Evaluation of the Polar-inductive and Mesomeric Effects exerted by *para*-Substituted Phenyl Rings on Contiguous Functionalities

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The *para* C-13 shifts of the phenyl ring in $PhCH_2Ar$ (**I**) is used as a monitor to evaluate, in terms of the previously defined σ_{I_B} constants, the polar-inductive effect exerted by some *para*-substituted aryl rings. Analogously, the *para* C-13 shift of the phenyl ring in PhNHAr (**IV**) is used as a monitor to evaluate, in terms of the previously defined σ_c^- constants, the blended polar-inductive and mesomeric effects exerted by such *para*-substituted aryl rings. The same *para* C-13 data offer access, through a biparametric (DSP) treatment, to σ_{R-} constants, which account for the mesomeric effects exerted by the same substituents. C-13 Shift data are also reported for the 4′-substituted sodium aryl(phenyl)amides PhN^-Ar (**VII**) which have been prepared in Me_2SO by deprotonation of PhNHAr. The σ_c^- values just obtained account successfully for the *para* C-13 shifts of the phenyl ring of (**VII**), for the *para* C-13 shifts of the phenyl ring of phenylhydrazones of *para*-substituted benzaldehydes, and for the acidity of aryl(phenyl)amines measured in Me_2SO–H_2O by Dolman and Stewart. The success of the biparametric treatment is limited by the small range of the σ_{I_B} values of the *para*-substituted aryl derivatives and by the scarcity of data. The σ_{I_B} set is linearly related to the set of σ_I constants obtained from substituted acetic acids. Both the σ_{I_B} and the σ_c^- sets account successfully for the acidity of *para*-substituted benzoic acids in H_2O, in Me_2SO, and in the gas phase: a rationale is given.

The effects of numerous 'primary' functionalities X acting as substituents on a contiguous group G have been characterized by: (i) the σ_{I_B} constants[1a] (polar-inductive parameters of benzylic type) which are related to the C-13 chemical shifts at the *para* position of systems (**I**)† through equation (1); (ii) σ_c^-

$$\delta(\text{C-13}) = 5.127\sigma_{I_B} + 125.29 \; (n\ 24;\ r\ 0.998) \qquad (1)$$

constants[1b] (blended parameters of polar-inductive and resonance effects) which are related to the C-13 shifts at the *para* position of systems (**IV**) through equation (2); (iii) σ_{R-} con-

$$\delta(\text{C-13}) = 8.46\sigma_c^- + 115.56 \; (n\ 17;\ r\ 0.991) \qquad (2)$$

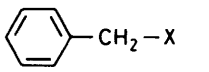
stants[1b] (the resonance contributions to the total substituent effects) which are also related to the *para* C-13 shifts of (**IV**) through the biparametric equation (3). It should be stressed that

$$\delta(\text{C-13}) = 6.71\sigma_{I_B} + 12.93\sigma_{R-} + 115.42 \; (n\ 18;\ r\ 0.9985) \qquad (3)$$

the above σ_{I_B}, σ_c^-, and σ_{R-} constants are designed to account for interactions developing between two functionalities, the reaction centre G and the substituent X which are contiguous: therefore their numerical values have little to do with the usual constants which account for substituent effects at a *remote* reaction centre.

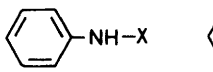
The 'primary' functionalities X so far studied[1] include the phenyl and 2-, 3-, and 4-pyridyl groups as the only aromatic and heteroromatic substituents. As part of our approach, we have now studied the C-13 spectra of families (**I**) and (**IV**) with the *para*-substituted phenyl rings indicated† as substituents: accordingly we report herein the σ_{I_B}, σ_c^-, and σ_{R-} values of such groups. The different types of constants have been interpolated by making use of equations (1)—(3).

† As previously,[1] substituents are identified by an arbitrary, progressive, arabic numbering while families are identified by roman numbers.

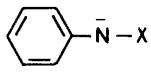


(**I**)

(**2**) X = Ph
(**39**) X = *p*-MeC_6H_4
(**41**) X = *p*-ClC_6H_4
(**42**) X = *p*-BrC_6H_4
(**43**) X = *p*-$H_2NC_6H_4$
(**45**) X = *p*-$MeOC_6H_4$
(**46**) X = *p*-$O_2NC_6H_4$
(**47**) X = *p*-NCC_6H_4
(**48**) X = *p*-$MeO_2CC_6H_4$



(**IV**)



(**VII**)

(**2**) X = Ph
(**39**) X = *p*-MeC_6H_4
(**40**) X = *p*-FC_6H_4
(**42**) X = *p*-BrC_6H_4
(**44**) X = *p*-$Me_2NC_6H_4$
(**45**) X = *p*-$MeOC_6H_4$
(**46**) X = *p*-$O_2NC_6H_4$

