Electron and charge demands of stabilizing groups in carbanions and nitroanions: the NMR approach

Silvia Bradamante and Giorgio A. Pagani

Dipartimento di Chimica Organica e Industriale dell'Università and CNR, Centro Speciali Sistemi Organici, Via C. Golgi 19, 20133 Milano, Italy

Abstract - Substituent effect treatment of DMSO acidities of families of di-activated carbon acids $XYCH_2$ provide sensitivities and intercepts (methane pK_a) that decrease on increasing the acidity of the parent carbon acid (Y=H). Charge demands q_X of substituents in X_2CH^- and $XYCH^-$ are obtained by applying an improved charge-C(13) shift relationship: the numerical values are smaller than those obtained from benzyl carbanions $PhCH^-X$. These results are interpreted as manifestations of saturation phenomena. The small charge demand of the cyano group is confirmed: steric hampering of resonance is evaluated in carbanions of α-activated phenylacetonitriles and of benzhydryl carbon acids relative to those of substituted acetonitriles and of benzyl carbanions. N(15) shifts of open chain and heterocyclic nitroanions provide a clue for interpreting the dichotomous dependence of shifts from charge: an extraordinary C(13)--N(15) shift relationship and a π charge-N(15) relationship is proposed.

INTRODUCTION

Evaluation of interactions between contiguous functionalities: substituent effect treatment and charge mapping as complementary approaches

In his book Louis P. Hammett states that "the principle (of linear free energy) is concerned with the reactivity of molecules whose structure can be divided into a reacting group X and a non reacting residue R. It asserts that in the absence of strong specialized interactions between R and X....". (ref.1) Although not openly declared it is surmised that this limitation is relative either to steric factors and/or to electronic interactions between proximate functionalities. The investigation whether the above limitation can be circumvented in the latter case has been the topic of our research in the last 8 years (ref. 2-15): in fact, the quantitative knowledge of how and to what extent contiguous functionalities interact is of primary importance in organic chemistry. Our approach has been the following: we have elected the n.m.r. method as structural probe and have chosen systems (A) as models for detecting the effect of the variable functionality X on the contiguous "involved" group G. We have been able to quantify both the mesomeric and the polar-inductive type of interac-

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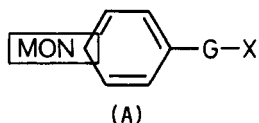
(I)	G = CH_2	(IV)	G = O$^-$
(II)	G = CHPh	(V)	G = N$^-$
(III)	G = NH	(VI)	G = CH$^-$

tions between G and X by monitoring the response of a remote magnetic monitor to the variation of the substituents X. Although the MON = H-1, C-13 and F-19 respond equally well, considerations of relative sensitivities and of product availability tend to prefer as a monitor the C-13 shift. The result of these studies has been the proposal of three scales of electron demands of substituents X: these include primary, aryl-substituted, and heterocyclic functionalities. (i) The σ_{IB} scale (I stands for inductive, B for benzylic) is relative to polar-inductive effects exerted by X on Mon in (I); (ii) the σ_R^- scale (R stands for resonance and the minus specifies it is relative to electron-withdrawing substituents X) is relative to mesomeric effects exerted by X on Mon in (III); (iii) the σ_c^- scale (c stands for contiguous and the minus has the above notation) is relative to the blend of the previous polar inductive and mesomeric effects exerted by X on Mon in (III). Values are reported in Table 1.

The σ_c^- scale is intended to account for the variation of a property in monoparametric rela-
tionships, and the σ_{IB} together with the σ_R- scales are intended for biparametric
relationships. The three scales served to account for variations of n.m.r. properties of
neutral and anionic systems in extrathermodynamic relationships, and for acidities of carbon
acids (in DMSO and in the gas phase), of nitrogen acids (in DMSO), of oxygen acids (in H_2O)
in thermodynamic relationships. It is clear that in thermodynamic relationships the property
monitoring the effect of structural variations of X, far from being remote from G, is instead
just associated with the involved G. Our approach revealed fruitful for understanding the
structural reorganization of carbon and nitrogen acids on their way to conjugate anions.
(ref. 6-8).

