ether. All tosylates and brosylates were stored at −10 °C. All of the sulfonate esters were previously prepared and characterized, hence structures were verified by comparison of melting points, where appropriate, with literature values and by characteristic IR and NMR spectra. Solvents were dried over 3A molecular sieves, purified by distillation, and stored in a desicator.

Kinetics. Rates were determined conductimetrically as previously described[23] but using conductimetric cells with pressure seals (Teflon) to prevent solvent loss. Each kinetic sample contained about 10 mL of solvent ca. 10^{-3} M in substrate and ca. 3 × 10^{-3} M in 2,6-lutidine.

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Registry No. HFIP, 920-66-1; PDT, 109-80-8; MeOTs, 80-48-8; EtOTs, 80-40-0; 2-PrOBs, 24767-70-2; 2-BuOBs, 91799-57-4; 2-BuOTs, 715-11-7; 3-pentyl-OBs, 28691-33-0; 3-Me-2-BuOTs, 26466-06-8; 3,3-Me_2-2-BuOBs, 26325-42-8; cyclopentyl-OTs, 3558-06-3; 2-adamantyl-OBs, 38680-00-1.

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(21) McManus, S. P. *J. Org. Chem.* **1981,** *46,* 635.

(22) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; New York: Wiley: New-York, 1967; p 1179.

(23) Hovanes, B. A.; Harris, J. M.; McManus, S. P. *Am. Lab.* **1984,** *16,* No. 6, 22. McManus, S. P.; Lam, D. H. *J. Org. Chem.* **1978,** *43,* 650.

Comparison of Substituent Constants for Correlation of Nuclear Magnetic Resonance Absorptions of β-Carbon Atoms in Ortho-Substituted Styrenes

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The nuclear magnetic resonance absorptions of β-carbon atoms in ten series of ortho-substituted styrenes have been studied. Each series included the following substituents: methoxyl, methyl, hydrogen, fluoro, chloro, bromo, and nitro. A set of substituent constants based on the present data corresponds fairly well with previously published sets. Dual substituent parameter analyses that neglect steric factors give significantly poorer correlations. Both the Charton and the Fujita–Nishioka three-parameter treatments that incorporate a steric factor give excellent correlations. The magnitude of the steric contribution in the correlations agrees well with expectation based on the total steric environment.

The early literature contains reports that ortho-substituted benzenes show unusual chemical behavior, which led to the belief that ortho substituents might exert both steric and electrical effects at a reaction center.[1] Accordingly, Hammett felt that the usual type of correlation between reactivity and substituent constant might be precluded because such correlations for meta and para substituents presuppose an absence or constancy of steric

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† Based in part on work described in the M.S. Thesis of James L. Horton, Memphis State University, August, 1982.

(1) Charton, M. *Prog. Phys. Org. Chem.* **1971,** *8,* 235–317. This article summarizes earlier work in the field.

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Table I. Carbon-13 Chemical Shifts for β-Carbon Atoms[a]

	substituent						
series	OCH_3	CH_3	F	H	Cl	Br	NO_2
3	120.67	122.00	123.51	120.79	123.39	123.53	125.58
4	122.49	123.05	124.52	122.09	124.63	124.98	127.45
5	81.35	84.18	84.64	82.73	85.82	86.14	88.68
6	126.37	128.04	128.42	126.58	129.06	128.98	130.58
7	102.34	104.67	105.26	103.16	106.32	106.51	108.69
8	109.77	111.76	112.19	110.32	113.32	113.59	115.32
9	118.80	110.34	120.98	118.43	120.98	121.09	123.36
10	134.72	135.53	136.51	134.71	136.92	137.01	138.24
11	96.92	97.11	99.33	96.39	99.08	99.18	101.65
12	94.72	96.85	97.30	95.12	98.23	98.34	100.25

[a] As ppm downfield from Me_4Si. All spectra were recorded from $CDCl_3$ solutions.

effects.[2] Despite this pessimistic view, the development of substituent constants has been explored from a variety of experimental standpoints, designed mainly to minimize steric effects. These have included the study of substances in which the reaction center is physically removed from the substituent but is capable of efficient polar interaction, as in phenylpropiolic acids and esters,[3] the use of polarographic techniques,[4,5] and the analysis of various infrared[6-10] and nuclear magnetic resonance absorptions.[11-16] In many instances, the observed property has correlated well with some particular set of substituent constants, but in some cases steric complications have been claimed.

