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 = $CONMe_2$), 18925-69-4; 1 (X = CO_2Me), 101-41-7; 1 (X = COMe), 103-79-7; 1 (X = COPh), 451-40-1; 1 (X = $COCF_3$), 350-92-5; 1 (X = NO_2), 622-42-4; 1 (X = CN), 140-29-4; 1 (X = SOMe), 824-86-2; 1 (X = SO_2Me), 3112-90-1; 1 (X = SOPh), 833-82-9; 1 (X = SO_2Ph), 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 = CH_2CN), 645-59-0; 1 (X = CH_2COMe), 2550-26-7; 1 (X = OH), 100-51-6; 1 (X = OMe), 538-86-3; 1 (X = NH_2), 100-46-9; 1 (X = NHCOMe), 588-46-5; 1 (X = $NMe_3^+Br^-$), 5350-41-4; 1 (X = Br), 100-39-0; 1 (X = SPh), 831-91-4; 2 (X = Ph), 519-73-3; 2 (X = $CONMe_2$), 957-51-7; 2 (X = CO_2Me), 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 = SO_2Me), 25195-40-8; 2 (X = SO_2Ph), 5433-76-1; 2 (X = CH_2COMe), 5409-60-9; 2 (X = OH), 91-01-0; 2 (X = $NMe_3^+Br^-$), 71964-91-5; 2 (X = SPh), 21122-20-3; 3 (X = H), 62-53-3; 3 (X = Me), 100-61-8; 3 (X = CH_2CN), 3009-97-0; 3 (X = OH), 100-65-2; 3 (X = OMe), 32654-23-2; 3 (X = NH_2), 100-63-0; 3 (X = NHCOMe), 114-83-0; 4 (X = H), 108-95-2; 4 (X = Me), 100-66-3; 4 (X = CH_2CN), 3598-14-9; 4 (X = CH_2COMe), 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 = SO_2Ph), 71964-92-6; 5 (X = $CONH_2$), 52787-17-4; 6 (X = Me), 352-70-5; 6 (X = Ph), 2367-22-8; 6 (X = NO_2), 402-67-5; 6 (X = $COCF_3$), 708-64-5; 6 (X = Br), 1073-06-9; 6 (X = OMe), 456-49-5; 6 (X = COMe), 455-36-7; 6 (X = CO_2Et), 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-hydroxybenzylium, 3441-73-4; 1-hydroxy-1-phenylethylium, 3441-74-5; 1-phenylethylium, 25414-93-1; 1-methyl-1-phenylethylium, 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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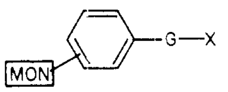
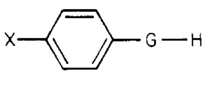
"Direct", phenyl-mediated interactions between groups G = –O– and –NH– and substituents X in Hammett systems *p*-XPhGH are linearly related to direct and contiguous interactions present in iso-Hammett systems PhGX; in fact shifts induced on O^1H and N^1H_2 of *p*-XPhOH and *p*-$XPhNH_2$ by a set of substituents X are linearly related to shifts induced by the same set on para monitors (^1H, ^{13}C, and ^{19}F) 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.

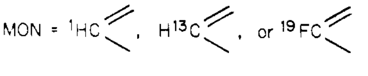
In an attempt to describe interactions between contiguous functionalities in terms of substituent effects, we have proposed[1] for investigation substrates of the general type **1**–**4**, in which the two functionalities are X and G, respectively, the former viewed as the substitutent and the latter 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 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.



1, G = CH_2
2, G = CHPh
3, G = NH
4, G = O



5, G = NH
6, G = O



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, ^{13}C, ^{19}F) 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

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[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.

0022-3263/80/1945-0114$01.00/0

Table I. Sets of σ^- Values[a]

entry	substituent	$\bar{\sigma}^-_{TA}$	$\bar{\sigma}^-_{TP}$	σ^-_{E}	σ^-_{H}	σ_c^-
1	H	0	0	0	0	0
2	Ph	0.14	0.14	0.11	0.18[b]	0.47
3	$CONMe_2$			*c*	*d*	0.70
4	CO_2Me	0.64	0.56	0.64	0.74	0.81, 0.74
5	COMe	0.75	0.75	0.84	0.82	0.82
6	COPh					0.81, 0.94
7	CHO			1.04	0.98	0.98[e]
8	$COCF_3$					1.09
9	NO_2	1.11	1.11	1.24	1.23	1.27[e,f]
10	CN	0.88	0.79	0.88	0.99	0.99, 0.88[g]
11	SOMe		0.67	0.73	0.73	
12	SO_2Me	0.97	0.88	0.98	1.05	0.99[h]
13	SOPh					0.76[e]
14	SO_2Ph					1.00[i]
15	SO_2NMe_2					0.84[j]
16	$PO(OEt)_2$					0.68, 0.58
17	$POPh_2$					0.58
19	2-py					0.55
20	3-py					0.58
21	4-py					0.73, 0.81

[a] $\bar{\sigma}^-_T$ values are belnded $\bar{\sigma}^-$ values from the Taft compilation;[3c] thus $\bar{\sigma}^-_{TP} = \sigma_I + \sigma_R^-{}_P$ for phenols and $\bar{\sigma}^-_{TA} = \sigma_I + \sigma_R^-{}_A$ for anilines; σ^-_H values are from the Hine tabulation,[3a] and σ^-_E values are from the Exner tabulation.[3b] All these sets were originally given to apply for para substituents. σ_c^- is the modified and extended set based on σ^-_H values proposed in this work for substituents directly bonded to oxygen and nitrogen groups. Whenever σ_c^- values for PhOX differ by more than 10% from values for PhNHX, two figures are given in the column, the first referring to PhOX and the second to PhNHX. [b] Value for the para position in *p*-XPhOH.[11] [c] The reported σ^- value for the $CONH_2$ group is 0.61. [d] The reported σ^- value for the $CONH_2$ group is 0.62. The σ^- value for *p*-$Me_2NCOPhNH_2$ is 0.40 as extrapolated from correlation of entry 17 in Table VIII. [e] Value from the PhNHX series only. [f] The value of 1.27 results from the 1.24 figure through an adjustment in both the *p*-$XPhNH_2$ and the PhNHX series.[6] [g] The value extrapolated from correlation of entry 4 in Table VII is 0.80, within 10% of the Exner value, which therefore is retained. [h] This is the value adjusted relative to the 1.05 Hine figure to account for an apparent overestimation in the *p*-$XPhNH_2$ and PhNHX series. [i] The σ^- value extrapolated from the correlation of entry 4 in Table VII is 0.98, adjusted to 1.0 in view of the adjustment of the SO_2Me value. [j] Extrapolated from correlation 9 in Table VIII.

