Table II

Alkyl groups	DARC descriptor[a]					$-E_s$ by ester hydrolysis	$-E_s^*$ by hydroboration with $(Sia)_2BH$	$\Delta(E_s^* - E_s)$
	A_1'	A_2'	A_1	A_2	A_3			
CH_3						0	0	
CH_2CH_3	0	0	0	0	0	0.07[b]	0.07	
$CH_2CH_2CH_3$	0	0	1	0	0	0.36[b]	0.56	0.20
$CH(CH_3)_2$	1	0	0	0	0	0.47[b]	0.66	0.19
$CH_2CH(CH_3)_2$	0	0	1	1	0	0.93[b]	1.06	0.13
$CH(CH_3)CH_2CH_3$	1	0	1	0	0	1.13[b]	1.15	0.02
$CH(CH_3)CH(CH_3)_2$	1	0	1	1	0		1.65	
$CH_2C(CH_3)_3$	0	0	1	1	1	1.74[b]	1.84	0.10
$CH(CH_3)C(CH_3)_3$	1	0	1	1	1	3.33[b]	2.43	0.90
$C(CH_3)_3$	1	1	0	0	0	1.54[b]	4.22	2.68
$C(CH_3)_2CH_2CH_3$	1	1	1	0	0	2.17[c]	4.72	2.55
$C(CH_3)_2CH(CH_3)_2$	1	1	1	1	0		5.21	
$C(CH_3)_2C(CH_3)_3$	1	1	1	1	1	3.90[b]	6.00	2.10

[a] When the A_i position is occupied by a C atom we note 1; when this position is not occupied or occupied by a H atom we note 0. [b] See ref 9. [c] See N. B. Chapman, J. R. Lee, and J. Shorter, *J. Chem. Soc. B*, 778 (1969).

radii into account. These clearly show that, in order to reach the transition state between the hydroboration reagent[15] and the 2-alkyl-1-propene, the shapes of tertiary alkyl substituents would be the only strong factor of hindrance. Whatever the real structure[5,17-19] of this transition state could be, it implicates simultaneously the two carbon atoms of the ethylenic linkage.

The present E_s^* scale could be a valuable tool in all the reactions in which the transition state is similar to that encountered in hydroboration of 2-alkyl-1-propenes. Moreover, we have checked[5] that in the reaction of tetrasiamyldiborane with methyl ketones, the E_s^* scale is a suitable expression of the reactivity, in spite of a noticeable polar effect.

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(15) We used THF as solvent in our kinetic studies on the hydroboration of 2-alkyl-1-propenes. In this medium the disiamylborane is present in its dimeric form only.[16]

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Aprotic Solvent Effects on Substituent Fluorine Nuclear Magnetic Resonance Shifts. III. *p*-Fluorophenyl-*p*′-substituted-phenyl Systems[1]

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Abstract: Studies of aprotic solvent effects on substituent fluorine nuclear magnetic resonance (F nmr) shifts of *p*-fluorophenyl labeled systems have provided evidence of general significance regarding the nature of solvation of molecules. The correlation of the aprotic polar solvent F nmr shifts with the σ_I parameter of the substituent and the E_T solvent polarity parameter is shown to be highly general. It is concluded that local fields of aprotic polar solvents enhance the electron-withdrawing effects of substituents principally by supporting greater separation of charge in polar σ bonds. In contrast, the π-electronic distribution in a neutral molecule is generally represented by a poorly solvated multipole of centers of relatively small charge spread over an extensive π-electron framework. Consequently, aprotic polar solvents effects show little or no dependence upon the σ_R parameter of the substituent. While the magnitudes of aprotic polar solvent effects on F nmr substituent shifts in a wide variety of systems have been found to be directly related (approximately) to the substituent σ_I value, the direction of the solvent effect in the systems considered depends upon whether shift components due to solvation of polar σ bonds or to the effective dielectric constant are predominant. For para-substituted fluorobenzenes and 10-substituted-9-fluoroanthracenes, the former components are thought to control the shift, accounting for the increasing *downfield* shifts which are observed with increasing substituent σ_I parameter and increasing polarity of the aprotic solvent. A similar result appears to hold for the para ^{13}C nmr substituent shifts for monosubstituted benzenes. In diphenyl systems of the structure I type (data reported herein), the effective dielectric constant component is believed to control the shift direction. As a consequence, the shifts for substituents, *e.g.*, *p*-NO_2, *p*-CN, *p*-CF_3, and *p*-halogen, are expected (as observed) to be increasingly shifted *upfield* with increasing solvent polarity. Although field effects apparently control the aprotic solvent effects on the F nmr substituent shifts for structure I systems, inductive transmission of substituent σ_I effects through the π-electron framework is found to be the dominant factor in the substituent shifts. Further aspects of results and interpretation are discussed.

Recent investigations of structural and medium effects on F nmr substituent shifts have prompted this further study. Relatively effective transmission of the effects of substituents, X, through a variety of neutral and charged cavities for structure I has been found.[2] These F nmr substituent shifts were usefully

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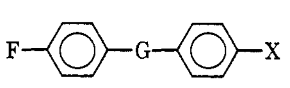
(1) This work was supported in part by the National Science Foundation. We also gratefully acknowledge their support in making available the nmr spectrometer of the University of California, Irvine, Chemistry Department.

(2) S. K. Dayal, S. Ehrenson, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 9113 (1972).



I

analyzed by means of the dual substituent parameter (DSP) equation (1)[2-4]

$$P^i = \sigma_I \rho_I{}^i + \sigma_R \rho_R{}^i = \rho_I{}^i(\sigma_I + \lambda\sigma_R) \qquad (1)$$

where P^i = the substituent effect property; σ_I and σ_R are the substituent polar and resonance effect parameters, respectively; ρ_I and ρ_R give the susceptibilities of the property to each of the substituent properties; the ratio or blend: $\rho_R/\rho_I \equiv \lambda$. The index i refers to the position of the substituent relative to the detector center.

The DSP equation has also been utilized to analyze the effects of aprotic solvents on the F nmr substituent shifts of para-substituted fluorobenzenes.[5] A useful analysis of the F nmr substituent shifts for appropriate 10-substituted-9-fluoroanthracenes has also been made[6] by eq 1. Aprotic solvent effects on these F nmr meso substituent shifts also have been reported[6] and are analyzed herein by means of eq 1. Finally, there has been a recent report of aprotic solvent effects on the ^{13}C nmr shifts for the para carbon of monosubstituted benzenes.[7] An analysis of these results by eq 1 is relevant and is included herein. In each of these systems, the key result is that the effects of aprotic solvent on substituent shifts are dependent upon the σ_I value of the substituent (*i.e.*, ρ_I is solvent dependent) but there is little or no dependence upon the substituent σ_R parameter (ρ_R is esentially solvent independent). Further, in each of these systems, the $-\rho_I$ value *increases* as the polarity of the solvent is increased.

The present work reports a study of the aprotic solvent effects on the substituent F nmr shifts for structure I systems with a variety of neutral G cavities. This work is made especially interesting and significant by the finding that in contrast to the results for the benzene-like systems, the structure I systems have $-\rho_I$ values which *decrease* with increasing solvent polarity. This contrasting behavior provides the basis for a more complete understanding of the origin of all of the aprotic solvent effects upon the substituent chemical shifts.

Experimental Section

The procedures of preparation of most compounds and of the F nmr measurements have been reported previously.[2] In this study solution concentrations of 0.03 *M* or less were used. Samples of the diphenyl ethers and sulfides were obtained from Dr. R. G. Pews, who made some preliminary shift measurements by earlier less accurate procedures. Shift measurements with the diphenyl sulfides at 0.01 *M* concentration in CH_2Cl_2 were more recently made by Dr. P. D. Heffley, and agree with those reported in Table VIII to ±0.04 ppm.