As an alternative approach, to improve the Spiesecke and Schneider charge-shift relationship
(1) (ref. 16) originally valid only for cyclic, aromatic, symmetric carbonaceous systems, we
have proposed equation (2) to account for π charge maps also in open chain carbanions and

$$\delta_{\pm}(^{13}C) = \delta_n - 160(q-1) \qquad\qquad eq. (1)$$

$$\delta_{\pm}(^{13}C) = 122.8 + \Sigma A_i - 160(q_C-1) \qquad\qquad eq. (2)$$

(where A_i is the shielding effect exerted by the ith residue, q_C is the
electron density on the trigonal, charged carbon atom).

carbenium ions (ref. 9). Since the generation of a negative π charge occurs whenever the CH
bond of the precursor carbon acid is contiguous to a carbanion stabilizing functionality, the
π electron density q_C residing on the carbanionic carbon is a descriptor of the withdrawing
power exerted by X from the carbanionic centre, and requires to consider the "involved" group
G as a monitor. The charge map approach in carbanions is therefore complementary with that
based on substituent parameters σ_c, and (σ_{IB}, σ_R-).

SATURATION PHENOMENA IN THE METHANE CARBON ACIDS AND
CONJUGATE CARBANIONS DI-SUBSTITUTED BY TWO ELECTRON-
WITHDRAWING PRIMARY FUNCTIONALITIES

A great deal of acidities have been measured in DMSO by F. Bordwell and his students for
di-activated carbon acids $XYCH_2$(1) (ref. 17-19). If X is allowed to vary and Y is kept
constant, it is possible to identify a number of families (Y = Ph, $CONMe_2$, CO_2Et, CN, SO_2Ph,
COPh, NO_2). The σ_c, and the (σ_{IB}, σ_R-) sets of parameters nicely account for the acidities of
the families. More interestingly, the acidity data may be treated assuming additivity of the
effects of substituents X and Y and thus considering the acids $XYCH_2$ as disubstituted
methanes. Equations (3) and (4) are for mono-parametric and di-parametric treatments
respectively (δ is the Leffler-Grunwald operator).

$$\delta p\underline{K}_a = (^X\sigma_c^- + ^Y\sigma_c^-)\, \varrho_c + s \qquad\qquad eq. (3)$$

$$\delta p\underline{K}_a = (^X\sigma_{IB} + ^Y\sigma_{IB})\, \varrho_I + (^X\sigma_R- + ^Y\sigma_R-)\, \varrho_R + t \qquad\qquad eq. (4)$$

Fitting parameters resulting from such treatments are reported in Table 2. It is observed
that on going from Y=Ph to $Y=NO_2$ either ϱ_c or ϱ_R and s or t decrease. On considering that the
already remarkable acidity of nitromethane is much less sensitive to effects of further
electron-withdrawing groups than the relatively weak acidity of acetonitrile (Y=CN, X=H) or
of toluene (Y=Ph,X=H), the decrements of sensitivity and of the values of s or t are clearly
due to saturation phenomena. For X=Y=H, the values of s or t would assume the meaning of the
p$\underline{K}_a$ of methane. It is evident that, because of saturation, such an extrapolation is devoid of
any significance. Both the ϱ and the (s, t) values are linearly related to the acidities of
monosubstituted methane carbon acids (for Y=H, CH_3X) and to the π charge demand of X, q_X
(vide infra). It is possible (ref. 15) to extrapolate from a combination of such
relationships the acidity of methane (p$\underline{K}_a$ in the range 71-73).
Further insights into the saturation phenomenon are obtained from the C-13 spectra of the
conjugated carbanions of the di-activated carbon acids, the acidity of which has been
discussed so far. The first step consisted in treating (ref. 14) with eq. 2 the C-13 shifts
of the carbanionic carbons of carbanions X_2CH^- (2) substituted with two identical groups X:
this gave access to the π electron densities q_C residing on the charged carbons. Such values

TABLE 1. Selected substituent parameters[a,b]

Substituent	σ_C^-	σ_{IB}	σ_R^-
H	0.00	0.00	0.00
Ph	0.47	0.10	0.26
CONMe$_2$	0.70	0.14	0.40
CO$_2$Me	0.74 (0.81)	0.26	0.39 (0.45)
COMe	0.82	0.20	0.47
COPh	0.94 (0.81)	0.21	0.52 (0.47)
CHO	0.98	0.26	0.49
COCF$_3$	1.09	0.58	0.42 (0.36)
NO$_2$	1.27	0.80	0.45
CN	0.88 (0.99)	0.43	0.33 (0.42)
SOMe	0.73	0.40	0.29
SO$_2$Me	0.99	0.59	0.33
SOPh	0.76	0.46	0.26
SO$_2$Ph	1.00	0.62	0.34
PO(OEt)$_2$	0.58 (0.68)	0.19	0.29 (0.38)
2-C$_5$H$_5$N	0.55-0.71[c]	0.12	0.31-0.42[c]
3-C$_5$H$_5$N	0.58	0.15	0.31
4-C$_5$H$_5$N	0.73	0.18	0.45

[a] From ref. 2,7. [b] Numbers in parentheses refer to values to be used with G=0. [c] From ref. 8.

