

nitrene and ethylene (Figure 10) or by hydrogen migration and formation of methylmethylenimine. This step has not been simulated, but by analogy with cyclopropane,³⁰ one can consider that it is likely to occur through comparable conditions. It leads to a molecule with a large internal energy, which is likely to dissociate and to yield a methyl radical. This sequence of elementary reactions may constitute the first steps in the formation of the saturated hydrocarbons experimentally obtained.

Other channels from the aziridine S_1 state are the formation of carbene (path e) or nitrene (path h) by simultaneous two-bond scission. The first one involves a decay from the S_1 to the S_0 surface under favorable conditions (Figure 13). The second leads directly to the formation of the fragments, following a PEC which has an inflexion point but is continuously decreasing.

From the T_1 triplet state, every reaction path is likely to occur, and no selectivity is predictable.

The second hypothesis assumes that aziridine is liable to react only from its Rydberg states, experimentally more easily accessible. In this case, only the CN bond rupture appears likely to occur. It leads to the formation of the intermediate II which can evolve as previously described.

In the condensed protic phase, the CC bond reactivity is modified. The disrotatory mode involves an intersystem

crossing after overcoming a 0.3-eV barrier (point D, Figure 8). The conrotatory mode leads directly to the intermediate I in its Z_1 state after overcoming a 0.8 eV barrier through a transition state which is near the products. It appears that experimentally the first situation is more favorable than the second. Let us note that intermediate I represents a stable species in its first singlet state, contrary to the corresponding trimethylene in the opening of the cyclopropane.³¹ This difference may explain why the diradical can be trapped by cycloaddition in the case of aziridine while it cannot in the case of cyclopropane.

In condensed protic media, the CC bond rupture ring opening can thus compete with the CN bond rupture ring opening, alone likely to occur in gas phase. Let us note that the quantum yield of the former reaction can be strongly reduced since the reverse cyclization reaction is spontaneous, i.e., no barrier prevents it, contrary to the CC bond rupture ring opening.

Registry No. Aziridine, 151-56-4.

(31) J. A. Horsley, Y. Jean, C. Moser, L. Salem, R. M. Stevens, and J. S. Wright, *J. Am. Chem. Soc.*, **94**, 279 (1972).

(32) It is clear that our model overemphasizes the influence of hydrogen bonding in protic solvent. Indeed, in the water molecule, the local charge on the hydrogen atom is only +0.3 eV [see, for example, M. S. Gordon et al., *J. Am. Chem. Soc.*, **97**, 1326 (1975)] while we have taken a +1.0 eV value. This crude model has been retained because a more complicated one (several water molecules) should require calculations beyond the scope of this paper in order to eliminate an arbitrary error worse than the lack of precision of the present model.

(30) J. A. Berson, L. D. Pedersen, and B. K. Carpenter, *J. Am. Chem. Soc.*, **98**, 122 (1976), and references therein.

Substituent Effect Treatment of Interactions between Contiguous Functionalities G-X. 1. Remote Response to Polar and Inductive Influence of X on $G = C(sp^3)$ and $-N<$

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¹H and ¹³C NMR shifts in Me₂SO for molecules of type PhGX and ¹⁹F NMR shifts for molecules of type *p*-FPhGX have been evaluated for measuring the direct effect of the substituent X on the contiguous group G ($G = CH_2$, CH(Ph), NH, O). The sensitivity of the substituent chemical shift (SCS) of the para monitor ¹³C in α -substituted benzhydryl derivatives Ph₂CHX (2) is 0.9 times that of α -substituted benzyl derivatives PhCH₂X (1), indicating a negligible partitioning of the substituent effect between the two rings. Para monitor (¹³C and ¹⁹F) substituent chemical shifts in PhNHX, where the X's are substituents capable of only polar-inductive (nonlocalizative) interactions with the NH group, are linearly related with those of 1, but their sensitivities are more than 2 times greater, indicating that the π -inductive effect plays an important role, together with a mesomeric component effect inductively controlled by the substituent X. SCS's in α -substituted benzyl derivatives 1 are linearly related to the acidities of α -substituted *p*-toluic acids and to ¹⁹F SCS's in meta-substituted fluorobenzenes (6). SCS's of several substituents in substrates 1-3 are fitted by the reported σ_1 values: there are, however, notable exceptions (e.g., the CN substituent) which remain unaccounted for by the DSP (dual substituent parameter) treatment. A basis set of reported σ_1 values which originate an excellent correlation for PhCH₂X is defined: hitherto unreported σ_1 values are then extrapolated together with new, adjusted, partially modified σ_{1B} scale gives excellent results with benzhydryl derivatives 2 and with meta-substituted fluorobenzenes (6). Reasons for the deviance of the cyano group and for the electron-withdrawing effect of the methyl group are proposed and discussed.

Molecules can be submitted to substituent-effect treatment whenever they present a variable substituent X, an involved (reacting) group G, and a monitor MON as discernible entities.¹ Effects exerted on the group G by a set of substituents X are evaluated by variations of a detector, either a thermodynamic function connected to

or a physical property of the monitor. In the thermodynamic approach the detector for substituent effects is represented by the ease (ΔG) or the barrier (ΔG^\ddagger) of the bond breaking or bond forming of the bond between the involved (reacting) group G and the monitor, while in the extrathermodynamic approach the detector is a property (e.g., NMR chemical shift) of the same monitor eventually bonded to the group G. Taft and co-workers presented overwhelming experimental evidence for the usefulness of σ constants derived from ¹⁹F NMR measures in predicting

(1) (a) L. P. Hammett, "Physical Organic Chemistry", 2nd ed., McGraw-Hill, New York, 1970, Chapter 11; (b) R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960).

Table I. Substituent Polar-Inductive Parameters

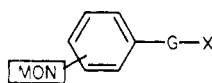
entry	substituent	σ_I	ref	σ_{IB}^a	entry	substituent	σ_I	ref	σ_{IB}^a
1	H	0.0	<i>b</i>	0.0	18	PPh ₃ ⁺			<i>f</i>
2	Ph	0.10	<i>b</i>	0.10	19	2-pyridyl			0.12
3	CONMe ₂	0.14			20	3-pyridyl			0.15
4	CO ₂ Me	0.26	<i>b</i>	0.30	21	4-pyridyl			0.18
			<i>c</i>	0.18	22	CH=CHPh			0.10
5	COMe	0.20	<i>b</i>	0.28	23	CH=NPh			
			<i>d</i>	0.22	24	N=CHPh			0.25
6	COPh	0.21			25	N=NPh	0.19	<i>g</i>	
7	CHO		<i>d</i>	0.26			0.25	<i>g</i>	
8	COCF ₃	0.58	<i>b</i>	0.45	26	Me	-0.04	<i>b</i>	-0.04 ^h (0.04) ⁱ
			<i>d</i>	0.41	27	CH ₂ CN	0.23	<i>g</i>	0.23
9	NO ₂	0.80	<i>b</i>	0.65	28	CH ₂ COMe	0.10	<i>j</i>	0.06
10	CN	0.43	<i>b</i>	0.56	29	OH	0.25	<i>b</i>	0.22
			<i>c</i>	0.45			0.16	<i>c</i>	
11	SOMe	0.40	<i>b</i>	0.50	30	OMe	0.27	<i>b</i>	0.40
12	SO ₂ Me	0.59	<i>b</i>	0.59	31	NH ₂	0.12	<i>b</i>	0.12
13	SOPh	0.46			32	NHCOMe	0.26	<i>b</i>	0.26
14	SO ₂ Ph	0.62			33	NMe ₃ ⁺	0.92	<i>g</i>	0.92
15	SO ₂ NMe ₂				34	Br	0.44	<i>b</i>	0.56
16	PO(OEt) ₂	0.19	<i>e</i>	0.24	35	SPh			0.30
17	POPh ₂	<i>f</i>	<i>e</i>	0.37					

^a σ_{IB} are constants derived from benzyl systems 1: values in italic form the basis set defined in the text. ^b Reference 2. ^c Me₂SO-corrected values from ref 12. ^d Reference 23. ^e Reference 24. ^f Insolubility prevented determination of shifts at the standard concentration. ^g Reference 12. ^h To be used when bonded to N, O, and C(sp²). ⁱ To be used when bonded to C(sp³). ^j Obtained from $\sigma^*_{COMe} = 1.65$ by assuming a methylene fall-off factor of 2.8 and $\sigma_I = 0.45\sigma^*$.

reactivities;² although the idea did not meet with general consensus,³ recent results strengthen its validity.⁴ Substituted phenols serve as a convincing example to show the internal coherence of the thermodynamic and the extrathermodynamic approach: the O-H bond dissociation constants (in H₂O)⁵ are in fact linearly related to the ¹H chemical shifts (in Me₂SO)⁶ and to IR stretching vibrations,⁷ both of the O-H group.