Table II. O^1H and N^1H_2 Chemical Shifts (ppm)

entry	X	*p*-XPhOH	*p*-$XPhNH_2$
1	H	9.25	4.97
2	Ph		5.21
3	$CONMe_2$		5.47
4	CO_2Me	10.26	5.94
5	COMe	10.25	6.03
6	COPh	10.37	6.18
9	NO_2		6.72
10	CN		6.14
12	SO_2Me	10.51	6.11
15	SO_2NMe_2		6.05

derived from Hine's compliation,[3a] Exner's compilation,[3b] and Taft's σ_I and σ_R^- values, the latter ones valid for anilines or phenols, respectively ($\bar{\sigma}^-_{TA} = \sigma_I + \sigma_R^-{}_A$; $\bar{\sigma}^-_{TP} = \sigma_I + \sigma_R^-{}_P$).[3c] All chemical shifts reported in Tables II–V are measured in Me_2SO dilute solution under standard conditions described in the preceding paper.[1a] Table II reports ^1H data relative to the G–^1H moiety of substrates **5** and **6**. Tables III and IV report ^1H_p, $^{19}F_p$, and ^{13}C (ortho, meta, para, and ipso) chemical shifts for substrates **3** and **4**. Table V collects additional ^1H parameters for substrates **3** obtained by fitting the experimental spectra with the LAOCOON III program.[4]

Correlations are schematized and defined as before[1a] as intermonitor, interpositional, intersystem, Hammett-type, and DSP (dual substituent parameter) correlations.[3c] All significant correlations found in this work are reported in Tables VI–IX; therein a correlation of two variables may be reported more than once with different inputs with the purpose of appreciating the effect of disregarding certain substituents on the slopes and on the correlation coefficients of the lines.

Entries 1–5 of Table VI report the generally excellent fitting parameters for intermonitor correlations. Since substrates **4** show strongly coupled ^1H NMR spectra even at 270 MHz, the ^1H_p shifts, evaluated by a first-order analysis of the spectra, are more approximate than the $^{13}C_p$ and $^{19}F_p$ shifts: this lower precision may be responsible for the somewhat worse *r* value of correlation 5 relative to that of 4. Entries 6–13 of Table VI report fitting parameters for interpositional correlations. Results show that in both substrates **3** and **4**, C_m is almost insensitive to substituent effects and that no correlation whatsoever exists between C_p and C_m. Instead, H_m and H_p in substrates **3** are found to be linearly related, although the correlation shows some scatter (entry 11). Ortho monitors (^1H and ^{13}C) in both substrates **3** and **4** are linearly related to the corresponding para monitors (entries 6, 9, and 12). However, while the H_o monitor is *more* sensitive to substituent effects than the H_p one, the reverse is found for C_o vs. C_p. A few substituents do not lie on the line of MON_o vs. MON_p: for C_o vs. C_p, X = Me, CH_2CN, and CN are deviant points in both substrates **3** and **4**, while for H_o vs. H_p deviances are found for X = $CONMe_2$, CN, and SO_2Me (the Me and CH_2CN points are missing). Entries 1–3 of Table VII report the fitting parameters for correlations between isomeric systems **3** and **5** and **4** and **6**: effects exerted by a set of remote substituents X on the G–^1H monitor of systems **5** and **6** are linearly related to those exerted by the same set directly bonded to groups G on the remote H_p monitor of systems **3** and **4**. Hammett

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(3) (a) J. Hine, "Structural Effects on Equilibria in Organic Chemistry", Wiley-Interscience, New York, 1975, p 73; (b) O. Exner in "Advances in Linear Free Energy Relationships", N. B. Chapman and J. Shorter, Eds., Plenum Press, New York, 1972, p 32; (c) S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Prog. Phys. Org. Chem.*, **10**, 13, 51 (1973); (d) C. D. Johnson, "The Hammett Equation", Cambridge University Press, 1973, p 29; (e) C. D. Ritchie and W. F. Sager, *Prog. Phys. Org. Chem.*, **2**, 323 (1964); (f) A. J. Hoefnagel and B. M. Wepster, *J. Am. Chem. Soc.*, **95**, 5357 (1973).

(4) A. A. Bothner-By and S. Castellano, "Computer Programs for Chemistry", D. F. deTar, Ed., 1968, p 10.

Table III. Proton,[a] Fluorine,[b] and Carbon[a] Chemical Shifts (ppm) for PhOX

entry	X	^1H_p	$^{19}F_p$	^{13}C ortho	meta	para	ipso
1	H	6.78	36.55	116.71	130.80	120.25	158.58
2	Ph	7.14		120.10	131.51	124.90	158.13
3	$CONMe_2$	7.23	44.74	123.34	130.67	126.51	152.82
4	CO_2Me	7.31	46.20	122.71	131.09	127.61	152.30
5	COMe	7.27	45.55	123.27	130.92	127.19	151.94
6	COPh	7.34	46.00	123.38	130.46	127.48	152.14
8	$COCF_3$	7.42	48.05	122.48	131.59	129.89	150.57
10	CN	7.44		116.97	132.41	128.72	154.05
12	SO_2Me	7.41	48.03	123.70	131.62	128.84	150.66
14	SO_2Ph	7.33	48.55	123.50	129.66	128.97	150.55
16	$PO(OEt)_2$	7.17	44.91	121.37	130.82	126.57	151.85
17	$POPh_2$	7.13	44.70	122.04	130.97	126.16	152.19
19	2-py	7.23		122.86	129.78	125.90	155.45
20	3-py	7.23		120.19	131.72	126.13	157.54
21	4-py	7.35		122.09	131.90	126.96	155.08
26	Me	6.95	38.51	115.36	130.90	121.91	161.46
27	CH_2CN	7.09		116.38	131.26	123.91	157.82

[a] Relative to (trimethylsilyl)propanesulfonic acid sodium salt (TSP). [b] Relative to hexafluorobenzene (see Experimental Section of the preceding paper[1a]).

Table IV. Proton,[a] Fluorine,[a] and Carbon[a] Chemical Shifts (ppm) for PhNHX

entry	X	^1H_p	$^{19}F_p$	^{13}C ortho	meta	para	ipso
1	H	6.50	32.88	115.39	130.23	117.14	150.03
2	Ph	6.84	39.23	118.26	130.61	121.14	144.96
3	$CONMe_2$	6.94	41.09	121.24	129.67	123.06	142.22
4	CO_2Me	7.01	42.05	119.72	130.14	123.80	140.51
5	COMe	7.05	43.23	120.54	130.12	124.46	140.84
6	COPh	7.14	44.11	121.92	130.09	125.14	140.68
7	CHO	7.11	44.13	120.49	130.10	125.00	140.02
8	$COCF_3$	7.16	46.74	123.05	130.30	126.38	137.67
9	NO_2	7.39	48.48	123.49	130.60	128.36	137.37
10	CN	7.05	41.65	116.32	130.83	123.88	139.84
12	SO_2Me	7.12	43.83	120.14	130.72	125.33	139.88
13	SOPh	6.95	43.42	119.35	130.56	123.56	143.30
14	SO_2Ph	7.03	44.67	121.63	130.72	125.59	139.19
15	SO_2NMe_2	7.05					
16	$PO(OEt)_2$	6.87	39.39	119.66	130.33	122.03	142.46
17	$POPh_2$	6.82	39.66	119.75	130.37	122.06	143.53
19	2-py	6.89	39.73	119.52	130.02	121.82	143.23
20	3-py	6.89		118.70	130.80	122.06	141.62
21	4-py	7.04	42.84	121.58	130.81	124.00	142.06
26	Me	6.51	32.66	113.05	130.04	116.69	150.69
27	CH_2CN	6.72		114.50	130.55	119.36	148.07

[a] See Table III.

