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Geometric Isomerism in Substituted 4-Picolyl Carbanions: A Probe for Ranking the Charge Demands of Electron-Withdrawing Groups

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Chain-substituted 4-picolyl carbanion sodium salts were prepared in DMSO and their ^{13}C NMR spectra investigated to monitor the competitive partitioning of the negative charge between the substituent and the pyridyl ring. The anisochrony of C(3) and C(5) carbon atoms of the heterocycle in the Ph-, PhS-, CN-, and PhSO-substituted carbanions 1^-–4^- probe the double bond between the carbanionic carbon and C(4) of the ring. Rotation about this bond is slow in sulfone and ester anions 5^- and 6^-. Because of the likely predominance of an enolate structure, the rotation is fast in the PhCO-substituted system 7^-, and therefore C(3) and C(5) of the pyridyl ring are isochronous. The extent of charge partitioning, and thus the double-bond character of the bond between C(4) and the carbanionic carbon, is dominated by the charge demand (c_X) of the substituent, defined as the fraction of π charge delocalized by group X. Previously reported π charge–^{13}C shift relationships (e.g., eq 4) incorporating the charge demands of the substituents are used to calculate the ^{13}C chemical shifts of the carbanionic carbon. The calculated and the experimental values compare very favorably.

It is commonly accepted[1] that charge delocalization is responsible for much of the intramolecular stabilization of trigonal carbanions. Physical and structural[2] evidence for delocalization is usually supplied by a change in the bond order of the atoms involved in the deprotonated site, as well as in those adjacent to, or conjugatively associated with, it. Observation of geometric isomerism about a bond is experimental validation of its high double-bond character, and therefore proof of delocalization. Delocalization has been associated with geometrical isomerism in substituted allyl,[3] 1-azaallyl,[4] 2-azaallyl,[5] dienyl,[6] and benzyl anions,[7] enolates,[8] α- and γ-*aza*heteroaryl-substituted carbanions,[9–15] and in nitranions.[16] To undergo enantioselective reactions with electrophiles,[17] a carbanionic carbon atom must be joined to an adjacent group with a high double-bond character. In addition, the barrier to free rotation has been used to characterize the π deficiency of heterocycles.[18]

The 4-pyridyl moiety is a strong electron-withdrawing group which provides considerable stabilization to adjacent carbanionic centers. This is confirmed by the high DMSO acidity of 4-picoline[19] and 4-benzylpyridine,[19] as well as by the high value of its charge demand c_X, defined as the fraction of the π charge withdrawn by a group X adjacent to the carbanionic center.[13,20–22] In picolyl carbanions, the high double-bond character of the bond between the

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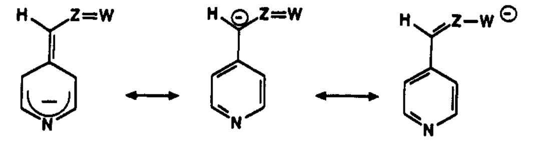
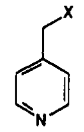
carbanionic carbon and the carbon atom of the ring is confirmed by the NMR anisochrony of the methylene protons of the 2-picolyl carbanion,[9] and by that of the C(3) and C(5) ^{13}C shifts in the anion of 4-benzylpyridine.[13,15] In the presence of an electron-withdrawing substituent X in ω-substituted 4-picolyl carbanions [(**B**): X = Z═W], the negative charge is competitively distributed between the pyridyl ring and the group X. When the charge demand of substituent X at the carbanionic center is increased, the double-bond character of the bond between the carbanionic carbon and C(4) of the heterocycle can be expected to decrease. Consequently, the rotational barrier around such a bond should also progressively decrease. For substituents with a charge demand higher than that of the 4-pyridyl group, anisochrony of carbons C(3) and C(5) of the heterocycle is expected to disappear.

We use a 4-pyridyl ring as a probe to monitor the relative contributions of the limiting resonance structures **A** and **C** in the description of ω-substituted picolyl carbanions **B**.



(A) (B) (C)

We report ^{13}C NMR results concerning the anisochrony of C(3) and C(5) in carbanions 1^-–7^- in which the electron-withdrawing capacities of the substituents have been varied from the low-ranked PhS to the highly efficient PhCO group.



(1) : X = SPh
(2) : X = Ph
(3) : X = CN
(4) : X = SOPh
(5) : X = SO$_2$Ph
(6) : X = CO$_2$Et
(7) : X = COPh

According to our treatment of ^{13}C shifts of trigonal carbanions,[14,20-23] eq 1 relates the actual ^{13}C shift of the carbanionic carbon to its π electron density q_C, the ^{13}C shift of ethene (122.8 ppm), and the shielding contributions A_i of the various substituents directly bonded to the anionic site.