Remoteness of the substituent from the involved (reacting) group G is the general, accepted constraint common to Hammett, Taft, and other classical systems.⁸ To our knowledge few and unsystematic attempts have been made so far to account in terms of substituent effects for interactions of contiguous functionalities.⁹

Using the extrathermodynamic NMR approach, we have pursued the general possibility of accounting for direct interactions between two adjacent functionalities. In this series of papers we report results for molecules of type A



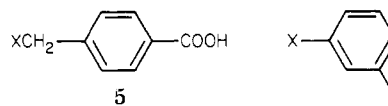
A

MON for 1-4 = ¹HC≡, ¹³C≡, or ¹⁹F≡

1, G = CH₂; 2, G = PhCH; 3, G = NH; 4, G = O

when submitted to substituent effect treatment by detecting variations of remote magnetic monitors induced by a set of substituents X directly bonded to the group G. Evidence will be offered¹⁰ that the para monitor's response depends on the nature of the interaction that the group G is capable of sustaining with the substituent X: thus where only polar interactions exist between the group G and the substituent X, the para monitor will respond to polar effects only, while when a resonance (delocalizative) interaction between the group G and the substituent takes place, the para monitor will respond to blended polar and mesomeric effects of X.^{10a}

In this paper we will be concerned with the response of various magnetic monitors to polar-inductive effects exerted by substituents X. We have considered either "formally" saturated groups G (G = CH₂, CH(Ph)) bonded to any substituent X or groups possessing available electron pairs (G = NH, O) bonded only to those substituents X incapable of any delocalizative mesomeric interactions with G. Effects of substituents in substrates 1-4 will be compared with those found in α -substituted *p*-toluic acids (5)¹¹ and in meta-substituted fluorobenzenes (6).¹² The



6

acidity dependence of acids 5 as function of the α substituent provides the thermodynamic counterpart of the present study.

Transmission of substituent effects in α -substituted toluenes has been previously investigated as part of the correlation of physical and chemical properties with molecular structure.^{9d,13} The ¹³C_p dependence of α -substi-

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Table II.^a ¹⁹F and ¹³C Shifts (ppm) of PhCH₂X and Ph₂CHX

entry	X	PhCH ₂ X					Ph ₂ CHX			
		¹⁹ F _p	C _o	C _m	C _p	C _{ipso}	C _o	C _m	C _p	C _{ipso}
1	H	44.43	130.38	129.69	126.81	138.82	129.85	129.85	127.43	142.72
2	Ph	45.59	129.85	129.85	127.43	142.72	129.81	130.52	127.72	145.25
3	CONMe ₂	45.95	130.45	129.65	127.67	137.43	129.68	130.36	127.99	141.70
4	CO ₂ Me	46.87	130.78	129.83	128.28	135.84	129.92	129.92	128.53	140.45
5	COMe	46.41	131.04	129.78	128.01	136.39	129.97	130.33	128.34	140.42
6	COPh	46.42	131.25	130.23	128.04	136.54	129.99	130.51	128.28	140.88
8	COCF ₃		131.44	129.67	129.90	132.45				
9	NO ₂		131.91	130.27	130.98	130.77				
10	CN	48.07	129.61	130.47	129.13	132.86	128.95	130.70	129.51	138.15
11	SOMe	48.42	131.47	129.59	128.96	132.75	129.92	131.06	129.32	138.80
12	SO ₂ Me		132.33	129.97	129.83	130.61	130.20	131.11	129.91	135.40
13	SOPh	48.64	131.89	129.56	129.28	130.54				
14	SO ₂ Ph	49.48	132.41	129.48	130.10	128.76	129.92	131.32	130.31	135.01
16	PO(OEt) ₂	46.48	131.23	129.69	127.93	133.75				
17	POPh ₂		<i>b</i>							
19	2-pyridyl		130.37	129.83	127.58	141.30				
20	3-pyridyl		130.14	130.14	127.71	141.97				
21	4-pyridyl		130.34	130.07	127.86	141.04				
22	CH=CHPh		129.98	129.98	127.49	141.53				
24	N=CHPh		<i>c</i>	<i>c</i>	128.25	141.08				
26	Me		129.29	129.85	127.16	145.29				
27	CH ₂ CN		129.92	129.92	128.18	140.34				
28	CH ₂ COMe		129.70	129.70	127.29	142.64				
29	OH	46.49	127.88	129.48	128.08	143.98	127.81	129.60	128.22	145.58
30	OMe		128.97	129.71	128.97	139.73	127.98	129.80	128.72	143.90
31	NH ₂		128.44	129.51	127.57	145.73				
32	NHCOMe		128.75	129.72	128.18	141.09				
33	NMe ₃ ^d		134.33	130.32	131.70	129.98	130.71	132.60	131.40	134.52
34	Br	49.63	130.13 ^c	130.73 ^c	129.77	139.48				
35	SPh	47.47	130.40 ^c	130.25 ^c	128.51	137.64	129.55	130.06	128.70	142.57

^a ¹³C shifts are relative to (trimethylsilyl)propanesulfonic acid sodium salt; ¹⁹F shifts are relative to C₆F₆ (see text). ^b Insoluble. ^c Assignment uncertain. ^d Bromide as counterion.

Table III. ¹H, ¹⁹F, and ¹³C Shifts (ppm) of PhNHX

entry	X	¹ H _p	¹⁹ F _p	¹³ C			
				ortho	meta	para	ipso
1	H	6.502	32.88	115.39	130.23	117.14	151.03
26	Me	6.514	32.66	113.05	130.04	116.69	150.69
27	CH ₂ CN	6.725		114.53	130.55	119.36	148.07
29	OH		37.21	114.47	129.86	120.68	153.54
30	OMe	6.818	38.73	114.57	130.21	121.77	150.77
31	NH ₂	6.586	34.36	113.20	130.02	118.44	153.65
32	NHCOMe	6.700	36.19	113.62	130.10	119.87	150.85

tuted toluenes in CDCl₃ has been studied¹⁴ by the DSP treatment and was interpreted to be dominated by the polar term of the substituent accompanied by a resonance contribution of opposite sign. Results of this analysis have been recently rejected by Kitching and Adcock,¹⁵ according to whom the CH₂X substituent as a whole exerts comparable polar-inductive and resonance contributions.

Table I reports the set of substituents¹⁶ which will be considered in this and future papers¹⁰ concerning substrates PhGX where G = O,^{10a} NH,^{10a,c} N⁻(Na⁺),^{10b} CH⁻(Met⁺),^{10b,c} and PhC⁻(Met⁺).^{10b} Their filing follows chemical analogy, although it has been impossible to consider all of them for each group G. Dimethyl sulfoxide (Me₂SO) was chosen as a solvent for recording NMR spectra of all compounds because of its special merits¹⁷ and

in particular for the following reasons: (a) correlations of σ^- values with NH₂ or OH chemical shifts of substituted anilines¹⁸ and phenols⁶ are particularly successful in this solvent and show higher sensitivities relative to other nonpolar aprotic solvents;¹⁹ (b) in considering carbanions as substrates having direct interactions with contiguous substituents, Me₂SO appears to be the solvent of choice, and in fact cations are believed to be extensively coordinated by Me₂SO,²⁰ thus causing alkali carbanides to be present as solvent-separated rather than intimate ion pairs. Disadvantages in the use of Me₂SO as solvent arise from the possibility of its specific interactions with polar (e.g., C≡N)²¹ or proton-donating (acidic) groups (e.g., OH).²²

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(16) We could not conform to Taft's suggestion² of using his proposed minimal basis set because in the cases of substrates 3 and 4 some of the compounds are unknown (e.g., PhONO₂) or too unstable (e.g., PhNHBr).