Diphenyl Ethers. The following 4-substituted-phenyl-4-fluorophenyl ethers were prepared by the reaction of potassium *p*-fluorophenoxide ion with the corresponding para-substituted bromobenzene: NH_2, Me, CF_3, and NO_2. The reaction of potassium *p*-methoxyphenoxide ion with *p*-bromofluorobenzene was used to obtain 4-methoxyphenyl 4-fluorophenyl ether. *p*-$FC_6H_4OC_6H_5$ was prepared as previously described.[8] The phenol (0.1 mol) and powdered potassium hydroxide (0.12 mol) were added to 50–60 ml of toluene and heated under reflux for 4–6 hr in a 100-ml flask equipped with a Dean and Stark apparatus and refluxing condenser. After removal of the water and toluene, the substituted bromobenzene (0.1 mol) and 50–60 ml of anhydrous diglyme were added to the phenoxide salt and the mixture was refluxed for 12–14 hr. The reaction mixture was poured into water and extracted with ether. Dilute KOH and water were used to wash the ether extract until neutral. The extract was dried over $CaCl_2$ and the ether evaporated. The diphenyl ether residue was then distilled or recrystallized. Yields were 40–70%. The following characterizations were obtained: NH_2, mp 65–66°; OMe, bp 115-116° (1.5 mm), $n^{25}D$ 1.5559; Me, bp 97–98° (1 mm), $n^{25}D$ 1.5488; CF_3, bp 88–90° (0.6–0.8 mm), $n^{25}D$ 1.4988; NO_2, mp 74–75°.

Diphenyl Sulfides. The following 4-substituted-phenyl 4-fluorophenyl sulfides were prepared by the reaction of the appropriate substituted benzenesulfenyl chloride with the *p*-fluorophenylmagnesium bromide: Me, Cl, and F. 4-Trifluoromethylphenyl-4-fluorophenyl sulfide was prepared by the reaction of *p*-fluorobenzene sulfenyl chloride with *p*-trifluoromethylphenylmagnesium bromide. These reactions were carried out by diluting the purified sulfenyl chloride with tetrahydrofuran and adding dropwise to the Grignard reagent at 0–5°. The reaction mixture was stirred for 0.5 hr, refluxed for 1 hr, cooled, poured onto crushed ice and concentrated H_2SO_4, and extracted with ether. The ether extract was dried over $CaCl_2$ and the ether removed *in vacuo*. The crude sulfide was treated with a small amount of Zn dust and dilute HCl in 95% ethanol to remove any disulfide. This reaction mixture was poured onto water and extracted with ether. The ether extract was washed with dilute KOH and water until neutral and dried over $CaCl_2$, and the ether was evaporated *in vacuo*. The sulfide was purified by vacuum distillation. *p*-$FC_6H_4SC_6H_5$ was prepared as previously reported.[8] 4-Nitrophenyl 4-fluorophenyl sulfide was prepared by the reaction of *p*-fluorophenylthiophene oxide ion with *p*-fluoronitrobenzene in methanol. After refluxing for 0.5 hr, the reaction mixture was poured onto water and extracted with benzene. The benzene extract was washed with dilute NaOH and water until neutral and dried over $CaCl_2$. Benzene was removed *in vacuo* and the product was recrystallized from methanol. The following characterizations were obtained: Me, bp 100-104° (0.3-0.5 mm), $n^{25}D$ 1.5947; F, bp 93–94° (1 mm), $n^{25}D$ 1.5822; Cl, bp 120–123° (0.5 mm), $n^{25}D$ 1.6112; CF_3, bp 94–95° (0.4–0.5 mm), $n^{25}D$ 1.5386; NO_2, mp 96–98.

Biphenyls. These were obtained from Peninsular Chem Research. Inc., except for 4′-CN and 4′-$IC_6H_4C_6H_4F$-4 which were prepared by the procedure of Dewar and Marchand.[9]

Results

The results are summarized in Tables I–VIII. Each table gives the shifts obtained with a given G cavity (structure I) in a graded series of aprotic polar solvents with the indicated set of substituents. The F nmr shifts (ppm) are listed as part (i) of the table. Part (ii) gives the results of analysis by the dual substituent parameter treatment. The best fit parameters are listed for comparison for fits to both $\sigma_R{}^0$ and $\sigma_{R(BA)}$ parameters.[2,4] The fits to other σ_R scales[2,4] are appreciably poorer and are not given. The fit parameter, $f \equiv$ SD/RMS, is italicized for the scale giving the best fit in each solvent. The results in the protic solvents CH_2Cl_2 and CH_3OH, if determined, are listed at the bottom of each solvent list in each table.

The precision of fits of the data achieved by the DSP equation is in accord with earlier results[2,4] ($f < 0.1$). The discrimination of best fits between the $\sigma_R{}^0$ and $\sigma_{R(BA)}$ scales is good for the more "extreme" type cavities, G. For example, in all solvents, $\sigma_R{}^0$ best

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[3] P. R. Wells, S. Ehrenson, and R. W. Taft, *Progr. Phys. Org. Chem.*, **6**, 147 (1968).

[4] S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *ibid.*, **10**, 1 (1973).

[5] R. T. C. Brownlee, S. K. Dayal, J. L. Lyle, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 7208 (1972).

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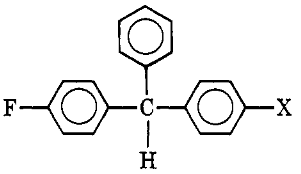
Table I. Results for the System

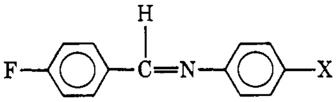


Set no.	Solvent	$f_{\text{ref}}^{\text{H}}$ [a]	NMe_2	OMe	F	Cl	Me	CF_3	NO_2 [b]
				(i) F Nmr Shifts (ppm)					
1	Cyclohexane	2.51	0.47	0.12	−0.35	−0.52	0.10	−0.94	−1.55
2	CCl_4	1.39	0.50	0.12	−0.30	−0.61	0.11	−0.96	−1.62
3	Benzene	2.68	0.45	0.14	−0.30	−0.47	0.11	−0.77	−1.50
4	THF	3.49	0.43	0.13	−0.28	−0.45	0.10	−0.70	−1.25
5	Acetone	4.14	0.41	0.14	−0.25	−0.42	0.10	−0.62	−0.97
6	CH_3CN	4.03	0.37	0.10	−0.28	−0.40	0.09	−0.60	−1.04
7	DMF	3.48	0.36	0.10	−0.30	−0.34	0.09	−0.57	−0.96
8	DMSO	2.37	0.37	0.10	−0.25	−0.33	0.08	−0.53	−0.94
9	CH_2Cl_2	2.83	0.47	0.15	−0.23	−0.39	0.14	−0.64	−1.11

Set	σ_R^0					$\sigma_{R(BA)}$				
no.	$-\rho_I$	$-\rho_R$	λ	SD	f	$-\rho_I$	$-\rho_R$	λ	SD	f
					(ii) DSP Results					
1	1.87	1.35	0.72	0.09	*0.128*	1.86	0.93	0.50	0.13	0.180
2	1.95	1.42	0.73	0.11	*0.144*	1.94	0.98	0.51	0.14	0.185
3	1.72	1.30	0.75	0.11	*0.160*	1.71	0.89	0.52	0.14	0.209
4	1.50	1.13	0.76	0.07	*0.110*	1.49	0.79	0.53	0.10	0.161
5	1.25	0.97	0.78	0.04	*0.084*	1.24	0.68	0.55	0.05	0.103
6	1.28	0.93	0.73	0.05	*0.093*	1.28	0.65	0.51	0.07	0.130
7	1.20	0.88	0.73	0.03	*0.073*	1.19	0.61	0.51	0.06	0.120
8	1.15	0.88	0.77	0.04	*0.090*	1.14	0.62	0.54	0.06	0.128
9	1.34	1.13	0.85	0.05	*0.091*	1.33	0.79	0.53	0.07	0.138

[a] Shift of the unsubstituted member relative to external reference of TCTFCB (60 wt % $CHCl_3$). [b] Shift of $(p\text{-}FC_6H_4)_2CHC_6H_4NO_2(p)$ relative to $(p\text{-}FC_6H_4)_2CHC_6H_5$.