TABLE 3. Pi electron densities on carbanionic carbons and charge demands q_X of electron-withdrawing groups X.

	PhCH$^-$X (3)		X$_2$CH$^-$ (2)	
X	q_{CH}	q_X	q_{CH}	q_X
Ph	1.42	0.29	1.42	0.29
CO$_2$Me	1.47	0.40	1.464	0.268
CONMe$_2$	1.45	0.42	1.45	0.275
COMe	1.38	0.51	1.35	0.325
COPh	1.35	0.56	1.32	0.34
NO$_2$	1.31	0.57	--	--
CN	1.55	0.28	1.586	0.207
SO$_2$Me	1.54	0.27	1.55	0.225
SOPh	1.56	0.26	1.514	0.243
			1.534	0.233
SO$_2$Ph	1.55	0.28	1.588	0.206
PO(OEt)$_2$	1.58	0.26	1.746	0.127
2Py	1.41	0.41	--	--

TABLE 2. Acidities in DMSO of Y-CH$_2$-X carbon acids: fitting parameters for eq. (3) and eq. (4) on varying the nature of Y.

Y	equation (3)				equation (4)				
	ρ_C	s	r[a]	n[b]	ρ_I	ρ_R	t	r[a]	n[b]
Ph	-36.50	66.62	.995	6	-15.49	-47.22	59.58	.986	8
CONMe$_2$	-20.66	49.85	.997	5					
CO$_2$Et	-20.52	46.52	.997	6	-22.75	-27.99	50.14	.997	12
CN	-22.73	42.20	.990	7					
SO$_2$Ph	-18.40	47.90	.981	8	-15.34	-27.53	48.22	.973	7
COPh	-13.19	36.38	.978	8	-11.71	-16.70	34.75	.987	6
NO$_2$	-10.19	30.55	.995	8	- 8.04	-14.92	30.55	.999	8

[a]Correlation coefficient. [b]Number of points, corresponding to the X substituents.

are related to the π charge demands q_X of the activating groups X: $q_X=(2-q_C)/2$. The q_X values are thus identified with the fraction of π charge transferred from the carbanionic carbon to the group X and are therefore a relative measure of the mesomeric electron-withdrawing capacity of electron-poor primary functionalities. These values are reported in Table 3, together with the values obtained for the same groups in benzylcarbanions PhCH$^-$X (3). It is immediately evident that the q_X values in the di-activated X$_2$CH$^-$carbanions are decreased relative to those in the benzyl systems PhCH$^-$X: this result is again interpreted in terms of saturation phenomena. In fact, while the (generally strong) electron-withdrawing group X has to compete with the relatively weak phenyl group in trasferring the negative charge from the carbanionic carbon in PhCH$^-$X, its competitor in X$_2$CH$^-$ is the same strong electron-withdrawing group X. The charge demands therefore are not "universal" constants, but vary from system to system. However, in the carbanions di-activated with the primary functionalities reported in Table 3, the charge demands are additive. This fact, and the predictive potentiality of eq. 2 is manifested in Fig. 1 which compares the experimental C-13 shifts of the charged carbon of carbanions di-activated with non-identical functionalities XYCH$^-$ and the values calculated