The consistency and the general applicability of the σ_{I_B} constants obtained are proved by the fact that they are linearly related to the set of σ_I constants obtained from substituted acetic acids.[2] In turn, the σ_c^- values have been used to treat successfully: (i) the *para* C-13 shifts of the sodium *N*-aryl-*N*-phenylamides (**VII-2**) and (**VII-39**)—(**VII-46**) which we prepared by deprotonation of the corresponding nitrogen acids (**IV**) with sodium dimsyl in Me_2SO; (ii) the acidity in Me_2SO–H_2O of some aryl(phenyl)amines reported by Dolman and Stewart;[3] and (iii) the *para* C-13 chemical shift of the phenyl ring in the phenylhydrazones of *para*-substituted benzaldehydes.[4] Finally, we have found that the acidities of *para*-substituted benzoic acids in water,[5] in Me_2SO,[6] and in the gas phase,[7] respond both to the σ_{I_B} and σ_c^- constants described herein: although this result may appear unexpected at first, we shall analyse it in detail.

Results and Discussion

C-13 Chemical shifts of some *para*-substituted diphenylmethanes have been reported previously for 2M solutions in [$^2H_6$]acetone:[8] however, since at the onset of our investigations[1] we chose to use more dilute (0.33M) solutions, in Me_2SO

Table 1. C-13 Chemical shifts of *para*-substituted diphenylmethanes[a]

Substituent	*ortho*	*meta*	*para*	*ipso*	*ortho'*	*meta'*	*para'*	*ipso'*	CH_2	Other
H	128.60[b]	128.31[b]	125.85	141.16	128.60	128.31	125.85	141.16	41.08	
Me	128.45	128.19	125.70	141.35	128.45	128.81	134.73	138.01	40.63	20.42 (Me)
Cl	128.30[c]	128.15[c]	125.93	140.60	130.34	128.51[c]	130.54	140.12	40.16	
Br	128.60	128.39	126.02	140.62	130.83	131.17	119.03	140.62	40.38	
NH_2	128.40	128.14	125.51	142.29	129.04	114.07	146.56	*d*	40.44	
OMe	128.41	128.17	125.65	141.50	129.49	113.76	157.47	133.03	40.16	54.88 (OMe)
NO_2	128.68	128.44	126.21	139.65	129.72	123.37	145.89	149.29	40.56	
CN	128.65	128.41	126.14	139.85	129.57	132.14	108.82	147.05	40.83	118.69 (CN)
CO_2Me	128.64	128.35	126.04	140.20	128.87	129.22	127.44	146.80	40.87	51.75 (Me), 166.00 (CO)

[a] Shifts are relative to TMS for 0.33M solutions in Me_2SO; primed positions indicate sites of the *para*-disubstituted phenylene ring and are relative to the CH_2 group. [b] These data complement and correct our previous data (ref. 1*a*) which attributed identical shifts to the *meta* and *ortho* positions. [c] Values may be interchanged among the three positions. [d] Uncertain assignment.

Table 2. C-13 Shifts of *para*-substituted diphenylamines and conjugate nitranions[a]

Substituent	Family	*ortho*	*meta*	*para*	*ipso*	*ortho'*	*meta'*	*para'*	*ipso'*	Other
H	(IV)[b]	116.63	128.98	119.51	143.33	116.63	128.98	119.51	143.33	
	(VII)[c]	117.12	128.06	109.47	157.91	117.12	128.06	109.47	157.91	
Me	(IV)	117.51	128.95	118.85	144.04	115.87	129.44	128.42	140.65	20.19 (Me)
	(VII)	116.44	128.20	108.28	157.80	117.78	128.81	117.78	155.28	20.40 (Me)
F[d]	(IV)	116.01	129.15	119.35	143.88	118.79[e]	115.57[f]	156.25[g]	139.72[h]	
	(VII)	116.33	128.23	108.77	157.67	117.24[i]	114.20[j]	151.06[k]	154.37	
Br	(IV)	118.07	129.04	120.28	143.02	117.38	131.60	109.98	142.64	
	(VII)	118.11	128.20	111.24	156.37	118.11	130.46	97.24	157.07	
NMe_2[d]	(IV)	114.02	128.74	117.33	146.01	121.30	113.77	146.01	132.68	40.79 (Me)
	(VII)	119.04	128.16	106.66	158.09	116.28	120.11	139.43	150.80	42.78 (Me)
OMe	(IV)	114.87	129.03	118.25	145.22	120.44	114.54	153.87	136.21	55.24 (MeO)
	(VII)	115.41	128.19	107.15	158.00	118.63	114.51	147.41	152.21	55.58 (MeO)
NO_2	(IV)	120.74	129.31	123.30	137.92	113.28	125.21	140.06	150.76	
	(VII)	119.76	128.62	115.39	154.28	121.30	126.79	125.93	159.68	

[a] Shifts are relative to TMS for 0.33M solutions in Me_2SO: primed positions indicate sites of the *para*-disubstituted phenylene ring relative to the NH or N^- group. [b] From ref. 1*a*,*b*. [c] From ref. 1*f*. [d] Assignments from proton-coupled spectra at 75.46 MHz. [e] $^3J_{CCCF}$ 6.1 Hz. [f] $^2J_{CCF}$ 22.5 Hz. [g] $^1J_{CF}$ 236 Hz. [h] $^4J_{CCCCF}$ 2.2 Hz. [i] $^3J_{CCCF}$ 6.6 Hz. [j] $^2J_{CCF}$ 20.6 Hz. [k] $^1J_{CF}$ 225 Hz.