Charton reviewed this field comprehensively in 1971 and analyzed 265 sets of data using eq 1 and 2. Equation 1

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h \qquad (1)$$

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + \psi r_{V,X} \qquad (2)$$

represents the standard, dual substituent parameter (DSP) treatment of Taft and Lewis,[17] in which the electrical effect of a substituent is factored into inductive and resonance contributions. Equation 2 includes a steric parameter based on the van der Waals radius of the substituent. Of the 265 sets treated, 210 gave what were considered to be significant correlations with eq 1, whereas only 7 required the inclusion of a steric parameter. Charton concluded that (1) the effect of ortho substituents is generally independent of steric effects, (2) it is impossible to define a single generally useful set of ortho substituent constants characteristic of the ortho electrical effect because there is no single pure characteristic ortho electrical effect, and (3) in the general case, the ortho effect is an electrical effect which may apparently be dissected into a normal component and a proximity component peculiar to the ortho position. To accommodate those situations in which a steric effect is found, Charton subsequently defined the steric parameter, ν_X, according to eq 3, showed that ν is

$$\nu_X = r_{V,X} - r_{V,H} \qquad (3)$$

related to the Taft parameter, E_S, and demonstrated convincingly that there is a steric effect in the reaction of ortho-substituted benzoic acids with diazodiphenylmethane.[18,19]

In 1976, Fujita and Nishioka[20] proposed eq 4, in which

$$\log k = \rho\sigma_0 + \delta E_S{}^0 + fF_0 + c \qquad (4)$$

the $\rho\sigma_0$ term is intended to account for the ordinary polar effect and the $\delta E_S{}^0$ and fF_0 terms separate the proximity effect into steric and polar effects, respectively. According to this treatment, para substituent constants are used to represent those for ortho substituents, and the most appropriate set of σ values is selected; i.e., σ, σ^+, σ^-, etc. Fujita and Nishioka, as well as Shorter,[21] have pointed out that correlation with a σ scale and F is equivalent to correlation with F and R. Thus, the Fujita–Nishioka treatment can be reformulated as involving F, R, and a steric term. The similarity between this and Charton's treatment, which involves σ_I, σ_R, and a steric term, is obvious. Accordingly, the major operational difference between the two approaches lies in the selection of the parameters to be utilized in a three-parameter equation. Fujita and Nishioka used the $E_S{}^0$ values of Kutter and Hansch[22] and the F values of Swain and Lupton, as modified by Hansch et al.[23] The innovation in this approach was in the successful treatment of data for ortho, meta, and para substituents with a single equation. Fujita subsequently extended this type of analysis to correlate structure and biological activity.[24]

In previous work we examined the ^{13}C NMR spectra of 17 series of substituted styrenes.[25] Each series incorporated nine para and seven meta substituents, as well as the parent, unsubstituted compound. Excellent correlations were found between the chemical shifts of the β-carbon atoms and a set of substituent constants, σ^{13}, that were

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(2) Hammett, L. P. *Physical Organic Chemistry*; McGraw-Hill Publishing Co.: New York, 1940; p 194.

(3) Solomon, I. J.; Filler, R. *J. Am. Chem. Soc.* **1963**, *85*, 3492–3496.

(4) Zuman, P. *Collect. Czech. Chem. Commun.* **1962**, *27*, 648–666.

(5) Hussey, W.; Diefendorfer, A. *J. Am. Chem. Soc.* **1967**, *89*, 5359–5362.

(6) O'Sullivan, D.; Sadler, P. *J. Chem. Soc.* **1957**, 2839–2840.

(7) Krueger, P.; Thompson, H. *Proc. R. Soc. London, Ser. A* **1959**, *250*, 22–38.

(8) Weigmann, H.; Malewski, G. *Spectrochim. Acta* **1966**, *22*, 1045–1052.

(9) Brooks, C.; Eglinton, G.; Morman, J. *J. Chem. Soc.* **1961**, 106–116.

(10) Forbes, W.; Myron, J. *Can. J. Chem.* **1961**, *39*, 2452–2465.

(11) Diehl, P. *Helv. Chem. Acta* **1961**, *44*, 829–843.

(12) Traynham, J.; Knesel, G. *J. Org. Chem.* **1966**, *31*, 3350–3352.

(13) Dietrich, M.; Nash, J.; Keller, R. *Anal. Chem.* **1966**, *38*, 1479–1484.

(14) Kondo, Y.; Kondo, K.; Takemoto, T.; Ikenoue, T. *Chem. Pharm. Bull.* **1966**, *14*, 1332–1337.

(15) Lynch, B.; MacDonald, B.; Webb, J. *Tetrahedron* **1968**, *24*, 3595–3605.

(16) Tribble, M.; Traynham, J. *J. Am. Chem. Soc.* **1969**, *91*, 379–388.

(17) Taft, R., Jr.; Lewis, I. *J. Am. Chem. Soc.* **1959**, *81*, 5343–5352.

(18) Charton, M. *Prog. Phys. Org. Chem.* **1973**, *10*, 81–204.

(19) Charton, M. *J. Org. Chem.* **1975**, *40*, 407–411.

(20) Fujita, T.; Nishioka, T. *Prog. Phys. Org. Chem.* **1976**, *12*, 49–89.

