

Contiguous Interactions in α -Substituted Nitrogen Acids and Conjugate Nitroanions: the Role of Mesomeric and Polar Components.

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^1H , ^{19}F , and ^{13}C n.m.r. parameters of α -substituted sodium phenyl amides PhN^-X (VII) are obtained in Me_2SO solution to study the interactions of the variable substituent X with the contiguous negatively charged nitrogen atom. Results probe the considerable structural reorganization undergone by the precursor nitrogen acids PhNHX (IV) upon deprotonation: the effect on ^{13}C shifts exerted by the [2.2.1] cryptand provides evidence for ion pairing and/or aggregation of the salts. Correlative analyses with the n.m.r. data probe the effect of the substituent in PhN^-X : in addition to the monoparametric treatment in terms of the σ_c^- constants, DSP analysis with the σ_{IB} and σ_{R} constants reveals that charge transfer from the nitrogen atom to the phenyl ring is dominated by the mesomeric component of the effects exerted by the substituent X. Unlike the analogous acid-base pair of toluene carbon acids PhCH_2X and of benzyl carbanions PhCH^-X , no correlation whatsoever is found between $\text{C}(p)$ of PhN^-X (VII) and Bordwell's acidities of PhNHX (IV) in Me_2SO . The DSP treatment of parent α -substituted nitrogen acids NH_2X and of their phenyl homologues reveals that the energetics of the deprotonation process is dominated by the polar-inductive component of the effect exerted by the substituent. The different sensitivities of charge release from nitrogen in nitroanions and of acidities of nitrogen acids are accounted for on plausible structural arrangements in these species. The pK_a of ammonia is extrapolated from the intersystem correlation between acidities of NH_2X and of PhNHX : the value (35.8) is in excellent accord with the value obtained (36.6) from the DSP treatment of NH_2X acidities.

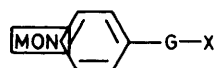
Ammonia behaves as a nitrogen base relative to the ammonium ion and as a nitrogen acid relative to the amide ion NH_2^- ; substitution of a hydrogen at the nitrogen atom of ammonia gives α -substituted nitrogen acids whose acidities are spread over a considerable range.¹⁻³ α -Substituted nitroanions are important intermediates in many organic reactions: di-isoalkyl and silyl nitroanions have found wide application as strong non-nucleophilic bases.⁴ Equilibria between nitrogen acids and their conjugate nitroanions, recently studied by ^{13}C n.m.r.,⁵ allowed the establishment of acidity functions.⁶⁻⁸ Acidities of a large number of carbon acids have been evaluated spectroscopically^{9,10} and by ^{13}C n.m.r.¹¹ using metal amides.

Relatively little effort has been put into understanding the effect of substituents at nitrogen on acid-base equilibria of nitrogen acids and on the structure of nitroanions. In this work we report the response to *N*-substituents of n.m.r. parameters of α -substituted *N*-phenylamides PhN^-X (VII)¹² and of the energetics of the acid-base equilibria of the parent nitrogen acids NH_2X (XI) and of their phenyl homologues PhNHX (IV).^{*} We have performed a detailed ^1H , ^{19}F , and ^{13}C n.m.r. study on α -substituted phenyl amides PhN^-X to obtain information concerning the interactions between the N^- and X functionalities. Interactions of this type have already found quantitative and successful expression, in terms of mono- and bi-parametric relationships based on σ_c^- , σ_{IB} , and σ_{R} sets of substituent constants,¹³ for parent oxygen acids XOH (X),¹⁴ parent carbon acids CH_3X (VIII),¹⁵ toluene carbon acids PhCH_2X (I),¹⁵ and nitro-activated methane carbon acids $\text{NO}_2\text{CH}_2\text{X}$.¹⁴

Results

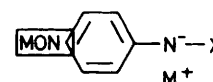
Nitroanions (VII) have been generated in Me_2SO , starting from nitrogen acids (IV):^{13a,b} solutions for ^1H and ^{19}F spectra were 0.1M in substrate, and 0.33M for ^{13}C experiments.

* For the number of substrates see Experimental section.