Table II. Results for the System



Set no.	Solvent	$-f_{\text{ref}}^{\text{H}}$ [a]	NMe_2	OMe	F	Cl	Me	CF_3	CN	NO_2
				(i) F Nmr Shifts (ppm)						
1	Cyclohexane	4.68	1.47	0.65	−0.21	−0.57	0.33	−1.26	−1.82	−2.11
2	CCl_4	5.64	1.48	0.64	−0.17	−0.53	0.33	−1.19	−1.74	−2.04
3	Benzene	4.70	1.46	0.61	−0.19	−0.54	0.30	−1.20	−1.86	−2.00
4	THF	3.83	1.58	0.70	−0.13	−0.32	0.33	−1.14	−1.51	−1.82
5	Acetone	3.42	1.51	0.65	−0.11	−0.46	0.31	−1.05	−1.41	−1.70
6	CH_3CN	3.45	1.47	0.64	−0.08	−0.43	0.30	−0.99	−1.35	−1.63
7	DMF	3.54	1.50	0.66	−0.08	−0.43	0.30	−0.99	−1.31	−1.58
8	DMSO	4.90	1.48	0.64	−0.06	−0.38	0.29	−0.98	−1.28	−1.57
9	CH_2Cl_2	4.66	1.52	0.63	−0.14	−0.49	0.33	−1.10	−1.59	−1.90

Set	σ_R^0					$\sigma_{R(BA)}$				
no.	$-\rho_I$	$-\rho_R$	λ	SD	f	$-\rho_I$	$-\rho_R$	λ	SD	f
					(ii) DSP Results					
1	2.52	2.99	1.19	0.07	*0.056*	2.56	2.14	0.83	0.10	0.081
2	2.41	2.95	1.23	0.08	*0.064*	2.45	2.11	0.86	0.09	0.079
3	2.45	2.93	1.20	0.09	*0.074*	2.49	2.09	0.84	0.11	0.090
4	2.12	2.97	1.40	0.08	0.071	2.16	2.13	0.99	0.08	*0.069*
5	2.02	2.76	1.37	0.11	0.099	2.06	1.99	0.97	0.03	*0.028*
6	1.92	2.68	1.40	0.10	0.101	1.96	1.94	0.99	0.03	*0.032*
7	1.88	2.69	1.43	0.11	0.114	1.92	1.95	1.01	0.02	*0.019*
8	1.83	2.66	1.45	0.11	0.106	1.88	1.92	1.02	0.03	*0.030*
9	2.23	2.88	1.29	0.09	0.082	2.27	2.07	0.91	0.07	*0.060*

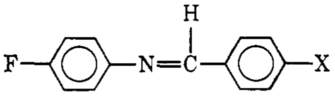
[a] Shift of unsubstituted member relative to external reference of TCTFCB (60 wt % in $HCCl_3$).

fits the data for G = $-CH(C_6H_5)-$ and –O–; and similarly, $\sigma_{R(BA)}$ best fits the data for G = –N=N–, –(biphenyl), and –S–. For intermediate types, *i.e.*, G = –CH=N–, –N=CH–, and –CH=CH–, best fits are generally obtained to σ_R^0 in hydrocarbon solvents and to $\sigma_{R(BA)}$ in polar solvents.

Discussion

The results from the data of this study are best discussed against the background of corresponding results for benzene-like systems taken from the recent literature. Table IX gives the DSP (eq 1) results for para-substituted fluorobenzenes[5] and for 10-substituted-

Table III. Results for the System

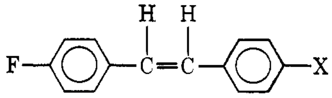


Set no.	Solvent	$\int_{\mathrm{ref}}^{\mathrm{H}}$[a]	NMe	OMe	F	Cl	Me	CN	NO_2
				(i) F Nmr Shifts (ppm)					
1	Cyclohexane	4.20	1.60	0.69	−0.26	−0.62	0.34	−1.91	−2.21
2	CCl_4	3.15	1.58	0.66	−0.21	−0.56	0.32	−1.80	−2.11
3	Benzene	4.17	1.55	0.62	−0.10	−0.55	0.29	−1.69	−1.99
4	THF	5.05	1.65	0.69	−0.14	−0.50	0.30	−1.50	−1.79
5	Acetone	5.47	1.56	0.58	−0.10	−0.44	0.29	−1.36	−1.64
6	CH_3CN	5.48	1.50	0.63	−0.09	−0.32	0.29	−1.32	−1.57
7	DMF	5.17	1.54	0.64	−0.07	−0.40	0.24	−1.28	−1.53
8	DMSO	3.68	1.52	0.64	−0.06	−0.38	0.26	−1.24	−1.50
9	CH_2Cl_2	4.29	1.51	0.63	−0.12		0.35	−1.55	−1.83

Set	σ_R^0					$\sigma_{R(BA)}$				
no.	$-\rho_I$	$-\rho_R$	λ	SD	f	$-\rho_I$	$-\rho_R$	λ	SD	f
					(ii) DSP Results					
1	2.72	3.20	1.18	0.07	*0.056*	2.74	2.28	0.83	0.09	0.066
2	2.56	3.11	1.21	0.08	*0.062*	2.59	2.20	0.86	0.08	0.065
3	2.40	3.01	1.25	0.10	0.084	2.42	2.15	0.89	0.08	*0.069*
4	2.18	2.97	1.36	0.13	0.118	2.21	2.14	0.97	0.02	*0.018*
5	1.99	2.74	1.38	0.14	0.130	2.02	1.98	0.98	0.04	*0.031*
6	1.87	2.70	1.44	0.10	0.105	1.90	1.94	1.02	0.05	*0.047*
7	1.85	2.69	1.46	0.14	0.139	1.88	1.95	1.04	0.03	*0.031*
8	1.80	2.66	1.48	0.13	0.136	1.83	1.92	1.05	0.03	*0.029*
9	2.16	2.91	1.35	0.07	0.060	2.27	2.05	0.90	0.05	*0.042*

[a] Shift of unsubstituted member relative to external reference of TCTFCB (60 wt % $CHCl_3$).