systems **5** and **6** are ca. twice as sensitive as their isomers **3** and **4** (MON = ^1H). Deviant points in correlation 3 (Table VII) are X = Ph and $CONMe_2$, the effect being much larger in systems **3** than in **5**. Entries 4–8 (Table VII) report the fitting parameters for **3** vs. **4** intersystem correlations: good values are obtained with a set of 11 substituents. Entry 5 shows that the five substituents X = CO_2Me, COPh, CN, $PO(OEt)_2$, and 4-py (4-py = 4-pyridyl) are somewhat deviant, suggesting that such groups require slightly different σ^- constants in the two series **3** and **4**. Entries 6 and 8 show that the experimental chemical shift for X = H in PhOX is also deviant: the reason for this is to be looked for in the specific interaction of PhOH with Me_2SO.[5] Correlation of entry 4 is used then to extrapolate the "corrected" chemical shift of the para monitor in PhOH, predicted in the absence of any specific interaction. This extrapolated value (δ $^{13}C_p$ = 122.08) is subsequently used in Hammett-type correlations. This has been done because the least-squares method confers strong weight to initial and final points:[3b,6] since the H point is invariably one of the first ones in every correlation, its misplacement confers high uncertainity to every correlation in which it is contained, shadowing more serious deviances. Entries 1–14 of Table VIII report Hammett-type correlations obtained by plotting $^{13}C_p$ shifts of PhOX and PhNHX vs. the four sets of σ^- values of Table I. For the 18 substituents studied in the PhNHX series there are available only seven σ^- values in the Hine and Exner sets and only six in the Taft scales. For PhNHX excellent five- and six-point lines are found by using Hine's available σ^- values (entries 1 and 2, Table VIII); a further improvement is obtained if the value for $\sigma^-_{NO_2}$ is adjusted at 1.27 (entry 3).[6] The σ^-_{CN} value of the Hine compilation seems to be inadequate (entry 4) and is, therefore, rejected for this series. The six σ^- values used in entry 3 are retained as the basis set for the PhNHX series: such a basis set contains the CO_2Me substituent, the effect of which has been shown to be incoherent in the PhNHX and PhOX systems. Correlation of entry 3 allows extrapolation of seven new σ^- values for those substituents which are co-

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[5] (a) D. Gurka and R. W. Taft, *J. Am. Chem. Soc.*, **91**, 4794 (1969); (b) R. W. Taft, D. Gurka, L. Joris, P. v. R. Schleyer, and J. W. Rakshys, *ibid.*, **91**, 4801 (1969); (c) L. Joris, J. Mitsky, and R. W. Taft, *ibid.*, **94**, 3438 (1972).

[6] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

Table V. ^{1}H NMR Parameters for PhNHX[a]

entry	X	H$_o$[b]	H$_m$[b]	J_{om}	J_{op}	J_{mp}	$J_{oo'}$	$J_{om'}$	$J_{mm'}$	error
1	H	657.908	701.382	7.980	1.135	7.533	1.710	0.529	2.404	0.031
2	Ph	711.664	724.599	8.193	1.135	7.267	2.167	0.433	1.718	0.054
3	$CONMe_2$	750.513	723.808	8.225	1.168	7.465	2.285	0.443	1.756	0.040
4	CO_2Me	750.461	729.464	8.214	1.085	7.539	2.122	0.437	1.844	0.042
5	$COCH_3$	762.407	731.575	8.031	1.179	7.532	2.083	0.501	1.852	0.040
6	COPh	785.958	738.835	8.148	1.199	7.510	2.090	0.530	1.951	0.044
7	CHO	765.004	735.433	8.247	1.095	7.403	1.995	0.357	1.531	0.047
10	CN	701.050	737.518	7.853	1.029	7.670	2.468	0.369	1.577	0.043
12	SO_2Me	725.545	735.077	8.154	1.094	7.505	2.382	0.515	1.528	0.029

[a] Best values (in Hz at 100 MHz) from LAOCOON III treatment. [b] Chemical shifts.

Table VI. Intermonitor and Interpositional Correlations[a]

entry	system	y	x	slope	intercept	r	n	X
1	PhNHX	$^{19}F_p$	$^{13}C_p$	1.38 ± 0.04	-129.05	0.992	18	H, Ph, $CONMe_2$, CO_2Me, COMe, COPh, CHO, $COCF_3$, NO_2, CN, SO_2Me, SO_2Ph, SOPh, $PO(OEt)_2$, $POPh_2$, 2-py, 4-py, Me
2		$^{13}C_p$	^1H_p	13.40 ± 0.43	29.74	0.992	18	H, Ph, $CONMe_2$, CO_2Me, COMe, COPh, CHO, $COCF_3$, NO_2, CN, SO_2Me, $PO(OEt)_2$, $POPh_2$, 2-py, 3-py, 4-py, Me, CH_2CN
3		$^{13}C_p$	^1H_p	13.54 ± 0.60	29.92	0.982	20	as entry 2 + SO_2Ph, SOPh
4	PhOX	$^{19}F_p$	$^{13}C_p$	1.35 ± 0.02	-126.48	0.999	11	H, $CONMe_2$, CO_2Me, COMe, COPh, $COCF_3$, SO_2Me, SO_2Ph, $PO(OEt)_2$, $POPh_2$, Me
5		$^{13}C_p$	^1H_p	13.60 ± 0.93	28.72	0.966	17	H, Ph, $CONMe_2$, CO_2Me, COMe, COPh, $COCF_3$, CN, SO_2Me, SO_2Ph, $PO(OEt)_2$, $POPh_2$, 2-py, 3-py, 4-py, Me, CH_2CN
6	PhNHX	$^{13}C_o$	$^{13}C_p$	0.72 ± 0.02	30.45	0.997	7	H, Ph, CO_2Me, COMe, NO_2, SO_2Me, SO_2Ph
7				0.70 ± 0.08	32.96	0.922	16	as entry 6 + $CONMe_2$, COPh, CHO, $COCF_3$, SOPh, $PO(OEt)_2$, 2-py, 3-py, 4-py
8				0.77 ± 0.23	24.84	0.622	20	as entry 7 + CN, $POPh_2$, Me, CH_2CN
9		^1H_o	^1H_p	1.94 ± 0.13	-6.06	0.991	6	H, Ph, CO_2Me, COMe, COPh, CHO
10				1.54 ± 0.45	-3.46	0.787	9	as entry 9 + $CONMe_2$, CN, SO_2Me
11		^1H_m	^1H_p	0.52 ± 0.05	3.68	0.963	9	as entry 10
12	PhOX	$^{13}C_o$	$^{13}C_p$	0.78 ± 0.11	22.96	0.903	14	H, Ph, $CONMe_2$, CO_2Me, COMe, COPh, $COCF_3$, SO_2Me, SO_2Ph, $PO(OEt)_2$, $POPh_2$, 2-py, 3-py, 4-py
13				0.83 ± 0.21	15.04	0.715	17	as entry 12 + CN, Me, CH_2CN

[a] For definition see the text.