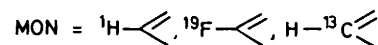


- (I) G = CH_2
 (II) G = CHPh
 (III) G = O
 (IV) G = NH
 (V) G = NMe
 (VI) G = CH^-
 (VII) G = N^-

- X—G—H
 (VIII) G = CH_2
 (X) G = O
 (XI) G = NH



(VII)



M = Na^+ , [Na(2.2.1) cryptand]⁺

- (1) X = H (12) X = SO_2Me
 (2) X = Ph (13) X = SOPh
 (3) X = CONMe_2 (14) X = SO_2Ph
 (4) X = CO_2Me (16) X = $\text{PO}(\text{OEt})_2$
 (5) X = COMe (17) X = POPh_2
 (6) X = COPh (18) X = P^+Ph_3
 (7) X = CHO (19) X = 2- $\text{C}_5\text{H}_4\text{N}$
 (8) X = COCF_3 (20) X = 3- $\text{C}_5\text{H}_4\text{N}$
 (9) X = NO_2 (21) X = 4- $\text{C}_5\text{H}_4\text{N}$
 (10) X = CN (26) X = Me

^{19}F Monitor shifts and benzenoid ^{13}C data for sodium *N*-phenylamides (VII) are reported in Table 1, together with data of a number of anions prepared in the presence of the [2.2.1] cryptand, known to bind strongly and selectively to the sodium cation. To make the relevant comparisons easier, we have also reported in Table 1 the ^{13}C shifts for nitroanions which have appeared in the literature since our preliminary reports.¹² ^1H Shifts and other ^1H parameters obtained by LAOCOON III¹⁵ fittings of the aromatic protons are reported in Table 2.

Table 3 collects intermonitor and interpositional correlations, as previously defined.¹³ Excellent correlations are found for $\text{C}(p)$ versus $\text{H}(p)$ and $\text{C}(p)$ versus $\text{F}(p)$: ^{19}F is ca. 19 times, and ^{13}C ca. 13 times more sensitive than the ^1H monitor. At least for a limited number of substituents, ^1H and ^{13}C monitors at the *ortho* position show inverted sensitivities relative to those at the *para* position.

Table 1. ^{19}F and benzenoid ^{13}C shifts (p.p.m.) of sodium *N*-phenylamide (VII)^a

Entry	X	Solvent	^{19}F	<i>ortho</i>	<i>meta</i>	<i>para</i>	<i>ipso</i>
1	H	$\text{Me}_2\text{SO} + [2.2.1]$	16.74	115.12	128.94	102.46	166.18
				113.83	127.87	100.68	163.75
2	Ph	THF ^b	27.68	117.12	128.06	109.47	157.91
				118.98	129.71	113.33	159.49
3	CONMe ₂		31.50	122.60	126.98	113.46	156.31
4	CO ₂ Me		34.31	122.34	127.16	116.08	153.71
5	COMe	$\text{Me}_2\text{SO} + [2.2.1]$	35.24	123.52	126.39	117.16	154.78
				122.29	127.06	117.38	151.52
6	COPh	$\text{Me}_2\text{SO} + [2.2.1]^c$	35.94	123.96	127.87	117.19	154.55
					127.07		
7	CHO			121.13	128.00	118.62	153.67
8	COCF ₃			123.87	127.36	119.30	151.52
9	NO ₂		41.69	122.53	127.54	122.37	148.33
10	CN		31.33	118.02	128.13	113.87	155.19
12	SO ₂ Me	$\text{Me}_2\text{SO} + [2.2.1]$	33.16	117.70	127.83	113.08	155.71
				119.81	127.52	115.36	151.04
13	SOPh	$\text{Me}_2\text{SO} + [2.2.1]^c$	33.10	119.57	127.90	115.58	150.09
				118.37	127.45	113.11	153.44
				125.48		156.35	
14	SO ₂ Ph	$\text{Me}_2\text{SO} + [2.2.1]$		118.16		112.11	
16	PO(OEt) ₂		33.97	120.41	127.61	115.98	150.03
		$\text{Me}_2\text{SO} + [2.2.1]$	29.81	121.38	127.54	112.82	154.22
				121.00	127.39	111.15	155.68
17	POPh ₂		29.24	121.98	128.08	112.05	155.39
18	PPh ₃ ⁺		34.68	122.61	<i>d</i>	116.49	150.93
19	2-C ₃ H ₄ N		32.64	120.62	127.84	114.42	155.06
20	3-C ₃ H ₄ N			117.59	128.14	111.28	153.03
21	4-C ₃ H ₄ N	$\text{Me}_2\text{SO} + [2.2.1]$	33.34	120.46	128.00	114.75	156.72
							156.05
				120.08	127.74	113.93	159.01
							158.60
							156.27
26	Me		16.97	111.28	125.28	101.73	162.62

^a Unless otherwise stated the solvent is Me_2SO ; shifts for ^{13}C are relative to TMS and for ^{19}F relative to C_6F_6 . Two values are reported whenever the assignment is uncertain. Unless otherwise stated the following ratios were used for spectra recorded in the presence of the [2.2.1] cryptand: [substrate]:[base]:[2.2.1] = 0.5:1:1.1. ^b Ref. 21. ^c [Substrate]:[base]:[2.2.1] = 0.5:0.5:0.55. ^d Assignment uncertain.

