Substituent Effects, Electronic Transmission and Structural Dependence of π Delocalization as Studied with the p-Fluorophenyl Tag[1]

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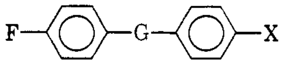
Abstract: The F nmr shielding effects of para substituents, X, in cations, anions, and molecules of the general formula $p\text{-FC}_6\text{H}_4\text{GC}_6\text{H}_4\text{X}_{(p)}$ have been determined for various molecular cavities, G. The results cannot be described satisfactorily by Swain's $\mathcal{F}$ and $\mathcal{R}$ treatment, but do conform satisfactorily to the dual substituent parameter (DSP) equation utilizing the σ_R scales recently defined independently by Ehrenson, Brownlee, and Taft. Values of ρ (ρ_R and ρ_I) vary with G by more than 40-fold. Use of the sensitive p-fluorophenyl tag measurement has permitted not only confirmation of structural classification of σ_R scales, but also the determination of systematic structural effects on the relative transmission of substituent polar and π delocalization effects. The importance of π induction in the F nmr shifts has been demonstrated. The results of this study support applications of the DSP equation to structural characterization of reaction transition states.

The objective of this work is the study of the nature and transmission of substituent electronic effects on the fluorine nuclear magnetic resonance (F nmr) shielding of p-fluorophenyl tagged systems. Specifically, both neutral, negatively, and positively charged systems of structure I have been studied



I

where X = general substituent.

The G constituent of I is a widely varied molecular cavity. Previously, work has established the sensitivity and general suitability of F nmr shielding for this type of investigation.[2]

The work has been stimulated by the results of a recent critical reexamination of substituent effects in the benzene series.[3] It has been demonstrated in terms of the dual substituent parameter treatment[4] (eq 1) that single substituent parameter treatments, *e.g.*, $\rho\sigma$, $\rho\sigma^-$, or $\rho\sigma^+$, lose precision and generality for two basically different reasons. First, the constraint of equal susceptibility of observed substituent effects to polar and resonance or π delocalization effects ($\rho_I = \rho_R = \rho$) is not generally valid.[5] Second, there are very significant dependencies of the resonance effects upon structural types.[6] With adequate recognition of these two factors it was shown that eq 1 achieves in the benzene series highly general and relatively precise correlations of rate, equilibrium, and spectral property substituent effects. In particular, F nmr shielding effects were shown to follow eq 1 with a

$$P^i \text{ (substituent effect from the } i\text{th position)} = \sigma_I\rho_I{}^i + \sigma_R\rho_R{}^i \quad (1)$$

generality and precision at least comparable to rate and equilibrium substituent effects.[3]

Equation 1 attributes the observed substituent effect to an additive blend of polar (I) and π delocalization (R) effects, each of which is given as a $\sigma\rho$ product. The susceptibility or mixing coefficients, $\rho_I{}^i$ and $\rho_R{}^i$, depend upon the position of the substituent (indicated by the index, i) with respect to the reaction or detection center, the nature of the measurement at this center, and the conditions of solvent and temperature. The σ_I scale of polar effects is held to have wide general applicability. The dependence of the π delocalization term, $\sigma_R\rho_R$, on structural type was recognized in the treatment by Ehrenson, Brownlee, and Taft in terms of four sets of σ_R parameters. Each parameter scale has limited generality and characteristic structural type.[3] These substituent parameters were designated as $\sigma_R{}^0$, σ_R(BA), $\sigma_R{}^+$, and $\sigma_R{}^-$ and the parameter values obtained from "basis sets" are summarized in Table I.

Previously reported F nmr shifts for structure I systems[2] were found to follow eq 1 with the discriminating best fits as shown in Table II.

Table II lists values of ρ_I and ρ_R and the ratio, $\rho_R/\rho_I \equiv \lambda$. Also given are the number of substituents in the data set, n, the standard deviation of the fit, SD, and the fit parameter, $f \equiv$ SD/RMS, where RMS is the root mean square of the data points. The present work was carried out in particular to provide critical tests of the $\sigma_R{}^-$ and $\sigma_R{}^0$ structural assignments, and to determine the structural effects of cavity G upon the relative transmission of the substituent polar and resonance effects as measured by λ. The $\sigma_R{}^-$ and $\sigma_R{}^0$ scales have not been previously tested by F nmr shifts of $p\text{-FC}_6\text{H}_4$ tags. With this purpose in mind, the following systems have been studied: G = $[>\text{CC}_6\text{H}_5]^-$ and $[>\text{C}{=}\ddot{\text{N}}{:}]^-$, both in DMSO solutions; G = $>\text{CH}_2$, $>\text{CHOH}$, $>\text{C(CH}_3)$-

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[1] This work was supported at UCI in part by the National Science Foundation, including support which made available the nmr spectrometer to the UCI Chemistry Department. Partial support (Brookhaven) was also provided by the Atomic Energy Commission.

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Table I. Substituted Parameters from Ehrenson, Brownlee, and Taft

Substituent	σ_I	$\sigma_R{}^0$ [a]	$\sigma_{R(BA)}$ [b]	$\sigma_{R(A)}{}^-$ [c]	$\sigma_R{}^+$ [d]
$-N(CH_3)_2$	0.06	−0.52	−0.83	−0.34	−1.75
$-NH_2$	0.12	−0.48	−0.82	−0.48	−1.61
$-NHCOCH_3$	0.26	−0.25	−0.36		−0.86
$-OCH_3$	0.27	−0.45	−0.61	−0.45	−1.02
$-OC_6H_5$	0.38	−0.34	−0.58		−0.87
$-SCH_3$	0.23	−0.20	−0.32	−0.14	*e*
$-CH_3$	−0.04	−0.11	−0.11	−0.11	−0.25
$-C_6H_5$	0.10	−0.11	−0.11	0.04	−0.30
-F	0.50	−0.34	−0.45	−0.45	−0.57
-Cl	0.46	−0.23	−0.23	−0.23	−0.36
-Br	0.44	−0.19	−0.19	−0.19	−0.30
-I	0.39	−0.16	−0.16	−0.11	−0.25
-H	0.00	0.00	0.00	0.00	0.00
$-SOCH_3$	0.50	0.00	0.00		0.00
$-SCF_3$	0.42	0.04	0.04	0.14	0.04
$-Si(CH_3)_3$	−0.10	0.06	0.06	0.14	0.06
$-SF_5$	0.57	0.06	0.06	0.20	0.06
$-SOCF_3$	0.64	0.08	0.08		0.08
$-CF_3$	0.45	0.08	0.08	0.17	0.08
$-SO_2CH_3$	0.59	0.12	0.12	0.38	0.12
-CN	0.56	0.13	0.13	0.33	0.13
$-CO_2R$	0.30	0.14	0.14	0.34	0.14
$-NO_2$	0.65	0.15	0.15	0.46	0.15
$-COCH_3$	0.28	0.16	0.16	0.47	0.16

[a] Defined from 14 sets of σ^0 type rates, equilibria, and F nmr shift data. [b] Defined from eight basis sets of rate and equilibrium data of the benzoic acid ionization type. [c] Defined from the basis set of anilinium ion ionization, H_2O, 25°. [d] Defined from two basis sets of rate data, solvolysis of *tert*-cumyl chlorides (Brown) and protonolysis of phenyltrimethylsilanes (Eaborn). [e] No single value found applicable.

OH, $>C(C_6H_5)OH$, and $>C(CF_3)OH$ in CH_2Cl_2 and/or benzene solutions. As a critical test of the range of applicability (or possible limitations) of the $\sigma_R{}^+$ scale, G = $[>CCH_3{}^-]^+$, $[>CH]^+$, and $[>CCF_3]^+$ have been investigated in FSO_3H. Finally, the unsaturated cavities G = −CH=CH−, −CH=N−, and −N=N− have been included.

Experimental Section

Synthesis. All the *p*-fluorophenyl derivatives were prepared by literature procedures reported for their unsubstituted phenyl analogs. Solids were recrystallized to a constant melting point. Liquids were fractionally distilled twice. All melting and boiling points given in Table III are uncorrected. The compounds were further characterized by infrared and proton nmr.