Table VII. Intersystem Correlations[a]

entry	system A[b]	system B[c]	y	x	slope	intercept	r	n	X
1	p-XPhOH	PhOX	O^{1}H	^1H_p	1.98 ± 0.06	-4.19	0.999	5	H, CO_2Me, COMe, COPh, SO_2Me
2	p-XPhNH$_2$	PhNHX	N$^1H_2$	^1H_p	1.99 ± 0.09	-7.81	0.993	8	H, CO_2Me, COMe, COPh, NO_2, CN, SO_2Me, SO_2NMe_2
3					2.20 ± 0.26	-9.51	0.946	10	as entry 3 + Ph, $CONMe_2$
4	PhNHX	PhOX	$^{13}C_p$	$^{13}C_p$	1.30 ± 0.06	-42.02	0.989	11	Ph, $CONMe_2$, COMe, $COCF_3$, SO_2Me, SO_2Ph, $POPh_2$, 2-py, 3-py, Me, CH_2CN
5					1.25 ± 0.09	-35.95	0.962	16	as entry 4 + CO_2Me, COPh, CN, $PO(OEt)_2$, 4-py
6					1.11 ± 0.08	-17.51	0.960	17	as entry 5 + H
7			^1H_p	^1H_p	1.20 ± 0.10	-1.82	0.957	16	as entry 5
8					1.09 ± 0.08	-0.96	0.963	17	as entry 6

[a] For the definition see the text. [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.

Table VIII. Hammett-Type Correlations

entry	system	y	x	ρ	intercept	r	n	X
1	PhNHX	$^{13}C_p$	σ^-_H	8.82 ± 0.55	117.10	0.994	5	H, CO_2Me, COMe, CHO, NO_2
2				8.55 ± 0.66	117.15	0.988	6	as entry 1 + SO_2Me
3				8.41 ± 0.56	117.20	0.991	6	as entry 2 (σ_{NO_2} = 1.27)
4				8.26 ± 0.93	117.14	0.970	7	as entry 2 + CN
5		$^{13}C_p$	σ^-_E	8.52 ± 0.71	116.96	0.986	6	H, COMe, CHO, CN, NO_2, SO_2Me
6				8.28 ± 0.85	117.35	0.975	7	as entry 5 + CO_2Me
7		$^{13}C_p$	$\bar{\sigma}^-_{TA}$	9.12 ± 1.17	117.21	0.969	6	H, CO_2Me, COMe, CN, SO_2Me, NO_2
8		$^{13}C_p$	$\bar{\sigma}^-_{TP}$	9.53 ± 0.95	117.33	0.980	6	as entry 7
9	PhNHX	^1H_p	σ_c^-	0.65 ± 0.04	6.50	0.985	17	H, Ph, $CONMe_2$, CO_2Me, COMe, CHO, COPh, $COCF_3$, CN, NO_2, SO_2Me, SOPh, $PO(OEt)_2$, $POPh_2$, 2-py, 3-py, 4-py
10	PhOX	$^{13}C_p$	σ^-_H	6.52 ± 0.25	122.04	0.998	4	H,[a] COMe, CN, SO_2Me
11				6.54 ± 0.50	122.18	0.991	5	as entry 10 + CO_2Me
12		$^{13}C_p$	σ^-_E	6.86 ± 0.99	122.31	0.970	5	as entry 11
13		$^{13}C_p$	$\bar{\sigma}^-_{TA}$	7.14 ± 0.74	122.26	0.984	5	as entry 11
14		$^{13}C_p$	$\bar{\sigma}^-_{TP}$	7.62 ± 1.15	122.35	0.967	5	as entry 11
15		$^{13}C_p$	σ_c^-	6.58 ± 0.27	122.09	0.992	11	as entry 10 + Ph, $CONMe_2$, $COCF_3$, SO_2Ph, $POPh_2$, 2-py, 3-py
16	p-$XPhNH_2$	^1H_2N	σ^-_H	1.30 ± 0.12	4.94	0.980	7	H, Ph,[b] CO_2Me, COMe, CN, SO_2Me, NO_2
17		^1H_2N	σ_c^-	1.34 ± 0.07	4.93	0.992	7	as entry 16

[a] Using the predicted value of ^{13}C shifts extrapolated from intersystem correlation 4 of Table VII. [b] Using σ^- = 0.22 for the p-Ph group.

Table IX. Fitting Parameters for DSP Treatments

entry	system	MON_p	σ_I	σ_R	ρ_I	ρ_R	f	SD	b[a]	r[a]	n	X
1	PhNHX	^{13}C	T	A	6.221 10	12.903 12	0.096	0.79	0.651	0.904	5	COMe, CO_2Me, CN, SO_2Me, NO_2
2		^1H	T	A	0.489 26	0.937 42	0.057	0.03	0.844	0.944	5	as entry 1
3		^{13}C	T	P	8.068 87	12.080 90	0.081	0.67	1.005	0.941	5	as entry 1
4		^{13}C	B	A	6.078 50	13.333 14	0.047	0.39	0.945	0.973	5	as entry 1
5		^{13}C	B	A	6.752 70	12.560 06	0.062	0.44	1.01	0.993	7	as entry 1 + Me, CH_2CN
6		^1H	B	A	0.426 45	1.033 50	0.068	0.04	0.92	0.963	15	Ph, $CONMe_2$, CO_2Me, COPh, $COCF_3$, COMe, CN, NO_2, SO_2Me, SOPh, SO_2Ph, $PO(OEt)_2$, 2-py, 3-py, 4-py
7	PhOX	^{13}C	T	A	7.123 77	7.521 27	0.082	0.49	1.11	0.844	4	COMe, CO_2Me, CN, SO_2Me
8		^{13}C	T	P	8.989 90	6.375 65	0.108	0.65	1.26	0.814	4	as entry 7
9		^{13}C	T	A	7.276 65	7.354 70	0.084	0.39	1.003	0.990	7	as entry 7 + Me, CH_2CN, CH_2Ac
10		^{13}C	T	P	8.702 17	6.720 15	0.112	0.52	0.981	0.983	7	as entry 9
11		^{13}C	B	A	6.764 63	8.991 83	0.105	0.63	1.02	0.746	4	as entry 7
12		^{13}C	B	A	6.994 87	8.777 71	0.108	0.50	0.995	0.984	7	as entry 9
13		^{13}C	B	A	6.026 46	8.870 08	0.046	0.23	1.05	0.987	8	Ph, $CONMe_2$, COMe, SO_2Me, SO_2Ph, 2-py, 3-py, 4-py
14		^{13}C	B	A	6.281 79	8.690 55	0.055	0.25	1.05	0.995	10	as entry 13 + Me, CH_2CN
15	p-$XPhNH_2$	N^1H_2	B	A	1.040 04	1.888 31	0.081	0.09	1.005	0.973	7	Ph, COMe, COPh, CO_2Me, CN, SO_2Me, NO_2

[a] r is the correlation coefficient of the relationship $\Delta\delta_{\text{exptl}} = b\Delta\delta_{\text{calcd}}$ + constant where the $\Delta\delta_{\text{calcd}}$ are the shifts calculated by using ρ_I and ρ_R in the same row.