Table 3. Polar-inductive (σ_{IB}), blended (σ_c^-), and resonance (σ_{R-}) substituent constants for *para*-substituted phenyl groups

Aryl	σ_{IB}[a]	σ_c^-[b]	σ_{R-}[c]
Ph	0.10	0.47	0.26
p-MeC_6H_4	0.08	0.39	0.22
p-FC_6H_4	0.10_5[d]	0.45	0.25
p-ClC_6H_4	0.12		
p-BrC_6H_4	0.14	0.56	0.30
p-$H_2NC_6H_4$	0.04		
p-$Me_2NC_6H_4$	(0.04)[e]	0.21	0.13
p-$MeOC_6H_4$	0.07	0.32	0.18
p-$O_2NC_6H_4$	0.17	0.91	0.52
p-NCC_6H_4	0.16_5		
p-$MeCO_2C_6H_4$	0.15		

[a] Obtained from relationship (1). [b] Obtained from relationship (2). [c] Obtained from relationship (3) using the σ_{IB} values reported in the first column. [d] Obtained by interpolation from relationship (14) of Table 4 using the pK_a value of *p*-fluorobenzoic acid. [e] Assumed to be equal to the value of the *p*-$H_2NC_6H_4$ group.

as solvent, we preferred to redetermine the shifts of the compounds under our standard conditions in order to avoid inhomogeneity in the collection of the derived σ_{IB} values. Table 1 reports the C-13 shifts of diphenylmethanes (**I**) and Table 2 collectes the C-13 shifts of systems (**IV**) and (**VIII**). Values of the σ_{IB} constants interpolated from equation (1) are reported in Table 3 together with the values of the σ_c^- constants interpolated from equation (2). The appropriateness of our redetermination of the shifts in Me_2SO becomes evident on considering that the reported shifts in acetone badly correlate with our values in Me_2SO (entry 1 of Table 4). We believe this is essentially due to association phenomena in acetone: the association of solutes is known to become important for concentrated solutions in rather poorly polar solvents. Data in Table 1 show that the polar-inductive effects exerted by *para*-substituted aryl groups are not very different from the one exerted by the unsubstituted phenyl ring. Supported by this observation, to make available the σ_{IB} values of all the substituents considered for system (**IV**), we have assumed that the *p*-$Me_2NC_6H_4$ aryl has a σ_{IB} value identical to that of the *p*-$H_2NC_6H_4$ group (σ_{IB} 0.04). The σ_{IB} value for the *p*-FC_6H_4 aryl was obtained by interpolation from the very precise relationship (that we will discuss below) between the acidities in H_2O of *para*-substituted benzoic acids[5] and the σ_{IB} values of the *para*-substituted aryls so far considered (entry 14 of Table 4). Having obtained the σ_{IB} values for the *para*-substituted aryl groups, we have interpolated the σ_{R-} values making use of equation (3): data are also reported in Table 3.

An extensive compilation of σ_I constants obtained from the acidities of substituted acetic acids is now available.[2] It is rewarding to note that the σ_{IB} values reported in Table 3, although numerically slightly different from those compiled by Charton, do correlate linearly with them (entries 2 and 3 of Table 4). No data are available regarding the error affecting the σ_{IB} values of Table 3: admittedly, it may be relatively high in view of the small range (0.70 p.p.m.) over which the *para* ^{13}C shifts vary. The success of correlations 2 and 3 of Table 4 is only fair possibly because of the uncertainties in the determination of the σ_{IB} values. The correlations are nonetheless certain evidence that the *para* carbon chemical shifts in compounds of family (**I**)

Table 4. Fitting parameters of monoparametric relationships[a]