Table IV. Results for the System



Set no.	Solvent	$-\int_{\mathrm{ref}}^{\mathrm{H}}$[a]	NMe_2	OMe	F	Cl	Me	CN	NO_2
				(i) F Nmr Shifts (ppm)					
1	CCl_4	24.98	1.59	0.72	−0.22	−0.61	0.37	−2.02	−2.36
2	Benzene	23.58	1.79	0.62[b]	−0.17	−0.53[c]	0.30	−1.74	−2.11[d]
3	THF	22.88	1.55	0.73	−0.08	−0.48	0.29	−1.59	−1.94
4	DMF	22.68	1.49	0.70	0.00	−0.34	0.33	−1.35	−1.68
5	DMSO	23.97	1.45	0.69	0.00	−0.35	0.30	−1.33	−1.69
6	CH_2Cl_2	23.47	1.49	0.66	−0.07	−0.46	0.34	−1.63	−2.02

Set	σ_R^0					$\sigma_{R(BA)}$				
no.	$-\rho_I$	$-\rho_R$	λ	SD	f	$-\rho_I$	$-\rho_R$	λ	SD	f
					(ii) DSP Results					
1	2.84	3.34	1.17	0.06	*0.041*	2.87	2.37	0.83	0.13	0.097
2	2.54	3.25	1.28	0.14	0.109	2.57	2.33	0.91	0.08	*0.060*
3	2.28	3.04	1.33	0.09	0.076	2.30	2.17	0.94	0.08	*0.069*
4	1.93	2.84	1.47	0.08	0.077	1.95	2.03	1.04	0.07	*0.064*
5	1.92	2.79	1.45	0.08	0.079	1.94	1.99	1.02	0.07	*0.071*
6	2.34	3.01	1.29	0.07	*0.059*	2.36	2.14	0.91	0.11	0.096

[a] Shift of unsubstituted member relative to external reference of perfluorocyclobutane (neat). [b] R. G. Pews and N. D. Ojha [*J. Amer. Chem. Soc.*, **91,** 5769 (1969)] gives 0.57. [c] Footnote *b* gives −0.54. [d] Footnote *b* gives −2.06.

9-fluoroanthracenes.[6] It will be noted that there is less than 5% variation of ρ_R values for either system over the complete range of polarities from hydrocarbon to DMSO solvents. On the other hand, $-\rho_I$ values increase appreciably over this solvent range, the increase being greater for the anthracene than the benzene system. This solvent dependence of ρ_I values for aprotic solvents is in fact well correlated by the empirical E_T scale of solvent polarities, obtained from uv charge-transfer spectra of betaines.[10,11] Figure 1 shows a plot of $-\rho_I$ values *vs.* E_T. The protic solvents CH_2Cl_2 and CH_3OH are not included in the correlation since their E_T parameters contain important contributions due to hydrogen bonding. The ρ_I values of Tables I–VIII place the polarity of CH_2Cl_2 at only somewhat greater than that of the hydrocarbon solvents.

Table X gives the results of a similar analysis of solvent effects on the para ^{13}C substituent shifts for substituted benzenes.[7] These data show identical trends to that for the F nmr shifts. Both the substitu-

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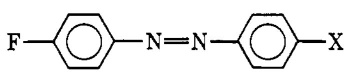
(10) K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Justus Liebigs Ann. Chem.*, **661,** 1 (1963).

(11) C. S. Giam and J. L. Lyle are the first to report useful generalized correlations of solvent effects of F nmr shifts with the E_T parameter, private communications: J. L. Lyle, Ph.D. Thesis, Texas A & M, 1971.

Table V. Results for the System

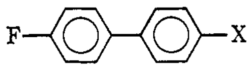


Set no.	Solvent	$-\int_{ref}^{H}$[a]	OMe	F	Cl	Br	I	Me	CF$_3$	COMe
				(i) F Nmr Shifts (ppm)						
1	CCl$_4$	3.67	1.10	−0.25	−0.73	−0.82	−0.85	0.51	−1.76	
2	Benzene	4.64	1.07	−0.19	−0.64	−0.73	−0.74	0.49	−1.61	−1.40
3	DMF	3.30	1.15	−0.08	−0.55	−0.64	−0.64	0.48	−1.45	

Set	σ_R^0					$\sigma_{R(BA)}$				
no.	$-\rho_I$	ρ_R	λ	SD	f	$-\rho_I$	$-\rho_R$	λ	SD	f
					(ii) DSP Results					
1	3.50	4.23	1.21	0.12	0.122	3.35	3.26	0.97	0.04	*0.042*
2	3.11	3.87	1.24	0.11	0.112	3.08	3.11	1.01	0.04	*0.039*
3	2.92	3.94	1.35	0.12	0.150	2.78	3.05	1.10	0.04	*0.049*

[a] Shift of the unsubstituted member relative to external reference of TCTFCB (60 wt % CHCl$_3$).

Table VI. Results for the System



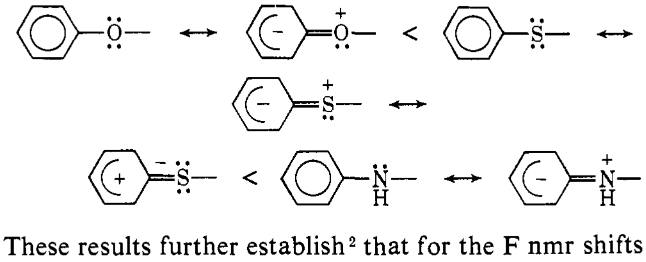
Set no.	Solvent	$-\int_{ref}^{H}$[a]	NH$_2$	F	Br	I	CN	NO$_2$
				(i) F Nmr Shifts (ppm)				
1	Cyclohexane	22.09	1.99	−0.27	−0.96	−1.05	−2.71	−3.11
2	CCl$_4$	23.37	1.97	−0.28	−0.97	−1.07	−2.79	−3.19
3	Benzene	21.94	1.88	−0.12[c]	−0.78[c]	−0.86[c]	−2.34[c]	−2.75[c]
4	THF	20.91	2.30	−0.08	−0.83	−0.88	−2.31	−2.76
5	Acetone	20.36	2.16	−0.08	−0.81	−0.88	−2.24	−2.68
6	CH$_3$CN	20.73	1.95	−0.06	−0.78	−0.85	−2.20	−2.62
7	DMF	20.97	2.36[c]	−0.03	−0.76	−0.80	−2.19	−2.64[c]
8	DMSO	22.63	2.34	−0.00	−0.73	−0.73	−2.15	−2.61
9	CH$_2$Cl$_2$	21.76	1.95	−0.10	−0.82	−0.91	−2.44	−2.91
10	CH$_3$OH	19.94	2.03	−0.10	−0.83	−0.91	−2.47	−2.84

Set	σ_R^0					$\sigma_{R(BA)}$				
no.	$-\rho_I$	$-\sigma_R$	λ	SD	f	$-\rho_I$	$-\rho_R$	λ	SD	f
					(ii) DSP Results					
1	3.89	4.75	1.22	0.17	0.085	3.88	3.22	0.83	0.15	*0.075*
2	3.98	4.80	1.20	0.15	*0.077*	3.98	3.24	0.81	0.17	0.084
3	3.35	4.41	1.32	0.15	0.088	3.35	2.99	0.89	0.14	*0.078*
4[b]	3.36	4.52	1.35	0.19	0.108	3.36	3.08	0.92	0.12	*0.069*
5[b]	3.27	4.44	1.36	0.20	0.119	3.27	3.04	0.93	0.11	*0.063*
6	3.19	4.38	1.37	0.19	0.117	3.19	2.99	0.94	0.11	*0.065*
7[b]	3.17	4.46	1.41	0.19	0.111	3.18	3.04	0.96	0.11	*0.066*
8[b]	3.10	4.47	1.44	0.17	0.105	3.10	3.04	0.98	0.11	*0.068*
9	3.52	4.63	1.31	0.17	0.091	3.54	3.12	0.88	0.15	*0.082*
10	3.50	4.69	1.34	0.18	0.098	3.50	3.19	0.91	0.13	*0.072*

[a] Shift of unsubstituted member relative to external reference of perfluorocyclobutane (neat). [b] Due to H bonding of the NH$_2$ group to basic solvent molecules, which gives a small upfield shift, the average of the shift for NH$_2$ in cyclohexane and in CCl$_4$ has been used for the DSP analysis in this solvent. [c] Reference 9 gives an earlier value. Average deviation of common values is ±0.04.

