3.82 (s, 6 H), 4.80–5.35 (m, 4 H), 5.50–6.27 (m, 2 H), 6.85 (s, 2 H); MS, *m/e* 282 (M^+). Anal. Calcd for $C_{14}H_{18}O_4S$: C, 59.55; H, 6.43. Found: C, 59.55; H, 6.37.

Registry No. **1a**, 5296-64-0; **1b**, 53439-63-7; **1c**, 592-88-1; **1d**, 72867-23-3; **1e**, 3393-13-3; **1f**, 6937-97-9; **1g**, 58965-04-1; **1h**, 82937-11-9; **1i**, 64871-50-7; **2a**, 82937-12-0; **2b**, 82937-15-3; **2c**, 82937-17-5; **2d**, 82937-21-1; **2e**, 82937-14-2; **2f**, 82937-19-7; **2h**, 82937-10-8; **2i**, 82937-24-4; **3a**, 82937-13-1; **3b**, 82937-16-4; **3c**, 82937-18-6; **3d**, 82937-22-2; **3e**, 83037-51-8; **3f**, 82937-20-0; **3h**, 82937-23-3; **3i**, 82937-25-5; **4**, 89889-98-5; **13a**, 89889-88-3; **13b**, 89889-90-7; **13c**, 89889-92-9; **13d**, 89889-94-1; **13e**, 89889-96-3; **14a**, 89889-89-4; **14b**, 89889-91-8; **14c**, 89889-93-0; **14d**, 89889-95-2; **14e**, 89889-97-4; **15a**, 89889-99-6; **15b**, 89890-00-6; **16a**, 89890-03-9; **16b**, 89890-04-0; **17a**, 89890-01-7; **17b**, 89890-02-8; **18a**, 89890-05-1; **18b**, 89890-06-2; **19**, 89890-07-3; MP, 922-67-8; DMAD, 762-42-5; $AlCl_3$, 7446-70-0; $FeCl_3$, 7705-08-0; $TiCl_4$, 7550-45-0; $EtAlCl_2$, 563-43-9; $BF_3 \cdot Et_2O$, 109-63-7; $SnCl_4$, 7646-78-8; $ZnCl_2$, 7646-85-7; 2,2-dimethoxypropane, 77-76-9.

Supplementary Material Available: The spectroscopic data of compounds **2a–i**, **3a–i**, **6(E)**, **6(Z)**, **11a,b** **13a–e**, and **14a–e** (Table III) (4 pages). Ordering information is given on any current masthead page.

Field and Resonance Substituent Constants for Aromatic Derivatives: Limitations of Swain's Revised *F* and *R* Constants for Predicting Aromatic Substituent Effects

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Received September 16, 1983

Two key limitations of Swain's revised *F* and *R* constants are pointed out. First, they provide an incomplete separation of field and resonance effects. Second, the range of precise applicability of *R* is restricted to systems following σ or σ^+ while it fails badly for systems following σ^-. The first limitation is attributed to inappropriate criteria used to separate field and resonance effects while the second is more fundamental. It reflects the fact that no single resonance scale can predict the whole range of aromatic reactivity due to very significant variations in substituent resonance effects with electron demand. It is concluded that the *F*,*R* model should be abandoned in favor of lines of research involving approaches intermediate in complexity between those of Swain and of Taft.

Introduction

Fifteen years ago, Swain and Lupton introduced two parameters, *F* and *R*, which were claimed to respectively represent substituent field and resonance effects.[2] They also claimed that only one resonance parameter was necessary for each substituent to predict substituent effects for a wide variety of properties and reactions according to eq 1, where P_x is the value of a particular property for a

$$P_x = fF + rR + h \qquad (1)$$

series of substituents X, *f* and *r* are transmission coefficients which only depend upon the reaction or property and conditions while *h* is the intercept for the correlation equation.[2] This approach contrasted with the earlier approach of Taft[3] who denoted the field and resonance components as σ_I and σ_R but presented detailed evidence that different resonance parameters ($\sigma_R{}^+$, σ_R(BA), $\sigma_R{}^0$ or $\sigma_R{}^-$) were necessary, depending upon the electron demand of the particular system or reaction.[4,5] Taft's was eq 2,

$$P_x = P_0 = \rho_I\sigma_I + \rho_R\sigma_R \qquad (2)$$

where P_0 is the value of the property for the parent molecule (X = H), σ_R is one of the four resonance scales listed above and ρ_I and ρ_R correspond to *f* and *r* in 1.