Table 2. ^1H N.m.r. parameters of sodium *N*-phenylamide (VII)^a

Entry	X	H_o	H_m	H_p	J_{op}	J_{mp}	$J_{oo'}$	J_{om}	$J_{om'}$	$J_{mm'}$	r^b
1	H	5.814	6.412	5.403	1.047	6.901	1.499	8.084	0.341	2.024	0.025
2	Ph	6.706	6.794	6.075	1.359	6.841	1.186	8.150	0.466	2.156	0.036
3	CONMe ₂	7.059	6.854	6.305	1.275	7.021	1.606	8.004	0.378	2.039	0.040
4	CO ₂ Me	7.254	6.960	6.502	1.174	7.137	1.629	8.196	0.453	2.295	0.041
6	COPh	7.366	7.037	6.602	1.214	7.175	1.669	8.140	0.171	1.665	0.038
10	CN	6.601	6.919	6.363	1.208	7.157	1.820	8.092	0.262	2.180	0.037
12	SO ₂ Me	6.863	6.988	6.495	1.141	7.177	2.221	8.268	0.202	2.142	0.032

^a Best values from LAOCOON III treatment. ^b Error.

Table 3. Intermonitor and interpositional correlations for sodium *N*-phenylamide (VII)

Entry	<i>y</i>	<i>x</i>	Slope	Intercept	<i>r</i>	<i>n</i>	X
1	F(<i>p</i>)	C(<i>p</i>)	1.20 ± 0.04	-105.46 ± 0.20	0.992	17	H, Ph, CONMe ₂ , CO ₂ Me, COMe, COPh, NO ₂ , CN, SO ₂ Me, SOPh, SO ₂ Ph, PO(OEt) ₂ , POPh ₂ , PPh ₃ ⁺ , 2-C ₃ H ₄ N, 4-C ₃ H ₄ N, Me
2	C(<i>p</i>)	H(<i>p</i>)	13.64 ± 0.35	27.41 ± 0.12	0.994	19	as entry 1 + COCF ₃ , 3-C ₃ H ₄ N
3	H(<i>o</i>)	H(<i>p</i>)	1.20 ± 0.17	-0.66 ± 0.07	0.961	6	H, Ph, CONMe ₂ , CO ₂ Me, COPh, SO ₂ Me
4	C(<i>o</i>)	C(<i>p</i>)	0.58 ± 0.07	54.82 ± 0.37	0.957	8	H, Ph, CONMe ₂ , CO ₂ Me, COMe, COPh, COCF ₃ , PO(OEt) ₂
5			0.46 ± 0.09	67.97 ± 0.37	0.779	19	as entry 2 + CHO, -Me

Table 4. Acidities (pK_a) of α -substituted nitrogen acids in Me_2SO

X	X-NH ₂	Ref.	<i>p</i> -XC ₆ H ₄ NH ₂	Ref.	Ph-NH-X	Ref.
H	(40) (41)	<i>a</i> <i>c</i>	30.7	<i>b</i>	30.7	<i>b</i>
Ph	30.7	<i>b</i>			24.95	<i>d</i>
CO ₂ Me	24.82	<i>e</i>				
COMe	25.5	<i>b</i>			21.45	<i>b</i>
COPh	23.35	<i>b</i>	24.4	<i>af</i>	18.8	<i>b</i>
CHO	23.5	<i>a</i>				
COCF ₃	17.15	<i>e</i>			12.59	<i>e</i>
CN	17.0	<i>c</i>	25.3	<i>f</i>		
NO ₂			21.0	<i>a</i>		
			20.9	<i>f</i>		
SO ₂ Me	17.5	<i>b</i>	25.6	<i>f</i>	12.94	<i>e</i>
SO ₂ Ph	16.1		24.9	<i>f</i>	11.91	
2-C ₅ H ₄ N	27.67	<i>e</i>				
3-C ₅ H ₄ N	28.51	<i>e</i>				
4-C ₅ H ₄ N	26.53	<i>e</i>				
SO ₂ CF ₃	9.7	<i>b</i>	21.8	<i>f</i>	5.7	<i>d</i>

^a Ref. 2c. ^b Ref. 2a. ^c Ref. 2e. ^d Ref. 2d. ^e Ref. 3. ^f Ref. 2b.