(21) Shorter, J. In *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; p 153.

(22) Kutter, E.; Hansch, C. *J. Med. Chem.* **1969**, *12*, 647–652.

(23) Hansch, C.; Leo, A.; Unger, S.; Kim, K.; Nikaitani, D.; Lien, E. *J. Med. Chem.* **1973**, *16*, 1207–1216.

(24) Fujita, T. *Anal. Chim. Acta* **1981**, *133*, 667–676.

(25) Slater, C.; Robinson, C.; Bies, R.; Bryan, D.; Chang, K.; Hill, A.; Moore, W.; Otey, T.; Poppelreiter, M.; Reisser, J.; Stablein, G.; Waddy, V.; Wilkinson, W.; Wray, W. *J. Org. Chem.* **1985**, *50*, 4125–4130.

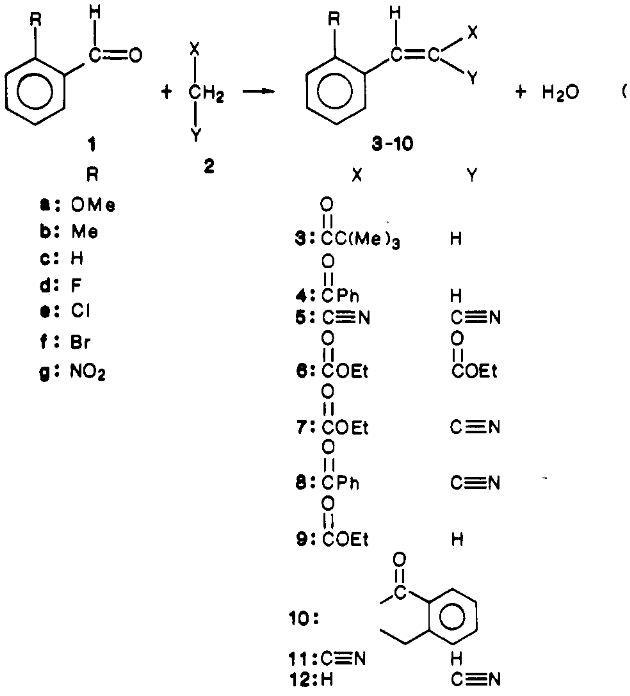
Table II. σ_o^{13} Values

series	substituent OMe	Me	F	Cl	Br	NO_2	r^a
3	−0.04	0.42	0.94	0.90	0.95	1.65	0.9943
4	0.13	0.31	0.79	0.83	0.93	1.74	0.9870
5	−0.22	0.24	0.31	0.50	0.55	0.97	0.9808
6	−0.06	0.39	0.49	0.66	0.64	1.07	0.9900
7	−0.16	0.29	0.40	0.61	0.64	0.98	0.9896
8	−0.11	0.29	0.38	0.61	0.66	1.01	0.9874
9	0.11	0.27	0.77	0.77	0.80	1.48	0.9881
10	0.00	0.29	0.64	0.79	0.82	1.25	0.9966
11	0.13	0.18	0.75	0.68	0.71	1.34	0.9742
12	−0.09	0.41	0.51	0.73	0.76	1.21	0.9904
mean	−0.03 ± 0.12	0.31 ± 0.08	0.60 ± 0.21	0.71 ± 0.12	0.75 ± 0.13	1.27 ± 0.28	0.9878

[a] Correlation coefficient for analysis according to eq 8 using the mean σ_o^{13} values. These analyses included the parent compound and used σ_o^{13} = 0.00 for hydrogen.

average values calculated from the chemical shift data and scaled to resemble other values. The σ^{13} constants closely matched σ^+ values for electron donors, but deviated from σ^+ values for electron withdrawers. With DSP treatments, the best correlation overall was found to be that using the revised Swain–Lupton parameters, *F* and *R*.[26] It became of interest to extend this study to include ortho-substituted styrenes. We wished to determine an empirical set of ortho substituent constants by the ^{13}C method, to compare them to other sets based on different types of measurements, to establish whether or not the data could be profitably analyzed with the DSP method, and, lastly, to see if a steric factor seemed to be necessary for significant correlation. Accordingly, we report here the results of measurements on ten series of compounds, each of which includes the parent compound and six ortho-substituted derivatives.

Compounds. Series **3**–**12** with substituents **a**–**g** were prepared according to eq 5, in which ortho-substituted benzaldehydes, **1**, were condensed with appropriate compounds, **2**, containing an active methylene group to give the ortho-substituted styrenes. The substituted ethyl cinnamates, **9**, were obtained by esterification of the acids that resulted from decarboxylative condensation with malonic acid.[27] The *trans*- and *cis*-cinnamonitriles **11** and **12** were prepared by cuprous oxide catalyzed decarboxylation[28] of the corresponding α-cyanocinnamic acids that resulted from condensation with sodium cyanoacetate.[29] These decarboxylations led to mixtures of **11** and **12**. Spectra were recorded and chemical shift assignments were made as previously described.[25] The solvent used in all cases was $CDCl_3$. Chemical shifts for the β-carbon atoms are collected in Table I.