herent in the intersystem correlation of entry 4 of Table VII (Ph, $CONMe_2$, $COCF_3$, SO_2Ph, $POPh_2$, 2-py, and 3-py) and of the remaining four substituents incoherent in the two series (CN, $PO(OEt)_2$, COPh, 4-py): these latter extrapolated values are, therefore, of more limited validity because they are usable only in the PhNHX series. The extrapolated value for σ^-_{CN} would be 0.80: however, to avoid proliferation of new σ^- constants, the value σ^-_{CN} = 0.88, derived from Exner's compilation, is retained, since it is within 10% of the extrapolated value. For the 15 substituents studied in the PhOX series, there are available only five σ^- values in Hine's set: one of these is for the CO_2Me substituent for which Hine's σ^- constant is expected to be inadequate. Entry 10 (Table VII) reports the fitting parameters for the four substituents whose σ^- values are found in Hine's set: from entry 11 it can be appreciated that Hine's $\sigma^-_{CO_2Me}$ = 0.74 is only slightly underestimated. Entry 15 reports the fitting parameters for the line containing the four substituents with Hine's reported σ^- values complemented by the seven σ^- values extrapolated from correlation 3 of Table VIII: the results are highly satisfactory. Correlation 15 is then used to extrapolate σ^- values for those substituents which are incoherent in the two series (CO_2Me, COPh, $PO(OEt)_2$, and 4-py): their validity will be limited, of course, to the PhOX series. All the extrapolated values complementing or modifying the original basis set of σ^- values complied by Hine are reported in Table I to form a new set of σ_c^- (contiguous and direct) constants, basically anchored to Hine's set but offering the possibility of dual constants for a few sustituents interacting directly with the oxygen or nitrogen functionalities. Entries 16 and 17 of Table VIII report the fitting parameters for the lines obtained by plotting N^1H shifts of system **5** either vs. Hine's σ^- constants or vs. the σ_c^- constants of Table I.

Exner's set gives for PhNHX (**3**) results which are equivalent to those obtained by using Hine's set, although somewhat better fits and intercepts are obtained with the latter (compare entries 2 and 5, and 4 and 6 of Table VIII). The para monitor's shifts of PhNHX and PhOX correlate satisfactorily also with Taft's set: it appears curiously, however, that phenol set $\bar{\sigma}^-_{TP}$ accounts better for the effects in the PhNHX series than the $\bar{\sigma}^-_{TA}$ set, and vice versa for the PhOX series. In any case sensitivities of the monitor (ρ's) are larger than with Hine's and Exner's sets.

$^{13}C_p$ of PhNHX and PhOX and ^1H_p of PhNHX have been submitted to the DSP treatment: according to Taft the SD and f values are indicative of the goodness of the fit. To further check the goodness of the fit, we have also reported the slope b and the correlation coefficient r of the line obtained by plotting the experimental $\Delta\delta$'s vs. the calculated shifts obtained from the plane equation by using the indicated ρ_I and ρ_R's. In the case of a perfect fit one would obtain both the slope b and r equal to 1. We believe that, particularly when only a few points are available, the b and r values are complementary to the SD and f values for appreciating how precisely the used σ constants account for substituent effects. Five couples of σ_I, $\sigma_R^-{}_A$ and σ_I, $\sigma_R^-{}_P$ are available from Taft's compilation for use in DSP treatment of $^{13}C_p$ and ^1H_p shifts of PhNHX (**3**), while for $^{13}C_p$ shifts of PhOX only four couples are available.[7] Fitting parameters are reported in entries 1–3 and 7–8 of Table IX, respectively. To improve the determination of the planes, we have added points relative to substituents X with zero mesomeric contributions in correlations of entries 9 and 10 (Table IX). Comparison of entries 7 vs. 9 and 8 vs. 10 shows that the ρ values vary negligibly as well as the SD and f values but that b and r are considerably improved, becoming closer to unity. The results also show that for PhNHX, but not for PhOX, Taft's set of σ_I, $\sigma_R^-{}_P$ parameters works better than the set of σ_I, $\sigma_R^-{}_A$ parameters: the σ_I, $\sigma_R^-{}_A$ set offers, instead, acceptable fitting parameters in both cases. To further improve the potentiality of the DSP treatment, we have substituted Taft's inductive constants σ_I by the complemented and partially modified set of σ_I constants derived from benzyl derivatives **1** (σ_{IB}),[1a] while for the mesomeric constants, Taft's $\sigma_R^-{}_A$ set has been retained. Entry 4 (Table IX) reports fitting parameters for the treatment of $^{13}C_p$ of PhNHX with the σ_{IB}, $\sigma_R^-{}_A$ set for the same points of entry 1, complemented in entry 5 by two more points having $\sigma_R \rightarrow 0$. Results show a considerable improvement relative to Taft's treatment of entry 1, both in the SD and f parameters and in the determination of the line (b and r values). Furthermore, ρ_I and ρ_R values of entry 5 do not differ from those obtained by the original Taft treatment by more than 7% and 3%, respectively. Correlation of entry 5 can then be used to extrapolate new σ_R^- values, taking advantage of the fact that several σ_{IB} values are available from our previous work.[1a] Extrapolated σ_R^- values obtained by this method are reported in Table X. The set formed by σ_{IB} and σ_R^- has been checked vs. ^1H_p of PhNHX (**3**), $^{13}C_p$ of PhOX (**4**), and N^1H of p-$XPhNH_2$ (**5**). Fitting parameters for the series **3** and **5** are reported in entries 6 and 15 of Table IX and are found to be highly satisfactory. The goodness of the fitting parameters for DSP treatment of PhOX $^{13}C_p$ data depends on the set of substituents X chosen. Correlations reported in entries 11 and 12 (Table IX) have f values at the limit of acceptability, although the latter is better determined (good b and r values). Correlation 12 (σ_{IB}, $\sigma_R^-{}_A$ set) has worse fitting parameters (f and SD) than correlation 9 (σ_{IT}, $\sigma_R^-{}_A$ set): this is undoubtedly due to the inadequacy of the first set to account for the effect of the CN group (compare σ_{IB} = 0.43 with σ_{IT} = 0.56), experimentally more electron withdrawing in series **4** than in series **3**. The CN group in series **4** thus requires enhanced constants, both in the mono (σ^-) and in the dual substituent parameter (σ_I, σ_R^-) treatment. To further support this result, we have treated

Table X. Set of σ_R^- Values[a]

entry	substituent	σ_R^-
2	Ph	0.26
3	$CONMe_2$	0.40
4	CO_2Me	0.39, 0.45
5	COMe	0.47
6	COPh	0.52, 0.47
8	$COCF_3$	0.42, 0.36
9	NO_2	0.45
10	CN	0.33, 0.42
12	SO_2Me	0.33
13	SOPh	0.26
14	SO_2Ph	0.34
16	$PO(OEt)_2$	0.29, 0.38
19	2-py	0.31
20	3-py	0.31
21	4-py	0.45

[a] Whenever σ_R^- values for PhOX differ by more than 10% from the values for PhNHX two figures are given in the column, the first referring to PhNHX and the second to PhOX.