Experimental Section

All new compounds were obtained commercially or were prepared by using standard methods: unknown fluorinated compounds were synthesized in analogy with their unlabeled counterparts. All new compounds gave satisfactory analytical data. The ^{19}F and ^1H spectra were recorded on an HA-94-100 D Varian spectrometer using 0.2 M sample solutions in Me_2SO (3.3 mm o.d. tubes). ^1H spectra of substrates 4 were obtained on a WH 270 Bruker spectrometer. Shifts were measured relative to 3-(trimethylsilyl)propanesulfonic acid sodium salt (TPS) as internal reference. ^{19}F shifts were measured relative to trifluoroacetic acid (neat) as external reference and then converted into shifts relative to hexafluorobenzene by using the relationship²⁵ $\delta_{\text{CF}_6} = \delta_{\text{CF}_3\text{CO}_2\text{H}} + 84.4$. ^{13}C spectra were obtained on either an XL-100-15 or an XL-100-12 WG Varian instruments at 25.18 MHz, using 0.33 M sample solutions in $\text{Me}_2\text{SO}-d_6$ (12 mm o.d. tubes): 16K data points were collected over a spectral width of 5000 Hz, resulting in a resolution of 0.05 ppm. Chemical shifts are relative to TPS as internal reference. Assignments of aromatic carbons were based on proton-coupled spectra.¹⁴

Results

Tables II–IV report ^{13}C and ^{19}F data for substrates 1–4. The number of substituents is necessarily limited to 6 or 7 for $\text{G} = \text{NH}$ and 3 or 4 for $\text{G} = \text{O}$, because of the restriction we imposed to the nature of substituents. For clarity, correlations are schematized as intermonitor, interpositional, Hammett-type, and DSP correlations. Intermonitor correlations are obtained by plotting shifts induced by a set of substituents on a monitor at a fixed position of one substrate vs. shifts induced on another monitor at the same position of the same family of substrates (e.g., $^{19}\text{F}_p$ of *p*-fluoroaniline vs. $^{13}\text{C}_p$ of aniline). Interpositional correlations are obtained by plotting shifts induced by a set of substituents on one monitor at two different positions (e.g., $^1\text{H}_p$ vs. $^1\text{H}_m$). Intersystem correlations are obtained by plotting variations of shifts, thermodynamic functions, etc. induced by a set of substituents in two different substrates (e.g., $^{13}\text{C}_p$ of 1 vs. $\text{p}K_a$ of 5). Hammett-type and DSP correlations have the usual significance. Results of the correlations are reported in Tables V–VIII.

Entries 1–4 of Table V report intermonitor correlations for $^{19}\text{F}_p$ and $^{13}\text{C}_p$: the excellent fits show that fluorine is more sensitive by a factor of 1.2–1.6. Entries 5 and 6 report fitting parameters for plots of $^{13}\text{C}_p$ shifts in Me_2SO vs. $^{13}\text{C}_p$ shifts in CDCl_3 ,¹⁴ and an excellent correlation is found if the point for $\text{X} = \text{OH}$ is omitted; evidently, the OH group, because of its hydrogen-bonding capacity, can be solvated by Me_2SO and CDCl_3 in widely different ways. Data here available allow interpositional correlations only of $^{13}\text{C}_p$ vs. $^{13}\text{C}_o$ and $^{13}\text{C}_m$ for substrates 1–4. No correlation whatsoever is found: this result is in line with what is known in monosubstituted benzenes^{26a,d} but is in contrast with recent findings of successful C_p/C_m and F_p/F_m correlations obtained for 1-X-substituted 4-phenylbicyclo[2.2.2]octanes.^{26e} Interpositional correlations will be further considered and

commented on in the accompanying paper.^{10a}

Entries 1–10 of Table VI report fitting parameters of NMR intersystem correlations (chemical shifts vs. chemical shifts), while entries 11–20 report chemical shifts vs. $\text{p}K_a$ and $\text{p}K_a$ vs. $\text{p}K_a$. Before the results are analyzed, it is convenient to recall that least-squares treatments confer a strong weight to initial and final points:²⁷ small variations in the positions of these points induce large differences in the fitting parameters of the equation. This consideration is in order since a significant discrepancy of the effect of the methyl group relative to hydrogen is observed in series 1–4, and indeed these points are our initial ones. In substrates 3 the methyl SCS is negative (high field shift = methyl electron donor) while in substrates 1 and 4 the SCS is positive (low field shift = methyl electron withdrawing). The positive methyl SCS in series 4 is, however, fictitious since the $^{13}\text{C}_p$ shift of phenol ($\text{X} = \text{H}$) is at abnormally high field due to the partial proton transfer to Me_2SO .²² The methyl SCS indeed becomes negative on using the extrapolated^{10a} value for phenol predicted in the absence of any solvent interaction. If the opposite sign of the methyl SCS in substrates 1 relative to 3 and 4 is retained, a considerable uncertainty is introduced in every correlation (intersystem, Hammett type, etc.) in which data of the benzyl derivatives 1 are used. This consequence would be quite annoying, since the toluene series 1, because of the availability of its numerous substituents, has the requisite for being considered a reference series, analogous to that represented by meta-substituted fluorobenzenes (6). To avoid this, we assumed arbitrarily, in analogy with series 3 and 4, a negative methyl SCS for toluene derivatives 1 and corrected the experimental $^{13}\text{C}_p$ shifts of toluene ($\text{X} = \text{H}$) and of ethylbenzene ($\text{X} = \text{Me}$) on the basis of results of intersystem correlations of 1 vs. 2 and of 1 vs. 3, having in mind the reservation of discussing later the “exceptionality” of the methyl substituent. An excellent fit is obtained for the intersystem correlation of substrates 1 and 2: comparison of entries 2 and 3 (Table VI) shows that the point for $\text{X} = \text{OMe}$ is slightly deviant. The correlation in which the point $\text{X} = \text{H}$ has been omitted (entry 1) is sufficiently determined and precise enough to be used for extrapolating the calculated chemical shift for $\text{X} = \text{H}$ in substrates 1 (toluenes): such a value (127.01 ppm) is very close to the experimental one and indicates that it is in ethylbenzene that some special effect occurs. To extrapolate the corrected value of the $^{13}\text{C}_p$ shift in ethylbenzene, we used the intersystem correlation between substrates 1 and 3. There are available seven experimental points (entry 4), and it appears that the OH group is deviant, since its omission (entry 5) increases considerably the correlation coefficient. Use of the correlation in entry 6 of Table VI, in which the Me and OH points have been omitted and the H point has the corrected value (to maximize the precision of the correlation), gives an extrapolated value of the $^{13}\text{C}_p$ shift in ethylbenzene of 126.85 ppm: the difference with the experimental value (0.3 ppm) is larger than that found for the H substituent. Entry 7 of Table VI reports the good fitting parameters of the intersystem correlation of substrates 4 vs. 1, showing a sensitivity ratio of about 1.5: the correlation, however, has a limited significance because of the paucity of data and because corrected $^{13}\text{C}_p$ chemical shifts both for ethylbenzene (126.85 ppm) and for phenol