Substituent Constants. Substituent constants were established by the same procedure previously applied for metal and para substituent constants. The scaling factor, *a*, in defining eq 6 was again that obtained by arbitrarily

$$\sigma_0^{13} \equiv a(\delta_X - \delta_H) \qquad (6)$$

setting σ_p^{13} for the dimethylamino group at −1.75 and that for hydrogen at 0.00. Viewed slightly differently, the defining reaction can be written as eq 7, in which the ρ value

$$\delta_X - \delta_H = \rho\sigma_0^{13} \qquad (7)$$

is that determined exclusively by the parent compound and the *p*-dimethylamino substituent. The same ρ value was used for all three types of substituents. Table II presents for each reaction series the individually calculated values of σ_0^{13}, their mean values, and standard deviations.

To test the correlative ability of the mean σ_0^{13} values thus determined, the data were reanalyzed using eq 8.

$$\delta_X = \rho\sigma_o^{13} + c \qquad (8)$$

The correlation coefficients for these analyses are also included in Table II. In all, the correlations are quite satisfactory, with coefficients ranging from 0.9742 to 0.9966 and a mean value of 0.9878. The nitro group, along with phenyl, iodo, and *tert*-butyl, has been frequently excluded from the analysis of ortho substituent effects because these groups sometimes give deviant results. Although the standard deviation of the σ_0^{13} value for the nitro group in the series reported here is larger than that for the other substituents, the overall correlations are still very good.

Because of previous reports that σ_p values can be used to correlate ortho substituent data,[11,14,15,30] several other correlations were tried with the present data. These attempts utilized σ_m^{13}, σ_p^{13}, σ_p, σ_I, and σ_R, but all gave very poor correlation coefficients. For the data reported here, it is clear that ortho substituent constants represent the

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[26] Swain, C.; Unger, S.; Rosenquist, N.; Swain, M. *J. Am. Chem. Soc.* **1983**, *105*, 492–502.

[27] Wiley, R. H.; Smith, N. R. In *Organic Syntheses*; Rabjohn, N., Ed.; Wiley: New York, 1964; Collect. Vol. IV, pp 731–734.

[28] Fairhurst, J.; Horwell, D.; Timms, G. *Tetrahedron Lett.* **1975**, 3843–3844.

[29] Lapworth, A.; Baker, W. In *Organic Syntheses*, 2nd ed.; Gilman, H., Ed.; Wiley: New York, 1941; Collect. Vol. I, pp 175–177.

[30] Charton, M. *Can. J. Chem.* **1960**, *38*, 2493–2499.

best possible single-parameter correlative scale.

It was of interest to compare the substituent constants arising from this study with those reported from other types of measurements. In his 1971 review, Charton tabulated 23 sets of proposed σ_o values. Unfortunately, several of these sets do not include a sufficient diversity of substituents; for instance, seven sets do not contain the nitro group, seven sets do not encompass the methoxy group, five sets do not include appropriate halogens, and five do not even incorporate the methyl group. In all, only six sets have all of the same substituents utilized in the present study and one other had all except the bromo substituent. Of these seven sets, three propose a smaller σ_o value for methyl than for methoxy. The remaining four sets all show moderately good correlations with the values reported here. The best correlation ($r = 0.9830$) is with the values of Barlin and Perrin derived from the pK_a's of benzoic acids in water.[31] Sets derived from the pK_a's of anilinium ions in water ($r = 0.9592$),[32] the $E_{1/4}$ for chronopotentiometric titration of phenylferrocenes in acetonitrile ($r = 0.9451$),[33] and the rates of alkaline hydrolysis of ethyl benzoates ($r = 0.9220$),[34] give less satisfactory results. Consequently, it appears that the present set of σ_o values should have about the same utility as other sets in correlating reactivity and other data; i.e., limited success, as would be predicted by Charton's analysis.