$$\delta C(13) = 122.8 + A_X + A_Y - 160 [(2-q_X-q_Y)-1] \qquad \text{eq. (5)}$$

with eq. 2, rewritten in the form (5). Since the q_X value is a measure of the aptitude of the group X to accept by transfer a fraction of πnegative charge from an adjacent carbanionic centre, and conversely the σ_R^- parameter is a measure, relative to the same group X, to entertain mesomeric interactions with an electron pair placed on an adjacent neutral nitrogen
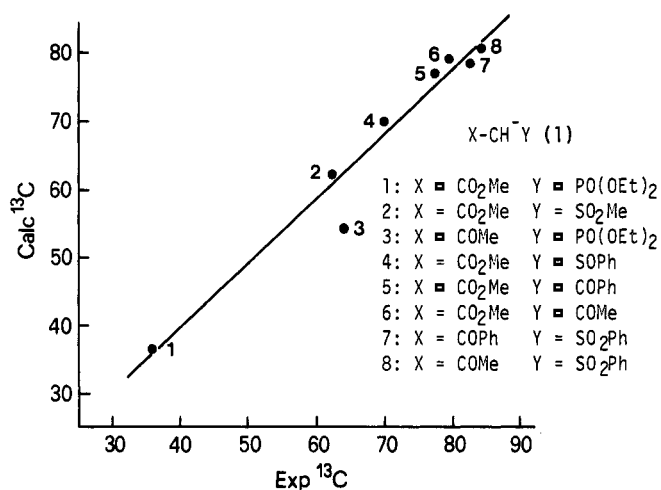
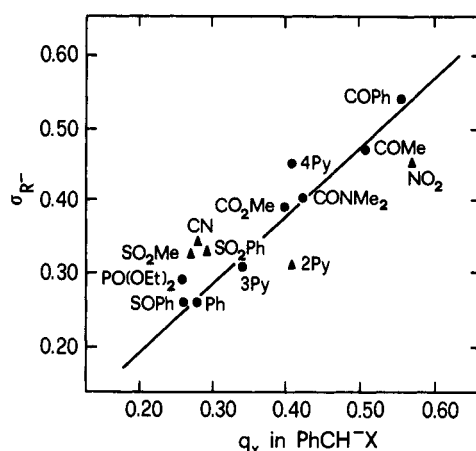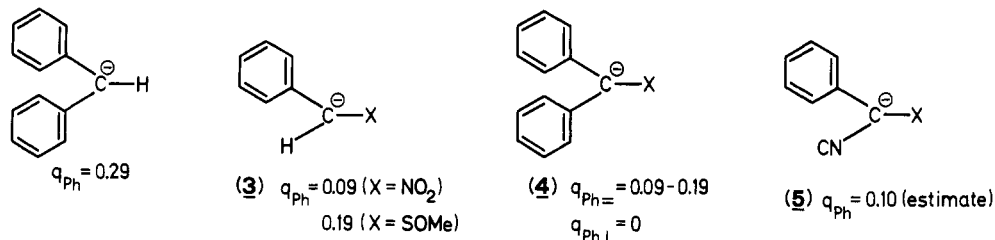Fig. 1. Predictive power of equation (5) for XYCH⁻ systems.

In the figure 1 legend area:

X-CH⁻Y (1)

1: X = CO_2Me Y = $PO(OEt)_2$
2: X = CO_2Me Y = SO_2Me
3: X = $COMe$ Y = $PO(OEt)_2$
4: X = CO_2Me Y = $SOPh$
5: X = CO_2Me Y = $COPh$
6: X = CO_2Me Y = $COMe$
7: X = $COPh$ Y = SO_2Ph
8: X = $COMe$ Y = SO_2Ph

Fig. 2. Plot of charge demands q_X in PhCH⁻X vs mesomeric electron demands of the same groups.

atom, it follows that a relationship of some sort between these two quantities should be expected. Indeed, as Fig. 2 shows, the σ_R- and q_X values are linearly correlated. This result is important because it provides evidence that the two independent approaches, the substituent effect treatment and the charge mapping, are internally consistent.

SATURATION PHENOMENA AND STERIC EFFECTS IN TRI-ACTIVATED CARBANIONS

The C-13 shifts of C(para) in benzyl systems PhCH⁻X do not correlate linearly with C(para) in benzhydryl systems Ph_2C⁻X (ref. 20). The evidence we had in hand (ref. 15) suggested that steric effects were operative in the latter case. To investigate in a quantitative way the aspect of steric inhibition of resonance in carbanions, we explored the possibility of predicting the shift of the carbanionic carbon in trisubstituted systems. We modulated the steric congestion around the carbanionic carbon on considering the benzhydryl carbanions Ph_2C⁻X (4) and the α-substituted phenylacetonitriles PhC⁻(CN)X (5): thus a cyano group, known to exert minimal steric requirements, substitutes in (5) one phenyl group in (4). Since the charge demand of the phenyl group in benzyl carbanions PhCH⁻X (q_{Ph}) is variable on varying X, we assumed, as indicated in the Scheme, an identically variable q_{Ph} for that phenyl group of the two that in the benzhydryl systems was supposed to be coplanar (Ph₌) with the C⁻-X moiety, while for the other phenyl we assumed it was orthogonal (Ph⊥) to the C⁻-X moiety and