Entry	System	y	x	Slope	Intercept	r	n	X
1	$PhCH_2X$	C_p[b]	C_p[c]	0.48 ± 0.09	64.56 ± 0.04	0.918	7	Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-BrC_6H_4, *p*-$MeOC_6H_4$, *p*-$H_2NC_6H_4$, *p*-$O_2NC_6H_4$
2	σ_{IB}	σ_{IB}	σ_I[d]	1.09 ± 0.15	0.02 ± 0.005	0.954	7	Ph, *p*-MeC_6H_4, *p*-FC_6H_4, *p*-ClC_6H_4, *p*-BrC_6H_4, *p*-$MeOC_6H_4$, *p*-$O_2NC_6H_4$
3				1.18 ± 0.12	0.01 ± 0.005	0.981	6	As entry 2 − *p*-BrC_6H_4
4	PhN^-X	C_p	σ_c^-	13.23 ± 0.83	103.31 ± 0.17	0.990	7	Ph, *p*-MeC_6H_4, *p*-FC_6H_4, *p*-BrC_6H_4, *p*-$Me_2NC_6H_4$, *p*-$MeOC_6H_4$, *p*-$O_2NC_6H_4$
5		C_p	σ_{R^-}	23.53 ± 1.63	103.31 ± 0.19	0.988	7	As entry 4
6[e]		C_p	σ_c^-	16.14 ± 0.53	102.49 ± 0.19	0.994	15	H, Ph, $CONMe_2$, CO_2Me, COMe, COPh, CHO, $COCF_3$, NO_2, $PO(OEt)_2$, $POPh_2$, 2-py, 3-py, 4-py, Me
7		C_p	σ_c^-	15.99 ± 0.51	102.45 ± 0.17	0.990	21[f]	As entry 6 + substituents of entry 4
8	PhNHX	pK_a[g]	σ_c^-	−12.38 ± 1.29	27.55 ± 0.29	0.979	6	Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-$MeOC_6H_4$, *p*-$H_2NC_6H_4$, *p*-$O_2NC_6H_4$
9		pK_a[g]	σ_{R^-}	−22.31 ± 1.67	27.64 ± 0.21	0.989	6	As entry 8
10		pK_a[i]	σ_c^-	−17.14 ± 2.84	32.05 ± 1.03	0.938	7	H, Ph, COMe, COPh, $COCF_3$, SO_2Me, SO_2Ph
11	PhNHN=CHX	C_p[j]	σ_c^-	2.61 ± 0.12	118.84 ± 0.03	0.995	6	Ph, *p*-MeC_6H_4, *p*-ClC_6H_4,[h] *p*-$MeOC_6H_4$, *p*-$Me_2NC_6H_4$, *p*-$O_2NC_6H_4$
12	XCO_2H	pK_a[k]	σ_{IB}	−8.81 ± 0.91	5.09 ± 0.03	0.979	6	Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-BrC_6H_4, *p*-$MeOC_6H_4$, *p*-$O_2NC_6H_4$
13				−8.87 ± 0.65	5.10 ± 0.03	0.987	7	As entry 12 + Me (0.04)
14				−9.39 ± 0.11	5.12 ± 0.005	0.999	6	As entry 13 − *p*-BrC_6H_4
15		pK_a[l]	σ_{IB}	−26.72 ± 2.30	13.56 ± 0.11	0.989	5	Ph, *p*-ClC_6H_4, *p*-$H_2NC_6H_4$, *p*-$EtOC_6H_4$, *p*-$O_2NC_6H_4$
16		(D-EA)[m]	σ_{IB}	−106.94 ± 10.99	31.52 ± 0.48	0.970	8	As entry 14 + *p*-FC_6H_4, *p*-NCC_6H_4
17				−105.68 ± 8.27	31.05 ± 8.27	0.985	7	As entry 16 − Ph
18		pK_a[k]	σ_c^-	−1.56 ± 0.11	4.89 ± 0.3	0.988	7	Ph, *p*-MeC_6H_4, *p*-FC_6H_4, *p*-BrC_6H_4, *p*-$MeOC_6H_4$, *p*-$O_2NC_6H_4$, Me (0.04)
19				−1.73 ± 0.11	5.00 ± 0.02	0.992	6	As entry 18 − Me
20		pK_a[l]	σ_c^-	−5.42 ± 0.64	13.60 ± 0.15	0.980	5	As entry 15
21		(D-EA)[m]	σ_c^-	−20.03 ± 2.48	30.52 ± 0.51	0.964	7	As entry 16 − *p*-NCC_6H_4
22	σ_c^-	σ_c^-	σ_{IB}	4.69 ± 0.47	0.003 ± 0.02	0.975	7	As entry 4
23				5.07 ± 0.25	0.02 ± 0.01	0.995	6	As entry 22 − *p*-BrC_6H_4
24	σ_p	σ_p[n]	σ_I	2.48 ± 0.38	−0.28 ± 0.01	0.947	7	As entry 2
25	σ_H	σ_H[o]	σ_I	11.45 ± 0.82	−1.42 ± 0.03	0.990	6	Ph (0.0), *p*-MeC_6H_4 (−0.17), *p*-FC_6H_4 (0.06), *p*-BrC_6H_4 (0.23), *p*-$MeOC_6H_4$ (−0.27), *p*-$O_2NC_6H_4$ (1.24)
26	σ_p°	$\sigma_p^{\circ o}$	σ_I	7.62 ± 0.52	−0.92 ± 0.02	0.993	5	Ph (0.0), *p*-MeC_6H_4 (−0.12), *p*-BrC_6H_4 (0.26), *p*-$MeOC_6H_4$ (−0.16), *p*-$O_2NC_6H_4$ (0.82)
27	σ_J	σ_J[o]	σ_I	7.57 ± 1.01	−0.94 ± 0.04	0.966	6	As entry 25 but *p*-$O_2NC_6H_4$ (0.78)
28	σ_c^-	σ_c^-	σ_H	0.35 ± 0.02	0.46 ± 0.01	0.991	7	As entry 25 + *p*-$Me_2NC_6H_4$ (−0.83)
29	σ_c^-	σ_c^-	σ_J	0.50 ± 0.04	0.46 ± 0.02	0.984	7	As entry 27 + *p*-C_6H_4 (0.06), *p*-$Me_2NC_6H_4$ (−0.60)
30	σ_c^-	σ_c^-	σ_p	0.56 ± 0.03	0.44 ± 0.01	0.995	6	As entry 26, *p*-$Me_2NC_6H_4$ (−0.44)
31				0.55 ± 0.04	0.43 ± 0.02	0.984	7	As entry 30 + *p*-FC_6H_4 (0.17)
32	PhNHX	C_p	σ_{II}	3.00 ± 0.19	119.44 ± 0.11	0.990	7	As entry 28
33		C_p	σ_J	4.33 ± 0.32	119.53 ± 0.13	0.986	7	As entry 29