Dual Parameter Correlations. According to Charton, most of the data sets available in 1971 gave significant correlations with eq 1, in which the ortho effect is considered to arise simply from an inductive and a resonance contribution. The σ_I scale has long been thought to be independent of position and σ_I values determined by a variety of experimental techniques usually agree quite closely.[35,36] On the other hand, it is widely recognized that σ_R values are position dependent, which raises the question of how best to estimate them for ortho substituents. Ehrenson, Brownlee, and Taft have tabulated values for the various scales (σ_R^0, $\sigma_{R(BA)}$, σ_R^-, σ_R^+) and have shown that some sets of data for ortho substituents correlate well with σ_I plus one or the other of these σ_R scales. Likewise, the successful treatments summarized by Charton have assumed the appropriateness of the σ_R values derived for para substituents.[1] In light of the resemblance of σ_p^{13} values to the σ_p^+ scale, it was expected that σ_R^+ might afford the best correlation. However, the enhanced value of σ_p^{13} for the nitro group, coupled with the suggestion of Krabbenhoft that in the styrene system, resonance, whether by electron supply or demand, makes the principal contribution to electron density variations at the β-carbon atom,[38] implied that the use of σ_R^+ for electron donors and σ_R^- for electron withdrawers should be tried. The multiple correlation coefficient, R, for each series with the various combinations of σ_I and σ_R is given in Table S-I. The mean values are 0.9282 ($\sigma_I + \sigma_R^0$), 0.9503 ($\sigma_I + \sigma_{R(BA)}$), 0.9437 ($\sigma_I + \sigma_R^+$), 0.9152 ($\sigma_I + \sigma_R^-$), and 0.9404 ($\sigma_I + \sigma_R^\pm$). The $\sigma_R^\pm$ scale used σ_R^- for the nitro group and σ_R^+ for all others.

Alternative dual parameter treatments gave similar R values. Swain's values of F and R gave a mean correlation coefficient of 0.9461 and those modified by Hansch, as used by Fujita and Nishioka, gave 0.9304. Correlations employing σ_p^{13} and Charton's steric parameter gave a mean R value of 0.9507. These analyses are also shown in Table S-I.

From a predictive standpoint, the DSP treatment of the present data is inadequate. In practical terms, the 95% confidence interval for predicting a given chemical shift using these equations and parameters covers a range of approximately 3–5 ppm. As seen in Table I, the average range of substituent-induced chemical shifts within a given series is only 5.3 ppm.

Correlations with Three Parameters. As noted previously, the two-parameter correlations using σ_I and a σ_R scale were best with $\sigma_{R(BA)}$, although σ_R^+ and $\sigma_R^\pm$ gave results nearly as good. In all cases, the correlation coefficients were less than 0.9510. Correlation coefficients for the three-parameter analyses of all series with σ_I, the various σ_R scales, and ν are given in Table S-II. The mean values are 0.9824 ($\sigma_I + \sigma_{R(BA)} + \nu$), 0.9846 ($\sigma_I + \sigma_R^+ + \nu$), 0.9616 ($\sigma_I + \sigma_R^- + \nu$), and 0.9882 ($\sigma_I + \sigma_R^\pm + \nu$).

The selection of parameters for the Fujita–Nishioka equation is possibly complicated by two factors. These authors tentatively defined σ_o as being equal to the appropriate σ_p (σ_p, σ_p^+, σ_p^-, etc.), but felt that in some instances this definition would underestimate the inductive influence and overestimate the resonance component. Two values of E_S were advanced for the nitro group, with the choice depending upon whether the group is expected to be coplanar with or perpendicular to the aromatic ring. Accordingly, the data for each series were analyzed in several ways. The first attempts utilized σ_p^{13}, as previously defined, to represent σ_o, the Swain value of F as modified by Hansch, and E_S for the perpendicular and parallel nitro groups. Correlation coefficients were 0.9855 and 0.9578, respectively. When σ_p^+ values were substituted for σ_p^{13}, correlation coefficients of 0.9870 and 0.9655 were found. To explore the suggestion that these correlations are tantamount to one involving the substitution of a resonance parameter for the appropriate σ value, correlations using F, R, and E_S were also tried using the Hansch parameters and both perpendicular and parallel nitro group E_S values. Correlation coefficients of 0.9763 and 0.9510, respectively, were found in these cases. These results are also summarized in Table S-II.

Perusal of the three-parameter results leads to two inescapable conclusions: (1) the use of a steric factor is required and (2) the treatments of Charton and of Fujita and Nishioka give virtually identical results. Which steric factor is used with a given set of inductive and resonance factors does not seem to matter. To illustrate, analysis using σ_I, σ_R^+, and E_S (nitro perpendicular) resulted in a mean correlation coefficient of 0.9921. Similarly, use of the unmodified Swain values for F and R in conjunction with E_S (nitro perpendicular) gave 0.9872.

Steric Effects. The best three-parameter treatment using Charton's approach as applied in eq 9 required σ_I, $\sigma_R^\pm$, and ν. The mean correlation coefficient was 0.9882. The best treatment using the Fujita–Nishioka approach of eq 10 used σ_p^+, F, and E_S (perpendicular nitro) and gave a mean correlation coefficient of 0.9870. These mean correlation coefficients compare very well with the value of 0.9878 found with the best single parameter σ_o^{13} constants. Accordingly, as indicated previously, it is necessary with the present data to include the steric term for satisfactory analysis. We wished next to examine the coef-

$$\delta_X = \alpha\sigma_I + \beta\sigma_R^\pm + \psi\nu \tag{9}$$

$$\delta_X = \alpha\sigma_p^+ + \beta F + \psi E_S \tag{10}$$

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[31] Barlin, G.; Perrin, D. *Q. Rev. Chem. Soc.* **1966**, *20*, 75–101.