Scheme 1

$q_{Ph} = 0.29$

(**3**) $q_{Ph} = 0.09\,(X = NO_2)$
      $0.19\,(X = SOMe)$

(**4**) $q_{Ph=} = 0.09\text{-}0.19$
      $q_{Ph\perp} = 0$

(**5**) $q_{Ph} = 0.10$ (estimate)

consequently we have labelled it with $q_{Ph} = 0$. Thus, the equation that would provide the shift of the carbanionic carbon in benzhydryl systems was rewritten in the form of eq. 6

$$\delta C(13) = 122.8 + 2A_{Ph} + A_X - 160\,[(2\text{-}q_{Ph} - q_X - 0)\text{-}1]\qquad\text{eq. (6)}$$

where q_{Ph} and q_X are the values previously obtained and operative (ref. 6) in the benzyl carbanions. Values of C-13 shift predicted by eq. 6 are plotted vs the experimental ones: a nice linear relationship is obtained as shown in Fig. 3.
Analogously, it was thought that in α-substituted phenylacetonitriles the frame NC-C⁻-X would leave poor chances to the phenyl group to exert fully its delocalizing capacity. Assuming that the copresence of X and CN on the carbanion would behave, owing to saturation phenomena, as a nitro group, we have assigned to the q_{Ph} in (5) the value of 0.10. For the anions of
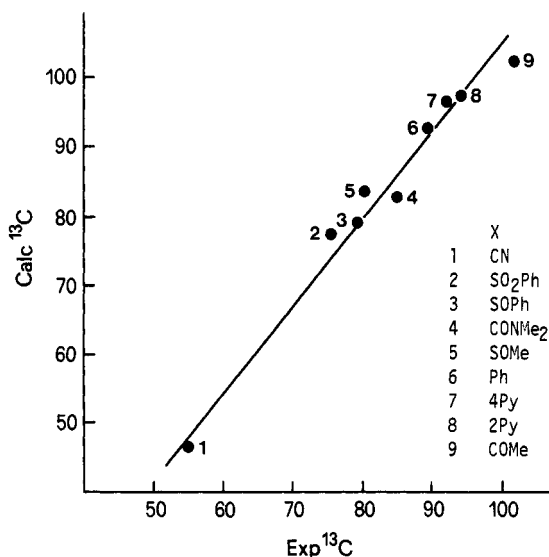
Fig. 3. Predictive power of equation (6) for Ph_2C^--X, where q_X and q_{Ph} are the values for $PhCH^-X$
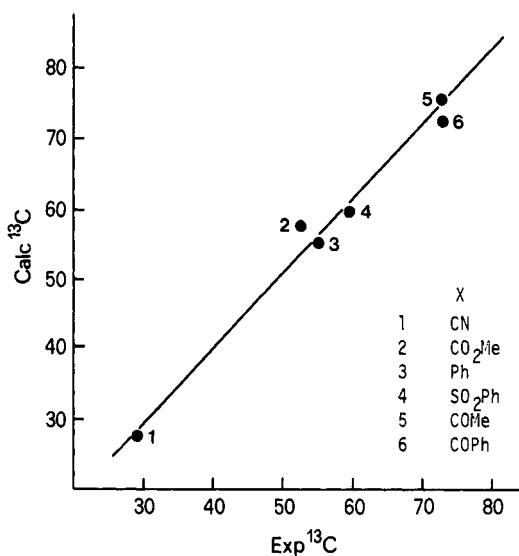
Fig. 4. Predictive power of equation (7) for $PhC^-(CN)X$, where q_{Ph} = 0.10, q_{CN} and q_X as in $CH^-(CH)X$

α-substituted phenylacetonitriles the equation providing the shift of the carbanionic carbon would take the form of eq. 7.

$$\delta_{\pm}C(13) = 122.8 + A_{CN} + A_X + A_{Ph} - 160 \left[(2-q_{CN} - q_{Ph} - q_X)-1\right] \qquad \text{eq.(7)}$$
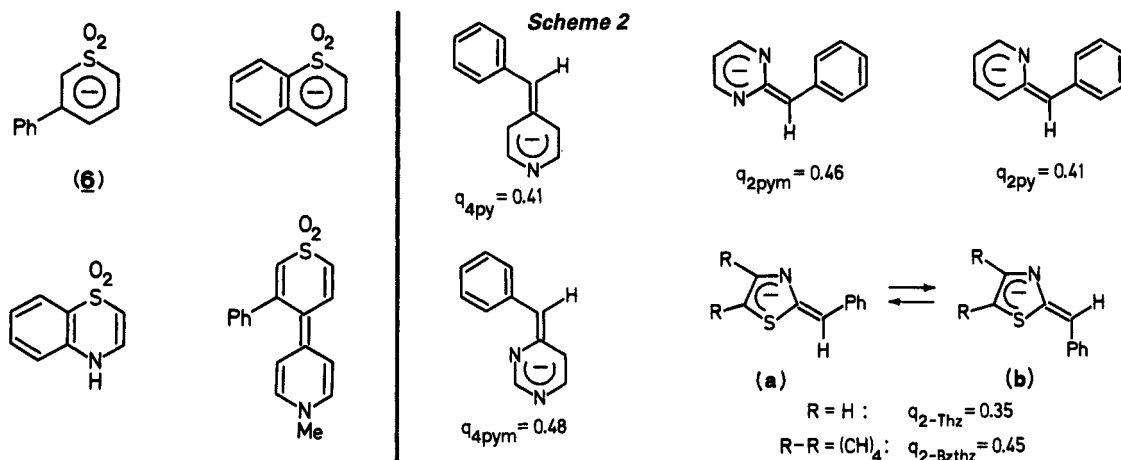
As indicated in Fig. 4, also in this case the plot of the values predicted by eq. 7 and the experimental shifts are nicely linearly correlated.