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Table IV. ^1H , ^{19}F , and ^{13}C Shifts (ppm) of PhOX

entry	X	$^1\text{H}_p$	$^{19}\text{F}_p$	^{13}C			
				ortho	meta	para	ipso
1	H	6.783	36.55	116.71	130.80	120.25	158.58
26	Me	6.950	38.51	115.36	130.90	121.91	161.46
27	CH_2CN	7.088		116.38	131.26	123.91	157.82
28	CH_2COMe			115.95	130.90	122.26	159.1

Table V. Intermonitor Correlations^a

entry	system	x	y	slope	intercept	r	n	substituents
1	PhCH_2X	$^{13}\text{C}_p$	$^{19}\text{F}_p$	1.45 ± 0.03	-139.34	0.999	9	Ph, CONMe ₂ , CO ₂ Me, COMe, COPh, CN, SO ₂ Ph, PO(OEt) ₂ , OH
2				1.50 ± 0.04	-145.63	0.998	10	as entry 1 + H
3	PhNHX	$^{13}\text{C}_p$	$^{19}\text{F}_p$	1.62 ± 0.06	-161.54	0.991	14	as entry 2 + SOMe, SOPh, SPh, Br
4	PhCH ₂ X	$^{13}\text{C}_p^b$	$^{13}\text{C}_p^c$	1.20 ± 0.05	-107.54	0.997	6	H, Me, OH, NH ₂ , NHCOME, OMe
5		$^{13}\text{C}_p^b$	$^{13}\text{C}_p^c$	1.03 ± 0.06	-5.23	0.994	6	H, Ph, CN, NO ₂ , Me, Br
6				1.01 ± 0.10	-2.21	0.976	7	as entry 5 + OH

^a For definition see the text. ^b Shifts in Me₂SO (Table II). ^c Shifts in CDCl₃.¹⁴

Table VI. Intersystem Correlations^a

entry	system A ^b	system B ^c	x	y	slope	intercept	r	n	substituents
1	Ph ₂ CHX	PhCH_2X	$^{13}\text{C}_p$	$^{13}\text{C}_p$	0.89 ± 0.03	14.03	0.994	12	Ph, CONMe ₂ , CO ₂ Me, COMe, COPh, CN, SO ₂ Me, SO ₂ Ph, SOMe, NMe ₃ ⁺ , SPh, OH
2					0.87 ± 0.02	16.30	0.994	13	as entry 1 + H
3					0.86 ± 0.04	17.13	0.988	14	as entry 2 + OMe
4	PhNHX	PhCH_2X	$^{13}\text{C}_p$	$^{13}\text{C}_p$	2.39 ± 0.37	-187.09	0.944	7	H, Me, CH ₂ CN, NH ₂ , NHCOME, OMe, OH
5					2.31 ± 0.29	-176.14	0.970	6	as entry 4 - OH
6					2.31 ± 0.18	-176.63	0.991	5	H*, CH ₂ CN, NH ₂ , NHCOME, OMe
7	PhOX	PhCH_2X	$^{13}\text{C}_p$	$^{19}\text{F}_m^e$	1.54 ± 0.18	-73.84	0.988	4	H*, Me*, CH ₂ CN, CH ₂ COMe
8	<i>m</i> -FPhX ^d	PhCH_2X^d	$^{13}\text{C}_p$	$^{19}\text{F}_m^e$	-0.92 ± 0.09	0.86	0.970	8	Me, Ph, NO ₂ , COCF ₃ , Br, OMe, COMe, CO ₂ Et
9					-0.85 ± 0.11	0.86	0.941	9	as entry 8 + CN
10					-0.97 ± 0.07	0.54	0.982	8	as entry 8 with H*, Me*
11	<i>p</i> -XCH ₂ PhCO ₂ H	PhCH_2X	$^{13}\text{C}_p$	$\text{pK}_{a,\text{EtOH}}^f$	-0.14 ± 0.01	24.44	0.997	5	H, Ph, OMe, NHCOME, Br
12					-0.14 ± 0.01	24.19	0.984	6	as entry 11 + OH
13					-0.17 ± 0.03	27.38	0.930	6	as entry 11 + CN
14					-0.14 ± 0.01	24.61	0.985	5	H, Ph, OMe, NHCOME, SO ₂ Ph
15					-0.14 ± 0.01	24.75	0.983	6	as entry 14 + OH
16					-0.15 ± 0.01	26.29	0.979	7	as entry 15 + Br
17					-0.16 ± 0.03	27.53	0.909	7	as entry 15 + CN
18	<i>p</i> -XCH ₂ PhCO ₂ H	<i>p</i> -XCH ₂ PhCO ₂ H	$\text{pK}_{a,\text{EtOH}}^f$	$\text{pK}_{a,\text{MCS}}^f$	1.03 ± 0.07	0.86	0.990	6	H, Ph, Br, CN, OMe, NHCOME
19					1.04 ± 0.11	0.83	0.972	7	as entry 18 + OH
20					0.94 ± 0.20	1.39	0.902	7	as entry 18 + CONH ₂

^a For definition see the text. Asterisked substituents (H*, Me*) indicate that for PhCH₂X, calculated instead of experimental values of chemical shift are used as inputs.

^b System whose monitor (column y) is reported as ordinate in the correlation. ^c System whose monitor (column x) is reported as abscissa in the correlation. ^d Inputs are shifts of the indicated monitor in a substituted substrate referred to that of the parent compound (X = H). ^e Reference 12. ^f Reference 11.

Table VII. Hammett-Type Correlations^a

entry	system	x ^b	y	ρ	intercept	r	n	substituents
1	PhCH ₂ X	σ _{1,T}	¹³ C _p	5.15 ± 0.41	126.96	0.952	18	H, Ph, CO ₂ Me, COMe, COCF ₃ , CN, NO ₂ , SOMe, SO ₂ Me, Me, CH ₂ CN, CH ₂ COMe, OH, OMe, NH ₂ , NHCOME, NMe ₃ ⁺ , Br as entry 1 with H*, Me*
2				5.20 ± 0.40	126.94	0.955	18	H, Ph, SO ₂ Me, Me, CH ₂ CN, NH ₂ , NHCOME, NMe ₃ ⁺ as entry 3 with H*, Me*
3				4.97 ± 0.22	127.00	0.994	8	
4				5.03 ± 0.11	126.97	0.999	8	
5				4.83 ± 0.24	126.94	0.989	11	
6			¹³ C _p	4.91 ± 0.20	127.055	0.993	11	
7	Ph ₂ CHX	σ _{1,corr}	¹³ C _p	4.36 ± 0.17	127.24	0.994	9	H, Ph, CO ₂ Me, COMe, CN, SOMe, SO ₂ Me, OH, NMe ₃ ⁺
8		σ _{1,T}	¹³ C _p	4.25 ± 0.21	127.50	0.994	7	
9		σ _{1,corr}	¹³ C _p	4.42 ± 0.17	127.40	0.995	9	
10		σ _{1B}	¹³ C _p	4.49 ± 0.14	127.38	0.995	13	
11				4.46 ± 0.19	127.36	0.989	14	
12	PhNHX	σ _{1,T}	¹³ C _p	13.25 ± 2.17	117.07	0.939	7	H, Me, CH ₂ CN, OH, OMe, NH ₂ , NHCOME
13		σ _{1B}	¹³ C _p	11.17 ± 0.52	117.08	0.996	6	H, Me, CH ₂ CN, OMe, NH ₂ , NHCOME
14	m-FPhX	σ _{1,T}	¹⁹ F _m	-6.36 ± 0.60	1.57	0.970	9	Ph, CO ₂ Et, COMe, COCF ₃ , CN ^c , NO ₂ , Me, OMe, Br
15		σ _{1B}	¹⁹ F _m	-5.04 ± 0.36	0.53	0.982	9	as entry 14

^a For asterisked substituents see footnote a in Table VI. ^b The σ_{1,T} set is formed by Taft's² polar-inductive constants reported in Table I; the σ_{1,corr} set contains "Me₂SO corrected" constants for CN, CO₂Me, and OH; the σ_{1B} set is the new adjusted and complemented set proposed in this work. ^c Using σ₁ = 0.56.