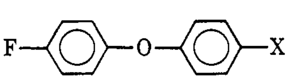
ent and solvent range are somewhat limited for the available data, however, and additional data would be very desirable to firm up quantitative aspects of ^{13}C shifts.

Turning now to the diphenyl systems (structure I), Table XI summarizes the F nmr results for structural variation in the neutral cavity G obtained in a given solvent CCl$_4$. It is abundantly established by the results in Table XI that the F-X distance is *not* the predominant variable determining either ρ_I or ρ_R. Instead, both $-\rho_I$ and $-\rho_R$ increase with increased conjugative interaction between the two phenyl rings. Over the range of G cavities, there is clearly more effect on ρ_R than on ρ_I (λ increases from 0.73 to 1.48). "Formally" saturated hydrocarbon cavities give rise to the lowest $-\rho_I$ and $-\rho_R$ values,[2] and atomic centers with polarizable lone-pair electrons give rise to the largest values of these parameters. For the latter, polarizable conjugative interaction increases in the following sequence



These results further establish[2] that for the F nmr shifts of structure I systems the transmission of substituent polar effects (σ_I) occurs predominantly through the π framework. That is, field effects make only secondary contributions.[2] The smaller $-\rho_I$ value for the stilbenes (-HC=CH-) than the biphenyls (-) could be a reflection of the smaller field effect contribution

Table VII. Results for the System

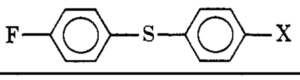


Set no.	Solvent	$\int_{ref}^{H}$[a]	NH_2	OMe	Me	CF_3	NO_2
			(i) F Nmr Shifts (ppm)				
1	Cyclohexane	7.00	2.06	1.29	0.68	−2.14	−3.29
2	CCl_4	6.01	1.99	1.24	0.65	−2.09	−3.29
3	Benzene	6.94	1.97	1.22	0.60	−1.89	−2.96
4	THF	7.83	2.45	1.30	0.62	−1.90	−2.88
5	Acetone	8.04	2.30	1.24	0.59	−1.88	−2.83
6	CH_3CN	8.28	2.09	1.14	0.54	−1.78	−2.75
7	DMF	7.79	2.44	1.20	0.56	−1.80	−2.67
8	DMSO	6.40	2.42	1.23	0.58	−1.76	−2.65
9	CH_2Cl_2	7.16	1.90	1.21	0.61	−1.90	−3.09

Set	σ_R^0					$\sigma_{R(BA)}$				
no.	$-\rho_I$	$-\rho_R$	λ	SD	f	$-\rho_I$	$-\rho_R$	λ	SD	f
					(ii) DSP Results					
1	3.85	5.21	1.35	0.02	*0.012*	4.15	3.44	0.83	0.20	0.094
2	3.84	5.07	1.32	0.04	*0.018*	4.13	3.35	0.81	0.20	0.095
3	3.41	4.84	1.42	0.05	*0.024*	3.69	3.21	0.87	0.16	0.085
4[b]	3.31	4.95	1.50	0.04	*0.020*	3.60	3.28	0.91	0.17	0.088
5[b]	3.27	4.87	1.49	0.06	*0.033*	3.55	3.23	0.91	0.14	0.075
6	3.15	4.77	1.51	0.12	0.064	3.43	3.18	0.93	0.08	*0.044*
7[b]	3.08	4.74	1.54	0.08	*0.047*	3.35	3.15	0.94	0.11	0.063
8[b]	3.03	4.71	1.55	0.06	*0.032*	3.30	3.12	0.95	0.14	0.077
9	3.89	4.94	1.27	0.16	*0.077*	4.18	3.27	0.78	0.24	0.120

[a] Shift of the unsubstituted member relative to external reference of TCTFCB (60 wt % $CHCl_3$). [b] Due to H bonding of NH_2 group to basic solvent molecules, which gives a small upfield shift, the average of the shift for NH_2 in cyclohexane and in CCl_4 has been used for the DSP analysis in this solvent.

Table VIII. Results for the System



Set no.	Solvent	$-\int_{ref}^{H}$[a]	F	Cl	Me	CF_3	NO_2
			(i) F Nmr (ppm)				
1	Cyclohexane	23.90	0.26	−0.81	1.05	−2.64	−3.95
2	CCl_4	24.90	0.23	−0.82	1.03	−2.60	−3.96
3	Benzene	23.97	0.33	−0.68	0.99	−2.38	−3.91
4	THF	23.08	0.31	−0.74	0.99	−2.43	−3.55
5	Acetone	22.78	0.33	−0.75	0.95	−2.37	−3.47
6	CH_3CN	22.69	0.35	−0.70	0.87	−2.43	−3.41
7	DMF	23.00	0.38	−0.68	0.91	−2.29	−3.30
8	DMSO	24.38	0.40	−0.66	0.96	−2.23	−3.24
9	CH_2Cl_2	23.70	0.35	−0.71	0.95	−2.36	−3.72

Set	σ_R^0					$\sigma_{R(BA)}$				
no.	$-\rho_I$	$-\rho_R$	λ	SD	f	$-\rho_I$	$-\rho_R$	λ	SD	f
					(ii) DSP Results					
1	4.59	6.94	1.51	0.17	0.076	4.77	5.97	1.25	0.10	*0.043*
2	4.59	6.86	1.49	0.16	0.073	4.77	5.90	1.24	0.09	*0.040*
3	4.14	6.53	1.58	0.16	0.078	4.31	5.61	1.30	0.09	*0.046*
4	4.14	6.41	1.55	0.18	0.090	4.31	5.52	1.28	0.10	*0.052*
5	4.05	6.26	1.55	0.19	0.097	4.21	5.41	1.28	0.10	*0.049*
6	4.00	6.26	1.56	0.18	0.096	4.17	5.40	1.30	0.09	*0.046*
7	3.84	6.11	1.59	0.19	0.100	4.00	5.28	1.32	0.09	*0.050*
8	3.76	6.07	1.62	0.19	0.105	3.92	5.24	1.34	0.12	*0.063*
9	4.21	6.62	1.57	0.16	0.081	4.38	5.70	1.30	0.07	*0.036*

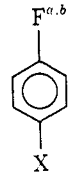
[a] Shift of the unsubstituted member relative to external reference of perfluorocyclobutane.

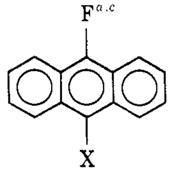
resulting from the greater F–X distance. Alternately, this result could arise simply from an attenuation in the transmission of the σ_I effects with distance along the π framework (or both).

The parameters from the DSP analysis results given in Tables I–VIII for structure I systems clearly show that the dominant effect of solvent polarity is upon the ρ_I value. The $-\rho_I$ values for each G cavity are well correlated for aprotic solvents by the empirical E_T solvent polarity parameter. These correlations are illustrated in Figure 1 with the results for G = –N=CH–, which are typical. Figure 1 further illustrates the dramatic contrast in behavior of structure I systems (negative slope) and for the benzene-like systems (positive slopes). Table XII presents a summary of the values of slope, *m*, for the various $-\rho_I$ *vs.* E_T correlations.