4′-Substituted-4-fluorobenzophenones were prepared according to the procedure of ref 2b. These compounds were convenient starting materials for most of the syntheses described below.

4′-Substituted-4-fluorobenzhydrols were prepared by either lithium aluminum hydride or sodium borohydride reduction of the ketones.

4′-Substituted-4-fluorodiphenylmethanes were prepared by formic acid and sodium formate reduction of benzhydrols.[7,8] For example, 5 g of *p*-fluorobenzhydrol was refluxed with 20 ml of formic acid (98%) and 2.5 g of sodium formate overnight. The reaction mixture was neutralized with sodium carbonate and extracted with ether. The solvent was evaporated and the residue on distillation yielded 3.5 g of the product.

α-Methyl-4′-substituted-4-fluorobenzhydrols were prepared by condensing methylmagnesium bromide with ketones.[2b]

α-Trifluoromethyl-4′-substituted-4-fluorobenzhydrols were prepared by condensing the appropriate Grignard reagent with *p*-fluorotrifluoroacetophenone (Pierce Chemical Co.).

4′-Substituted-4-fluoroazobenzenes were prepared by condensing equimolar amounts of 4-fluoronitrosobenzene with the appropriate amine in absolute ethanol containing trace amounts of glacial acetic acid. The compounds were recrystallized from absolute ethanol. 4-Fluoronitrosobenzene (mp 40–41°) was obtained in about 30% yield by zinc and ammonium chloride reduction of 4-fluoronitrobenzene.

4′-Substituted-4-fluorostilbenes (trans) were prepared by condensing diethyl 4-fluorobenzylphosphonate with 4-substituted benzaldehydes in dimethylformamide containing sodium methoxide (10% in excess). The compounds showed a strong band at 990–965 cm^{-1} in infrared indicating the trans structure.

4-Fluoro-4′-substituted-triphenylcarbinols were prepared by condensing phenyl magnesium bromide with ketones.[2b]

4-Fluoro-4′-substituted-triphenylmethanes were obtained by the formic acid and sodium formate reduction of the corresponding carbinols (above).

Table II. Best Fit Parameters of Literature Data to Eq 1

	Solvent	Type	$-\rho_I$	$-\rho_R$	λ^p	*n*	SD	*f*	Ref
$p-FC_6H_4C_6H_4X_{(p)}$	C_6H_6 or DMF	$\sigma_R(BA)$	3.23	3.32	1.03	8	0.18	0.110	2c
$p-FC_6H_4COC_6H_4X_{(p)}$	CH_2Cl_2	$\sigma_R(BA)$	2.55	2.71	1.06	9	0.07	0.059	2b
$p-FC_6H_4C(OBF_3)C_6H_4X_{(p)}$	CH_2Cl_2	$\sigma_R{}^+$	6.42	6.25	0.97	6	0.19	0.068	2b
$p-FC_6H_4C(OBCl_3)C_6H_4X_{(p)}$	CH_2Cl_2	$\sigma_R{}^+$	7.86	7.23	0.92	6	0.21	0.065	2b
$p-FC_6H_4C(OBBr_3)C_6H_4X_{(p)}$	CH_2Cl_2	$\sigma_R{}^+$	7.87	7.44	0.95	5	0.06	0.018	2b
$p-C_6H_4C(OH)C_6H_4X_{(p)}{}^+$	H_2SO_4	$\sigma_R{}^+$	7.91	7.91	1.00	7	0.36	0.089	2b
$p-FC_6H_4C(C_6H_5)C_6H_4X_{(p)}{}^+$	H_2SO_4	$\sigma_R{}^+$	10.98	11.25	1.02	7	0.75	0.088	2a

Table III. Boiling Point Data, °C (mm), and Melting Point Data, °C

G	NMe_2	OMe	F	Cl	Me	H	CF_3	MeCO	CN	NO_2
$-CH_2-$	85–90	165 (0.4)	62–65	130 (0.4)	140 (0.4)	140 (0.4)	155 (0.4)			
−C(Ph)H−	110 (0.5)	80[a] (0.1)	118–120[a,b]	136 (0.4)	110 (0.1)	80–84 (0.5)	140 (0.25)			
−C(OH)H−	74–75	145 (0.4)	140 (0.4)	165 (0.4)	155 (0.25)	130 (0.5)	65–66			81–82
$-C(CH_3)OH-$	80–83	110 (0.4)	128 (0.25)	130 (0.4)	120 (0.4)	120 (0.25)				Oil
−C(Ph)OH−	115–117	170–175 (0.5)	120 (0.1)	130 (0.4)	Oil[a]	120–122	140 (0.25)			
$-C(CF_3)OH-$	89–94	110 (0.25)	98–100 (0.4)		130 (0.5)	120 (0.4)	138 (0.4)			
−CH=N−	143–145	96	58	74–75	58	40	Oil		98–100	98
−N=CH−	134–136	53–54	58	57–59	68	56			137–139	112–113[c]
−CH=CH−	183–185	147–149[c]	130–131	142[c]	150	124–125[c]			138–140	135–137
−N=N−		91	97	126–128	98–100	83–84	54–56	74–75		

[a] L. D. McKeever, Ph.D. Dissertation, the University of California, Irvine, 1966. [b] Bis-*p*-difluoro-*p*-nitrotriphenylmethane. [c] Prepared and supplied by Dr. R. G. Pews.

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Table IV. F Nmr Substituent Shielding Effects (ppm)

Set no.[a]	$\int_{\mathrm{ref}}^{\mathrm{H}}$ [b]	NMe_2	OMe	F	Cl	Me	SMe	CF_3	MeCO	SO_2Me	CN	NO_2
1	3.84	0.53	0.19	−0.23	−0.37	0.12		−0.69				
2	2.83	0.47	0.15	−0.21	−0.39	0.14		−0.64				−1.11[c]
3	2.48	0.65	0.23	−0.23	−0.43	0.17		−0.78				−1.44
4	2.06	0.65	0.23	−0.26	−0.47	0.16		−0.81				
5	4.36	0.72	0.27	−0.27	−0.46	0.18		−0.82				−1.52
6	1.31	0.58	0.17	−0.21	−0.40	0.15		−0.71				
7	−0.67	0.56	0.21	−0.39		0.18		−0.82				
8	−0.72	0.56	0.20	−0.45		0.18		−0.85				
9	−4.70	1.46	0.61	−0.19	−0.54	0.30		−1.20			−1.86	−2.00
10	4.17	1.55	0.62	−0.10	−0.55	0.29					−1.69	−1.99
11	2.07	1.79	0.62	−0.17	−0.53	0.30					−1.74	−2.11
12	−6.42	2.32	0.80	−0.16	−0.51	0.46		−1.29				−2.00
13	−3.72	2.35	0.94	−0.23		0.46	0.32	−1.41				
14	−3.67		1.07	−0.19	−0.64	0.49	−0.73[e]	−1.61	−1.40			
15	−23.22		1.43	−0.65		0.53					−3.60	−3.87
16	−7.09		1.97	−0.17		0.54					−2.50	−3.00
17	−36.06	38.73[d]	17.62	1.88	−0.55	6.20		−10.39				
18	−45.30	48.06[d]	19.92	2.46	−0.57	6.73		−12.27				
19	−54.38		38.44	5.96		16.65		−22.04				
20	14.89	4.10	3.30	0.00	−1.60	1.30		−6.12				−12.61[c]
21	5.95	0.23	0.14	−0.24	−0.24	0.12	−0.39	−3.40		−10.33		

[a] Set no. refers to the number designation used in Table V. [b] Shift of unsubstituted member relative to external reference of TCTFCB (60 wt % in $HCCl_3$). [c] Measurement made with (p-$FC_6H_4)_2CHC_6H_4NO_2$ relative to (p-$FC_6H_4)_2CC_6H_5$. [a] In trifluoroacetic acid. [e] Result for Br. For I substituents, −0.74.

4′-Substituted-4-fluorodiphenylketimines were prepared by condensing the appropriate Grignard reagent with p-fluorobenzonitrile in ether. The complexes were hydrolyzed with anhydrous methanol[9] and filtered. The hydrochlorides were precipitated with HCl gas. The hydrochlorides were found to sublime over a wide temperature range. The imine salts were converted to free bases by the method of Hantzsch and Kraft.[10] A solution of the salt in chloroform is treated with dry ammonia. Due to the very hygroscopic nature of these bases, they were used without further purification.