[a] Substituent parameters for *para*-substituted aryls are in Table 3, those of primary groups are in ref 1*b*. [b] Chemical shifts in Me_2SO. [c] Chemical shifts in C_3D_6O (ref. 8). [d] The σ_I values are from Table 7 of ref. 2. [e] From ref. 1*f*. [f] The number of points is 21 and not 22 since the Ph substituent is common to both entries. [g] Acidities in aqueous Me_2SO (ref. 3). [h] The σ_c^- value for the *p*-ClC_6H_4 substituent has been assumed to be identical to that of *p*-BrC_6H_4. [i] Absolute acidities in Me_2SO (ref. 9). [j] Shifts in $CDCl_3$ from ref. 4. [k] Acidities in H_2O from ref. 5. [l] Acidities in Me_2SO (ref. 6). [m] Gas-phase acidities in kcal mol^{-1} from ref. 7. [n] Values for *para*-substituted benzenes from Table 27 of ref. 2. [o] The Hammett (σ_H), Jaffé (σ_J), or σ_p° values for the group at the *para* position of the benzene rings which we have used for the substituent in the aryl are reported in the column of X near each group and are from ref. 12.

are sensitive exclusively to the polar-inductive effects of substituents X.

The C-13 data at position 4 of the sodium aryl(phenyl)amides (**VII-39**)—(**VII-46**) are fitted excellently by the σ_c^- values (entry 4 of Table 4): the sensitivity of the relationship is somewhat lower than that of entry 6 which treats systems in which a structural variation is introduced directly on the nitrogen atom and not in a remote position as in the present case. Incorporation of the data for substituents (**39**)—(**46**) into the correlation of entry 6 (entry 7 of Table 4) does not cause any appreciable deterioration of the fit, although the sensitivity is again somewhat lowered.

The DSP treatment of data of substrates (**VII-39**)—(**VII-46**) gives a satisfactory fit (entry 3 of Table 5): however, the polar inductive sensitivity is affected by an intolerably high standard deviation and the sensitivity to mesomeric effects of the aryl derivatives is lower than in the correlation of entry 4, valid for PhN^-X systems in which a structural variation occurs directly at the nitrogen atom. Again, incorporation of the present data into the correlation of entry 4 to give entry 5 leads to a somewhat decreased sensitivity to mesomeric effects. We believe that all this should be ascribed to the fact that the polar-inductive demand of the substituted aryls varies but little: indeed, as entry 5 of Table 4 clearly shows, the variation of the C-4 chemical shift of substrates (**VII-39**)—(**VII-46**) is accounted for as well simply by the σ_{R^-} values of the aryls. In conclusion, the mesomeric

Table 5. Fitting parameters for the DSP treatment of data using the σ_{IB} and σ_{R-} values[a]