In addition to the opposite directions of aprotic polar solvent effects for the benzene and anthracene as compared with structure I systems, Table XII re-

Table IX. DSP Equation Analysis of Solvent Effect on F Nmr Substituent Shifts for Para-Substituted Fluorobenzenes and for 10-Substituted-9-fluoroanthracenes

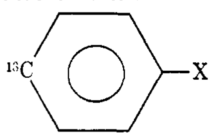




Solvent	$-\rho_I$	$-\rho_R$	λ	SD	f	$-\rho_I$	$-\rho_R$	λ	SD	f
c-C_6H_{12}	7.82	31.00	3.96	0.64	0.079					
CCl_4	8.13	31.04	3.82	0.60	0.074	13.08	28.76	2.20	0.79	0.111
C_6H_6	8.17	31.14	3.81	0.61	0.076	13.57	29.00	2.14	0.75	0.105
1,4-Dioxane						14.36	28.95	2.02	0.68	0.095
$(CH_3)_2C{=}O$	9.19	31.74	3.45	0.60	0.073					
DMF	9.35	31.85	3.41	0.60	0.073	16.66	30.12	1.81	0.88	0.114
DMSO	9.36	31.43	3.36	0.63	0.078					
MeOH	9.34	31.07	3.33	0.70	0.086	16.03	29.94	1.87	0.92	0.121

[a] Each data set is best correlated with the use of the $\sigma_R{}^0$ parameter in eq 1. [b] For substituents included in analysis, *cf.* ref 5. [c] The data for six substituents free of severe steric effects were used in the analysis (NH_2, CH_3, F, Cl, Br, and CN). Due to hydrogen bonding of the NH_2 group to basic solvent molecules, which gives substantial upfield shifts, the observed NH_2 shift (12.3 ppm) in CCl_4 has been used for the DSP analysis in all solvents.

Table X. DSP Equation Analysis of Solvent Effects on the Para-Carbon ^{13}C Substituent Shifts of Monosubstituted Benzenes[a]



Solvent	c-C_6H_{12}	CCl_4	$(CH_3)_2CO$	CH_3OH
$-\rho_I$	3.96	4.20	4.99	5.16
$-\rho_R$	20.70	20.62	21.49	21.52
λ	5.23	4.91	4.30	4.17
SD	0.44	0.36	0.34	0.30
f	0.067	0.055	0.050	0.044

[a] Data for the following substituents were available and were used for the analysis: NH_2, OMe, Me, MeCO, and NO_2. Since the NH_2 group is known to hydrogen bond to basic solvents (ref 7) (which produces an additional upfield shift), the observed shift for this substituent in c-C_6H_{12} was used in the DSP equation analysis in the solvents $(CH_3)_2CO$ and CH_3OH. Discriminating best fits to the $\sigma_R{}^0$ scale were obtained for each data set. The sign of ρ values is determined by utilization of the F nmr shift convention, namely, that downfield shifts are negative.

Table XI. Values of ρ_I and ρ_R for Structure I Systems in CCl_4 Solvent

G	$-\rho_I$	$-\rho_R$	σ_R scale[a]	$\lambda = \rho_R/\rho_I$
$-CH(C_6H_5)-$[b]	1.95	1.42	$\sigma_R{}^0$	0.73
$-CH{=}N-$	2.41	2.95	$\sigma_R{}^0$	1.23
$-N{=}CH-$	2.56	3.11	$\sigma_R{}^0$	1.21
$-CH{=}CH-$	2.84[e]	3.34[e]	$\sigma_R{}^0$	1.17
$-N{=}N-$	3.35	3.26	$\sigma_{R(BA)}$	0.97
———[c]	3.98	3.24	$\sigma_{R(BA)}$	0.81
-O-	3.84[f]	5.07[f]	$\sigma_R{}^0$	1.32
-S-	4.77[g]	5.90[g]	$\sigma_{R(BA)}$	1.24
-NH-[d]	5.99	8.85	$\sigma_R{}^0$	1.48

[a] σ_R scale which gives best fit of the substituent shifts in CCl_4. [b] In CH_2Cl_2 solution, essentially identical ρ_I and ρ_R values are obtained for both this and G = CH_2, *cf.* ref 2. [c] ——— refers to biphenyls. [d] Unpublished results of Dr. J. L. Lyle. [e] For less precise fit with $\sigma_{R(BA)}$ parameters: $-\rho_I = 2.87$ and $-\rho_R = 2.37$. [f] For less precise fit with $\sigma_{R(BA)}$ parameters: $-\rho_I = 4.13$ and $-\rho_R = 3.35$. [g] For less precise fit with $\sigma_R{}^0$ parameters: $-\rho_I = 4.59$ and $-\rho_R = 6.86$.

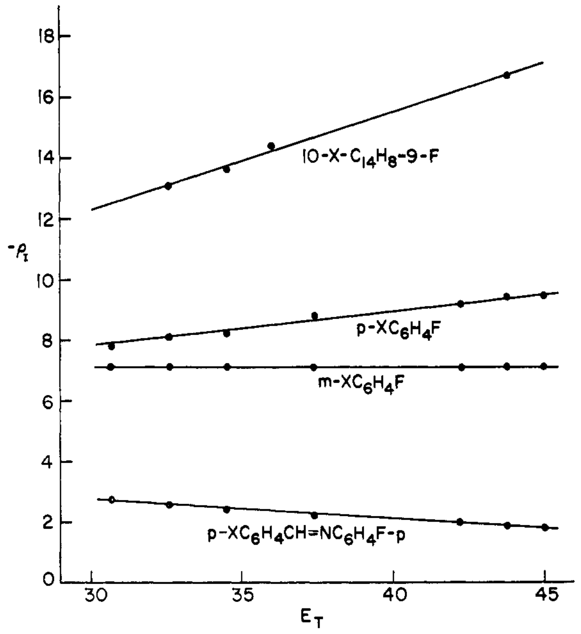


Figure 1. Correlation of aprotic solvents effects on ρ_I values by the solvent polarity parameter, E_T.

veals a second striking result. Values of *m* are essentially equal for all the structure I systems, irrespective of the size or nature of G or of the orientation of the phenyl groups about G. A value of $m = -0.060 \pm 0.010$ describes adequately all of the data. Since values of $-\rho_I$ in a given solvent vary with the nature of G over a range of 250% (*cf.* Table XI), this constant aprotic polar solvent effect clearly shows that there are components to the observed shifts which are both medium sensitive and medium insensitive. Between cyclohexane and DMSO, $-\rho_I$ values for the various G cavities decrease by 0.8 ± 0.1. This is indeed a minor but significant variation compared with that shown in Table XI for structural changes in G.

The polar solvent effects on the ρ_R parameters of Tables I–VIII in contrast to those for the ρ_I parameters are small and variable. For the biphenyls, the azobenzenes, and the azomethines ($-CH{=}N-$), $-\rho_R$ changes between cyclohexane and DMSO (CCl_4 and DMF for $-N{=}N-$) by 0.22 or less. This solvent

Table XII. Correlation of ρ_I Values with Solvent Polarity Parameter, E_T

G	n^a	m^b
(i) Structure I Types		
-CH(C$_6$H$_5$)-	7	−0.057
-CH=N-	7	−0.049
-N=CH-	7	−0.051
-CH=CH-	5	−0.071
-N=N-	3	−0.045
——	7	−0.050
-O-	7	−0.058
-S-	7	−0.055
(ii) Benzene Type		
m-FC$_6$H$_4$X	7	0.00^c
p-FC$_6$H$_4$X	7	0.112
9-FC$_{14}$H$_8$X-10	4	0.326

[a] The number of aprotic solvents. [b] The correlation equation is: $-\rho_I = mE_T +$ constant; it should be borne in mind that the change in $-\rho_I$ between solvents (Tables I–VIII) gives (eq 1) the corresponding F nmr shift in ppm for the hypothetical substituent with $\sigma_I = 1.00$. [c] *Cf.* R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 709 (1963). A value of zero is assigned on the basis that the meta-substituent effects generally have no significant dependence upon the polarity of aprotic solvents.

effect is so small and uncertain as to be trivial. On the other hand, for G = -N=CH-, -CH=CH-, -O-, -S-, and -CH(C$_6$H$_5$)-, the changes in ρ_R values parallel the changes in ρ_I values and appear to be large enough to be significant. In no case, however, are the changes as large for ρ_R as for ρ_I. In only one case, G = -CH(C$_6$H$_5$)-, is the variation in ρ_R values large enough that $\lambda \equiv \rho_R/\rho_I$ = constant, independent of solvent. In all other cases, λ increases with increasing solvent polarity.