4-Fluoro-4′-substituted-diphenylazomethines (and isomers) were synthesized[11] by 1–2 hr refluxing of equimolar amounts of appropriate amine and aldehyde in ethanol. Purification to a constant melting point was carried out by means of recrystallization from ethanol.

Measurements. All solvents were dried suitably prior to their use. Fluorosulfonic acid (Allied Chemical Co.) was distilled in glass apparatus under argon. A center cut (bp 163°) was collected in glass ampoules and sealed for storage.

Fluorine chemical shifts were recorded on a Varian HA-60 spectrometer at 56.4 MHz in conjugation with an NMR Specialties SD 60-B heteronuclear spin decoupler and Varian V4343 temperature controller. The procedure followed was generally that previously reported.[12] The external capillary locking technique was employed and all fluorine shifts are reported in ppm from TCTFCB (60 wt % in $CHCl_3$). In order to extend the range from TCTFCB, the following references were employed (shifts are relative to TCTFCB): octafluorocyclobutane (neat), +23.78 ppm; 1,1,1-trichloro-2,2,2-trifluoroethane (60 wt % in $CHCl_3$), −31.38 ppm.[13] Samples of 0.05–0.10 M concentrations were typically used. For systems in which the substituent effects are relatively small (sets 1–14 Table V) greater experimental precision (±0.02 ppm) was obtained by putting the compounds (each at 0.05 M) in the same nmr tube. The measurements in FSO_3H were carried out in the following way. About 3 to 4 mg of the compound to be ionized was dissolved in 0.025 ml of CH_2Cl_2 in an nmr tube. The tube was flushed with dry argon and then cooled in a Dry Ice–acetone bath. FSO_3H (0.25 ml) was introduced slowly by means of a capillary pipette with thorough mixing. Measurements were done at −60° with the temperature cooled nmr probe. The negative ions were generated at room temperature by reacting 3 to 4 mg of the compound in 0.25 ml of DMSO with 0.25 ml of a 0.25 M solution of sodium methylsulfinylmethide[14] in DMSO and in an atmosphere of argon. The substituent effects were determined at room temperature. The proton transfer in these systems was found to be slow compared to the nmr time scale, so peaks for the neutral and the ionized species could be observed simultaneously. In all cases duplicates were run and for substituent shifts in FSO_3H and DMSO (sets 15–21, Table V), the precision is estimated to be ±0.10 ppm.

Results

In Table IV are given the F nmr substituent shielding effects (in ppm) observed for the 19 sets determined in this study. The first column of Table IV gives the shifts, $\int_{\mathrm{ref}}^{\mathrm{H}}$, of the unsubstituted member relative to tetrachlorotetrafluorocyclobutane (60 wt % in $CHCl_3$) as an external reference. The subsequent columns are the shifts for the indicated 4′-substituent relative to the unsubstituted member.

Table V gives the results of the best fits of the data to eq 1. In addition to values of ρ_I^p and ρ_R^p, values of λ^p, n, SD, and f = SD/RMS are listed as given (and defined) for Table II. Table VI shows the comparative values of SD and the fit parameter, f, for fits by eq 1 to the four σ_R scales and to Swain's $\mathcal{F}$ and $\mathcal{R}$ parameters.[5]

Discussion

σ_R^0 Sets. All of the series wherein G is a "formally saturated" cavity are best fitted by the σ_R^0 parameters. Since resonance effects are relatively small for these sets, the discriminatory precision achieved with these parameters over that obtained with the σ_R(BA) parameters is not highly dramatic. However, the pattern is completely consistent and the better fits are by factors which we believe to be generally significant (*cf.* Table VI, results for sets 1–8). Thus, the relatively sensitive F nmr measurements do support the utility of the σ_R^0 scale in achieving a more precise description of substituent effects. However, the utility appears even more valuable with respect to discriminating between structural types (*cf.* subsequent discussion of results.)

The effects of substantial structural variation in the "saturated" cavity G and, of solvent variation, on the ρ_I and ρ_R values are quite minor but significant (*cf.*

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[13] We are indebted to Dr. John Thompson for this measurement.

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Table V. Best Fit Parameters of Eq 1 for Substituent F Nmr Shielding Effects

Set	Type	Solvent	$-\rho_I$	$-\rho_R$	λ^p	n^a	SD	f
1. p-$FC_6H_4CH_2C_6H_4X_{(p)}$	σ_R^0	CH_2Cl_2	1.311	1.175	0.90	6	0.03	0.079
2. p-$FC_6H_4CH(C_6H_5)C_6H_4X_{(p)}$	σ_R^0	CH_2Cl_2	1.339	1.133	0.85	7*	0.05	0.091
3. p-$FC_6H_4CH(OH)C_6H_4X_{(p)}$	σ_R^0	CH_2Cl_2	1.676	1.537	0.92	7*	0.07	0.106
4. p-$FC_6H_4CH(OH)C_6H_4X_{(p)}$	σ_R^0	C_6H_6	1.573	1.421	0.90	6	0.04	0.088
5. p-$FC_6H_4COH(CH_3)C_6H_4X_{(p)}$	σ_R^0	CH_2Cl_2	1.782	1.655	0.93	7*	0.07	0.097
6. p-$FC_6H_4COH(C_6H_5)C_6H_4X_{(p)}$	σ_R^0	CH_2Cl_2	1.368	1.241	0.91	6	0.04	0.087
7. p-$FC_6H_4COH(CF_3)C_6H_4X_{(p)}$	σ_R^0	CH_2Cl_2	1.599	1.301	0.81	5	0.03	0.067
8. p-$FC_6H_4COH(CF_3)C_6H_4X_{(p)}$	σ_R^0	C_6H_6	1.688	1.306	0.77	5	0.04	0.081
9. p-$FC_6H_4CH{=}NC_6H_4X_{(p)}$	σ_R^0	C_6H_6	2.451	2.931	1.20	8*	0.09	0.074
10. p-$FC_6H_4N{=}CHC_6H_4X_{(p)}$	$\sigma_R(BA)$	C_6H_6	2.423	2.150	0.89	7*	0.08	0.070
11. p-$FC_6H_4CH{=}CHC_6H_4X_{(p)}$	$\sigma_R(BA)$	C_6H_6	2.569	2.334	0.91	7*	0.08	0.060
12. p-$FC_6H_4COC_6H_4X_{(p)}$	$\sigma_R(BA)$	CH_2Cl_2	2.554	2.739	1.07	7*	0.12	0.091
13. p-$FC_6H_4C{=}NH(C_6H_4X_{(p)})$	$\sigma_R(BA)$	$CHCl_3$	2.883	2.925	1.01	6	0.08	0.069
14. p-$FC_6H_4N{=}NC_6H_4X_{(p)}$	$\sigma_R(BA)$	C_6H_6	3.076	3.111	1.01	8	0.04	0.039
15. p-$FC_6H_4CH{=}NH{-}C_6H_4X_{(p)}{}^+$	$\sigma_R(BA)$	FSO_3H^b	5.139	4.458	0.87	5	0.13	0.052
16. p-$FC_6H_4NH{=}CH{-}C_6H_4X_{(p)}{}^+$	σ_R^+	FSO_3H^b	3.800	2.908	0.77	5	0.16	0.082
17. p-$FC_6H_4C(CH_3)C_6H_4X_{(p)}{}^+$	σ_R^+	FSO_3H^b	20.31	22.79	1.12	6	0.62	0.034
18. p-$FC_6H_4CHC_6H_4X_{(p)}{}^+$	σ_R^-	FSO_3H^b	24.73	27.72	1.12	6	1.37	0.062
19. p-$FC_6H_4C(CF_3)C_6H_4X_{(p)}{}^+$	σ_R^+	FSO_3H^b	42.42	48.64	1.15	4	1.28	0.054
20. p-$FC_6H_4C(C_6H_5)C_6H_4X_{(p)}{}^-$	σ_R^-	DMSO	10.37	12.80	1.23	7	0.36	0.063
21. p-$FC_6H_4C{=}N(C_6H_4X_{(p)})^-$	σ_R^-	DMSO	8.475	8.055	0.95	8	1.47	0.382

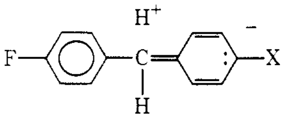
[a] Sets marked with asterisks meet the minimal basic set requirements of Wells, Ehrenson, and Taft, ref 4. [b] *Cf.* Experimental Section for details of this solvent.