In conclusion, in trisubstituted carbanions in which at least one of the activating groups has minimal steric requirements (e.g. the CN), no steric inhibition of resonance is evidenced, or at least not larger than in $PhCH^-X$. Instead, in the benzyhydryl systems steric inhibition of resonance is operative: just for the sake of simplicity, we have labelled one phenyl as completely conjugated and the other phenyl group as conjugatively inactive: it is clear that the real system will adopt an average conformation within these two limits.

α-CYANO- AND α-SULFONYLCARBANIONS

One important aspect that remains to be fully appreciated arises when it is considered that the charge demands exerted by the cyano group and by functionalities incorporating second row elements (SO_2R, $O=P(OEt)_2$) are weak indeed. In malononitrile anion almost 60% of the negative charge resides on the carbanionic carbon! As previously discussed (ref. 6), all this indicates that the charge transfer from a carbanionic carbon to the adjacent X of the kind as above is not the primary mechanism of stabilization of the anionic species. A stabilization mechanism in the anion must be nonetheless operative: evidence for this is manifested by the large increase in acidity provided by the cyano group in phenylacetonitrile relative to toluene, even larger than that caused by the methoxycarbonyl group, a functionality that, upon forming an enolate, typically provides stabilization by charge transfer. The cause of stabilization in α-cyano-, α-sulfinyl-, α-sulfonyl-, α-phosphonylcarbanions must be looked for then in the formation of a π bonding between the carbanion centre and the X functionality, with negligible or almost no charge transfer. It is evident that the VB formalism is a poor descriptor of this situation: within such theory, in fact, stabilization of a species is associated and accounted for with mesomerism among different limit structures which are interconnected to one another by electron (and thus charge) transfer. The description of α-cyanocarbanions as keteneimine nitroanions would require some association of the negatively charged nitrogen with cations and its involvement in hydrogen bonding. Absence of effects between protic and aprotic solvents on the acidity of malononitrile (ref. 19) and on the n.m.r. spectra of its conjugate anion (ref. 14) are against such a description.

Evidence for essentially localized π bonding between the carbanionic carbon and an adjacent cyano (ref. 21), sulfonyl (ref. 22), and sulfinyl (ref. 23) group have been provided by beautiful crystallographic investigations carried out independently by Gais and by Boche: their results essentially confirm the suggestions forwarded by the n.m.r. work (ref. 6). Almost 15 years ago, in connection with the exceptional, aromatic-like stability of thiin-1,1-dioxide anion (6) (ref. 24) and its benzo-congeners (ref. 25), we approached the problem of bonding in α-sulfonyl carbanions by evaluating the X-ray structures of some aza-analogs of the carbanions (ref. 26). In every case a strengthening of the SO_2-C bond and a slight involvement of the S-O bond was found, in strict analogy with the more recent Gais and Boche results.

Scheme 2

$q_{4py} = 0.41$

$q_{2pym} = 0.46$

$q_{2py} = 0.41$

$q_{4pym} = 0.48$

(6)

(a)   (b)

R = H : $q_{2-Thz} = 0.35$

R-R = (CH)$_4$: $q_{2-Bzthz} = 0.45$

HETEROCYCLIC AZINES AND AZOLES AS ELECTRON-WITHDRAWING GROUPS

Despite the universally accepted classification of heteroaromatics in π-excessive and π-deficient systems, a quantitative ranking in only partially available (ref. 27) or missing at all. The study of benzyl anions PhCH$^-$X in which X is either a pyridyl, pyrimidyl, pyrazinyl, or pyridazinyl ring has ascertained that these heteroaromatics do stabilize very efficiently a contiguous carbanionic center by mesomeric mechanisms. Substantial negative charge is transferred from the carbanionic centre to the heterocycle, involving high π bond character of the bond connecting these two sites. As a consequence geometrical isomerism of the anions may exist, simultaneously with room temperature shift non equivalence (ref. 20).