(122.08 ppm)^{10a} have been used. Entries 8–10 of Table VI report fitting parameters for plots of ¹⁹F shifts in meta-substituted fluorobenzenes (6)¹² vs. ¹³C_p shifts of substrates 1, both in Me₂SO solution. Considering all the available nine substituents, only a fair correlation is found (entry 9): upon the exclusion of the deviant cyano group (entry 8) and inclusion of the predicted values for X = H and Me for toluenes 1 (entry 10), good fits are obtained. Entries 11–18 of Table VI report fitting parameters for plots of pK_a values of α-substituted *p*-toluic acids (5) determined¹¹ in 50% (by volume) aqueous ethanol and 80% (by weight) aqueous methyl Cellosolve (MCS) vs. ¹³C_p shifts of substrates 1. The results show a satisfactory linear correlation provided that the deviant CN and OH points are omitted. Although the OH substituent decreases the *r* values of correlations 11 and 14 (Table VI), its influence on the slopes, unlike the CN group, is negligible. Entries 18–20 report fitting parameters for plots of the pK_a values determined in the two solvents: these correlations show that groups capable of different hydrogen bonding with the two solvents (X = OH and CONH₂) decrease considerably the goodness of the correlations.

Entries 1–11 of Table VII show correlations of ¹³C_p shifts relative to substrates 1–2 with previously reported σ₁ constants. Of the overall 29 substituents considered for substrates 1, there are available only 18 σ₁ values, and for the overall 14 substituents considered for substrates 2 there are available only nine σ₁ values. The 18-point lines obtained for substrates 1 by using either experimental or predicted shifts for X = H and Me (entries 1 and 2, respectively) are fair but not completely satisfactory: somewhat deviant points appear to be X = OH, OMe, Br, CN, COMe, and NO₂. Although statistically imprecise, the ρ₁ value obtained with the 18-point line of entry 1 is physically significant: in fact the ratio of ρ₁'s for substrates 1 and 2 is very close to the slope of the intersystem correlation of substrates 1 and 2 (4.36/5.15 = 0.85, to be compared with the experimental value 0.87 ± 0.2 of entry 2 of Table VI). Instead, ¹³C_p shifts of substrates 2 respond linearly to σ₁ values with an appreciably high degree of precision (entry 7, Table VII). Exclusion from correlations 1 and 2 of substituents either apparently deviant (X = OMe, Br) or with possibly solvent-dependent σ₁ values (X = OH, CN, CO₂Me, COMe, SOMe, NO₂) originates very good eight-point lines whose fitting parameters are reported as entries 3 and 4 (Table VII). Introduction of the CN, CO₂Me, and OH points, with either normal or "Me₂SO corrected" σ₁ values¹² (entries 5 and 6, Table VII), decreases the slope and the *r* values but in the latter case less than in the former. Instead, comparison of entries 7 and 8 (Table VII) shows that for substrates 2 the goodness of the fit is insensitive whether normal or "Me₂SO corrected" σ₁ values are used. Because of its imprecision, the 18-point correlation of entry 1 (Table VII) cannot be used to extrapolate any new σ₁ value: however, the eight-point correlation reported in entry 4 (Table VII) appears sufficiently determined and precise enough to extrapolate adjusted σ₁ values for those substituents excluded from the correlations and for the nine substituents with hitherto unreported σ₁ values. Table I reports such new values anchored to the Taft σ₁ values of eight substituents chosen as a basis set (NH₂, NHCOME, Ph, CH₂CN, SO₂Me, NMe₃⁺, H, Me). Systems 2 and 6 have been used to check in a stepwise fashion the validity of the adjusted and of the new σ₁ constants. Experimental data thus have been treated either with Taft's or with the newly calculated σ₁ constants, and the results are reported in entries 12–15 of Table VII. ¹³C_p shifts of substrates 3 correlate poorly with

Table VIII. Fitting Parameters for DSP Treatment of PhCH₂X

entry	x	y	z	ρ_I	ρ_R	f	SD	n	substituents
1	$\sigma_{I,T}$	¹³ C _p	σ_{R°	5.55	-0.06	0.17	0.32	8	Ph, CO ₂ Me, COMe, NO ₂ , Me, NH ₂ , NHCOMe, Br
2	$\sigma_{I,T}$	¹³ C _p	σ_{RBA}	5.55	0.05	0.17	0.32	8	as entry 1
3	$\sigma_{I,T}$	¹³ C _p	σ_{R°	4.97	-0.66	0.22	0.43	11	as entry 1 + CN, SOMe, OMe
4	$\sigma_{I,T}$	¹³ C _p	σ_{RBA}	4.95	-0.39	0.23	0.43	11	as entry 3

Taft's σ_I values (seven points, entry 12); an almost perfect six-point line is obtained, however, by changing the σ_I value of the OMe from the tabulated 0.27 to the aforesaid 0.40 and by omitting the OH point (entry 13). The slope of the line is in accord with that predicted from the intersystem correlation between substrates 1 and 3 (11.17/5.03 = 2.22, to be compared with the experimental 2.31 ± 0.18 of entry 6 in Table VI). Entry 14 of Table VII reports the good fitting parameters obtained from the correlation of ¹³C_p vs. σ_I values in system 4: phenol is a coherent point provided that the extrapolated value is used.^{10a}

Entries 1-4 of Table VIII report fitting parameters for DSP treatment of ¹³C_p shifts induced by 11 substituents in system 1. Both σ_{R° and σ_{RBA} sets have been checked: in both cases the f and SD values are out of the range of acceptability defined by Taft and co-workers.² No improvement in the fitting parameters is obtained on omitting the OMe, SOMe, and CN points (Table VIII, entries 1 and 2).

Meta ¹³C shifts in substrates 1-4 are considerably less sensitive than ¹³C_p to the effects induced by substituents X. The SCS of this monitor are not accounted for by any type of correlation (intersystem, e.g. vs. ¹⁹F_m in meta-substituted fluorobenzenes; Hammett type, e.g. vs. σ_I values). Even intersystem correlations obtained by plotting ¹³C_m of one substrate vs. ¹³C_m of another substrate are unsuccessful.

Discussion

Results here reported clearly show that para monitors (¹H, ¹⁹F, ¹³C) of substrates 1-4 respond linearly to polar-inductive interactions that the substituent X sustains with the group G. This is manifested by the good quality of intersystem relationships which afford relative sensitivities of different substrates and of different monitors. As a corollary, the para monitor SCS's respond to σ_I constants defined by Taft, although a number of deviances are found. The Discussion section will treat different substrate's sensitivities in connection with mechanisms of transmission of effects, plausible reasons for variance of substituent effects of some groups, including that of the methyl group bonded to a saturated carbon.

Transmission of Polar-Inductive Effects. Several mechanisms of the polar category have been proposed for the transmission of effects. σ -Inductive effects are the consequence of the transmission through σ bonds of the inductive electron withdrawal or repulsion exerted by the X substituent. *Direct-* (electrical) *field effects* arise by through-space polarization, induced by the polar X group, of the bonds by which the monitor is linked (e.g., the C-¹⁹F bond): their magnitude depends upon angle and distance factors. π -Inductive effects are due to the benzene π cloud polarization and cause aromatic charge redistribution: their magnitude depends upon the nature of the intervening dielectric material. *Hyperconjugative* effects arise because of C-X and/or C-H hyperconjugation with the benzene π cloud. Taft²⁹ and Stock³⁰ suggested that π -in-

ductive effects play an important role: Reynolds,³¹ Brownlee and Topsom,³² and others³³ have stressed, on grounds of firm experimental and theoretical evidence, that π effects can even be dominant, depending upon the substrate.