Table 5. Intersystem correlations

Entry	System A(<i>y</i>)	System B(<i>x</i>)	<i>y</i>	<i>x</i>	Slope	Intercept	<i>r</i>	<i>n</i>	X
1	PhNHX	PhN ⁻ X	C(<i>p</i>)	C(<i>p</i>)	0.53 ± 0.02	61.31 ± 0.12	0.991	14	H, Ph, CONMe ₂ , CO ₂ Me, COMe, COPh, CHO, COCF ₃ , NO ₂ , PO(OEt) ₂ , POPh ₂ , 3-C ₅ H ₄ N, 4-C ₅ H ₄ N, Me
2					0.54 ± 0.03	60.37 ± 0.14	0.979	18	as entry 1 + SO ₂ Me, SO ₂ Ph, SOPh, CN
3					0.54 ± 0.03	60.58 ± 0.17	0.968	19	as entry 2 + 2-C ₅ H ₄ N
4	PhCH ⁻ X	PhN ⁻ X	C(<i>p</i>)	C(<i>p</i>)	1.38 ± 0.09	-45.63 ± 0.33	0.982	10	Ph, CONMe ₂ , CO ₂ Me, COMe, COPh, NO ₂ , PO(OEt) ₂ , POPh ₂ , 3-C ₅ H ₄ N, 4-C ₅ H ₄ N
5					1.38 ± 0.10	-46.20 ± 0.35	0.975	11	as entry 4 + 2-C ₅ H ₄ N
6					1.36 ± 0.12	-43.55 ± 0.36	0.952	15	as entry 5 + CN, SO ₂ Me, SOPh, SO ₂ Ph
7	PhNHX	NH ₂ X ^a	<i>pK_a</i>	<i>pK_a</i>	1.05 ± 0.04	3.77 ± 0.21	0.997	6	Ph, COMe, COPh, SO ₂ Me, SO ₂ Ph, COCF ₃
8					1.08 ± 0.3	3.22 ± 0.20	0.998	7	as entry 7 + H ^b

^a The extrapolated value of the pK_a of NH_3 is 35.81 using a pK_a of PhNH_2 of 30.55. ^b Using the value of 36.61 obtained from the correlation of entry 5 of Table 7.

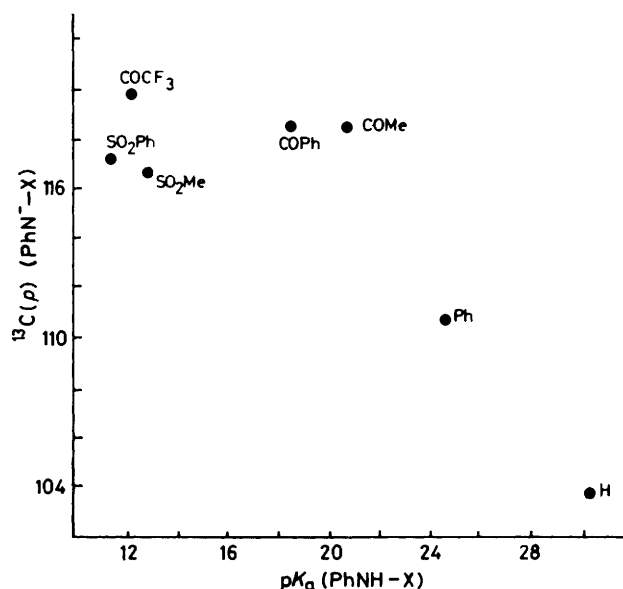


Figure 1. $^{13}\text{C}(p)$ Chemical shifts of PhN^-X as a function of pK_a values of PhNH-X , in Me_2SO

Acidity data in Me_2SO for nitrogen acids NH_2X (XI) and PhNHX (IV) are collected in Table 4; intersystem correlations are collected in Table 5. Acidities of the NH_2X and PhNHX nitrogen acids are linearly related with a high degree of precision and with unit slope (entry 7 of Table 5). Unlike the analogous α -substituted benzyl carbanions (VI), no correlation whatsoever is found between the *para* ^{13}C monitor of *N*-phenyl amides (VII) and the pK_a values of the precursor nitrogen acids PhNHX (IV) (Figure 1). Good intersystem correlations are, however, found for the *para* ^{13}C monitors of *N*-phenyl amides (VII) and of the precursor nitrogen acids (IV), the sensitivity to substituents of the former being almost twice as large (Table 5, entry 1). Some scatter is also introduced on considering the SO_nR ($n = 1, 2$; $\text{R} = \text{Me, Ph}$), CN , and 2-pyridyl groups (Table 5, entries 2 and 3). The same trend is also observed for the intersystem correlation of the *para* ^{13}C monitor in (VII) and in (VI); in PhCH^-X (VI) the monitor is *ca.* 30% more sensitive.