The n.m.r. evidence (comparison with spectra of specially tailored methyl derivatives, coupling constants, and NOE esperiments) supports the preference for the geometrical isomer in which the phenyl group is <u>cis</u> to the nitrogen atom, as shown in Scheme 2. In the case of benzylanions of diazines, saturation phenomena are again present, as it is shown by the small increase of the charge demands of 2- and 4-pyrimidyl groups relative to the 2- and 4-pyridyl groups, which instead are sizeably incremented relative to the phenyl group (q_{Ph} = 0.29 in diphenylmethane).

NITROANIONS: RESPONSE OF N-15 SHIFTS TO σ AND π CHARGE

Relative to the neutral precursors, N-15 shifts of nitroanionic species derived from aromatic and heteroaromatic amino- and amido functionalities are present at lower fields (Table 4). Instead, the N-15 shifts of the pyridyl nitrogen in carbanionic and nitroanionic species in which the pyridyl nitrogen is conjugated with the anionic centre, is displaced towards high-field. This dichotomous behaviour is interpreted on considering that the generation of a negative charge (electron pair) in an sp^2 orbital of a trigonal nitrogen causes a low-field shift, while an increment in the π electron density on a trigonal nitrogen with the electron pair residing in the p orbital causes a high-field displacement. Two facts support this interpretation. (a) The low-field suffered by the N-15 nitrogen of pyrrole upon formation of the nitroanion, displacement that cannot be ascribed to any pyramidal $\longrightarrow$ trigonal rehybridization. (b) The high-field shift of N-15 of pyridine upon formation of the pyridinium ion: in this latter case the displacement is due both to the disappearance of the sp^2 lone pair and to the increase of π electron density on nitrogen as resulting from an augmented π withdrawl of this atom from the ring. Recognition that an electron pair is

generated in an sp^2 orbital upon deprotonation of activated nitrogen acids of the type NH$_2$X and PhNHX beautifully explains the different sensitivities of nitrogen acids relative to carbon acids. In fact, sensitivities of carbon acids CH$_3$X and PhCH$_2$X and of analogous nitrogen acids NH$_2$X and PhNHX to polar-inductive and mesomeric effects exerted by substituents X are just opposite: while acidities of carbon acids are dominated by the mesomeric effects exerted by X (ref. 7), acidities of nitrogen acids are dominated by the polar-inductive effects exerted by X (ref. 8). The nitroanion sp^2 electron pair has not the right symmetry for being delocalized onto X and thus does not participate directly by a mesomeric mechanism to the stabilization of the nitroanion: instead, polar-inductive interactions with the contiguous functionality X will be primarily responsible for acidity variations. Substitution of a N-H bond with and sp^2 electron pair will decrease the electron demand of nitrogen: as a consequence, the electron pair sitting in the p orbital of a trigonal nitrogen of a nitroanion will be more available for delocalization on π acceptor groups. The high-field shift experienced by the pyridyl N-15 nitrogen shift on going from 2- and 4-aminopyridine to the corresponding nitroanions should be interpreted in the above terms, as an indirect release of the p-π electron pair of the anionic nitrogen.

Quantitative relationships between N-15 shifts and π electron density residing therein have been previously proposed (ref. 28): their variable success depended upon the sophistication of the calculation providing the π electron density. In fact, while the sensitivity of C-13 to π electron density has been directly obtained, without the need of any MO calculation, simply by plotting experimental shift variations vs the total π charge residing on cyclic symmetrical aromatic ions divided by the number of trigonal carbon atoms, in the case of nitrogen heteroaromatics, because the π electron density is unevenly distributed between nitrogen and carbon atoms, the nitrogen π charge densities must originate from theoretical calculations.

The theoretically expected linear dependence of N-15 shifts from π electron density is experimentally warrented by the extraordinary C(13)-N(15) shift linear relationship reported in Fig. 5: the straight line can be expressed analytically in the form of eq.(8) and is

$$\delta N(15) = 2.275 \, \delta C(13) -77.41 \quad (r = 0.994) \qquad \text{eq. (8)}$$

obtained by plotting C-13 shifts of carbocycles and heterocycles vs the shifts of N-15 atoms occupying analogous positions of correspondingly isoelectronic and isostructural aza-systems. The relationship of eq.(8) is also particularly important because it documents, on an experimental and quantitative basis, the several times declared analogy of cyclopentadienyl

Table 4. ^{15}N Chemical shifts of nitroanions sodium salts and their precursors .