The fact that λ is solvent independent only for a $\sigma_R{}^0$ set with $\lambda \simeq 0.75$ (*i.e.*, the -CH(C$_6$H$_5$)- set) appears consistent with earlier ideas regarding the polar resonance effect.[12] Namely, there is a limiting case in which the polar and resonance effects of the *p*-X substituent take on an immutable combination, namely, when they act in combination only as the polar effect of the *p*-C$_6$H$_5$X group as a whole. Previous work in this series suggests that this limit is reached when the above condition is fulfilled.[2,4]

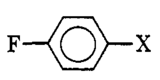
For G = -S-, the change in the magnitude of the ρ_R values obtained between cyclohexane and DMSO is 0.73. This result must be accepted with great caution, since the substituent data set for this series is clearly deficient in substituents with relatively large $-\sigma_R$ values. That is, while the range of σ_I values covered by the available substituent data is probably good enough to ensure a reliable evaluation of ρ_I values, this is not true for σ_R and ρ_R values. In particular, before solvent effects on ρ_R for this system are reliably known, data for X = NMe$_2$ and OMe are required (the minimum basis set requirement would then be met).

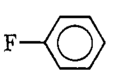
The present study provides further evidence that correlations of substituent chemical shifts with single substituent parameters, *e.g.*, $\sigma_{(p)}$, are not general but may be largely accidents of solvent, system, and precision of fit. For example, Ager, Phillips, and Tewsan[13] have plotted the F nmr substituent shifts for 4-substituted-4′-fluoro-*trans*-stilbenes in CCl$_4$ *vs.* $\sigma_{(p)}$ and report a linear correlation. Visual inspection of this plot reveals quite clearly, however, a curved rather than linear relationship. Curvature such as this by now has been commonly observed in varying extents.[2,4] In the DSP analysis, the curvature dissolves upon relaxation of the apparently unjustified constraint $\lambda = \rho_R{}^p/\rho_I{}^p = 1.00$ which is required of a linear fit to $\sigma_{(p)}$. The data of Table IV clearly reveal that only in DMF and DMSO does $\lambda \simeq 1.00$. In other solvents λ is significantly less than unity for the 4-X-4′-fluoro-*trans*-stilbenes. On the other hand, in other data sets $\lambda \simeq 1.00$ is either not found in any solvent (*cf.* Tables VII and VIII), or it holds for hydrocarbons but not for polar aprotic solvents (*cf.* Table V). Consequently, the DSP treatment provides a generalized correlation of relatively high precision, whereas fits to $\sigma_{(p)}$ of comparable precision are instead accidents of the variable transmissions of σ_I and σ_R substituent effects with system and solvent.

Interpretation

Aprotic polar solvents may enhance the effects of an electron-withdrawing substituent by supporting greater separation of charge, principally in the polar σ bonds. Enhancement of only the electron-withdrawing polar effect follows for two reasons. The σ-bond polarities are frequently large enough for the local fields of polar solvents to "get their molars in." On the other hand, a π-electronic distribution in a neutral molecule generally is represented by a poorly solvated multipole of centers of relatively small charge spread over an extensive π-electron framework. Secondly, the solvation of the polar σ bond generally cannot be spherically symmetric, due to structural considerations.[14] Thus, for example, the F center of the C$^+$–F$^-$ σ-bond dipole in say C$_6$H$_5$F is more accessible to the polar solvent fields than is the carbon center. The consequence of solvation is therefore a greater electron-withdrawing effect. Similar considerations apply to substituents, *e.g.*, CF$_3$, CN, NO$_2$, etc. Since the σ_I value of the substituent is a polarity measure, the extent of the solvent-enhanced electron-withdrawing effect is approximately proportional to this parameter. In the DSP treatment, the solvent-induced effect is placed as a variable in the ρ_I parameter.

For a para-substituted fluorobenzene, for example, the observed substituent effect is the shift between structures II and III at very high dilution in a given solvent. In light of the above considerations, the observed substituent shift must clearly be considered to consist mainly of three components. First, a solvent which supports greater separation of charge in the σ bonds of the electron-withdrawing substituent X (positive σ_I) will increase electron withdrawal and


II


III

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[13] I. G. Ager, L. Phillips, and T. J. Tewsan, *Progr. Nucl. Magn. Resonance Spectrosc.*, **7**, 64 (1971), as quoted by J. W. Emsley and L. Phillips.

[14] M. J. S. Dewar and P. J. Grisdale, *J. Amer. Chem. Soc.*, **84**, 3548 (1962); *cf.* also H. D. Holtz and L. M. Stock, *ibid.*, **86**, 5188 (1964); W. A. Adock and M. J. S. Dewar, *ibid.*, **89**, 379 (1967).

further deshield[5] the F for II relative to that in III. Second, greater charge separation in the C^{+}–F^{-} σ bonds of II and III will also be involved with such a solvent. The polarization of the solvated C–F σ bond by the solvated X substituent will give rise to a C–F σ bond of II which will be less polarized by the polar solvent than that of III. This second component to the observed shift will provide additional deshielding of F in II compared with that in III. Thirdly, the solvent may change the effective dielectric constant[15] of the medium through which pass the lines of force between the (solvated) substituent dipole and the (solvated) C–F dipole. This dielectric effect of the polar solvent will consequently reduce the observed deshielding substituent effect. In the DSP treatment, the dielectric effect is also a variable determining the ρ_I value. We assume that in comparing II and III (as well as in other similar comparisons) there is no differentiation due to the van der Waal interactions with the solvent.[16]

For structure I systems, the negative value of the slope of $-\rho_I$ *vs.* E_T ($m = -0.060 \pm 0.010$) may be attributed to predominance of the third (effective dielectric) contributing component of the polar solvent shift. That is, evidence is definitely provided for a field effect contribution to the F nmr polar substituent effects in I. The nearly constant field effect contribution for the various G cavities (*cf.* Table XII) can be rationalized on the basis that the F–X distance, while not constant, does not vary greatly. The considerations of variable orientations of the phenyl groups about G (with accompanying uncertainties about variations in the effective dielectric constant) can negate any result expected solely on the basis of small differences in F–X distance. While the field effect appears to be small based upon the observed polar solvent effects on ρ_I values, it must be borne in mind that the observed shift effects may contain measurable contributions from the first two components (X and C–F solvation effects) which will materially reduce effects expected solely on a simple field effect basis. Further, the variation of the effective dielectric constants for structure I systems in the range of solvents from cyclohexane to DMSO is probably not large since even in these systems the solvent molecules tend to be blocked from effective positions.

For benzene-like systems, *i.e.*, para-substituted fluorobenzenes and 10-substituted-9-fluoroanthracenes, the positive values of m (Table XII) indicate that the sums of the first and second components to the shifts (*i.e.*, X and C–F solvation effects) are predominant. This is a reasonably expected result since the much closer distance between the substituent and the fluorine atom raises the magnitude of components 1 and 2 compared to those for structure I systems. Further, the polarizable aromatic cavities of the benzene-like systems are expected to better exclude intervening solvent and thus to maintain a more constant (lower) effective dielectric constant.