Recently Utley,³⁴ using one single framework alternatively substituted at two different positions, was able to directly compare sensitivities to field and to field plus π -inductive effects of substituents. The substituent effects exerted by CH₂-X groups, either present as a side chain or embedded in a ring fused onto a benzene or naphthalene nucleus bearing the magnetic monitor, have been investigated by both Dewar's and Adcock's group. Dewar has concluded that the σ -inductive effects are unimportant³⁵ for ¹⁹F chemical shifts compared to electrostatic polarization of the C-F bond and to hyperconjugative effects.^{13a} Hyperconjugative charge transfer to the aromatic rings is favored by Sheppard³⁶ and McBee³⁷ in the case of halomethyl groups and by Adcock³⁸ even for the tricyanomethyl group. Cooperation of both π -inductive and direct-field effects is elsewhere admitted by Adcock,^{13b,39} while direct-field effects are predominant in substrates in which the substituent is very remote from the monitor as in 1-substituted 4-(p-fluorophenyl)bicyclo[2.2.2]octanes.⁴⁰ It has been pointed out that the controversy is semantic.^{31c}

If substituent effects were transmitted to ¹³C_p of substrates 1 and 2 by the π -inductive and/or the direct-field effects exclusively, one would expect equal monitor sensitivities in the two cases; if, however, substituent effects were transmitted by the σ -inductive mechanism exclusively, one would expect the sensitivity of system 2 to be half of that of system 1 as a result of equal partitioning of the effect between the two rings. This is not found, and the actual response in 2 is 0.9 times that in 1. We interpret this result as evidence that negligible partitioning of the effect occurs, and thus π -polarization and/or the direct-field effect are predominant mechanisms of substituent-effect transmission.

Substituent chemical shifts for substrates 3 are nicely related in a linear way to those of substrates 1: their sensitivity however is more than two times greater. Besides

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the aforeoutlined mechanism of transmission of effects in CH_2X -substituted benzenes, another important mechanism can be envisaged in NHX -substituted benzenes. The substituent X can operate an inductive electron withdrawal (or donation) on the π electrons of nitrogen: the reduced π -electron availability on nitrogen reduces the extent of π interaction with the adjacent π cloud of the benzene ring. Thus, through a polar mechanism the substituent X would interfere with the mesomeric interaction of the NH group with the aromatic ring, and since $^{19}\text{F}_p$ and $^{13}\text{C}_p$ shifts are related to π -electron charge density at C_p ^{26b-d} it would ultimately affect ^{19}F and ^{13}C shifts. Conversely, the π aromatic cloud in substrates 3 (and 4) is more electron rich than in toluenes 1 and hence more polarizable: the efficiency of the π -inductive effect depends upon the extent of polarizability of the dielectric material intervening between the substituent and the monitor. The enhanced inductive mechanism of transmission and the polar interference with mesomeric charge distribution outlined above are in our opinion responsible for the exalted sensitivity of systems 3 relative to 1. An analogous situation has been recently discussed in the case of *N*-alkylacetamides.^{26f}

In view of the fact that both $^{13}\text{C}_m$ and $^{13}\text{C}_o$ do not linearly respond to any treatment discussed herein, their usefulness as monitors for substituent effects has not been further considered.

Variance of Substituent Effects. Para monitors (^{19}F and ^{13}C) of benzyl derivatives 1 respond linearly with ^{19}F shifts of meta-substituted fluorobenzenes (6) and with $\text{p}K_a$'s of α -substituted *p*-toluic acids: the correlations have fair to good fitting parameters if the deviant point relative to the cyano substituent is omitted. This substituent is less electron withdrawing in benzyl derivatives 1 than in meta-substituted fluorobenzenes (6) and α -substituted *p*-toluic acids (5). Since it is well accepted that the ^{19}F monitor in meta-substituted fluorobenzenes^{8,27b} and the acidity of α -substituted *p*-toluic acids^{2,11} respond to polar-inductive effects only, it follows that also in benzyl derivatives 1 $^{19}\text{F}_p$ and $^{13}\text{C}_p$ are sensitive to polar-inductive effects only. The deviance of the CN group is real since it cannot be accounted for by resonance components present in the DSP treatment. Fitting parameters (*f* and SD) of the DSP treatment of ^{13}C data for benzyl derivatives 1 are unacceptable by the suggested Taft standards. The small value of ρ_R relative to ρ_I and the fact that ρ_R assumes either a positive or a negative value depending upon the set of substituents chosen clearly indicate that ρ_R has zero as the limiting value, the nonzero value originating as a mathematical artifact of the regression. Intersystem correlations between systems 2 and 5 or 6 for comparing directly the effects of substituents cannot be used because substituents common within the series are too few: substituent effects must thus be compared through the intermediacy of σ_I constants. There is no detectable deviance for the CN substituent in series 2, and the precision of the fit is almost insensitive to the introduction of solvent-corrected σ_I values. We believe, however, that the deviance for X = CN between series 1 and 5 and series 1 and 6 is real and finds explanation in physical phenomena occurring in either case.

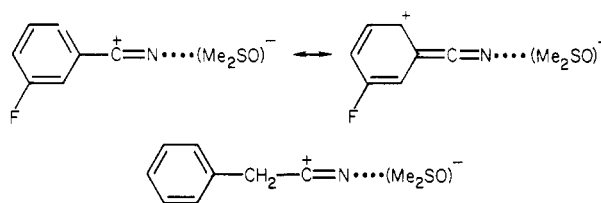
Aryl cyanides are known²¹ to interact strongly with Me_2SO , and 1:1 complexes have been proposed and evidenced. In such complexes the nitrogen of the cyano group acts as a base toward the positive pole of the sulfur atom: the net result is that both π -inductive effects and mesomeric interaction of the cyano group with the aromatic ring are greatly exalted, because of the charge transfer and

Table IX. Effects of Methyl Substitutions on $^{13}\text{C}_p$ Shifts of Monosubstituted Benzenes

substrate	R = H	R = Me	ref
PhR	128.7	125.6	a
PhCH ₂ R	125.6	125.9	b
PhCOR	134.7	131.6	a
PhCOCH ₂ R	131.6	131.1	a
PhC(R)OH ⁺	148.9	145.3	c
PhC(R)CH ₃ ⁺	161.6	155.9	c

^a Reference 45. ^b Reference 44. ^c Reference 50.

charge redistribution in the aromatic ring. The meta fluorine monitor therefore is affected by the partially positive cyano group and not by the neutral uncomplexed substituent. Complexation would undoubtedly take place in the case of benzyl cyanide: this complexation, however, would affect the para monitor through space only and not by charge transfer. It is easy to anticipate that the effect of the complexation in this case is considerably weaker than in the case of aryl cyanides. Different σ_I constants are anticipated for these two considerably different electronic situations.



It seems somewhat more difficult to account for the deviance of the cyano group between systems 1 and 5. It seems logical to assume that the cyano group shows similar coordinating properties toward protic solvents and Me_2SO . This seems reasonable in view of the fact that, e.g., malononitrile has similar $\text{p}K_a$ values in water⁴¹ and in Me_2SO .⁴²

Another substituent with a variable effect is the methoxy group, which appears to be more strongly electron withdrawing in benzyl derivatives 1 and *N*-substituted anilines (3) ($\sigma_I = 0.40$) than in benzhydryl derivatives 2 where the reported $\sigma_I (=0.27)$ is instead quite satisfactory. It appears difficult to envisage specific interactions with the solvent: it should be recalled, however, that aromatic methoxyl shifts are extremely sensitive to concentration in CCl_4 .⁴³

The fact that the $^{13}\text{C}_p$ shift of ethylbenzene is actually to low field of that of toluene, although not unprecedented,⁴⁴ is certainly interesting because it shows a feeble electron-withdrawing capacity of the methyl group when considered a substituent at a saturated sp^3 hybridized carbon.⁴⁶ There is considerable confusion about the polar-inductive effects exerted by alkyl groups originated by their inconstant and often opposite behavior dependent upon the substrate, the site of substitution, the monitoring property, and the phase (gas or condensed) under which the effect has been evaluated.⁴⁷ The status of understanding of the polar-inductive effects of alkyl groups on

(41) R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953).