Swain's approach is clearly the simpler of the two since it involves only two fixed scales. Probably for that reason, *F* and *R* constants have been quite extensively used, particularly in correlations of spectroscopic and biological data.[6] However, both the derivation and the utility of this approach have been seriously criticized by other leading physical organic chemists in articles, reviews, and books.[7] Nevertheless, Swain has recently reported revised values of *F* and *R* based upon a larger data set and more sophisticated statistical analysis, but still using the same basic, previously criticized, assumptions.[8] Although Swain presents what appears to be impressive statistical data to support his claim that he has developed a universal resonance scale,[8] close inspection reveals that certain of his conclusions result from the use of incomplete data sets and are unjustified. Consequently, we felt that it was important to point out the problems with the *F*,*R* approach so that organic chemists who make occasional use of dual (field and resonance) substituent constants would be aware of the serious limitations of this attractively simple model.

Discussion

(i) The Choice of R = 0 for $N(CH_3)_3{}^+$ as a Criterion for Separating *F* and *R* and Defining the Resonance Scale. The original *R* scale was determined by using the assumption that R = 0 for $N(CH_3)_3{}^{+2}$. It was quickly pointed out by several others that this assumption was probably incorrect and that *R* was consequently not a pure resonance scale.[7a,7b,9] However, the same

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(1) (a) University of Toronto. (b) La Trobe University. Correspondence may be addressed to either author.

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Table I. Testing of the Ability of F and σ_I To Predict the Acidities of 3 and 4

system	variable	constant(s)	h[a]	$f(\rho_I)$	C[b]	F[c]	std dev[d]	n[e]
3	$-\Delta pK_A$[f]	F	0.06 ± 0.17	3.11 ± 0.28	0.9330	128	0.403	21
3	$-\Delta pK_A$	σ_I[g]	0.14 ± 0.06	5.17 ± 0.16	0.9907	1000	0.152	21
4	$-\Delta pK_A$[i]	F	−0.06 ± 0.08	1.89 ± 0.14	0.9551	187	0.199	20
4	$-\Delta pK_A$	σ_I	0.02 ± 0.03	3.04 ± 0.09	0.9927	1225	0.081	20

[a] Parameters for variable = $fF + h$ or variable = $\rho_I\sigma_I + h$. [b] Correlation coefficient. [c] F test of the variance. [d] Standard deviation of the estimate. [e] Number of points in the correlation. This includes all neutral substituents from ref 31 and 32 for which both F and σ_I values are available (see Table III). [f] Data from ref 31 plus F and R constants from ref 8. [g] Results of correlation with F and R; 3 (C = 0.967, F = 131, std dev = 0.29), 4 (C = 0.975, F = 164, std dev = 0.15). Note that the F test should increase if the second term is significant.[28] [h] σ_I from ref 30. [i] pK_A values from ref 32.

assumption was made in deriving revised R scale.[8] While the authors note that this is a "critical condition upon which the validity of the whole analysis depends", they also state that "there is no evidence of electron supply from $N(CH_3)_3^+$".[8] In fact, there is a large amount of data which suggests that $N(CH_3)_3^+$ (along with NH_3^+) is a modest π donor with a resonance effect similar to that for the isoelectronic $C(CH_3)_3$ group. Revelant data include ^{13}C[10,11] and ^{19}F[12,13] chemical shifts, infra-red intensity measurements,[14,16] pK_A measurements,[17,18] secondary isotope effects,[19] product distributions in electrophilic aromatic substitutions,[19,20] and theoretical calculations.[10,11,21,22] The only contrary evidence offered by Swain is the purported meta-directing properties of $N(CH_3)_3^+$ in electrophilic aromatic substitution plus the observation that the electronic spectrum of benzene is essentially unaltered by the $N(CH_3)_3^+$ group. However, $N(CH_3)_3^+$ is a meta-para director for bromination[23] and both $N(CH_3)_3^+$ and NH_3^+ are meta-para directors for nitration.[19,20] Ridd has argued that the nitration results are only compatible with opposing field and resonance effects for NR_3^+ groups.[20] Furthermore, wavelength shifts provide an unreliable quantitative measure of resonance effects.[24] Thus, the balance of evidence strongly supports the view that $R < 0$ for $N(CH_3)_3^+$, invalidating Swain's basis for separation of field and resonance effects.