[32] Clark, J.; Perrin, D. *Q. Rev. Chem. Soc.* **1964**, *18*, 295–320.

[33] Little, W.; Reilley, C.; Johnson, J.; Lynn, K.; Sanders, A. *J. Am. Chem. Soc.* **1964**, *86*, 1376–1381.

[34] Taft, R., Jr. *J. Am. Chem. Soc.* **1953**, *75*, 4231–4238.

[35] Exner, O. In *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; pp 500–525.

[36] Charton, M. *Prog. Phys. Org. Chem.* **1981**, *13*, 119–251.

[37] Ehrenson, S.; Brownlee, R.; Taft, R. *Prog. Phys. Org. Chem.* **1973**, *10*, 1–80.

[38] Krabbenhoft, H. *J. Org. Chem.* **1978**, *43*, 1830–1832.

Table III. Coefficients for Correlation Using Equations 9 and 10

	coefficients[a]			
series	α	β	ψ	$\%\psi$
3	4.950	2.298	1.821	20.1
4	5.507	2.250	1.523	16.4
5	5.292	4.287	3.612	27.4
6	3.425	2.225	2.561	31.2
7	4.985	3.560	3.446	28.7
8	4.434	3.112	3.446	31.4
9	5.266	1.977	1.326	15.5
10	3.651	1.698	1.810	25.3
11	6.021	1.888	0.913	10.3
12	4.434	3.006	3.421	31.5
3	1.830	3.065	−1.060	17.8
4	1.699	3.879	−0.990	15.1
5	3.582	1.714	−1.887	30.5
6	1.738	1.656	−1.376	28.8
7	2.891	2.114	−1.782	26.3
8	2.464	2.038	−1.732	27.8
9	1.500	3.798	−0.854	13.9
10	1.299	2.403	−0.916	19.8
11	1.426	4.636	−0.658	9.8
12	2.361	2.078	−1.787	28.7

[a] The values at the top of the table are those from eq 9. Those at the bottom are from eq 10. Note that in eq 9, α and β are the coefficients for the inductive (field) and resonance component, respectively, but that this is reversed in eq 10.

Table IV. Field, Resonance, and Steric Contributions

	contribution[a]		
series	% field	% resonance	% steric
4	59.3	24.3	16.4
9	61.5	23.0	15.5
11	68.2	21.5	10.3
8	40.3	29.3	31.4
7	41.6	29.7	28.7
5	40.1	32.5	27.4
4	59.0	25.9	15.1
9	61.7	24.4	13.9
11	69.0	21.2	9.8
8	32.7	39.5	27.8
7	31.1	42.6	26.3
5	19.6	49.9	30.5

[a] The analyses at the top of the table are based on eq 9; those at the bottom are derived from eq 10.

ficients found in eq 9 and 10 to see if they were interpretable in terms of the perceived steric environment.

Charton[40] has recently given a quantitative description for planar π-bonded substituents ortho to a nonplanar active site based on eq 11, in which Q_X is the property to

$$Q_X = L\sigma_{IX} + D\sigma_{DX} + S\nu_X + h \tag{11}$$

be correlated, σ_{IX} is the substituent constant for the localized electrical effect, σ_{DX} is the substituent constant for the delocalized electrical effect, and ν_X is the steric parameter. He also provided a method of correcting σ_{DX} and ν_X for those substituents for which the steric effect is expected to be particularly significant; e.g., NO_2, Ph, and COZ where Z is OMe, OEt, NH_2, Me, H, and Ph. According to this treatment, the percent steric contribution is given by eq 12. We have employed this approach to

$$P_S = |S|100/(|L| + |D| + |S|) \tag{12}$$

estimate the steric contribution in the present data, although we have not included the correction procedure because the nitro group has offered no anomalies in the correlations. It should be noted, however, that the steric parameter for a perpendicular nitro group afforded the best correlations in the Fujita–Nishioka analyses.

In all the series analyzed, the α-carbon atom bears the substituted aromatic nucleus and a hydrogen atom, such that there is no variation in the steric environment at that locale. With regard to the disposition of substituent groups around the ethylenic unit, however, three different situations are encompassed. In series **3**, **4**, **9**, and **11**, a hydrogen atom is cis to the aromatic ring. In series **5**, **7**, **8**, and **12**, a cyano group occupies this position, while in series **6** a carbethoxy group is located there. Series **10**, with a methylene group cis to the phenyl ring, should perhaps lie sterically somewhere between those series with a cis cyano group and that with a cis carbethoxy group.