Table 6 reports the treatment of the *para* ^{13}C shifts of (VII) and of the acidity of PhNHX (IV) in terms of the σ_c^- constants: Table 7 collects the fitting parameters for the treatment of the same monitors in terms of the DSP approach based on the σ_{1B} and σ_R^- constants. Results show that, while the delocalization of the negative charge in the phenyl ring of phenylamides (VII) is

Table 6. Monoparametric Hammett-type correlations

Entry	System	y	x	Slope	Intercept	r	n	X
1	PhN ⁻ X	C(p)	σ_c^-	15.09 ± 0.96	102.75 ± 0.32	0.969	18	H, Ph, CONMe ₂ , CO ₂ Me, COMe, COPh, CHO, COCF ₃ , NO ₂ , CN, PO(OEt) ₂ , POPh ₂ , SO ₂ Me, SO ₂ Ph, SPh, 3-C ₅ H ₄ N, 4-C ₅ H ₄ N, Me
2				15.16 ± 0.89	102.72 ± 0.27	0.972	19	as entry 1 ^a + 2-C ₅ H ₄ N ^b
3				16.14 ± 0.53	102.49 ± 0.19	0.994	14	as entry 2 - 2-C ₅ H ₄ N, CN, SO ₂ Me, SO ₂ Ph, SPh
4	NH ₂ X	pK _a	σ_c^-	-23.61 ± 3.72	42.13 ± 0.71	0.904	11	Ph, CO ₂ Me, COMe, COPh, COCF ₃ , CN, SO ₂ Me, SO ₂ Ph, 2-C ₅ H ₄ N, 3-C ₅ H ₄ N, 4-C ₅ H ₄ N
5				-14.42 ± 1.91	36.71 ± 0.28	0.959	7	as entry 4 - COCF ₃ , CN, SO ₂ Me, SO ₂ Ph
6			σ_{IB}	-24.84 ± 2.62	30.93 ± 0.50	0.953	11	as entry 4
7	p-XPhNH ₂	pK _a	σ_c^-	-5.92 ± 0.54	30.52 ± 0.19	0.984	6	H, COMe, COPh, CN, SO ₂ Me, SO ₂ Ph

^a Using σ_c^- (CO₂Me) = 0.81. ^b Using σ_c^- (2-C₅H₄N) = 0.71.

Table 7. Fitting parameters for the DSP treatment of data using σ_{IB} and σ_R^- values^a

Entry	System	y	ρ_I	ρ_R	Intercept	b ^a	r ^a	n	X
1	PhN ⁻ X	C(p)	8.54 ± 1.32	27.69 ± 2.15	102.13 ± 0.70	1.00 ± 0.05	0.979	18	H, Ph, CONMe ₂ , CO ₂ Me, COMe, COPh, CHO, COCF ₃ , NO ₂ , CN, SO ₂ Me, SO ₂ Ph, PO(OEt) ₂ , 2-C ₅ H ₄ N, 3-C ₅ H ₄ N, 4-C ₅ H ₄ N, Me
2		C(p)	9.60 ± 0.09	26.98 ± 1.43	101.67 ± 0.50	0.999 ± 0.04	0.990	18	as entry 1 ^b
3		C(p)	10.94 ± 1.03	26.01 ± 1.40	101.84 ± 0.47	1.00 ± 0.03	0.993	15	as entry 2 - CN, SO ₂ Me, SO ₂ Ph
4	NH ₂ X	pK _a	-23.90 ± 4.82	-15.06 ± 2.92	36.93 ± 1.01	1.00 ± 0.08	0.983	7	Ph, CO ₂ Et, ^c COEt, ^c COPh, 2-C ₅ H ₄ N, ^d 3-C ₅ H ₄ N, 4-C ₅ H ₄ N
5			-24.46 ± 0.82	-13.99 ± 2.14	36.61 ± 0.92	1.00 ± 0.03	0.996	10	as entry 4 + COCF ₃ , SO ₂ Me, SO ₂ Ph
6			-25.52 ± 2.43	-10.38 ± 6.26	35.14 ± 2.69	1.00 ± 0.09	0.966	11	as entry 5 + CN
7			-25.08 ± 0.95	-13.14 ± 2.59	36.36 ± 1.12	1.00 ± 0.03	0.994	11	as entry 6 ^e
8	PhNHX	pK _a	-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 ₂ Me, SO ₂ Ph

^a As previously reported and defined. ^b Using σ_R^- (CO₂Me) = 0.45, σ_R^- [PO(OEt)₂] = 0.39, σ_R^- (2-py) = 0.42. ^c CO₂Et and COEt are treated as if they were CO₂Me and COMe, respectively. ^d Using σ_R^- (2-C₅H₄N) = 0.42. ^e Using σ_{IB} (CN) = 0.56 instead of 0.43.

dominated by the resonance parameter of the substituent X, acidities of nitrogen acids are dominated by the polar inductive component of the substituent effect (Table 7, entries 4–8) (Figure 2).