Table VI. Comparative Fits of Eq 1 with Different Parameter Scales

Set	σ_R^0		$\sigma_R(BA)$		$\sigma_R^-(A)$		σ_R^+		$\mathcal{F}$ & $\mathcal{R}$	
no.[a]	SD	f	SD	f	SD	f	SD	f	SD	f
1	0.03	0.079	0.04	0.105	0.10	0.241	0.09	0.229	0.03	0.074[b]
2	0.05	0.091	0.08	0.138	0.10	0.174	0.13	0.242	0.04	0.072[b]
3	0.07	0.106	0.11	0.157	0.13	0.180	0.18	0.263	0.08	0.076[b]
4	0.04	0.088	0.05	0.091	0.12	0.249	0.11	0.221	0.03	0.058[b]
5	0.07	0.097	0.11	0.143	0.15	0.200	0.19	0.248	0.08	0.104[b]
6	0.04	0.087	0.04	0.090	0.11	0.251	0.09	0.217	0.02	0.045[b]
7	0.03	0.067	0.06	0.120	0.13	0.255	0.11	0.220	0.05	0.097[b]
8	0.04	0.081	0.06	0.120	0.13	0.263	0.11	0.215	0.06	0.116[b]
9	0.08	0.068	0.10	0.083	0.38	0.324	0.26	0.219	0.06	0.057[b]
10	0.09	0.074	0.09	0.076	0.41	0.346	0.25	0.210	0.05	0.046[b]
11	0.08	0.077	0.07	0.064	0.36	0.344	0.22	0.208	0.04	0.048[b]
12	0.25	0.193	0.12	0.091	0.63	0.478	0.13	0.096	0.06	0.052[b]
13	0.21	0.177	0.08	0.069	0.58	0.479	0.12	0.093	0.15	0.181[b]
14	0.11	0.112	0.04	0.038	0.29	0.300	0.13	0.136	0.12	0.126
15	0.19	0.077	0.13	0.052	0.43	0.174	0.27	0.108	0.22	0.089
16	0.26	0.132	0.20	0.102	0.52	0.265	0.16	0.082	0.27	0.135
17	5.15	0.285	3.37	0.186	10.15	0.562	0.62	0.034	2.52	0.262[b]
18	6.78	0.308	4.54	0.206	12.77	0.580	1.37	0.062	2.64	0.241[b]
19	5.28	0.222	5.27	0.221	9.23	0.387	1.28	0.054	6.03	0.253
20	1.50	0.262	1.97	0.344	0.36	0.063	2.60	0.456	1.26	0.213[b]
21	2.16	0.561	2.33	0.606	1.47	0.382	2.70	0.655	1.91	0.465[b]

[a] Set no. refers to the number designation used in Table V. [b] Datum for NMe_2 substituent not included due to critical omission of an $\mathcal{R}$ value. Although the f parameters are adjusted by the modified RMS in an attempt to compensate for the omission, the results must be accepted with less confidence since a more limited range of substituent effect properties is covered by the data treated.

Table V, results for sets 1–8). The carbinols (sets 3–8) have somewhat larger ρ values than the methanes (sets 1 and 2), suggesting that transmission occurs at least in part through no-bond resonance forms,[15] *e.g.*, with III and IV more important than I and II. The importance of double bond–no-bond resonance forms has recently been supported by theoretical studies of charge distributions and bond separation energies.[16] Comparable studies with alkaryl fluorides, *e.g.*, p-$FC_6H_4C(R)FC_6H_4X_{(p)}$, would be of interest in this connection.



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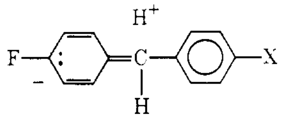

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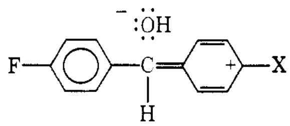
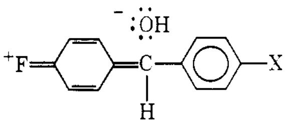


III



IV

The ratio of ρ_R to ρ_I, *i.e.*, $\lambda \equiv \rho_R/\rho_I$, is of interest. For sets 1–8 of Table V, $\lambda = 0.87 \pm 0.05$. This result is apparently roughly characteristic of the relative transmission of para-substituent resonance and polar effects for a number of systems involving no significant through-conjugation (*i.e.*, direct conjugation between the para substituent and the atomic center in the cavity G which is bonded to the benzene ring).

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(15) *Cf.* E. T. McBee, I. Serfaty, and T. Hodgins, *J. Amer. Chem. Soc.*, **93**, 5711 (1971).

(16) L. Radom, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 289 (1971).

Table VII. Fits by Eq 1 with σ_R^0 Values for Ar–X and ArCH$_2$–X Systems[a]

	$-\rho_I^p$	$-\rho_R^p$	λ^p	n	SD	f
Conjugated Substituent, Ar–X						
p-XC$_6$H$_4$F, F nmr shift, cyclohexane, 25°	7.03	30.58	4.35	22	0.56	0.076
p-XC$_6$H$_4$CH$_2$F, F nmr shift, CCl$_4$, 25°[b]	−8.96	−20.6	2.30	7	0.74[b]	0.138[b]
p-XC$_6$H$_4$CO$_2$H, ionization, 50% aq EtOH, 25°[b]	−1.54	−1.73	1.12	14	0.07[b]	0.118[b]
p-XC$_6$H$_4$CH$_2$CO$_2$H, ionization, 50% aq EtOH, 25°	−0.755	−0.646	0.86	11	0.02	0.060
Nonconjugated Substituent, ArCH$_2$–X						
p-XCH$_2$C$_6$H$_4$F, F nmr shift, CCl$_4$, 25°	10.51	−0.91	−0.09	10	0.37	0.100
p-XCH$_2$C$_6$H$_4$CO$_2$H, ionization, 50% aq EtOH, 25°	−0.903	0.018	−0.02	8	0.03	0.082

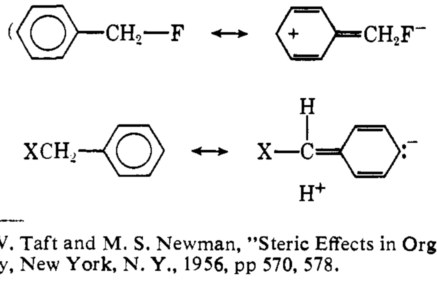
[a] All figures are from ref 3, which cites original literature. [b] Better fit is achieved with this set using σ_R(BA) parameters. However, to make direct comparison of all ρ_R values of Table VII, eq 1 has been applied to all sets using σ_R^0 parameters.

Similar λ values were found by Ehrenson, Brownlee, and Taft[3] for the ionization of phenylacetic acid, and the rates of saponification of their esters and of β-phenylpropionic esters ($\lambda = 0.85 \pm 0.02$).

Nonzero values of λ for these structural types in either rate, equilibrium, or F nmr shift data are expected, of course, since delocalization of π charge from the substituent, X, gives rise to polarization of the benzene ring (the resonance polar effect)[17] which is transmitted through G by field and internal π induction to the reaction or detector center. However, if the CH$_2$ cavity is interposed between the substituent X and the benzene ring (*i.e.*, Ar–CH$_2$X), the results of the dual substituent parameter analysis of F nmr shifts and acid ionizations (for Ar–CH$_2$X) are strikingly different than for corresponding Ar–X systems. These results which are relevant to the present discussion are given in Table VII.

For sets with conjugated substituent, Ar–X, λ^p varies from 0.86 to 4.35. For the "nonconjugated" ArCH$_2$X substituent sets, λ^p is essentially zero. This wide variation in λ^p results from the effect on ρ_R values, since ρ_I values are of comparable magnitudes for all of the F nmr sets or all of the acid ionizations. It is of interest in this connection that for the ArX sets, the interposition of a CH$_2$ cavity between the benzene ring and the detector (F) or reaction center (CO$_2$H) produces in each case the expected reduction in ρ_R^p and λ^p. For acid ionization there is a similar reduction in ρ_I^p values.