Values of α, β, and ψ from eq 9 and 10 are given in Table III. Examination of these coefficients indicates that the different steric environments are indeed reflected in the correlations, regardless of treatment. Because E_S values are all negative and ν values are all positive, the sign of ψ differs in the two treatments. For the present purpose, the sign can be ignored. In both treatments, the steric contribution is indeed smallest for series **3**, **4**, **9**, and **11**, as predicted. Those for series **5**, **7**, **8**, and **12** are distinctly larger, with series **6** included among those with the largest contribution from the steric term. In all, the general trend closely parallels expectation, although the steric contribution in series **10** is somewhat smaller than might have been supposed. This is perhaps related in some fashion to the diminished rotational freedom in the cyclopentanone ring system.

The Charton and Fujita–Nishioka treatments give a remarkably consistent analysis of the steric contribution, as can be seen in Table III. The deviation from the mean for the two treatments is 13.9% in the worst case (series **10**); in all others the agreement is approximately twice as good, or better. An interesting difference does emerge, however, when the overall mix of field, resonance, and steric contributions is considered. We note that if the hydrogen atom cis to the aromatic ring in series **4**, **9**, and **11** is replaced by a cyano group, series **8**, **7**, and **5**, respectively, result. A comparison of the two treatments of these series is presented in Table IV.

According to the results in Table IV, both treatments agree that in the parent series (**4**, **9**, and **11**), the field, resonance, and steric contributions amount to approximately 63%, 23%, and 14%, respectively. With the cis hydrogen atom replaced by a cyano group, the relative contributions become 41%, 30%, and 29%, respectively, according to the Charton treatment, and 28%, 44%, and 28%, respectively, according to the Fujita–Nishioka treatment. Thus, although both analyses agree that the steric contribution approximately doubles with this change, the Fujita–Nishioka approach suggests that the resonance effect plays a much larger role at the expense of the field effect than that suggested by the Charton approach. Unfortunately, we currently have no means at hand of assessing the validity of either approach.

In conclusion, it may be said that the ortho-substituted series dealt with here resemble the analogous meta and para series previously reported[25] in at least one important respect. Although a suitable single substituent parameter can be devised for predictive purposes, explication of the electrical effect requires a dual parameter analysis. Satisfactory correlations for the ortho series can be obtained with an additional steric parameter based solely on the size of the substituent groups. Such correlations suggest that the steric effect comprises 10–30% of the total substituent

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(39) Reynolds, W.; Gomes, A.; Maron, A.; MacIntyre, D.; Tanin, A.; Hamer, G.; Peat, I. *Can. J. Chem.* **1983**, *61*, 2376–2384.

(40) Charton, M. *J. Org. Chem.* **1983**, *48*, 1016–1021.

influence. It is possible, however, that a more refined analysis of the ortho effect, such as that suggested by Charton,[40] would lead to a somewhat diminished contribution from the steric component.

Registry No. **3a**, 67962-17-8; **3b**, 67962-16-7; **3c**, 67962-18-9; **3d**, 29569-91-3; **3e**, 67962-23-6; **3f**, 67962-20-3; **3g**, 103457-25-6; **4a**, 22965-99-7; **4b**, 22966-01-4; **4c**, 22966-06-9; **4d**, 614-47-1; **4e**, 22966-11-6; **4f**, 22966-10-5; **4g**, 53744-31-3; **5a**, 2834-10-8; **5b**, 2698-44-4; **5c**, 2698-43-3; **5d**, 2700-22-3; **5e**, 2698-41-1; **5f**, 2698-42-2; **5g**, 2826-30-4; **6a**, 6768-22-5; **6b**, 24331-75-7; **6c**, 2262-52-4; **6d**, 5292-53-5; **6e**, 6768-20-3; **6f**, 93098-67-0; **6g**, 17422-56-9; **7a**, 14533-89-2; **7b**, 24393-41-7; **7c**, 103457-26-7; **7d**, 2169-69-9; **7e**, 24393-43-9; **7f**, 103457-27-8; **7g**, 68792-18-7; **8a**, 103457-28-9; **8b**, 103457-29-0; **8c**, 103457-30-3; **8d**, 101220-25-1; **8e**, 103457-31-4; **8f**, 103457-32-5; **8g**, 103457-33-6; **9a**, 24393-54-2; **9b**, 24393-48-4; **9c**, 89760-42-9; **9d**, 4192-77-2; **9e**, 24393-51-9; **9f**, 91047-77-7; **9g**, 24393-59-7; **10a**, 103457-34-7; **10b**, 103457-35-8; **10c**, 103457-36-9; **10d**, 17434-21-8; **10e**, 103457-37-0; **10f**, 103457-38-1; **10g**, 51813-41-3; **11a**, 57103-26-1; **11b**, 26155-19-1; **11c**, 91319-60-7; **11d**, 1885-38-7; **11e**, 51220-00-9; **11f**, 51220-04-3; **11g**, 51991-49-2; **12a**, 57103-24-9; **12b**, 57103-23-8; **12c**, 91319-61-8; **12d**, 24840-05-9; **12e**, 51219-99-9; **12f**, 51220-03-2; **12g**, 74845-04-8.