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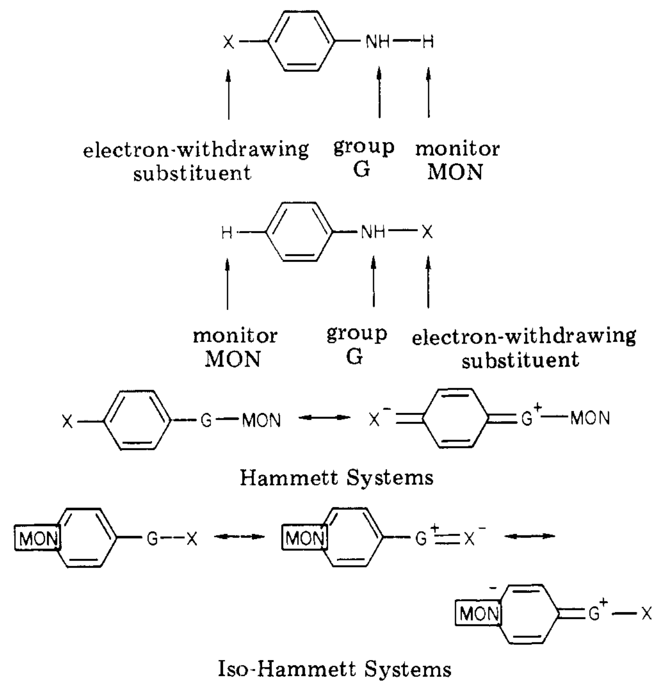
[7] It has been authoritatively pointed out that multiple regressions with less than 20 points may not be worthwhile.[8] In our case we could not conform to this warning because of the natural limitedness of electron-withdrawing groups and the availability of σ_I and σ_R^- constants. We tried to counterbalance this difficulty by considering suspect all correlations based on a few points, unless the four significant statistics f, SD, b, and r were all simultaneously satisfactory.

[8] Reference 3b, p 18.

Scheme I



the $^{13}C_p$ data of PhOX by considering only those substituents coherent with the PhNHX series: the results for eight and ten points are reported in entries 13 and 14 of Table IX, respectively, and in both cases very good fitting parameters are obtained. Correlation 14 can be used then to extrapolate σ_R^- values valid for the PhOX series relative to those substituents incoherent within the two series **3** and **4**. Such values are reported in Table X.

Discussion

Monitor Response in Contiguous and Phenyl-Mediated Interactions. Systems **3** and **4** are related to Hammett systems **5** and **6** simply by a positional interchange of the monitor with the substituent: the former ones can thus be regarded as iso-Hammett systems. While in the Hammett systems the "direct" conjugative interaction of the group G with the remote substituent X is actually "mediated" by the phenyl ring, in the iso-Hammett systems **3** and **4** the interaction is really direct and contiguous: what is "mediated" instead is the response of the monitor MON (see Scheme I). The present results firmly establish that "direct" delocalizative interactions mediated by the phenyl ring in Hammett systems **5** and **6** as detected by the proximate monitor MON = H are linearly correlated with "direct" and contiguous interactions in iso-Hammett systems **3** and **4** as detected by the remote para monitor. It is found also that the remote monitor in iso-Hammett systems has, relative to Hammett systems, a falloff factor of about 2. A falloff factor could be anticipated on considering that the electron availability on G partitions between the substituent X and the phenyl ring, while in the Hammett systems delocalization occurs with the aryl ring only. Chemical shifts of the para monitors in substituted benzenes are known to be linearly related to electron densities at the carbon para to the substituent.[9] The electron density at the para position for a certain substituent X in **3** and **4** will be the one G can donate to the ring when X = H, lessened by the amount that X withdraws, competitively with the phenyl ring, from G. Therefore, to a greater delocalizative interaction of X with G will correspond a smaller negative charge transfer from G to the para position, originating larger shifts of the monitor relative to X = H. In view of the existence of a linear relationship between Hammett and iso-Hammett systems, it is no wonder that the para monitor of the latter ones responds to σ_p^- constants of substituents X. This is fully consistent with our picture, according to which the para monitor in iso-Hammett systems responds to σ constants, the nature of which (inductive or mesomeric) is dictated by the nature of the interaction developing between the group G and the substituent X.

Another result of considerable relevance is the greatly enhanced effect exerted by X = Ph and $CONMe_2$ in iso-Hammett relative to Hammett systems. We ascribe this increase to steric inhibition of conjugation. Various σ^- values have been proposed for the *p*-Ph group: 0.11,[3b] 0.16,[10] and 0.18.[11] A phenyl group contiguous to the involved (reacting) center also presents variable stabilizing properties. Substitution with a phenyl for a hydrogen in carbanions α-substituted with electron-withdrawing groups (EWG) increases the acidity of the parent carbon acid in Me_2SO by ca. 7.5 pK_a units:[12] a larger increase (10.5 pK_a units) is, however, observed for EWG = CN. Streitweiser has elegantly shown[13] that the small increase of the acidity of 9-phenylfluorene relative to that of the parent compound is associated with steric inhibition of resonance. Other evidence for a decreased efficiency of the phenyl group in stabilizing adjacent carbanions has been recently offered.[14] Our analysis shows that the ratio of resonance to polar-inductive contribution is 2.5:1, in better agreement with Streitweiser's (2:1) than with Bordwell's estimate (4:1). We also ascribe the small conjugative capacities of X = Ph and $CONMe_2$ in Hammett systems to steric inhibition of conjugation. We base this conclusion for the two isomers *p*-phenylaniline and diphenylamine on the fact that in diphenyl derivatives the two aromatic rings are twisted relative to one another,[15] while molecular models of diphenylamine do not show any feature which would prevent complete coplanarity and coalignment of interacting orbitals to achieve maximum conjugation. We believe that an analogous situation applies for the *N*,*N*-dimethylcarbamido group, although in this case we are lacking any support from structural studies. To check, however, the validity of this reasoning, we looked for the σ_p^- constant required by the *p*-$CONMe_2$ group in anilines **5** by using the correlation reported in entry 17 of Table VIII. The interpolated value ($\sigma^-_{p\text{-CONMe}_2} = 0.40$) is close to the one reported[3b] for $CONH_2$ in the para position of benzoic acids ($\sigma_p = 0.38$) rather than to the σ_p^- constant for *p*-$CONH_2$ in anilines ($\sigma_p^- = 0.62$), [3a,b,e,f] a clear indication that the $CONMe_2$ group in Hammett compounds **5** is incapable of achieving complete coplanarity with the aryl ring and thus of exerting fully its electron-withdrawing capacity.

The alternative meta and ortho positions for monitors have been considered in iso-Hammett systems **3** and **4** for

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[9] (a) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961); (b) T. K. Wu and B. P. Dailey, *ibid.*, **41**, 2796 (1964); (c) G. E. Maciel and J. J. Natterstad, *ibid.*, **42**, 2427 (1965); (d) G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Am. Chem. Soc.*, **94**, 3089 (1972).

[10] I. G. Traynham and G. A. Knesel, *J. Org. Chem.*, **31**, 3350 (1966).

[11] H. v. Bekkum, P. E. Verkade, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **78**, 815 (1959).

[12] F. G. Bordwell, J. E. Bares, J. E. Bartmess, G. J. McCollum, M. Van Der Puy, N. R. Vanier, and W. S. Matthews, *J. Org. Chem.*, **42**, 321 (1977).

[13] (a) E. Jvaristi and A. Streitwieser, Jr., *J. Org. Chem.*, **43**, 2704 (1978); (b) A. Streitwieser, Jr., and L. L. Nebenzahl, *ibid.*, **43**, 598 (1978).

[14] F. Hibbert, *J. Chem. Soc., Perkin Trans. 2*, 1171 (1978).