The greater value of m for the anthracenes than the benzenes is in accord with the larger aromatic framework acting to minimize the variation in effective dielectric constant and thus the contribution of the opposed third (effective dielectric) component of the shifts. More effective transmission through the π-inductive mechanism may also contribute.[6] The effect of orientation of the substituent in the fluorobenzenes also is understandable in these terms, *i.e.*, a greater effective dielectric shift component is expected for meta- than for para-substituted fluorobenzenes. That is, more lines of force pass through solvent for meta- than for para-substituted benzenes. In this view, the insensitivity to aprotic polar solvents of the meta-substituted fluorobenzenes shifts[17] results from essentially an exact cancellation of the third with the first and second components of the shifts. In short, the order of increasing slopes in Figure 1 conforms to that expected on the basis of increasing exclusion of solvent from the "molecular cavity." It is of further interest that aprotic polar solvent effects on 3-fluoropyridine are downfield shifts.[18] Since the 3-N substituent is more embedded in its cavity than is the 3-substituent of meta-substituted fluorobenzenes, this result fits consistently the views formulated here.

The ρ_R values for all systems show small and uncertain but consistent trends with the solvent polarity which parallel the ρ_I values. The significance of these trends is open to question in view of their relative unimportance. If significant, there are several possible causes for these effects. First, the ρ_R trends could be an artifact of the quantitative separation of polar and resonance effects. That is, σ_I and σ_R parameters may be deficient in a completely quantitative separation.

Secondly, the ρ_R could be an artifact of the dual substituent parameter treatment of the aprotic solvent effects. That is, errors due to the assumption that the aprotic solvent effect on the substituent shift is directly related to the σ_I value of every substituent may lead to apparent rather than real ρ_I effects. A more rigorous analysis of the aprotic solvents on the para-substituted fluorobenzene shifts does show that for equal σ_I values, substituents which give rise to a charge distribution of the type $C_{ar}{}^{+}$–X^{-}–Y, *e.g.*, halogens, OMe, and SCF_3, are less sensitive. That is, the solvent effects plotted *vs.* σ_I give two family lines, the one of lesser slope is for the former type and that of greater slope is for substituents which give a charge distribution of the type C_{ar}–X^{+}–Y^{-}, *e.g.*, NO_2, CN, CF_3, and F_3CCO. In the less accurate but apparently useful DSP treatment, a single (intermediate) slope of solvent effects *vs.* σ_I is assumed.

Thirdly, it is possible that the greater electron-withdrawing effects of a polar unsaturated substituent, *e.g.*, NO_2, which result from solvation by local fields of polar solvents involve both polar and π-electron delocalization interactions. That is, both ρ_I and ρ_R values may be increased (or decreased) by substituent solvation effects. It is clear from the data of Tables II–IV that the π-electron delocalization effects of the strong $-R$ para substituents, NMe_2 and OMe, involve little or no influence of aprotic polar solvents. The shifts for these substituents show no obvious systematic trends with solvents. On the other hand, the relatively large systematic trends with solvent polarity exhibited

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(16) J. W. Emsley and L. Phillips, *Mol. Phys.*, **11**, 437 (1966).

(17) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 709 (1963).

(18) Unpublished results of Dr. J. L. Lyle.

by para substituents, *e.g.*, CF_3, CN, and NO_2 (*cf.* Tables I–VIII), could have some small (secondary) π-delocalization effect contributions (R effects) as well as the predominant polar effect contributions (I effects). However, the previously reported equal solvent sensitivity for the "completely twisted" and the "coplanar" NO_2 substituents does not appear at first sight to support this possibility. However, unpublished results of Mr. Imuta appear to invalidate this evidence.[19]

Fourthly, for structure I type systems, the ρ_R effects may be apparent from the resonance polar effects[12] of the substituents. Such a result would be expected, however, to lead to $\lambda \equiv \rho_R/\rho_I$ = constant, independent of solvent. Only the G = $HC(C_6H_5)$ data set gives this result (*cf.* Table I).

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[19] Unpublished results of Mr. M. Imuta. With both 4-nitro-3,5-dimethylfluorobenzene and 4-cyano-3,5-dimethylfluorobenzene, Mr. Imuta has found significantly greater shift sensitivity to polar aprotic solvents than for the corresponding para-substituted fluorobenzene. Consequently, it appears very probable that the equality of 4-nitro-3,5-di-*tert*-butylfluorobenzene and *p*-nitrofluorobenzene solvent shifts is coincidental. The 3,5-di-*tert*-butyl groups probably play two additional roles besides giving rise to "complete twisting." There is steric hindrance to solvation of the "completely twisted" NO_2 which reduces the solvent induced electron-withdrawing polar effect compared with the "coplanar" *p*-NO_2 of the fluorobenzene. This reduction, however, is probably totally compensated by the lower effective dielectric constant applicable for the former, which gives rise to greater effective transmission of the reduced substituent solvation effect—thus a coincidental stand-off.

Effects of Ring Substituents on the Type II Photoreactions of Phenyl Ketones. How Interactions between Nearby Excited Triplets Affect Chemical Reactivity

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Abstract: The effects of various ring substituents on the type II reactions, phosphorescence, and uv and epr spectra of phenyl alkyl ketones have been determined. Phenyl, methoxy, methyl, *o*-chloro, and *p*-chloro substituents decrease the chemical reactivity of the ketone triplets; trifluoromethyl substituents double reactivity; fluoro and *m*-chloro substituents produce little change; and *p*-hydroxy, *p*-bromo, and *p*-thiomethoxy substitution completely suppresses type II reaction. All ring substituents which affect triplet reactivity lower the O–O phosphorescence band energies of phenyl alkyl ketones. With phenyl-, methoxy-, thiomethoxy-, and methyl-substituted ketones, the observations of $\Delta M = 2$ epr signals and phosphorescence lifetimes greater than 0.1 sec indicate π,π^* lowest triplets. The spectroscopic behavior of the *p*-chloro ketone suggests virtually isoenergetic n,π^* and π,π^* triplet levels. The fluoro-, trifluoromethyl-, *m*- and *o*-chloro-substituted ketones retain n,π^* lowest triplets. The decreased reactivity of the *o*-chloro ketone probably reflects a steric effect. The increased reactivity of the trifluoromethyl ketones probably reflects a weak inductive effect. The triplet-state reactivity of ketones with π,π^* lowest triplets decreases as the energy gap ΔE_T between the π,π^* and n,π^* triplets increases. This effect is produced as substituents become more electron donating ($CH_3S > CH_3O > CH_3 > Cl$) and as the solvent is changed from benzene to methanol. Observed rates of triplet state γ-hydrogen abstraction respond identically with changes in C–H bond strength and to inductive effects of γ and δ substituents for both *p*-methoxy and unsubstituted phenyl ketones. This behavior suggests that the *p*-methoxy ketones react primarily from equilibrium concentrations of upper n,π^* triplets, with a ΔE_T of 2.8 kcal in benzene and 4.2 kcal in methanol. Intersystem crossing yields of the methoxy ketones are nearly unity in polar and nonpolar solvents. Consideration of the spectroscopy and the low triplet-state reactivity of naphthyl and biphenylyl ketones suggests that vibronic mixing of n,π^* and π,π^* triplets is very ineffective at promoting chemical reactivity when $\Delta E_T > 2$ kcal. With the methyl- and *p*-chloro-substituted phenyl ketones, $\Delta E_T < 2$ kcal and the two triplets may be strongly mixed. If they are, reaction may take place from equilibrium populations of both states.

Correlation of the effects of substituents on the reactivity of benzene derivatives is one of the principal weapons of physical and mechanistic organic chemistry. Determination of the effects of ring substituents on the photochemistry of phenyl ketones[2-4] has turned out to be a very complicated business. Any effect of substituents on the reactivity

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