Discussion

Ion Pairing and Structural Reorganization in Nitroanions.—

The transformation of nitrogen acids (IV) into nitroanions (VII) causes the variation of all the n.m.r. parameters, as a result of differential structural reorganization promoted by both external and intrinsic factors.

External factors are associated with the nature of the solvent and of the cation. Data from Table 1 provide evidence for ion pairing between the nitroanions and the sodium cation, despite the considerable capacity of Me₂SO in co-ordinating alkali-metal cations,¹⁷ and sodium in particular.¹⁸ Since the [2.2.1] cryptand selectively binds the sodium cation,¹⁹ we believe it disrupts the association of sodium with the nitroanions. The effect of the [2.2.1] cryptand on ¹³C shifts, although discernible, are rather small. Breakdown of the nitroanion-cation association is anticipated to inhibit the dispersion of the negative charge from the negatively charged nitrogen towards the metal ion, thus leaving on the 'naked' anion a large π electron availability free to delocalize on the phenyl ring: in terms of shift variations, the expected result is a highfield displacement of the *para* ¹³C resonance. The prediction is nicely fulfilled for PhNH⁻,

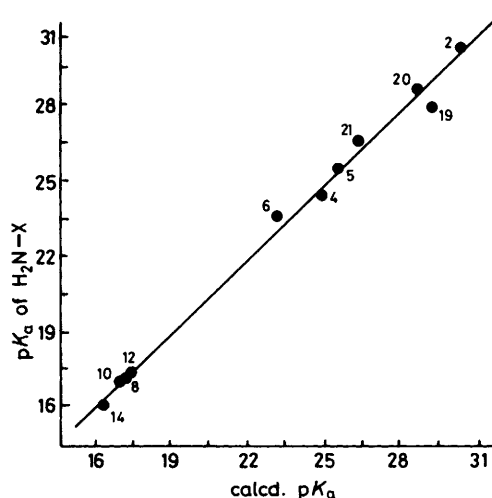


Figure 2. Experimental versus calculated pK_a values of NH₂X: the line refers to entry 7 of Table 7. Numbering of the points follows the arbitrary identification number of the substituents as reported in Table 1

PhN⁻CN, PhN⁻PO(OEt)₂, PhN⁻CO₂Me, PhN⁻SPh, and PhN⁻4-pyridyl but not for PhN⁻COMe and PhN⁻SO₂Me which instead show a lowfield displacement. We have no explanation at present for this result: in view of the structural

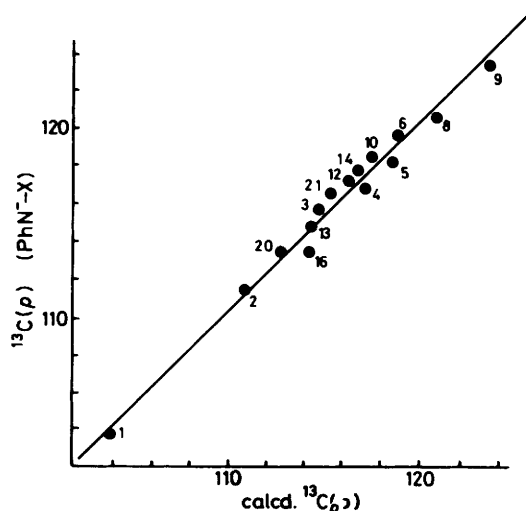


Figure 3. Experimental versus calculated $^{13}\text{C}(p)$ shifts of PhN^-X (Table 7): numbering of the points follows the arbitrary identification number of the substituents as reported in Table 1

complexity of metal amides so far isolated as solvates and adducts,²⁰ any guess concerning the structures responsible for the above n.m.r. variations appears unwarranted. Instead, the large variations found on comparing the shifts of (VII-1) and (VII-2) in THF²¹ and in Me_2SO indicate that tighter aggregation is unequivocally present in THF.