[15] H. Suzuki, *Bull. Chem. Soc. Jpn.*, **32**, 1340 (1959); see also a detailed discussion in H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy", Wiley, New York, 1965, pp 389–407.

evaluating their response to polar-inductive and mesomeric effects. In systems **3** and **4** relative sensitivities of ortho vs. para monitors are puzzling since C_o is less sensitive than C_p, irrespectively of the nature of the group (G = O or NH), while H_o is more sensitive than H_p. Furthermore, correlations show a considerable scatter, and the fit, if some substituents are not excluded, is certainly very poor. In analogy with their para analogues, ortho monitors are affected by polar-inductive and resonance effects but should be more sensitive both to σ-inductive and field effects: these components represent, however, only a portion, possibly minor, of the total polar-inductive effect. We have previously shown[1a] that in α-substituted toluenes (**1**), where the substituent X exerts polar-inductive effects only, variations of C_o are unpredictable, and no linear response to σ_I constants exists. The resonance component of the total effect at the ortho position should be linearly related to that at the para position since mesomeric charge transfer from the group G to the ortho position is proportional to that at the para one. It is evident then that if the total gross substituent effect at the ortho position is made up of a resonance component linear with that at the para position and of a polar-inductive term, a part of which is apparently random, the ortho monitor's response will be approximately related to that of the para one, with a less precise and more scattered linearity. This interpretation accounts nicely for the large deviations found in MON_o vs. MON_p plots for those substituents X with exclusively or predominantly polar-inductive contributions (Me, CH_2CN, CN). The large deviance of the $CONMe_2$ group in interpositional (ortho vs. para) correlations is not accounted for by this interpretation. We believe, however, that unusual anisotropy effects on proximate ortho monitors should be expected in this case because of the special steric requirements of the $CONMe_2$ group.

Another feature open to interpretation is the peculiar response of meta monitors. Taft found[16] that ^{19}F shifts in meta-substituted fluorobenzenes respond linearly to polar-inductive effects and are not linearly related to ^{19}F shifts in para-substituted fluorobenzenes. It has been recognized for a long time that $^{13}C_m$ shifts in monosubstituted benzenes are almost insensitive to substituent effects,[9a,b,17] in analogy with our results for substrates **3** and **4**. Our finding that ^1H_m and ^1H_p in **3** are linearly related, finds an analogy in Kloosterziel's results on several monosubstituted benzenes in which the side chain is either neutral or positively or else negatively charged.[18] It is evident, therefore, that the nature of the meta monitor is critical in the type of response obtained. On concluding this section, it must be admitted then that ortho and meta monitors are specifically sensitive to still unaccounted for factors, different from those affecting para monitors.

Influence of G on Substituent Constants. A relatively high number of substituents X (H, Ph, $CONMe_2$, COMe, $COCF_3$, SO_2Me, SO_2Ph, $POPh_2$, 2-py, 3-py) exert coherent effects in the PhOX and PhNHX series: the 1.30-fold larger sensitivity of the para monitor in PhNHX relative to that in PhOX is evidence that substituents X interact more strongly with the NH than with the O functionality. Higher sensitivity in nitrogen-containing substrates is also found for the acid–base equilibria of ring-substituted anilines and phenols:[19] the ratio of the ρ values for the corresponding Hammett plots is ${\rho_{ArNH_2}}^{H_2O}/{\rho_{ArOH}}^{H_2O} = 2.39/2.23 = 1.29$, a figure quite close to that found in iso-Hammett systems **3** and **4**, despite the different solvents involved. Cyano and ester groups (CO_2R, $PO(OEt)_2$) interact more strongly with the oxygen than with the nitrogen functionality: the reverse appears to be true for the carbonyl substituents (COPh, $COCF_3$). The case of the 4-pyridyl (4-py) and $COCF_3$ groups is somewhat special. The 4-py substituent in PhOX is less electron withdrawing than in PhNHX, although the divergence is only of 10%: in the DSP treatment, however, the σ_{R^-A} value extrapolated from PhNHX nicely accounts also for the PhOX series. The reverse situation applies for the $COCF_3$ substituent, for which a common $\sigma^-_{COCF_3} = 1.09$ accounts for the effect in both the PhOX and the PhNHX series, while the DSP treatment gives two slightly different σ_{R^-A} constants ($\sigma_{R^-A} = 0.42$ for PhNHX and $\sigma_{R^-A} = 0.37$ for PhOX, a 12% difference). It is remarkable that a duality of values for a number of substituents is required not only in the monosubstituent parameter (σ_c^-), but also in the DSP treatment of data. This is particularly meaningful since it shows that the DSP treatment is unable to accommodate dichotomies of substituent effects. We do not wish to stress this as an indication of a failure of Taft's DSP treatment, but we believe, instead that this is evidence for different modes of interactions between contiguous functionalities. The requirement of different substituent constants in the PhNHX and PhOX series is indicative either of different polar-inductive or of different mesomeric components in substituent effects. If we retain Taft's suggestion[3c] that σ_I constants are "universal", we are left with variable mesomeric components of substituent effects, that is with variable σ_{R^-} values. We are unable to account in a detailed manner for the different mesomeric modes of contiguous interactions of all the dichotomous substituents investigated: we believe, however, that the stronger interaction that the C≡N group is capable of sustaining in PhOC≡N relative to PhNHC≡N can be accounted for on considering that in the former case the sp-hybridized oxygen can more advantageously interact than the sp^2-hybridized nitrogen with the sp-hybridized carbon of the C≡N group to form a wholly cylindrical fragment. The modified and complemented set of constants (σ_c^-) has been differently tested to check its validity. Inclusion of the seven substituents coherent in the two series **3** and **4** in the plot of entry 10 originates the plot reported in entry 15 (Table VIII): a straight line of remarkable precision is obtained. The fact that the ratio of slopes for PhNHX and PhOX vs. σ_c^- is almost coincident with the slope of the intersystem plot for PhNHX vs. PhOX (8.41/6.58 = 1.28, to be compared with the value of 1.30 ± 0.06 of entry 4 of Table VII) offers an idea of how precisely the new proposed σ_c^- values can account for the effect of substituents. Treatment of the ^1H monitors of PhNHX and p-$XPhNH_2$ with the proposed σ_c^- set is also highly satisfactory (entries 9 and 17 of Table VIII). The latter case is particularly relevant since the fitting is better than with Hine's original basis set. Also in this case the ratio of the slopes of the lines reported in entry 17 and 9 gives a value very close to that obtained from the intersystem plot for PhNHX vs. p-$XPhNH_2$ (1.34/0.65 = 2.06, to be compared with the experimental value of 1.98 ± 0.06 of entry 1 of Table VII).

Taft's DSP Treatment. System **3** where X represents substituents capable of polar-inductive effects only, show for $^{13}C_p$ a sensitivity considerably higher ($\rho_I = 11.51 \pm$

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

[17] G. P. Syrova, V. F. Bystrov, V. V. Orda, and L. M. Yacupolskii, *Zh. Obshch. Khim.*, **39**, 1395 (1969); cited in G. J. Martin, M. L. Martin, and S. Odiot, *Org. Magn. Reson.*, **7**, 2 (1975).

[18] H. Kloosterziel and G. J. Heiszwolf, *Recl. Trav. Chim. Pays-Bas*, **89**, 413 (1970).