However, for the F nmr shifts which are more highly sensitive to π electron effects, the magnitudes of ρ_I^p are actually greater for both the p-XC$_6$H$_4$CH$_2$F and p-XCH$_2$C$_6$H$_4$F sets than for the p-XC$_6$H$_4$F set. This is a highly significant result which we believe can be accounted for by the pseudounsaturation present in "formally saturated" cavities and by the noncolinearity of X and F in the former sets. The ρ_I^p values for the p-XC$_6$H$_5$CH$_2$F and p-XCH$_2$C$_6$H$_4$F sets are presumably composites of the "normal" polar effect (which may be enhanced in these sets by conformations which shorten the X–F distance) and the polar effect of X on the no-bond resonance forms



The contribution of the "normal" polar effect to the observed ρ_I^p value will tend to decrease with the interposition of the CH$_2$ cavity, as observed for acid ionization. However, the polar effect on hyperconjugation makes a very significant contribution to π electron sensitive F nmr shifts, resulting in the observed ρ_I^p values actually increasing in magnitude in the p-XC$_6$H$_4$CH$_2$F and p-XCH$_2$C$_6$H$_4$F sets compared to the p-XC$_6$H$_4$F set.

Comparison of the DSP fitting parameters for p-XC$_6$H$_4$F$_{(p)}$ (Table VII) and p-XC$_6$H$_4$CH$_2$H$_4$F$_{(p)}$ (Table V) systems is also instructive, *cf.*, Table VIII. The large apparent fall-off factor in the ρ_I values of Table VIII is consistent with the above discussion. The differences in ρ_R values are probably not significant in view of the markedly different λ blends.

Table VIII. DSP Parameter Comparison

Set	$-\rho_I^p$	$-\rho_R^p$	λ^p
p-XC$_6$H$_4$CH$_2$C$_6$H$_4$F$_{(p)}$, CH$_2$Cl$_2$	1.31	1.18	0.90
p-XCH$_2$C$_6$H$_4$F$_{(p)}$, CCl$_4$	10.51	−0.91	−0.09

$\sigma_{R(BA)}$ Sets. All of the series wherein G is a neutral but unsaturated cavity, *i.e.*, –N=CH–, –CH=N–, –CH=CH–, –C(O)–, –C(NH)–, and –N=N– are fitted very satisfactorily by the σ_R(BA) scale (Tables V and VI, sets 9–14). The latter three sets are fitted better with σ_R(BA) than σ_R^0 parameters by factors greater than twofold, whereas the former three sets give essentially indiscriminate fits between these two scales (*cf.*, Table VI, sets 9–14). For all of these sets, both $-\rho_I$ and $-\rho_R$ values are substantially greater than corresponding values for the σ_R^0 type sets (*cf.*, sets 1–8, Table V). The larger $-\rho$ values are in accord with the expected alteration in the relative contribution of the F nmr shift active forms,[18] $:\ddot{\mathrm{F}}\text{–Ar}$ and $^{+}:\ddot{\mathrm{F}}{=}\mathrm{Ar}^{-}$, resulting from increased transmission of the substituent's polar and resonance interaction effects through the more mobile π bonds. Further, the larger values of $-\rho_R$ and $-\rho_I$ for G = –$\ddot{\mathrm{N}}$=$\ddot{\mathrm{N}}$– than –CH=CH– may be ascribed to the increased $\mathrm{C_{ar}}\overset{--}{-}\ddot{\mathrm{N}}$ π bonds provided by the interaction of the nitrogen lone pairs. ρ values are strongly enhanced by protonation of G = –C(H)=N–: $-\rho_I$ increases by a factor of 2.7; $-\rho_R$ by a factor of

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(17) R. W. Taft and M. S. Newman, "Steric Effects in Organic Chemistry," Wiley, New York, N. Y., 1956, pp 570, 578.

(18) R. T. C. Brownlee and R. W. Taft, *J. Amer. Chem. Soc.*, **92**, 7007 (1970).

Table IX. Summary of σ_R^+ Fitting Results

G	Solvent	$-\rho_I^p$	$-\rho_R^p$	λ^p	n	SD	f
$-\mathrm{NH{=}CH^+}$	$\mathrm{FSO_3H}$, 25°	3.80	2.91	0.77	5	0.16	0.082
$>\mathrm{C{=}OBF_3}$	$\mathrm{CH_2Cl_2}$, 25°	6.42	6.25	0.97	6	0.19	0.068
$>\mathrm{C{=}OBCl_3}$	$\mathrm{CH_2Cl_2}$, 25°	7.86	7.23	0.92	6	0.21	0.065
$>\mathrm{C{=}OBBr_3}$	$\mathrm{CH_2Cl_2}$, 25°	7.87	7.44	0.95	5	0.06	0.018
$>\mathrm{C{=}\dot{O}H^+}$	$\mathrm{H_2SO_4}$, 25°	7.91	7.91	1.00	7	0.36	0.089
$>\mathrm{CC_6H_5^+}$	$\mathrm{H_2SO_4}$, 25°	10.98	11.25	1.02	7	0.75	0.088
$>\mathrm{CCH_3^+}$	$\mathrm{FSO_3H}$, 25°	20.31	22.8	1.12	6	0.62	0.034
$>\mathrm{CH^+}$	$\mathrm{FSO_3H}$, 25°	24.7	27.7	1.12	6	1.37	0.062
$>\mathrm{CCF_3^+}$	$\mathrm{FSO_3H}$, 25°	42.4	48.6	1.15	4	1.28	0.054

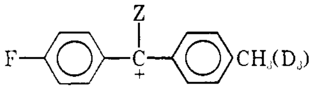
2.0 (*cf.* sets 9 and 15, Table V). This enhancement also may be ascribed to the improved overlap of the $\mathrm{C_{ar}}\overset{---}{—}\mathrm{CH}$ and $\mathrm{C_{ar}}\overset{---}{—}\underset{\cdot\cdot}{\mathrm{N}}$ π orbitals in the electron-deficient system.

The fits achieved with σ_R(BA) values used in eq 1 clearly support the conclusion of Ehrenson, Brownlee, and Taft[3] that this scale is applicable on a limited generality basis to systems which involve only very moderate direct conjugation between the para substituent and the atomic center in G which is bonded to the phenyl ring.

σ_R^+ Sets. All of the series wherein G is an unsaturated neutral or positively charged cavity with the p-$\mathrm{XC_6H_4}$ ring bonded to an appreciably electron deficient atomic center (having no unshared electron pairs, *e.g.*, with carbonium ion character) are best fitted with eq 1 by very significant factors using the σ_R^+ parameters (*cf.* sets 16–19, Table VI). Present results together with previously reported F nmr shifts are summarized in Table IX.

It is striking that the results of Table IX show a greater than 10-fold variation in ρ_I and ρ_R values. Within this range there are closely equivalent values (0.06 ± 0.03) of the fit parameter $f \equiv$ SD/RMS. This represents a very significant test of the σ_R^+ scale and shows the "limited generality" of the scale to be of broad scope. It is also significant that λ^p increases in a generally regular sequence with increasing value of $-\rho_R$. Clearly, the latter increases with electron demand at the carbonium ion center, due presumably to better orbital overlap of the π bonds, which accompanies the greater importance of the direct para-quinoidal structures.

Since the values of $-\rho_I$ also increase in this sequence (although not quite as sharply), it is also clear that the $\sigma_I\rho_I$ terms are determined predominantly by π electron transmission. That is, the simple field effect model is not capable of accounting for the greater than 10-fold variation in ρ_I values in view of the roughly comparable F–X distances. Another manifestation of the electron demand at the carbonium center is provided by the H–D p-$\mathrm{CH_3}$ isotope effect on the F nmr shift,[19] *i.e.*, for the carbonium ion series



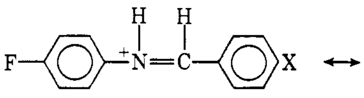
These methyl isotope effects are shown in Table X, together with the shift of the unsubstituted p-fluorophenyl carbonium ion relative to a fixed external reference standard (TCTFCB, 60% in $\mathrm{HCCl_3}$, Table IV) and the $-\rho_R$ value from Table IX. All of the quantities increase as Z becomes more electron attracting.