(42) W. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, J. F. Cornforth, G. E. Drucker, Z. Margolin, R. J. McCallum, G. J. McCollum, and N. R. Vanier, *J. Am. Chem. Soc.*, **97**, 7006 (1975).

(43) C. Heathcock, *Can. J. Chem.*, **40**, 1865 (1962).

(44) R. W. Woolfender, Ph.D. Thesis, University of Utah, 1965; cited in ref 45, p 97.

(45) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972, Chapter 3.

(46) W. Adcock and T.-C. Khor, *J. Org. Chem.*, **43**, 1272 (1978).

(47) J. F. Sebastian, *J. Chem. Educ.*, **48**, 97 (1971).

acidities of carbon and oxygen acids has been recently reviewed and thoroughly discussed;⁴⁸ it has been even proposed,^{8,49} authoritatively, that small positive or small negative σ_I values for the methyl group would indifferently accommodate existing data. Table IX shows that methyl substitution for hydrogen at a trigonal carbon α to a benzene ring invariably causes a shielding of the para ¹³C resonance: the methyl group in such instances thus works as an electron-releasing substituent. Theoretical calculations have suggested⁵⁰ that the methyl group bonded to an sp²-hybridized carbon is σ electron withdrawing but electron releasing by hyperconjugation and that σ electron withdrawal increases as hyperconjugative donation increases. When bonded to an sp³-hybridized carbon, methyl hyperconjugative donation is negligible: if, indeed, in a σ -bond framework the methyl group has a negative inductive effect both toward an sp²- and sp³-hybridized carbon, the total effect on the sp³-hybridized carbon, in the absence of hyperconjugative effects, would still be negative, in accord with results here reported. This picture, however, does not seem to be supported by STO-3G minimal basis set calculations⁵¹ for toluene and ethylbenzene which predict equal charge densities at the para carbon. Once again the polar effect of the methyl group appears dominated by the mesomeric charge delocalization involving the groups to which the alkyl is bonded, in analogy both with *N*-alkylacetamides^{26f} and with the previously discussed case for the transmission of the polar effect through the groups G = CH₂ and NH.

Toluene Model for Polar-Inductive Constants. A number of substituents induce on para monitors shifts which are very precisely accounted for by Taft's σ_I constants. This set is taken as a basis set to extrapolate new σ_I values. Both the nature of the points of the basis set and the validity of the calculated σ_I constants deserve comment. Points of the basis set cover a large span of σ_I : they are rather evenly spaced, although admittedly most of them are between 0.2 and 0.3. Hine recommends⁸ great care in using charged substituents, and this certainly applies to the trimethylammonium group, NMe₃⁺, we used as the extreme point in the basis line. We included it for two reasons: (a) to have a point in the upper positive region and (b) because it seems that the NMe₃⁺ group is quite well-behaved since it shows identical σ_I values both in weakly protic and in aprotic dipolar media; furthermore, it has been successfully used⁵² to define a line in Me₂SO with much fewer points. The check of the calculated σ_I values (σ_{IB}), anchored to the eight-point basis set, has been performed on substrates 2 and 6: results are highly satisfactory. Entries 7 and 9 of Table VII consider for substrates 2 the same set of points but the former with Taft's and the latter with calculated σ_{IB} values: the good fit already obtained with Taft's constants is further improved with the calculated σ_{IB} values and remains unchanged upon expansion of the set to 13 substituents (entry 11): the ratio of ρ_I 's for 2 and 1 gives precisely the value of the slope found for the intersystem correlation of 1 vs. 2 (4.49/5.03 = 0.89, to be compared with 0.89 ± 0.03 of entry 1 in Table VI). The use of calculated⁵³ instead of Taft's σ_I values in

Hammett-type correlations of meta-substituted fluorobenzenes improves considerably the fit: furthermore, while the ratio of ρ_I 's for 6 and 1 (5.04/5.03 = 1.002) compares favorably with the experimental value (0.97 ± 0.07 reported in entry 10 in Table VI), the ratio obtained by using Taft's σ_I values does not (6.25/5.03 = 1.24).

Our analysis of substituent effects in α -substituted toluenes is in general accord with Shapiro's results.¹⁴ Adcock's¹⁵ and Shapiro's¹⁴ DSP analyses of α -substituted toluenes differ because for the former the substituent is the whole CH₂X moiety, while for the latter the substituent is represented by the X group alone. Adcock rejects Shapiro's analysis since resonance constants ($\sigma_{R^*}, \sigma_{RBA}$) were used for substituents X not directly bonded to the aromatic ring, as the σ_R definition would require.² The CH₂ moiety, thanks to hyperconjugation, is a sort of unsaturated cavity: hence, in analogy with substituted ethylenes and acetylenes,⁵⁴ the use of σ_R constants for X substituents of the CH₂X groups should be legitimated.⁵⁵ The fact is that, although the CH₂ can conjugate, the extent of such a conjugation is almost insensitive to the nature of X.⁵⁶ This is not unprecedented: Taft² analyzed acidities of α -substituted *p*-toluic acids in terms of σ_I and σ_R (σ_{R^*} and/or σ_{RBA}) constants of groups X, pointing out that "the interposed CH₂ moiety does eliminate conjugation of the substituent X with the ring system (but not necessarily that of the CH₂ group)".

Values of σ_I constants, anchored on the toluene model, may differ considerably from Taft's values, relative to which some are enhanced (COCF₃, NO₂, OMe, Br) and some decreased (CO₂Me, COMe, CN, SOMe, PO(OEt)₂). It is gratifying to note that the adjustments relative to normal Taft σ_I values for CO₂Me, OH, and CN are in the same sense as corrections Taft suggested because of interactions with Me₂SO as solvent. Some of the σ_I constants proposed in the set of Table I differ also from the values obtained from aliphatic substrates:⁵⁸ the trimethylammonio group can serve as an example since it requires a value of $\sigma_I = 0.73$ in substituted acetic acids, while the enhanced value of $\sigma_I = 0.92$ accounts for the effect in aromatic substrates. We believe that such discrepancies can be ascribed to the different components contributing to the total polar-inductive effect in aromatic and aliphatic substrates: the π -inductive effect, shown to have a strong weight in aromatic systems,²⁹⁻³³ vanishes in aliphatic substrates where the field effect becomes instead predominant.

Conclusion

Magnetic monitors para to groups G interacting with adjacent functionalities X by nondelocalizative mechanisms, respond linearly to polar-inductive effects exerted by such substituents X: the response of extrathermodynamic (NMR) monitors is coherent with that of a thermodynamic monitor represented by the ionization of α -substituted *p*-toluic acids. Coherence of effects is also found with meta-substituted fluorobenzenes: α -substituted

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(49) (a) M. Charton, *J. Am. Chem. Soc.*, **97**, 3691 (1975); (b) F. G. Bordwell and H. E. Fried, *Tetrahedron Lett.*, 1121 (1977).

(50) (a) G. A. Olah, P. W. Westerman, and D. A. Forsyth, *J. Am. Chem. Soc.*, **97**, 3419 (1975); (b) G. A. Olah and D. A. Forsyth, *ibid.*, **97**, 3137 (1975).

(51) W. J. Hehre, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 1496 (1972).

(52) F. G. Bordwell, M. Van der Puy, and N. R. Vanier, *J. Org. Chem.*, **41**, 1883, 1885 (1976).

(53) The $\sigma_I(\text{CN}) = 0.56$ has been retained because it was felt that *m*-cyanofluorobenzene constitutionally requires such an enhanced value; see foregoing discussion.

(54) See, e.g., A. R. Katritzky and R. D. Topsom, *Chem. Rev.*, **77**, 639 (1977).

(55) Adcock himself analyzed 1-substituted 4-(*p*-fluorophenyl)bicyclo[2.2.2]octanes^{26a,40} in terms of the DSP treatment by using the σ_I and σ_R of groups X and not of groups C₆H₄X.