[19] A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 388 (1961).

0.71)[1a] than that obtained in this investigation through the DSP treatment of the same system where X represents substituents capable of both polar-inductive and mesomeric effects. This inconsistency is real and cannot be ascribed to the uncertainity of the fits. If the substituent-effect analyses were correct in both cases, the ρ_I values were expected to be equal. We believe this discrepancy is inherent in the definition of σ_I constants, proposed as universal but having their reference in the benzene ring of the benzoic acids. We have in fact previously ascribed the enhanced ρ_I value of **3** (X represents substituents capable of polar-inductive effects only) to two factors: the greater polarizability of the aromatic ring (relative to that of toluene) and the charge transfer from nitrogen to the ring, inductively controlled by the substituent X. Because of their definition of universality, the σ_I constants cannot become enhanced in order to account for the above two factors, the effect of which must then show up in the enhanced ρ_I value. In the DSP treatment, instead, it is up to the mesomeric term to account for these two factors, and, consequently, the ρ_I value comes out to have a figure quite similar to that of the α-substituted toluenes. Since into the mesomeric term there are poured variable (from system to system) amounts of inductively controlled terms which are not accounted for by the universal σ_I constants, the ratio $\lambda = \rho_R/\rho_I$ may assign fictitious importance to polar-inductive and resonance contributions. The danger of separating polar-inductive and mesomeric contributions via statistical correlations only may be overcome by also analyzing, when possible, individual or cluster sets of raw data.

Conclusion

Contiguous delocalization interactions between two adjacent functionalities are accounted for by σ^- values originally devised for "direct" interactions mediated by a p-phenylene ring. Exceptions are noted for a few substituents having special steric constraints to full delocalization when present in a position para to the interacting group G. A set of σ_c^- constants is thus proposed to account for contiguous interactions between adjacent functionalities: this set overlaps with Hine's σ^- set for the majority of substituents but provides new values for substituents incoherent in the Hammett and iso-Hammett series. A duality of values is recognized for certain substituents depending on whether the adjacent group G is O or NH. Taking advantage of the recently proposed σ_{IB} set (inductive constants derived from α-substituted toluenes), the scale of σ_{R^-} values based on Taft's σ_{R^-A} set is expanded and partially modified.

Registry No. **3** (X = H), 62-53-3; **3** (X = Ph), 122-39-4; **3** (X = $CONMe_2$), 101-42-8; **3** (X = CO_2Me), 2603-10-3; **3** (X = COMe), 103-84-4; **3** (X = COPh), 93-98-1; **3** (X = CHO), 103-70-8; **3** (X = $COCF_3$), 404-24-0; **3** (X = NO_2), 645-55-6; **3** (X = CN), 622-34-4; **3** (X = SO_2Me), 1197-22-4; **3** (X = SOPh), 14933-97-2; **3** (X = SO_2Ph), 1678-25-7; **3** (X = SO_2NMe_2), 4710-17-2; **3** (X = $PO(OEt)_2$), 1445-38-1; **3** (X = $POPh_2$), 6190-28-9; **3** (X = 2-py), 6631-37-4; **3** (X = 3-py), 5024-68-0; **3** (X = 4-py), 22961-45-1; **3** (X = Me), 100-61-8; **3** (X = CH_2CN), 3009-97-0; **4** (X = H), 108-95-2; **4** (X = Ph), 101-84-8; **4** (X = $CONMe_2$), 6969-90-0; **4** (X = CO_2Me), 13509-27-8; **4** (X = COMe), 122-79-2; **4** (X = COPh), 93-99-2; **4** (X = $COCF_3$), 500-73-2; **4** (X = CN), 1122-85-6; **4** (X = SO_2Me), 16156-59-5; **4** (X = SO_2Ph), 4358-63-8; **4** (X = $PO(OEt)_2$), 2510-86-3; **4** (X = $POPh_2$), 1706-96-3; **4** (X = 2-py), 4783-68-0; **4** (X = 3-py), 2176-45-6; **4** (X = 4-py), 4783-86-2; **4** (X = Me), 100-66-3; **4** (X = CH_2CN), 3598-14-9; **5** (X = Ph), 92-67-1; **5** (X = $CONMe_2$), 6331-71-1; **5** (X = CO_2Me), 619-45-4; **5** (X = COMe), 99-92-3; **5** (X = COPh), 1137-41-3; **5** (X = NO_2), 100-01-6; **5** (X = CN), 873-74-5; **5** (X = SO_2Me), 5470-49-5; **5** (X = SO_2NMe_2), 1709-59-7; **6** (X = CO_2Me), 99-76-3; **6** (X = COMe), 99-93-4; **6** (X = COPh), 1137-42-4; **6** (X = SO_2Me), 14763-60-1.

Stereochemistry of Tetrahydropyran-2-yl Ions, Radicals, and Related Species. Conjugative and Inductive Effects[1]

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The inductive effect discriminates against a planar geometry at the trivalent center in tetrahydropyran-2-yl radicals in favor of a bent geometry. Conjugation between the nonbonded carbon orbital, ψ, and the two lone-pair orbitals of the adjacent oxygen atom discriminates against both a planar geometry and a bent geometry with ψ pseudoequatorial in favor of a bent geometry with ψ pseudoaxial. The result is an asymmetrical inversion potential. Conjugation in the present model also favors a pseudoaxial ψ in the anions but favors planarity in the cations. The neglect of overlap leads to qualitatively different results for the radicals and anions. Similar results are obtained for related species.

Oxygen-substituted alkyl radicals in which the trivalent carbon atom is bonded to one or more oxygen atoms have attracted a great deal of experimental attention.[2-10] Both the overall geometry of such radicals and the local geometry at the trivalent carbon are of some interest. Considerations of the inductive effect[11] lead to the conclusion that

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[1] Issued as NRCC No. 17931.

[2] A. Hudson, *J. Chem. Soc. A*, 2513 (1969).

[3] A. Hudson and K. D. J. Root, *Tetrahedron*, **25**, 5311 (1969).

[4] A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc. A*, 124 (1971).

[5] A. L. J. Beckwith and P. K. Tindal, *Aust. J. Chem.*, **24**, 2099 (1971).

[6] I. Biddles, A. Hudson, and J. T. Wiffen, *Tetrahedron*, **28**, 867 (1972).

[7] S. O. Kobayashi and O. Simamura, *Chem. Lett.*, 699 (1973).

[8] (a) C. Gaze and B. C. Gilbert, *J. Chem. Soc., Perkin Trans. 2*, 116 (1977); (b) 754 (1977); (c) 1161 (1977).

[9] G. Brunton, K. U. Ingold, B. P. Roberts, A. L. J. Beckwith, and P. J. Krusic, *J. Am. Chem. Soc.*, **99**, 3177 (1977).

[10] V. Malatesta, R. D. McKelvey, B. W. Babcock, and K. U. Ingold, *J. Org. Chem.*, **44**, 1872 (1979).

[11] A. D. Walsh, *Discuss. Faraday Soc.*, **2**, 18 (1947); H. A. Bent, *Chem. Rev.*, **61**, 275 (1961); L. Pauling, *J. Chem. Phys.*, **51**, 2767 (1969).

0022-3263/80/1945-0122$01.00/0