The intrinsic factors affecting the n.m.r. variations undergone by nitroanions (VII) relative to the neutrals (IV) depend on the nature of the substituent X and on its ability to withdraw the negative charge. The variation of the n.m.r. parameters of the aromatic portion offers unequivocal evidence for delocalization of the negative charge on the phenyl ring: in fact, both *ortho* and *para* ^{13}C shifts in anions (VII) are invariably displaced toward high field relative to the neutral precursors. Also, $^3J_{\text{H,H}}$ variations are consistent with extensive structural reorganization: in fact, such couplings in the anions (VII) are more similar to the values presented by benzyl carbanions (VI)²² than to those of their neutrals (IV).¹³ In particular, the $^3J_{\text{m,p}}$ values invariably decrease in the anions relative to the precursors. Although the mechanism of the $^3J_{\text{H,H}}$ coupling is dominated by σ electrons,²³ a decrease of $^3J_{\text{H,H}}$ in aromatic systems has been consistently associated²⁴ with a decrease of the intervening C=C bond order P , according to relationships of the type $^3J = aP + b$.²⁵ Variations of $^3J_{\text{o,m}}$ in the anions relative to the precursors are less informative because they are small and of inconstant sign.

The DSP treatment of the *para* ^{13}C data indicates that the charge transfer from the negatively charged nitrogen atom to the *para* position is dominated by the resonance component of the effects exerted by the substituent X (Figure 3). The response to the resonance component is greatly enhanced in nitroanions (VII) relative to the neutral species (IV).

Instead, the acidity of nitrogen acids PhNHX (IV) and NH_2X (XI) is dominated by the polar-inductive component of the effects exerted by the substituent (entry 7 of Table 7). To ascertain whether substituents endowed with high polar-inductive effects such as the SO_2Me , SO_2Ph , COCF_3 , and CN groups control the treatment affording fitting parameters which could be an artifact, we have repeated the DSP analysis neglecting these points. We have obtained the same result as before (entry 4 of Table 7). The response of α -substituted nitrogen acids and of α -substituted carbon acids¹⁵ to the polar-inductive and mesomeric components of the effects exerted by the substituent are thus just the opposite. The present results indicate that the

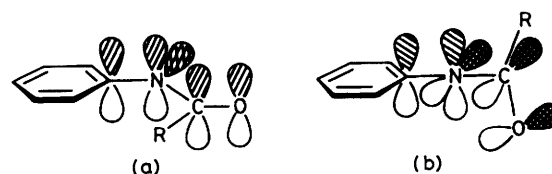


Figure 4. Configurations in nitroanion and π overlap with contiguous substituents

lone pair developing on the nitrogen atom upon deprotonation has limited chances to provide mesomerically an extra stabilization to the anion relative to the neutral. A planar sp^2 configuration for the nitrogen atom with the two electron pairs occupying a p orbital and an sp^2 orbital [Figure 4(a)] appears to be indicated by theoretical *ab initio* studies of NH^-CHO ,²⁶ NH^-CN ,²⁶ and R-NH^- ($\text{R} = \text{alkyl}$).²⁷ If nitroanions (VII) we have studied similarly adopt such a configuration at nitrogen and collinearity of the p orbitals of the phenyl ring, of the nitrogen atom, and of the substituent X (e.g. $\text{X} = \text{COR}$ with $\text{R} = \text{H}$, NMe_2 , OMe , Me , Ph) [Figure 4(a)], the electron pair residing in the sp^2 orbital of nitrogen, while unable to overlap with the p orbital of the substituent, can nonetheless enhance the electron release from the nitrogen atom both to the phenyl and to the substituent. Absence of a direct overlap of the nitrogen sp^2 orbital and of the p orbital of X explains why the acidity of nitrogen acids is only marginally affected by substituents with strong resonance electron-withdrawing power.

Some time ago Stewart and O'Donnell^{7b} suggested an alternative configuration of the nitrogen atom in metal diarylamides: they proposed an sp -hybridized nitrogen whose orthogonal p orbitals, both occupied by electron pairs, would overlap with the p orbitals of the aryl rings, also orthogonal to one another. This arrangement could also be considered [Figure 4(b)], although so far there has been found neither experimental nor computational evidence. However, it would not show accord with our results as good as that of the preceding model. In fact, while it would accommodate the partitioning of the negative charge between the substituent and the aryl ring, it would also support control of the acidity of nitrogen acids by the mesomeric component of the effect exerted by the substituent X.