There are two other serious problems with the use of $N(CH_3)_3^+$ as an anchor point for defining substituent constants for neutral substituents.[6,7b] First, the electronic effect of a charged substituent is particularly sensitive to changes in solvent and/or counter ion,[20,25,26] e.g., note the large uncertainty in σ_m and σ_p (±0.2) for $N(CH_3)_3^+$.[27] Second, the electrostatic effect of a monopole (charged) group varies as r^{-1} while that for a dipole follows r^{-2}.[6] Thus, the field effect of a monopole will decrease more slowly with increasing distance than that for a dipole. For example, Wepster has shown that inclusion of data for $N(CH_3)_3^+$ in Hammett plots of aromatic acidities gave "constants" for this substituent which increased dramatically in size with increasing distance.[25] These results can be quantitatively rationalized in terms of the different distance dependencies of monopoles and dipoles.[28] Thus, one should not really even include $N(CH_3)_3^+$ in a correlation of dipolar substituents,[26] let alone use it as an anchor point for a dipolar substituent scale.[29]

(ii) The Validity of the F Scale as a Pure Field Effect Scale. pK_A values for 14 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids (1) in 50% w/w ethanol water were used as standards for the original F scale (assuming $r = 0$ for this system).[2] This provided F values for fourteen substituents with the remainder estimated from σ_m and σ_p[2]. The F values roughly parallel σ_I[2], although they give generally poorer correlations than σ_I for a variety of properties likely to depend solely on field effects.[30]

The primary defining system for the revised F values was switched from 1 to *trans*-4-X-cyclohexane-1-carboxylic acids (2), although there are only data for six substituents in the latter system.[8] While other data for similar systems, including that for 1, were included in the data matrix used to define F and R, this still included only the same 14 (of 43) substituents. However, there are at least two far more extensive data sets in the literature which would appear to be at least as suitable for defining F. These are the aqueous acidities for 4-substituted quinuclidinium ions (3, 39 neutral substituents)[31] and 3-(XCH_2)-pyridinium ions (4, 27 neutral substituents),[32] both of which are predicted to have insignificant resonance contributions[31,32] and which have been used to define polar substituent constants.[31,32]

To compare the relative abilities of F and σ_I to predict polar (field) effects, we have correlated F (without and with R) and σ_I against pK_A values for systems 3 and 4 (see Table I). σ_I is clearly superior to F. While F plus R give improved correlations (see footnote g of Table I), the resonance term is of marginal statistical significance. Interestingly, when we separate the substituent set for 3 into "primary" (e.g., those where F and R are defined from both aliphatic and aromatic data) and "secondary" (those for which only aromatic data were used) substituents, the former give an excellent correlation against F alone (C = 0.998) while the latter give a noncorrelation with F (C = 0.888), but a fair correlation with F and R (C = 0.958, see Figure 1). The first correlation suggests that 3 is free of true resonance effects, while the second indicates major errors in F for many secondary substituents, presumably partly due to incomplete separation of field and resonance effects. The R term reflects this incomplete separation. Consequently, σ_I is still superior to F as a polar (field) scale.[30,33]

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Table II. Testing of the Ability of F and R To Predict Properties for a Variety of Aromatic Systems in Protic Media[a]

system[a,b]	variable	h[c]	f	r	c	F	std dev	n
5	$-\Delta G°$	0.11 ± 0.20	2.18 ± 0.33	0.73 ± 0.10	0.9209	59	0.527	24
6	$-\Delta G°$	0.26 ± 0.24	2.39 ± 0.40	1.51 ± 0.13	0.9608	111	0.570	21
5 M	$-\Delta G°$	0.06 ± 0.07	1.84 ± 0.11	0.28 ± 0.29	0.9819	257	0.147	22
7	σ	0.00 ± 0.03	0.56 ± 0.05	0.20 ± 0.11	0.9809	267	0.066	21
8	σ	−0.03 ± 0.01	0.51 ± 0.02	0.31 ± 0.05	0.9961	2144	0.037	37
9	$-\Delta G°$	−0.34 ± 0.15	3.40 ± 0.25	2.19 ± 0.07	0.9925	563	0.379	20
10	σ	−0.06 ± 0.03	0.33 ± 0.05	0.52 ± 0.01	0.9941	843	0.070	23

[a] The systems are described in the text. [b] The substituents included in the correlations are listed in Table III. [c] For meanings of headings, see Table I.