Supplementary Material Available: Tables showing multiple correlation coefficients for analyses of β-carbon chemical shifts with two- and three-parameter equations, F values for two- and three-parameter correlations, and the estimated error in the steric parameter for three-parameter correlations (5 pages). Ordering information is given on any current masthead page.

Notes

Resonance and Solvent Effects on Absorption Spectra. 4. Effects of 5-Substituents on Electronic Spectra of Some 2-Nitroaniline Derivatives

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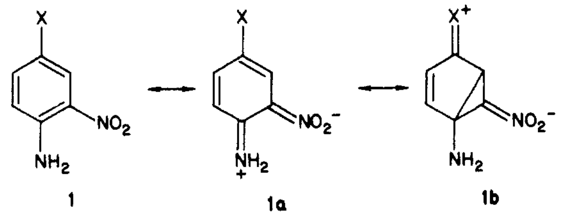
In Part 3 of this series,[1] we reported that positions of [$>N^+=C(1) \rightarrow C(2)=NO_2^-$] bands in the electronic spectra of some 4-X-2-nitroaniline derivatives (**1**) were well correlated (r = 0.994–0.998) by dual substituent parameter (dsp) equations involving σ_I and σ_R^+. The multiple linear regression equations in cyclohexane (CH) and dimethylformamide (DMF) were given by eq 1a,b.

$$\nu(1)_{max}^{CH} = 26.42 + 1.84\sigma_I + 2.44\sigma_{R^+} \times 10^3 \text{ cm}^{-1} \quad (1a)$$

$$\nu(1)_{max}^{DMF} = 24.39 + 2.05\sigma_I + 2.38\sigma_{R^+} \times 10^3 \text{ cm}^{-1} \quad (1b)$$

That σ_{R^+} in eq 1a,b resulted in better statistical goodness of fit than σ_{R° or σ_{R^-} was rationalized on the basis that, in addition to primary canonical structures like **1a**, there are also important resonance contributions to the electronic excited states by meta-bridged canonical structures like **1b**, wherein positive charge is delocalized from the amine nitrogen to π-donor substituents in the 4-position.



1 1a 1b

Similar *meta*-quinoidal structures had earlier been invoked by Kamlet et al.[2] to rationalize solvent and substituent effects on 3-nitroaniline spectra, by Porto et al. to rationalize substituent effects on 2-nitrodiphenyl sulfide spectra,[3] and by Rapoport et al.[4] in connection with nitrophenol spectra.

The excellent fit to eq 1a,b accorded with an earlier suggestion by Brownlee and Topsom[5] that UV/visible spectra should follow high-precision linear free energy relationships only when the substituents being varied are external to the chromophore being measured.

The present investigation is an extension of the earlier work to the 5-X-2-nitroanilines (**2**), where the substituent being varied is again external to the chromophore being studied. This time, however, the substituents are meta to the amino and para to the nitro group.

Experimental Section

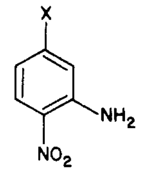
Materials. Samples were prepared by the methods described in the literatures. All solvents were purified by removing acidic or basic impurities, through drying and taking a narrow cut of fractional distillate.

UV–Visible Spectra. The instrument was Hitachi 220A double-beam spectrometer. Measurements were carried out four times at each of three different concentrations at 25 °C.

^{15}N NMR Spectra. Measurements were made with JEOL FX90Q FT-NMR spectrometer at ^{15}N natural-abundance level using $HCONH_2$ as external standard at room temperature. Samples were run as 1.7 M Me_2SO-d_6 solution.

Results and Discussion

Positions of ν_{max} for the lowest energy transitions in the spectra of eight 5-X-2-nitroanilines (**2**) are assembled in



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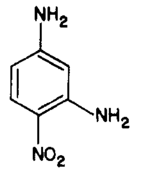

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(1) Yokoyama, T.; Taft, R. W.; Kamlet, M. J. *Spectrochim. Acta* **1984**, *40A*, 669.

(2) Kamlet, M. J.; Jones, M. E.; Taft, R. W.; Abboud, J.-L. M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 342.

(3) Porto, A. M.; Altieri, L.; Castro, A. J.; Brieux, J. A. *J. Chem. Soc. B* **1971**, 1360.

(4) Rapoport, M.; Hancock, C. K.; Meyers, E. A. *J. Am. Chem. Soc.* **1961**, *83*, 3487.

(5) Brownlee, R. T. C.; Topsom, R. D. *Spectrochim. Acta* **1972**, *29A*, 385.

0022-3263/86/1951-3540$01.50/0