(56) Proposed^{15,54} values for σ_{R^*} of CH₂X substituents are remarkably small, with the exception of X = metal.⁵⁷

(57) (a) W. Adcock, D. P. Cox, and W. Kitching, *J. Organomet. Chem.*, **133**, 393 (1977); (b) W. Adcock, B. D. Gupta, W. Kitching, and D. Dodder, *ibid.*, **122**, 297 (1975).

(58) M. Charton, *J. Org. Chem.*, **29**, 1222 (1964).

toluenes serve thus as alternative models for extrapolating new σ_{IB} constants whose values may differ from those obtained from aliphatic systems. These differences are expected to depend upon the relevance of π -inductive effects induced by the substituent on a monitor bonded to an aromatic framework.

Registry No. 1 (X = H), 108-88-3; 1 (X = Ph), 101-81-5; 1 (X = CONMe₂), 18925-69-4; 1 (X = CO₂Me), 101-41-7; 1 (X = COMe), 103-79-7; 1 (X = COPh), 451-40-1; 1 (X = COCF₃), 350-92-5; 1 (X = NO₂), 622-42-4; 1 (X = CN), 140-29-4; 1 (X = SOMe), 824-86-2; 1 (X = SO₂Me), 3112-90-1; 1 (X = SOPh), 833-82-9; 1 (X = SO₂Ph), 3112-88-7; 1 (X = PO(OEt)₂), 1080-32-6; 1 (X = 2-pyridyl), 101-82-6; 1 (X = 3-pyridyl), 620-95-1; 1 (X = 4-pyridyl), 2116-65-6; 1 (X = CH=CHPh), 5209-18-7; 1 (X = N=CHPh), 780-25-6; 1 (X = Me), 100-41-4; 1 (X = CH₂CN), 645-59-0; 1 (X = CH₂COMe), 2550-26-7; 1 (X = OH), 100-51-6; 1 (X = OMe), 538-86-3; 1 (X = NH₂), 100-46-9; 1 (X = NHCOMe), 588-46-5; 1 (X = NMe₃⁺Br⁻), 5350-41-4; 1 (X = Br), 100-39-0; 1 (X = SPh), 831-91-4; 2 (X = Ph), 519-73-3; 2 (X =

CONMe₂), 957-51-7; 2 (X = CO₂Me), 3469-00-9; 2 (X = COMe), 781-35-1; 2 (X = COPh), 1733-63-7; 2 (X = CN), 86-29-3; 2 (X = SOMe), 2863-45-8; 2 (X = SO₂Me), 25195-40-8; 2 (X = SO₂Ph), 5433-76-1; 2 (X = CH₂COMe), 5409-60-9; 2 (X = OH), 91-01-0; 2 (X = NMe₃⁺Br⁻), 71964-91-5; 2 (X = SPh), 21122-20-3; 3 (X = H), 62-53-3; 3 (X = Me), 100-61-8; 3 (X = CH₂CN), 3009-97-0; 3 (X = OH), 100-65-2; 3 (X = OMe), 32654-23-2; 3 (X = NH₂), 100-63-0; 3 (X = NHCOMe), 114-83-0; 4 (X = H), 108-95-2; 4 (X = Me), 100-66-3; 4 (X = CH₂CN), 3598-14-9; 4 (X = CH₂COMe), 621-87-4; 5 (X = H), 99-94-5; 5 (X = Ph), 620-86-0; 5 (X = OMe), 67003-50-3; 5 (X = NHCOMe), 1205-58-9; 5 (X = Br), 6232-88-8; 5 (X = OH), 3006-96-0; 5 (X = CN), 50685-26-2; 5 (X = SO₂Ph), 71964-92-6; 5 (X = CONH₂), 52787-17-4; 6 (X = Me), 352-70-5; 6 (X = Ph), 2367-22-8; 6 (X = NO₂), 402-67-5; 6 (X = COCF₃), 708-64-5; 6 (X = Br), 1073-06-9; 6 (X = OMe), 456-49-5; 6 (X = COMe), 455-36-7; 6 (X = CO₂Et), 451-02-5; 6 (X = CN), 403-54-3; 6 (X = H), 462-06-6; benzene, 71-43-2; benzaldehyde, 100-52-7; 1-phenyl-1-ethanone, 98-86-2; 1-phenyl-1-propanone, 93-55-0; α -hydroxybenzylum, 3441-73-4; 1-hydroxy-1-phenylethylum, 3441-74-5; 1-phenylethylum, 25414-93-1; 1-methyl-1-phenylethylum, 16804-70-9.

Substituent Effect Treatment of Interactions between Contiguous Functionalities G-X. 2. Remote Response to Polar-Inductive and Mesomeric Influence of X on G = -O- and -NH-

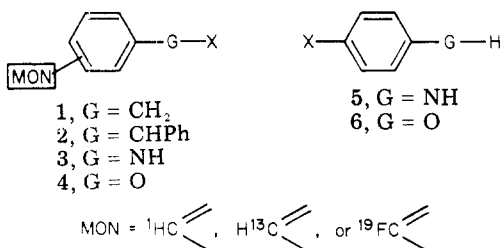
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"Direct", phenyl-mediated interactions between groups G = -O- and -NH- and substituents X in Hammett systems *p*-XPhGH are linearly related to direct and contiguous interactions present in iso-Hammett systems PhGX; in fact shifts induced on O¹H and N¹H₂ of *p*-XPhOH and *p*-XPhNH₂ by a set of substituents X are linearly related to shifts induced by the same set on para monitors (¹H, ¹³C, and ¹⁹F) of PhOX and PhNHX, respectively. Thus para monitors in PhGX detect the type and extent of interactions between contiguous functionalities G and X, respectively regarded as the involved (reacting) group and the substituent. A number of σ_p^- values valid for true Hammett systems (Hine's compilation) accounting precisely for interactions between G and X in PhGX are taken as a basis set to build up the σ_c^- scale valid for contiguous and direct interactions. Gross total contiguous interactions have been dissected into polar-inductive and mesomeric components by the DSP treatment of the data: the usefulness and limitations of Taft's DSP treatment are discussed. The response of monitors present at positions other than the para one is also evaluated.

In an attempt to describe interactions between contiguous functionalities in terms of substituent effects, we have proposed¹ for investigation substrates of the general type 1-4, in which the two functionalities are X and G, respectively, the former viewed as the substituent and the latter as the involved (reacting) group (or "cavity").² We first focused our attention on substrates where only polar-inductive interactions could occur between the group G and the substituent X:^{1a} thus G was either a saturated group flanked by a substituent of any kind as in 1 and 2 or, alternatively, a group possessing available electron pairs, as in 3 and 4, flanked by properly chosen substituents X



(1) (a) S. Bradamante and G. A. Pagani, *J. Org. Chem.*, preceding paper in this issue; (b) S. Bradamante, F. Gianni, and G. A. Pagani, *J. Chem. Soc., Chem. Commun.*, 478 (1976).

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

incapable of π -delocalizative interactions with G. We have shown that polar-inductive interactions exerted by a variety of substituents X are satisfactorily accounted for by the response of a spin-active monitor present at the para position of the substrates.

In this paper we consider in substrates 3 and 4 the effects of substituents X capable of mesomeric interactions with groups G (G = -O- and -NH-).^{1b} Evidence will be offered that shifts induced by a set of substituents X on a certain para monitor of 3 and 4 are linearly related to those induced on ¹H monitors of the G-H moiety of the true Hammett systems 5 and 6. Also, we will show that the response of the para monitor accounts properly for the blend of polar-inductive and mesomeric components of the total interactions, the choice of the monitor (¹H, ¹³C, ¹⁹F) being independent of the type of interaction considered. The response of monitors present at the ortho and meta positions of 3 and 4 will be further explored.

Results

Table I reports the set of substituents under consideration in this and in the preceding paper,^{1a} together with four sets of available σ^- constants, chosen among the multitude reported in the literature.³ These sets are