Table X. Effect of Electron Withdrawal by Z for G = -CZ-

Z	$-\int_{\text{ext ref}}$, ppm	$\int_{p\text{-CD}_3}^{p\text{-CH}_3}$, ppm	$-\rho_R$
$\mathrm{CH_3}$	36.1	0.044[a]	22.8
H	45.3	0.062	27.2
$\mathrm{CF_3}$	54.4	0.170[a]	48.6

[a] Unpublished results of Dr. John Thompson.

The different best fits of the isomeric protonated Schiff's bases (*cf.* Table VI, sets 15 and 16) are instructive with respect to structural classification of the σ_R parameters. The resonance forms, V and VI, clearly anticipate that this system will involve (as observed) direct conjugation of the σ_R^+ type. The value λ^p = 0.77 (Table V, set 16) may be rationalized on the basis that form V makes a substantially greater contribution than forms VI and VI′. However for the isomeric system (set 15, Table V), resonance form VII′ is of little importance. The shifts for this set accordingly are found to be of the σ_R(BA) type.



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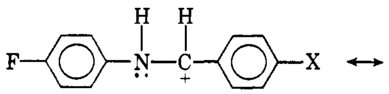

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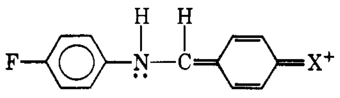
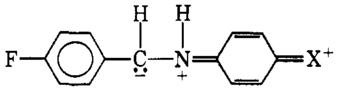


VI′



VII′

σ_R^- Sets. The F nmr substituent effect shifts are best correlated for the trityl anions (set 20, Table VI) by very substantial margins with the use of the σ_R^- parameters. This result offers the first confirmation of this scale obtained by the F nmr p-$\mathrm{FC_6H_4}$ tag method. It appears significant that λ^p = 1.23 (Table V, set 20) is greater than that found for any of the carbonium ions of the previous section (*cf.*, Table IX), even though ρ values for the trityl cation (ρ_I = −10.98; ρ_R =

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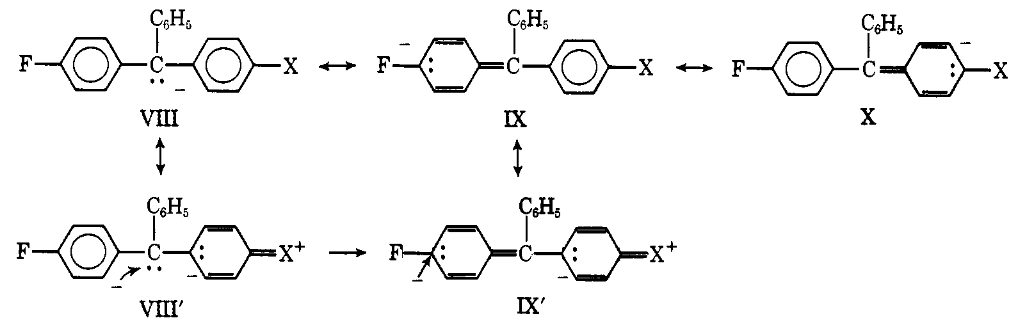
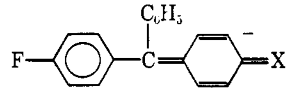
[19] J. W. Timberlake, J. A. Thompson, and R. W. Taft, *J. Amer. Chem. Soc.*, 93, 274 (1971).

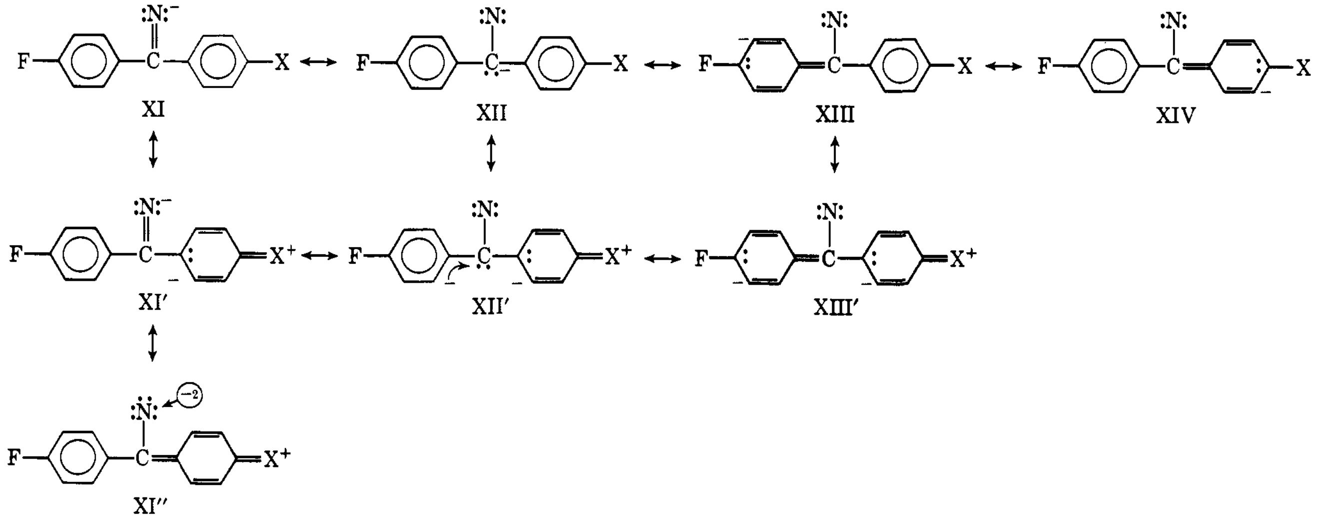


-11.25) and trityl anion ($\rho_I = -10.37$; $\rho_R = -12.80$) are of comparable magnitudes. This result indicates that the ratio of the substituent π delocalization to polar effects is enhanced in electron-rich systems. The effect is above and beyond the enhancements for +R substituents which are accommodated by the enhanced σ_R^- values for these substituents. Another manifestation of the role of the mobile π electron framework in the transmission of resonance effects is therefore obtained from the results for this system which is rich in π electron density.

Important information is also provided on the question of whether the sensitivity of the p-FC_6H_4 F nmr shift depends upon the F atom charge densities. The unsubstituted p-$FC_6H_4C(C_6H_5)_2^+$ ion is about 43 ppm downfield from the p-$FC_6H_4C(C_6H_5)_2^-$ ion, indicating an appreciably smaller (perhaps ~0.05)[20] F π charge density for the former. Since the ρ_I and ρ_R values of these two systems are very comparable, there is no evidence of any important dependence of ρ values upon this variable.



X′



The transmission of the π electron effects can be pictured in terms of the resonance forms for the trityl anion VIII–X and the para-substituent interaction forms, *e.g.*, VIII′ and IX′.

Form IX′ undoubtedly makes a minor contribution compared to forms VIII–X but small contributions from form IX′ are effective in the F nmr shielding. Form VIII′ is of very little importance (adjacent charge rule). The contribution of form IX′ increases with increasing $-\sigma_R^-$ value of the p-X substituent. For +R substituents, the interaction form, X′, increases in importance with increasing σ_R value and does so at the expense of form IX. Thus, an effective deshielding mechanism is available.

The results obtained with the diphenylimine conjugate bases (set 21, Tables V and VI) are equally interesting and instructive. This set is not satisfactorily correlated by eq 1 with any of the four scales of σ_R parameters. Since these results show a rational pattern of behavior, it seems clear that the failure of eq 1 is due not to faulty data, but rather to unique behavior associated with the molecular structure of this system. The shifts for −R substituents are notable for their very small magnitudes (*cf.*, set 21, Table IV). If these −R substituent effects alone are fitted by eq 1 using either σ_R^0 or σ_R^- values, the fit is to SD = 0.05, which is acceptable, with $-\rho_I \simeq 1.0$ and $\lambda^p \simeq 0.8$. That is, these substituent effects are rather similar to those obtained with both −R and +R substituents when G = "saturated" cavity (sets 1–8, Table VI). The low transmission of −R para-substituent effects in the diphenylimine conjugate base system may be considered in terms of the valence bond structures XI–XIV and their substituent interaction forms XI′, XII′, and XIII′.