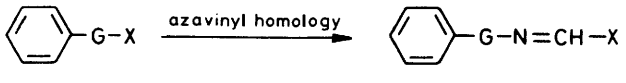
Entry	System	Monitor	ρ_I	ρ_R	Intercept	b[b]	r[b]	n	X
1	PhNHX	pK_a[c]	43.33 ± 24.83	−37.42 ± 8.77	27.43 ± 0.42	1.00 ± 0.05	0.995	6	Ph, *p*-MeC_6H_4, *p*-ClC_6H_4,[d] *p*-$MeOC_6H_4$, *p*-$O_2NC_6H_4$, *p*-$H_2NC_6H_4$
2[e]		pK_a[f]	−23.09 ± 1.21	−11.80 ± 1.84	30.61 ± 0.64	1.00 ± 0.03	0.997	7	H, Ph, COMe, COPh, $COCF_3$, SO_2Me, SO_2Ph
3	PhN^-X	C_p	16.61 ± 14.49	17.66 ± 5.36	103.18 ± 0.47	1.00 ± 0.06	0.991	7	Ph, *p*-MeC_6H_4, *p*-FC_6H_4, *p*-BrC_6H_4, *p*-$MeOC_6H_4$, *p*-$Me_2NC_6H_4$, *p*-$O_2NC_6H_4$
4		C_p	10.94 ± 1.03	26.01 ± 1.40	101.84 ± 0.47	1.00 ± 0.03	0.993	15	H, Ph, $CONMe_2$, CO_2Me, COMe, COPh, CHO, $COCF_3$, NO_2, SOPh, $PO(OEt)_2$, 2-py, 3-py, 4-py, Me
5		C_p	11.45 ± 1.05	24.68 ± 1.32	102.08 ± 0.41	1.00 ± 0.03	0.990	21[g]	As entries 3 + 4
6	PhNHN=CHX	C_p[h]	4.63 ± 4.41	3.04 ± 1.56	118.81 ± 0.07	0.99 ± 0.04	0.996	6	Ph, *p*-MeC_6H_4, *p*-ClC_6H_4,[d] *p*-$MeOC_6H_4$, *p*-$Me_2NC_6H_4$, *p*-$O_2NC_6H_4$
7	XCO_2H	pK_a[i]	−3.60 ± 1.75	−1.82 ± 0.60	5.03 ± 0.06	1.00 ± 0.05	0.995	6	Ph, *p*-MeC_6H_4, *p*-FC_6H_4, *p*-BrC_6H_4, *p*-$MeOC_6H_4$, *p*-$O_2NC_6H_4$

[a] The values used for *para*-substituted aryls are in Table 3, those of primary groups are in refs. 1*a*,*b* [b] As previously defined (ref. 1*b*). [c] Acidities in aqueous Me_2SO (ref. 3). [d] Substituent parameters for the *p*-ClC_6H_4 substituent have been assumed to be identical to those of *p*-BrC_6H_4. [e] From ref. 1*f*. [f] Absolute acidities in Me_2SO (ref. 9). [g] The number of points is 21 and not 22 since the Ph substituent is common to both entries. [h] Values in $CDCl_3$ from ref. 4. [i] Acidities in H_2O from ref. 5.

effects exerted by the substituted aryl derivatives dominate the response of the C-4 chemical shift.

To bring further convincing evidence for the general applicability of the σ values obtained, we have treated the acidities of some aryl(phenyl)amines, as determined by Dolman and Stewart,[3] who used a H_- function in aqueous Me_2SO. The data that can be treated with the present substituent constants is limited to the six substituted aryl compounds which are shared by our and their series. The monoparametric treatment offers a good fit (entry 8 of Table 4), but the slope is somewhat smaller than that of correlation of entry 10 of Table 4 for the PhNHX acids in Me_2SO.[1f] The DSP treatment of the data (entry 1 of Table 5) offers an excellent fit. As before, the polar inductive component of the substituent effect is poorly determined: because of this limitation, the postivie sign of ρ_I is meaningless. As entry 9 of Table 4 clearly shows, the mesomeric effects exerted by the *para*-substituted aryl derivatives dominate not only the C_p chemical shifts of compounds (**VII-39**)—(**VII-46**) of family (**VII**), but also the acidities of aryl(phenyl)amines. The monoparametric treatment of aciditities of aryl(phenyl)amines would give for aniline a pK_a of *ca.* 27.5, and the biparametric treatment a value of *ca.* 27.4. These values are lower by 3 pK_a units relative to the pK_a of aniline determined by Bordwell[9] in anhydrous Me_2SO, a quite reasonable and interesting result since it fits nicely in the general scheme of anions which can entertain favourable hydrogen-bonding interactions with the medium.[10] Also, the decreased sensitivity of acidities in the aqueous solvent relative to anhydrous Me_2SO should be associated with the levelling effect of water.[11]

We have also treated the recently reported[4] C-4 shifts for the phenyl ring of phenylhydrazones of *para*-substituted benzaldehydes.



(**IV**) (**XII**)

It can be seen that the mono- and bi-parametric treatments in terms of σ_c^-, σ_{IB}, and σ_{R-} values are quite successful (entries 11 of Table 4 and 6 of Table 5). Regarding systems (**XII**) as azavinyl homologues of family (**IV**) it is worth noting that the fall-off factor associated with the interpolation of the azavinyl moiety between the PhNH fragment and the substituted aryl functionality is *ca.* 3.5, judged from the relative slopes of entry 11 of Table 4 and that of equation (2).