(iii) The Use of a Single Resonance Parameter for Different Aromatic Systems. Swain and Lupton claimed that a single resonance scale was sufficient for a wide range of aromatic systems.[2] However, Exner quickly pointed out that F and R reproduced σ_p^+ and σ_p^- with very low precision.[26] Subsequent analyses of very considerable amounts of data almost invariably gave better results by using eq 2 than eq 1.[5,34] For example, ca. 85% of the aromatic data sets investigated by Taft gave better correlations with σ_I and σ_R than with F and R. R was really only applicable to systems of moderate electron demand, since of 60 data sets where σ_R^+ or σ_R^- gave the best fit of the σ_R scales, only two gave better fits with F and R. This is consistent with Taft's basic assumption that resonance effects are significantly modified by varying π electron demand. In fact, recent theoretical[35,36] and experimental[37-39] evidence demonstrates that substituent resonance effects alter dramatically, even to the extent of changing sign, in situations of extreme electron demand.

Despite this, Swain has reasserted his claim that only a single resonance scale is needed.[8] He supports this with what appears to be highly impressive statistical evidence. For example, σ_p^- (based on phenol acidities) is predicted by F and R with a correlation coefficient, $C = 0.9940$, while σ_p^+ is predicted with similar precision, $C = 0.9945$.[8] Furthermore, both correlations show the same relative response to field and resonance effects (%r is respectively 59% and 62%). This leads Swain to conclude that the idea of enhanced resonance effects in systems following σ_p^+ or σ_p^- is "*only an artifact or illusion*".[8] This conclusion contradicts the results of many previous investigations in this area.[40] Fortunately, it can be easily checked. if σ_p^+ and σ_p^- can be predicted by the same blend of field and resonance effects, then σ_p^- (or the corresponding $\Delta G°$ values for the proton transfer equilibrium for phenol) should be linearly related to σ_p^+. This is clearly not true, provided that one uses a well-balanced set of substituents (see Figure 2). Thus, there must be some major flaw(s) in Swain's analysis of aromatic substituent effects. A logical starting point in searching for the flaw(s) is to consider the actual data sets used in ref 8.

Of the aromatic data sets used to define F and R,[8] σ_m, σ_p, σ_m^+, and σ_p^+ all provide extensive substituent sets, including reasonable numbers of strong π donor and π acceptor groups. However, the σ_p^- set, although it contains 17 substituents, has no π donor groups stronger than CH_3, even though the relevant data was readily available.[38,41] It is apparent from Figure 2 that omission of strong π donor groups will lead to the totally unjustified conclusion that σ_p^- is linearly related to σ_p^+. Similarly, the correlation of σ^0 with F and R ($C = 0.9906$) is based upon a substituent set containing only one strong π donor (OCH_3).[8] In view of these omissions, the claim that F and R can accurately predict aromatic properties in systems following σ^- or σ^0 must be regarded as suspect. Many of the other data sets used to define or test F and R can also be questioned since only 9 of 46 satisfy Taft's minimal substituent set requirements for investigations of aromatic substituent effects.[5,42]

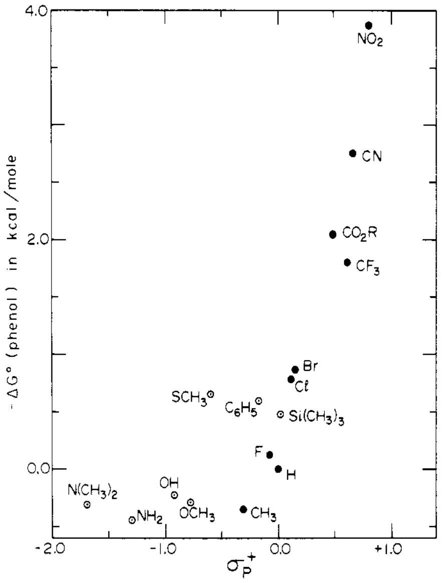

Figure 2. Plot of substituent effects on acidities of 4-substituted phenols (in terms of $-\Delta G°$ in kcal/mol) against Brown's σ_p^+ scale. Filled circles are points included in Swain's correlations of both σ_p^- and σ_p^+ against F and R while open circles are for points omitted from the σ_p^- correlation. By the use of the former points only, the correlation of $\Delta G°$ vs. σ_p^+ gives a correlation coefficient, $C = 0.957$. For all points, $C = 0.770$.