Structures XII′, like VIII′, may be considered unimportant. So also are structures XI″. The results can be interpreted then on the basis of quite minor contributions of XIII′ relative to the small contributions made by structures XI′ (in contrast to the more important contribution of structures IX′ for the trityl anions). This possibility appears very rational in

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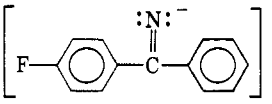
(20) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 3146 (1963).

terms of the greater electronegativity of the N than C, which favors XI′ over XIII′. Such an explanation is also in accord with the much smaller upfield shift of



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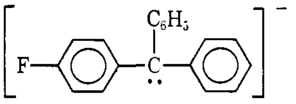
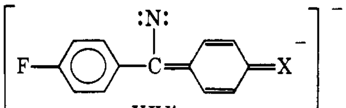


(*cf.*, Table IV).

The large substituent effects of the +R para substituents in the diphenylimine conjugate base system (*cf.* Table V, set 21) are readily accounted for by structure XIV′ in the same manner as discussed above for structure X′.



XIV′

It is also of interest to note that the *p*-SMe substituent exerts a net electron withdrawing effect (−0.39 ppm, *cf.*, Table IV) in this anion system, whereas normally this substituent is electron donating (*cf.*, for example, set 13, Table IV). Acceptor orbitals on sulfur (presumably 3d) have been shown to be important in π electron-rich systems.[21]

Additional Conclusions. Equation 1 purports to separate on a quantitative basis the measured substituent effects (on rate, equilibrium, or spectral quantity) to the sum of effects which are proportional to the σ_I values and to the sum of effects which are proportional to the appropriate σ_R parameter. The broad applicability which has been demonstrated for this treatment, *i.e.*, to measurements having very different dependences on bonding interactions, electric distributions, chemical state change, molecular motions and solvation, permits important conclusions, as follows.

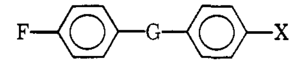
The σ_I scale of substituent effects is to useful approximation shown to be independent of the atomic center to which the substituent is bonded, or of the molecular framework or the space (empty or solvent and/or molecule filled) through which the polarization is propagated. The effects of these latter variables act as scaling constants within a data set, *i.e.*, their effects appear in variable ρ_I values. Specifically included within variables of the latter kind are variations in π or σ electron densities in the substituent X or on the atom to which X is bonded. It may be inferred from the data sets for which eq 1 holds (to the precision we have discussed, *i.e.*, SD/RMS $\leq$ 10%) that such variations, while small perhaps, are appreciable in view of the oppositely charged molecular cavities (G) which have been included in this study. The extent of independence of the σ_I scale from the nature of the atomic center to which the substituent is bonded has not received severe test in this work (only C_{ar} and C_{aliph} results are included in this paper). However, applications to X–P and X–S bonded systems have been made in other studies[21b,22] with quite acceptable results. More stringent tests of the transferability of the σ_I scale using other atomic centers and molecular cavities would be of substantial interest and significance.

It may be concluded from all of the critical rate, equilibrium, and F nmr shift data sets which follow eq 1 that the effects of at least four specific interaction mechanisms may be included among those effects which in general follow the σ_I scale: the σ and π bond inductive, the electrostatic field, and second order effects due to the mutual interactions of the first three.[23]

With respect to the F nmr shielding effects alone more specific conclusions appear applicable. Brownlee and Taft[18] have presented evidence from CNDO/2 theoretical calculations of charge distributions that the σ_I dependent term in the F nmr shielding effects of *meta-* and *para*-substituted fluorobenzenes may be identified with the fluorine atom σ electron density (and the σ_R^0 dependent term with the fluorine π electron density). The electrostatic field interaction between the dipolar substituent and the C_{ar}–F bond was indicated to be the mechanism leading to variable fluorine atom σ charge density. However, in systems of structure I, much larger $-\rho_I$ values have been observed for the cations and anions (sets 15–18 of Table V) than those for the *meta-* and *para*-substituted fluorobenzene shifts (*cf.* Table IX). These results cannot be accounted for by only electrostatic field or σ bond inductive effects. Accordingly, it appears that the π bond inductive effect, which leads to polarizations of the fluorine atom π and σ charge densities that follow the σ_I scale, must be a very important contributor to the $\sigma_I\rho_I$ terms for the F nmr shifts.

Stock and his students[24] have recently presented strong evidence that significant transmission of polar (σ_I) effects occurs through the π electron framework, especially in the F nmr shielding of 10-substituted-9-fluoroanthracenes.

Summary. The F nmr shielding effects of para substituents, X, in cations, anions, and molecules of the general formula



have been determined by systematically varying the molecular cavity, G. The results have been analyzed with the use of the dual substituent parameter treatment, eq 1. Because of the sensitivity of the p-FC_6H_4 tag it has been possible to vary the ρ values, ρ_R and ρ_I, more than 40-fold, and the ratio of π delocalization to polar effects, $\lambda \equiv \rho_R/\rho_I$, by nearly twofold with G. Using *p*-X substituents which within each series cover wide ranges of electronic properties (frequently, sets which meet the requirements of a minimal basis set[4] have been utilized), it has been established that the sensitive p-FC_6H_4 tag method supports the utility of the four scales of π delocalization effects recently defined completely independently by Ehrenson, Brownlee, and Taft.[3] Twenty of the p-FC_6H_5 tagged systems from the present study and seven literature sets are found to be fitted to a precision better than 0.100 in $f \equiv$ SD/RMS, with best fits which very generally discriminate by a factor of 2 or more between the four π delocalization scales as

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[21] (a) E. L. Wehry, *J. Amer. Chem. Soc.*, **89**, 41 (1967); (b) W. A. Sheppard and R. W. Taft, *ibid.*, **94**, 1919 (1972).

[22] J. W. Rakshys, R. W. Taft, and W. A. Sheppard, *ibid.*, **90**, 5236 (1968).

[23] *Cf.* A. R. Katritzky and R. D. Topsom, *J. Chem. Educ.*, **48**, 427 (1971).

[24] G. L. Anderson, R. C. Parish, and L. M. Stock, *J. Amer. Chem. Soc.*, **93**, 6984 (1971).

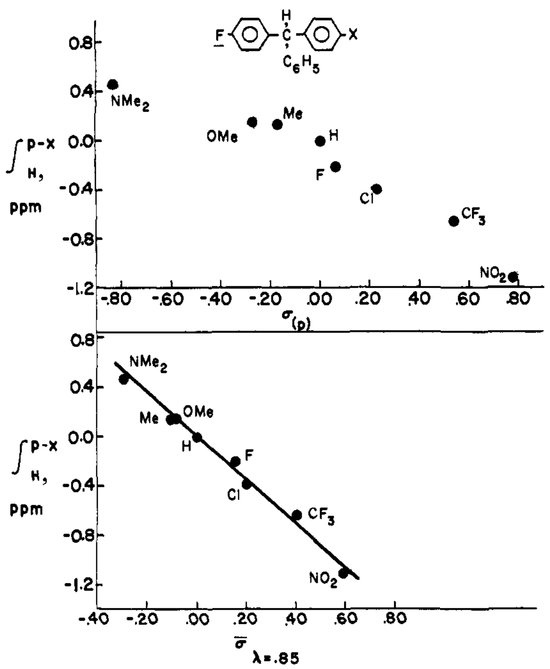


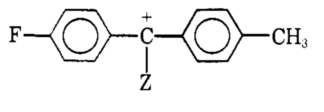
Figure 1. F nmr shifts for set 2, Table V, plotted *vs.* $\sigma_{(p)}$ (upper) and $\bar{\sigma}$ (lower); *cf.* ref 4.

expected on structural grounds. The results are illustrated in Figures 1 and 2 for a $\sigma_R{}^0$ and $\sigma_R{}^-$ set, respectively, which show comparative plots of shifts *vs.* $\sigma_{(p)}$ and $\bar{\sigma}$ (λ = 0.85 using the $\sigma_R{}^0$ scale) and of $\sigma_{(p)}{}^-$ and $\bar{\sigma}$ (λ = 1.23 using the $\sigma_R{}^-$ scale).