The Role of the Polar-Inductive Component of the Substituent Effects exerted by Substituent X on the Acidity of Nitrogen Acids.—Since mesomeric interactions between the nitrogen lone pair and the adjacent π system (if any) of the substituent X are already present in the neutral nitrogen acids, stabilization of the nitroanion cannot be provided by electron-withdrawing groups which act predominantly by mesomeric processes. Instead, stabilization can be provided by those functionalities that constitutionally stabilize an adjacent negative charge without, or with very limited, charge transfer. From our investigations on carbanions,²² the most eligible among such groups are the cyano and the sulphonyl functions. Although it has been known for a long time that the sulphonyl and cyano groups enhance dramatically the acidity of adjacent nitrogen acids, this is the first time that it is possible to evaluate and discriminate quantitatively the role of polar-inductive and mesomeric effects of substituents on the acidity of α -substituted nitrogen acids. Although the stabilization effect in nitroanions shows up in the DSP treatment as due to the polar-inductive component, this result should be understood in a wider sense and ascribed to a localized effect as opposed to a mesomeric one, irrespective of whether it involves a purely electrostatic interaction or a localized π bonding between the negatively charged centre and the substituent.

Finally, we note that on the basis of the foregoing discussion it is expected that the monoparametric treatment of NH_2X acidities based on σ_c^- constants should be rather unsatisfactory: indeed the σ_c^- constants have a large mesomeric component and a small polar-inductive component.¹⁵ The prediction is experimentally verified (entries 4–6 of Table 6). In contrast, the acidities of *p*-substituted anilines respond satisfactorily to the monoparametric treatment based on σ_c^- constants (entry 7 of Table 6): the reason why this set of constants, in principle inappropriate for remote interactions, accounts as well for the effects of the substituents is due to the fact it has been anchored to the σ_p^- set of values.¹³

Extrapolations.—Ammonia is less acidic than dimethyl sulphoxide: its $\text{p}K_a$ in this solvent therefore can be only extrapolated. Bordwell has estimated a value of 41:^{2e} our estimates are at least 4–5 $\text{p}K_a$ units lower. Our values originate from two sources, either from the intersystem relationship linking acidities of NH_2X and of PhNHX (entry 7 of Table 5 gives a value of 35.81) or from the DSP treatment of acidities of NH_2X (entry 7 of Table 7 gives a value of 36.36). The obtained values are thus in good accord and for this reason we believe that a value of ca. 36 is more dependable than Bordwell's estimate. Thus, NH_3 is only 1 $\text{p}K_a$ unit less acid than dimethyl sulphoxide: the ready and quantitative formation of sodium dimsyl upon reaction of Me_2SO with sodamide is no doubt associated with the possibility of shifting the equilibrium to the right thanks to the evolution of ammonia from the solution.

Conclusions

While the acidity of α -substituted carbon acids CH_3X and PhCH_2X is dominated by the mesomeric component of the effect exerted by the substituent X, the acidity of α -substituted nitrogen acids NH_2X and PhNHX is dominated by the polar-inductive component of the effects exerted by the substituent. The reason for this different behaviour is identified in the fact that while for carbon acids conjugation of the electron pair on carbon develops only in the final carbanion, for the nitrogen acids conjugation of the nitrogen lone pair with the adjacent substituent is already present in the reactant neutral: thus, stabilization in nitroanions cannot be provided primarily by delocalizative mechanisms involving the substituent. The cyano and the sulphonyl functionalities stabilize α -carbanions through a localized interaction with the adjacent negatively charged centre without involving an appreciable charge transfer: the same mechanism appears to operate also for nitroanions.

The heuristic potentiality of correlative analysis and the validity of the σ_c^- , σ_{IB} , σ_R^- sets of substituent constants is reaffirmed. Accordingly, the $\text{p}K_a$ value of ammonia extrapolated in Me_2SO from the NH_2X – PhNHX intersystem correlation is in agreement with the value obtained from the DSP treatment of NH_2X acidities.

Experimental

Substrates: Source and Numbering.—Nitroanions (VII) were prepared starting from the corresponding nitrogen acids.¹³ As previously,^{15,22} for clarity and conciseness, compounds with a variable substituent X are identified by a roman and an arabic number, the former characterizing the 'family' to which the compound belongs, the latter the substituent X: substituents which have been considered so far are listed in Table 1 of ref. 13a and their number is retained throughout the present and future papers.

Preparation of the Nitroanions and N.m.r. Measurements.—The preparation of the dimsyl solution for n.m.r. experiments

and the preparation of the nitroanions directly in the n.m.r. tubes for ^1H , ^{19}F , and ^{13}C experiments are strictly analogous to those previously described for carbanions.^{22,28} Also, concentrations, internal reference standards, scales, and conversion factors have been reported previously.^{22,28}

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