We have chosen seven data sets to rigorously check Swain's claim that F and R can predict properties for a wide variety of aromatic systems. These are aqueous acidities of 4-substituted phenols (**5**), 4-anilinium ions (**6**) (both σ^- systems[5]), and 3-substituted phenols (**5M**, a σ^0 system[5]), Wepster's σ_p^n scale (**7**, also representative of a σ^0 system),[43] σ_p (**8**), acidities of 4-substituted pyridinium ions (**9**), and σ_p^+ (**10**) (the last two are σ^+ systems[5]). Mainly para-substituted derivatives were chosen since they should be particularly sensitive to enhanced resonance effects.[5] Furthermore, in each case, an extensive and well-balanced[44] sub-

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[33] For further evidence and discussion, see: Charton, M. *J. Org. Chem.*, the third paper in this series.

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[40] See ref 6b and 26 for summaries of earlier work in this area.

[41] The previously included σ_p^- value for OCH_3 (−0.13)[2] is now excluded on the grounds of "dubious reliability".[8] However, in a critical compilation of acid dissociation constants (Kortum, G.; Vogel, W.; Andrussow, K. *Pure Appl. Chem.* **1960**, *1*, 188) the pK_A value for 4-methoxyphenol (10.20) used to derive σ_p^- for OCH_3 (Cohen, L. A.; Jones, W. M. *J. Am. Chem. Soc.* **1963**, *85*, 3397) is classified as reliable.

[42] Including hydrogen, the recommended minimal substituent set includes nine key substituents ranging from $N(CH_3)_2$ and/or NH_2 to CN and/or NO_2.

[43] Hoefnagel, A. J.; Wepster, B. M. *J. Am. Chem. Soc.* **1973**, *95*, 5357.

stituent set was available. Charged substituents were avoided for reasons discussed in part i and ref 25, 26, 29, 30, and 33.

Results of correlations against *F* and *R* are summarized in Table II. *F* and *R* give very good correlations for the three systems following σ or σ^+ (**8**–**10**) but deteriorate progressively from σ to σ^- systems (**7**, **5M**, **6**, **5**). System **5** is regarded as the outer limit for a σ^- system in solution.[5] The dramatic difference between our correlation for **5** ($C = 0.921$) and that reported by Swain ($C = 0.994$) clearly illustrates the importance of using well-balanced substituent sets.[29] It is obvious from these results that *R* is not a universal resonance scale and that *F* and *R* are really applicable only to systems following σ and σ^+. Their success in this limited area undoubtedly reflects the fact that the data matrix used to define *F* and *R* is dominated by systems following σ or σ^+.[45] Note also that correlations of gas phase acidities for six of these systems against *F* and *R* are of generally low precision (average $C = 0.962$, see Table IV in supplementary material).

(iv) Reasons for the Limitations of *F* and *R* and Directions for Future Research. There appear to be two major problems with this scale. First, the unfortunate choice of $R = 0$ for $N(CH_3)_3^+$ combined with the fact that *F* and *R* constants for the majority of substituents were determined soley from aromatic data results in the incomplete separation of field and resonance effects. This is particularly reflected in the poor correlations for systems dominated by a single effect, e.g., **3** and **4**. This problem might be overcome by a change in reference and use of a more complex data matrix. However, the second problem is insurmountable, given Swain's basic assumptions. It is simply that no single resonance scale can adequately account for the entire range of aromatic properties, given the major variations in substituent resonance effects with electron demand.[5,34-39] *R*, as currently defined, is applicable to σ and σ^+ systems and even in these cases, the weighting factors (*f* and *r*) are of dubious significance due to incomplete separation of substituent effects.

In our view, there is little value in pursuing this approach further since its fundamental limitations outweigh its attractive simplicity. A more fruitful line of research would be to develop a model which recognizes the variability of substituent resonance effects but which requires fewer fixed resonance scales than the five (counting $\sigma_R^-(P)$ for phenols) required in the Taft approach.[36,46]

Acknowledgment. We thank Dr. A. Tanin for help in carrying out the correlations reported in this paper.

Supplementary Material Available: Table III, listing of all substituents, values of parameters, and sources of parameters used for the correlations in Tables I and II and Table IV correlations of gas phase acidities against *F* and *R*; Figure 1, a plot of ΔpK_A of **3** vs. *F* along with correlations for primary and secondary substituent sets (5 pages). Ordering information is given on any current masthead page.

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[44] Well balanced in the sense of having at least four strong π donors ($R < -1.0$) and four strong π acceptors ($R > 0.5$).

[45] 165 of the 195 aromatic data points in the data matrix used to define *F* and *R* are for benzoic or naphthoic acid acidities or cumyl chloride solvolyses,[8] i.e., systems which follow σ or σ^+. Of the remaining 30 data points, only one is for a strong π donor.

[46] Reynolds, W. F.; Tanin, A., to be published.