Finally we have found that the acidity of the carboxylic acids XCO_2X in H_2O,[5] in Me_2SO,[6] and in the gas phase[7] are accounted for by linear relationships both with the σ_c^- and the σ_{IB} sets reported in Table 3 (entries 12—21 of Table 4). The success of correlating the acidity of substituted formic acids XCO_2H with parameters representative of the polar-inductive effect of X even in the case when X is a substituted phenyl ring is unprecedented and may appear at first unexpected on considering that the acidity of the same acids regarded as substituted benzoic acids *p*-$YC_6H_4CO_2H$ is firmly established to be a function both of the polar-inductive and of the resonance effects exerted by the Y group. Indeed we have also found that the biparametric treatment of acidities of XCO_2H in H_2O in terms of the σ_{IB} and σ_{R-} sets is highly satisfactory (entry 7 of Table 5).

The reason why the acidities of XCO_2H correlate both with the sets of σ_{IB} and σ_c^- values is due to the fact that the σ_{IB} parameters and the σ_c^- values do indeed correlate (entries 22 and 23 of Table 4). This last linear relationship should not raise doubts that the polar-inductive effect of X has been incorrectly separated from the mesomeric contributions. In fact, the Charton σ_I set for X = *p*-YC_6H_4 not only correlates with σ_p° of X (entry 24 of Table 4) but also with Hammett σ_H, σ_p°, and Jaffé σ_J sets of constants for the group Y as substituent (entries 25—27 of Table 4). Evidently the polar-inductive effects of *para*-substituted aryl rings have a memory of the polar-inductive and mesomeric contributions of the *para* group Y. It is found also that the σ_c^- set of parameters correlates with the σ_H, σ_J, and σ_p° constants of the Y group (entries 28—31 of Table 4). The slopes of correlations of entries 28—31 may be considered a measure of the efficiency of the phenyl ring in transmitting the effects of the Y group present at the *para* position. In view of these results it is not surprising then that σ_c^- and σ_{IB} correlate (entry 22 of Table 4). Furthermore it seems quite justified *a posteriori* to interpolate the value of σ_{IB} of the *p*-FC_6H_4 substituent from the very good correlation of entry 14 of Table 4.

The sensitivity of the acidity of XCO_2H to the nature of X is

three times larger in Me_2SO than in H_2O (entry 20 of Table 4) and *ca.* 10 times larger in the gas phase than in H_2O (entry 21 of Table 4).* The factor of 3 between Me_2SO and H_2O finds analogy in the acidity of arylcyclopentadiene carbon acids[11] and a factor of *ca.* 10 was already observed by Kebarle[7] on comparing directly the acidities of benzoic acids in the gas phase and in H_2O.

Although the C-4 data of substrates (**IV-39**)—(**IV-46**) served to obtain the σ_c^- and σ_{R-} values of *para*-substituted aryls as substituents, the same data could have been treated alternatively along the classical approach of using the *para* constants typical of the variable, remote, benzenoid 4′-substituent (Me, F, Br, *etc.*). The treatment of the C-4 data of (**IV-39**)—(**IV-46**) with Hammett σ_H and Jaffé σ_J values (all as given in Exner's compilation)[12] afforded results which, as reported in entries 32—33 of Table 4, are highly dependent upon the set chosen: the choice for the best set appears difficult.

On comparing the two alternative approaches, the classical one and our own, characterized by considering the whole *para*-substituted aryl group as a substituent, the latter treatment gives better, or at least comparable, results than the former. Our own approach however presents the invaluable advantage of treating both contiguous and remote structural variations with the same co-ordinated set. We can thus affirm that the effect exerted by a contiguous benzoyl group (σ_c^- 0.94) on the PhNH fragment is equivalent to that of the *p*-nitrophenyl group (σ_c^- 0.91) or else that a *p*-bromophenyl group is approximately equivalent to a 3-pyridyl group. Furthermore, the effect exerted by a *p*-nitrophenyl group (σ_c^- 0.91) on the nitrogen atom of the PhNH fragment is reduced only to a quarter relative to the effect exerted by nitro group directly attached to the nitrogen atom (σ_c^- 1.24).

Experimental

Materials.—Diphenylmethane, diphenylamine, and 4-nitrodiphenylamine were commercial products (Fluka). 4-Chloro-, 4-bromo-, and 4-methoxy-diphenylmethane were prepared as described[13] by the reduction of the corresponding benzophenones. 4-Nitrodiphenylmethane was prepared from *p*-nitrobenzyl alcohol and benzene.[14] Catalytic reduction of 4-nitrodiphenylmethane in MeOH and in the presence of 5% Pd–C under the usual conditions gave *p*-benzylaniline, m.p. 34 °C (from hexane) (lit.,[14] 34—35 °C). Methyl *p*-benzylbenzoate was prepared as described[15] by esterification of the corresponding acid with methanol. 4-Fluoro-,[16] 4-methyl-,[17] 4-methoxy-,[18] and 4-(*NN*-dimethylamino)-diphenylamine[19] were prepared according to known procedures by thermal decarboxylation of the corresponding *N*-(*para*-substituted)phenylanthranilic acids.