Compound[b]	State[c]	$\delta_{N(amine)}$	Δ[d]	$\delta_{N\ (py)}$	Δ[d]
Ph-NH$_2$	N	58.2			
	A[e]	124.8	+66.6		
2-NH$_2$py	N	72.8		265.7	
	A	146.5	+73.7	246.0	-19.7
4-NH$_2$py	N	67.8		275.0	
	A	150.0	+82.2	234.3	-40.7
PhNHCOMe	N	133.0			
	A[e]	206.4	+73.4		
2-PhCH$_2$py	N			314.5	
	A			256.2	-58.3
4-PhCH$_2$py	N			309.0	
	A			212.4	-96.6
Pyrrole	N	154.1			
	A	239.0	+84.9		

[a]Nitrogen shielding relative to liquid NH$_3$(0.0 ppm), 380.23 ppm from neat nitromethane; [b] py= pyridine; [c]N = neutral: Me$_2$SO-d$_6$ solution 1M in substrate, A = anion: Me SO$_2$solution 0.5M in substrate, 1M in base; [d] Δ = δ(anion)-δ(neutral): positive values represent lowfield displacements; N(15)-enriched substrate used for the anionic solution.
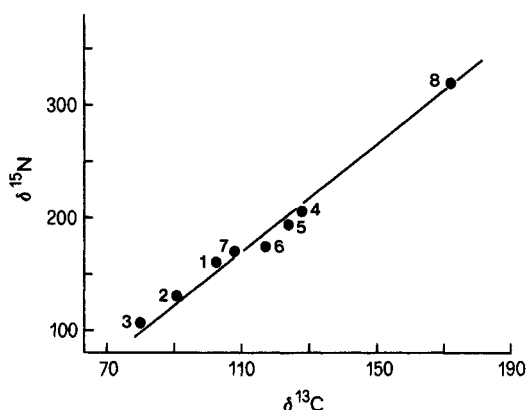

Fig. 5 Plot of C(13) vs N(15) shifts of isoelectronic and isostructural aza-systems. Points are as follows.

C-13:
1, cyclopentadienyl anion;
2, C-1(C-3) of indenyl anion;
3, C-9 of fluorenyl anion;
4, benzene;
5, C-3 of pyridine;
6, C-2 of N-Me-pyrrole;
7, C-3 of N-Me-pyrrole;
8, C-1 of Ph-Li.

N-15:
1, pyrrole;
2, indole;
3, carbazole;
4, pyridinium ion;
5, NH of pyrimidine monocation;
6, NH of N-Me-pyrazolium;
7, NH of N-Me-imidazolium;
8, pyridine.

Scheme 3

Charge maps in 2- and
4-benzylpyridine carbanions.

$$Q_{Ph} = 6.179; \quad \Sigma q^{\pi} = 13.962 \qquad Q_{Ph} = 6.185; \quad \Sigma q^{\pi} = 14.005$$
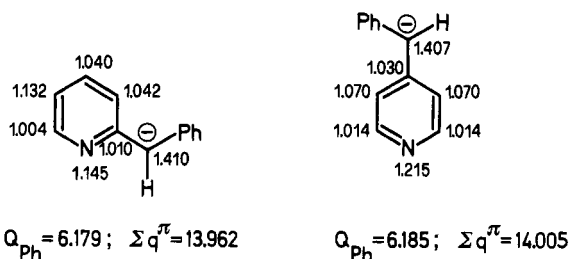
anion and pyrrole, indenyl anion and indole, fluorenyl anion and carbazole, phenyl lithium
and pyridine, benzene and pyridinium ion. Equation (8) does not provide however the
sensitivity of N-15 from π-electron density. The best theoretical approach to π-electron
densities appears to be provided by Fliszar (ref. 29) for the series of pyridine, pyrimidine,
pyrazine, and sym-triazine. Accordingly, eq. (9) would results. If both eq. (2) and eq.(9)

$$\delta N(15) = 347.35 - 626.76 (q_N - 1) \qquad\qquad \text{eq. (9)}$$

are applied to the C-13 and N-15 shifts of 2- and 4-benzylpyridine carbanions, the charge
maps reported in Scheme 3 are obtained. It is rewarding to note that the total number of
π-electrons Σq obtained upon summation of the local π-electron densities is extremely close
to the theoretical values of 14 e⁻, simply obtained by adding the electron pair of the
carbanion to the 12 π electrons of the two rings.

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