The results obtained for G = "formally saturated" carbon cavities (variously substituted) support the view that much of the relatively small transmission occurs through double bond–no bond pseudounsaturation. Less than unit values of $\lambda \equiv \rho_R/\rho_I$ are found for many rate, equilibrium, and F nmr shift data sets for this structural type. The markedly different values of λ found for $ArCH_2$–X as compared with Ar–X systems have been discussed.

The results for G = unsaturated neutral or charged cavities, which are expected to have only minor direct conjugation with the *p*-X substituent, are all well fitted by the σ_R(BA) scale. The ρ values for these systems are all substantially larger than those systems (above) which are best fitted by the $\sigma_R{}^0$ parameters. This result is attributed to the enhanced transmission of the more mobile π electrons.

The limited generality of the $\sigma_R{}^+$ scale has been critically tested with data sets involving greater than 10-fold variations in ρ_R and ρ_I values. The ratio of π delocalization to polar effects, as measured by $\lambda = \rho_R/\rho_I$, is found to increase gradually with increasing $-\rho_R$ values. The CH_3 secondary β-deuterium isotope F nmr shift for cations



is also found to increase sharply in the same sequence.

The $\sigma_R{}^-$ scale has been confirmed for the first time by the *p*-FC_6H_4 tag F nmr method utilizing para-substituted trityl anions in DMSO solution. The λ value obtained for this system (1.23) is the largest

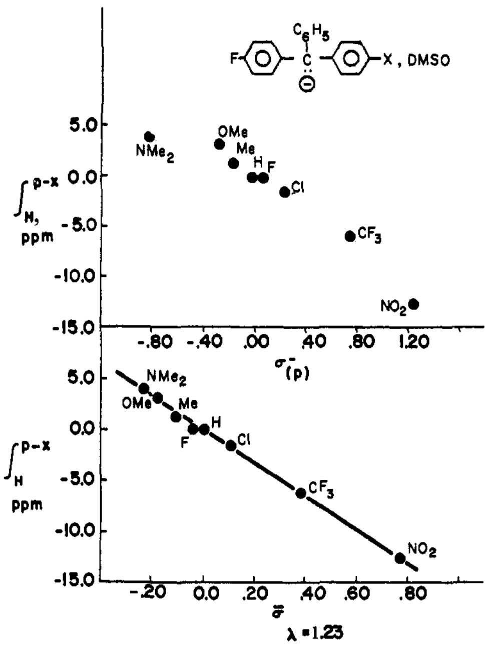


Figure 2. F nmr shifts for set 20, Table V, plotted *vs.* $\sigma_{(p)}{}^-$ (upper) and $\bar{\sigma}$ (lower); *cf.* ref 4.

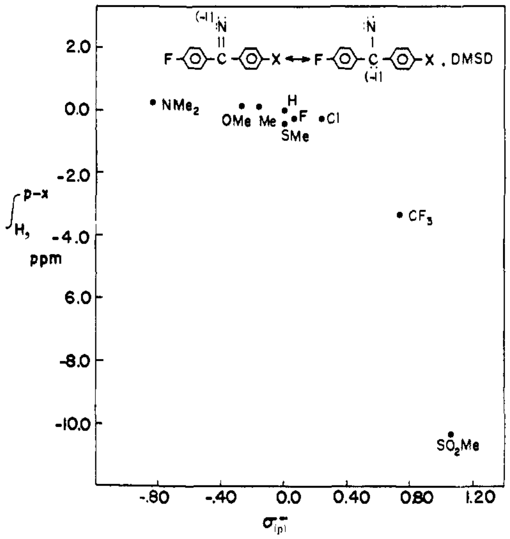
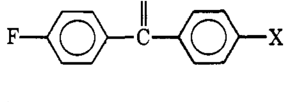


Figure 3. F nmr shifts for set 21, Table V, plotted *vs.* $\sigma_{(p)}{}^-$.

that has been observed for a structure I type. This result is attributed as a characteristic of the F nmr measurement in systems in which G has a relatively large delocalizable π electron density.

The anionic series



has provided the only example for which shielding data are not satisfactorily described by eq 1 with one of the four scales of σ_R values. The results are accounted for in terms of the unique structure, wherein +R and −R para substituents experience grossly different transmission modes. This result is illustrated in Figure 3 by a plot of shifts *vs.* $\sigma_{(p)}{}^-$. No possible value of $\lambda = \rho_R/\rho_I$ with eq 1 will relieve the curvature shown.

Comparison of the various ρ values for F nmr shifts obtained in this study leads to the conclusion that π bond inductive effects follow the σ_I scale and contribute substantially to observed shifts.

Implied applications of eq 1 to structural characterization of reaction transition states are supported by the results of this study. Ehrenson, Brownlee, and Taft have discussed such applications.[3]

Acknowledgment. We are pleased to acknowledge the contribution of Dr. John Thompson of unpublished results and general assistance at the outset of this work. We are also indebted to Dr. R. G. Pews for samples of *trans*-4′-substituted-4-fluorostilbenes.

Bonding Studies in Group IV Substituted Anilines. III. Electron Spin Resonance Spectra of the Radical Cations and the Ground-State Bonding Description[1]

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Received May 30, 1972

Abstract: The radical cations of *p*-*tert*-butyl-, *p*- and *m*-trimethylsilyl-, and *p*-trimethylgermyl-*N*,*N*-dimethylaniline, generated electrolytically in acetonitrile with sodium perchlorate as the supporting electrolyte, have been studied by esr spectroscopy. These first examples of group IV organometallic cation radical esr spectra provide insight as to the bonding interactions in the ground states of these molecules. Semiempirical molecular orbital calculations using the CNDO/2 approximation, which correlate well with experimental ground-state properties and radical cation spin densities, indicate that both hyperconjugative p–pπ interaction and dπ interaction contribute to the stabilization of the ground state observed when carbon is replaced with silicon. Based on the results of the CNDO/2 calculations, the interaction of the d orbitals appears more important than hyperconjugation in the ground state and accounts almost entirely for the stabilization of the highest occupied molecular orbital.

The electron spin resonance spectra of several anion radicals containing group IV metals have been reported.[2] While these esr experiments have demonstrated a small delocalization of the unpaired electron through the d orbitals of the metal, they suffer from the disadvantage that the odd electron occupies a π^* molecular orbital. The d-orbital interactions observed are therefore excited state interactions, and the conclusions strictly are valid for only $(p \rightarrow d)\pi^*$ overlap.[3] In a radical cation the unpaired electron resides in a bonding molecular orbital providing a system more appropriate for the study of ground-state interactions.

In our studies of the ground-state properties of group IV substituted anilines, we observed a small but significant increase in the ionization potential of the molecules when silicon or germanium was substituted for carbon. The results indicated a stabilization of the highest filled molecular orbital (HFMO) for *p*-trimethylsilyl- and *p*-trimethylgermyl-*N*,*N*-dimethylaniline of 0.30 and 0.24 eV, respectively, relative to the *p*-*tert*-butyl compound.[4] This is consistent with electron withdrawal from the HFMO by the trimethylsilyl or trimethylgermyl group. Such ground-state stabilizations are commonly observed in unsaturated organosilicon compounds and have generally been attributed to d-orbital interaction with the bonding π orbitals. An alternative explanation has been suggested which ascribes the stabilization to a σ–π or hyperconjugative interaction between the metal and the unsaturated system.[5] Although the hyperconjugative description of the bonding in group IV substituted π systems appears reasonable, and has been suggested for other systems,[6] very little experimental evidence for this type of σ–π interaction appears in the literature.[5,6] Of this evidence, most is based on correlations with charge transfer data. We found that such charge transfer studies provide unreliable measurements of ground-state energies in our studies of group IV substituted anilines.[4]

In order to determine whether it is more appropriate to attribute the electron withdrawal to d-orbital interaction with the ground-state molecular orbitals or to a hyperconjugative σ–π effect, we have investigated the properties of the radical cations of the para-substituted

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