N.m.r. Measurements and Assignments.—Solutions for n.m.r. spectra of families (**I**) and (**IV**) were in Me_2SO (0.33M in substrate): solutions for nitranions (**VII**) were in Me_2SO (0.33M in substrate and 0.66M in base). ^{13}C Spectra were obtained either on a Varian XL-100-12 WG instrument operating at 25.18 MHz with the procedure previously described[1f] or on a Bruker WP 80 SY instrument operating at 20.15 MHz: the deuterium lock required by the Bruker instrument for the nitranions was provided by neat $[^2H_6]Me_2SO$ contained in an internal 4 mm tube, coaxial with the 10 mm tube containing the solution of the anion. ^{13}C Shifts were measured relative to trimethylsilylpropanesulphonic acid sodium salt (TPS) as internal reference and then converted into shifts relative to tetramethylsilane (TMS) using the relationship $\delta_{TPS} - \delta_{TMS} = 1.63$ p.p.m. Assignments of the ^{13}C resonances to every carbon atom of the different substrates was based on: (i) the different intensities of *ortho* and *meta*, *para*, and *ipso* and *ipso′* carbons; (ii) additivity of the shielding effects, relative to the unsubstituted parent compounds (**Ia**) and (**IVa**), of substituents as deduced from data of mono-[20] and di-substituted benzenes;[21] and (iii) proton-coupled spectra in a number of cases, as specified in the Tables.

Preparation of Nitranions.—The procedure as previously described[1f] was followed for the preparation of the anions directly in the n.m.r. tube.

4-*Benzylbenzonitrile.*—The aromatic halide displacement effected by copper(I) cyanide[22] was followed essentially. 4-Bromodiphenylmethane (10.5 g, 42.5 mmol) in dimethylformamide (6.5 ml) was added to freshly prepared copper(I) cyanide (4.38 g, 48.9 mmol): the mixture was then heated at reflux (4 h), cooled, and poured into 5% hydrochloric acid (35 ml) containing iron(III) chloride (17 g). The mixture was then heated at 60 °C for 30 min under stirring, cooled to 40 °C, and extracted at this temperature with benzene (4 × 20 ml). The combined extracts were washed with 15% hydrochloric acid, 10% aqueous sodium hydroxide, and water and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue was crystallized from EtOH to give the title compound (4.1 g, 51%), m.p. 49—50 °C (lit.,[23] 50—51 °C).

4-*Benzylbenzoic Acid.*—A solution of 4-benzylbenzonitrile (2.4 g, 12.4 mmol) in a mixture of 50% aqueous acetic acid (10 ml) and concentrated sulphuric acid (5 ml) was heated at reflux for 3 h. The precipitate was filtered off and dissolved in 5% aqueous NaOH: the solution was filtered and acidified with hydrochloric acid. The solid was collected by filtration and crystallized ($EtOH–H_2O$) to give the title compound (2.2 g, 84%) m.p. 156 °C (lit.,[24] 157—158 °C).

(4-*Bromophenoxybenzylidene*)*aniline.*—The synthesis follows essentially the method described by Chapman[25] for analogous compounds. *N*-Phenylbenzimidoyl chloride (9.30 g, 43 mmol) in ether (20 ml) was slowly added to a magnetically stirred solution of sodium *p*-bromophenoxide prepared by dissolving *p*-bromophenol (8.0 g, 46 mmol) in ethanol (20 ml) with sodium ethoxide (3.12 g, 46 mmol). After 12 h at room temperature, the solution was evaporated under reduced pressure: the residue, taken up with water, afforded a solid which, after drying at room temperature, was crystallized (EtOH) to give the title compound (7.91 g, 53%), m.p. 86—87 °C (Found: C, 65.0; H, 4.0; N, 4.0. $C_{19}H_{14}BrNO$ requires C, 64.8; H, 4.0; N, 4.0%).

N-*Benzoyl*-4-*bromodiphenylamine.*—The preceding compound (7.8 g, 22 mmol) was carefully melted in a small apparatus and then heated at 300 °C for 30 min.; temperature control was given by a thermometer immersed in the melt. After cooling, the oily residue was taken up with hexane: the solid was collected and crystallized (from 80% aqueous ethanol) to give the title compound (3.72 g, 47%), m.p. 112 °C (Found: C, 64.5; H, 3.9; N, 3.9. $C_{19}H_{14}BrNO$ requires C, 64.8; H, 4.1; N, 4.0%).

4-*Bromodiphenylamine.*—A solution of *N*-benzoyl-4-bromodiphenylamine (3.70 g, 10.5 mmol) in ethanol (20 ml) was treated with 50% aqueous potassium hydroxide (7 ml) and heated at reflux under nitrogen for 1 h. The solution was evaporated to dryness and taken up with water. The solid was filtered off and crystallized (from dilute methanol) to give the title compound (2.08 g, 80%), m.p. 86—87 °C (lit.,[26] 87—88 °C).

* The (D-EA) values used in entries 16 and 21 of Table 4 are expressed in kcal mol^{-1}: the factor of 9 takes into account the fact that 1.35 pK_a units correspond to a variation of 1 kcal mol^{-1} in ΔG.

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