$$\delta^{13}\mathrm{C} = 122.8 + \sum A_i - 160(q_C - 1) \qquad (1)$$

The π electron density q_C on the carbanionic carbon is equal to 2 (the electron pair) minus the fraction of π charge withdrawn from this carbon by the substituents directly bonded to it. The fraction of π charge withdrawn by a group X from the carbanionic center was defined as the charge demand c_X[14] (previously[20-22] denoted as q_X). It therefore derives that

$$q_C = 2 - \sum c_X \qquad (2)$$

Table I. Shielding Contributions A_i and Charge Demands of Various Groups

X	A_i[a]	$c_{\mathrm{X}}^{\mathrm{Ph}\,a}$	$c_{\mathrm{X}}^{\mathrm{X}\,b}$
Ph	13.00	c	0.29[d]
CONMe$_2$	5.88	0.42	0.275
CO$_2$Me	6.20	0.40	0.268
CO$_2$Et	6.00	0.40[e]	0.268[e]
COMe	14.90	0.51	0.325
COPh	9.30	0.56	0.341
CN	−14.60	0.28	0.207
SPh	9.4[f]	0[g]	0[g]
SOPh	20.18	0.26	0.233
SO$_2$Ph	17.46	0.28	0.206
PO(OEt)$_2$	3.95	0.26	0.122
Me$_3$N$^+$	20.5[h]	0[g]	0[g]
2-Py[i]	13.82	0.411	0.278[j]
4-Py	12.70	0.408	0.277[j]
2-Pym[k]	13.90[l]	0.430[l]	0.286[j]
4-Pym	10.50[l]	0.501[l]	0.318[j]
3-Pyd[m]	11.50[l]	0.417[l]	0.281[j]
Pyz[n]	10.50[l]	0.446[l]	0.294[j]

[a] From ref 20 if not otherwise noted. [b] From ref 22 if not otherwise noted. [c] In PhCH$^-$X (ref 20) the average charge demand of the phenyl ring $c_{\mathrm{Ph}}^{\mathrm{Ph}}$ is 0.175 ± 0.053. [d] In diphenylmethane. [e] The same value of the corresponding methyl ester is assumed. [f] Obtained by using the value of 132.18 ppm of C(1) of PhSCH═CH$_2$ (Reynolds, W. F.; McClelland, R. A. *Can. J. Chem.* **1977**, *55*, 536–540). [g] Theoretical value when no π charge delocalization occurs. [h] Obtained by using the value of 143.3 of C(1) of Me$_3$N$^+$CH═CH$_2$ (ref 30, p 295). [i] 2-Pyridyl. [j] Obtained by interpolation of the straight line of eq 3 and using the corresponding $c_{\mathrm{X}}^{\mathrm{Ph}}$ values. [k] 2-Pyrimidyl. [l] From ref 14. [m] 3-Pyridazinyl. [n] Pyrazinyl.

Experimental access to charge demands was obtained by applying the previously described extended π charge–^{13}C shifts relationship.[20-23] The values of the substituent charge demands depend on the system studied. The study of benzyl carbanions PhCH$^-$X originated[13,14,20,21] the $c_{\mathrm{X}}^{\mathrm{Ph}}$ values, whereas the study of symmetrically diactivated carbanions $^-$CHX$_2$ (X = COR, CO$_2$R, CN, SO$_n$R, NO$_2$, etc.) originated[22] the $c_{\mathrm{X}}^{\mathrm{X}}$ values. In charge demand notation, the subscript identifies the group and the superscript identifies the system (benzylic or symmetrically disubstituted): e.g., $c_{\mathrm{CN}}^{\mathrm{Ph}}$ is the charge demand of the cyano group in PhCH$^-$CN, whereas $c_{\mathrm{CN}}^{\mathrm{CN}}$ is the charge demand in $^-$CH(CN)$_2$. The $c_{\mathrm{X}}^{\mathrm{X}}$ values are smaller than the $c_{\mathrm{X}}^{\mathrm{Ph}}$ values because of saturation phenomena,[21,24] the two sets of values being linearly related through eq 3.[22]

$$c_{\mathrm{X}}^{\mathrm{Ph}} = 2.216c_{\mathrm{X}}^{\mathrm{X}} - 0.205 \qquad (n = 8, r = 0.990) \qquad (3)$$

In addition, charge demands may be further decreased because of resonance inhibition due to steric effects, as in trisubstituted systems such as Ph$_2$C$^-$X.[24] Anions 1^-–7^- are a special case of diactivated disubstituted carbanions $^-$CHXY[22] in which Y = 4-pyridyl. To predict the ^{13}C shift of their carbanionic carbon using the charge demands of the substituents, eqs 1 and 2 must be applied. Accordingly, eq 1 is rewritten in the form of eq 4: Table I shows the A_i, $c_{\mathrm{X}}^{\mathrm{X}}$, and $c_{\mathrm{X}}^{\mathrm{Ph}}$ values.[13,14,20,22] As before,[20] A_i values reported for the first time have been obtained from the shift difference of the values of C(1) of XCH═CH$_2$ and ethylene (122.8 ppm).

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Table II. ^{13}C NMR Shifts[a] of ω-Substituted 4-Picolines $PyCH_2X$ and Conjugate Carbanions in DMSO[b]

			pyridine ring positions							
compd	X	state[c]	2[d]	3[d]	4	5	6	Cα	^1J/Hz[e]	other groups
1	SPh	N	149.52	123.76	146.82	123.76	149.52	35.40	142.0	C_i = 135.02; C_o = 128.66; C_m = 128.98; C_p = 126.18
		A	145.21	106.50	153.98	111.16	146.64	51.44	173.2	C_i = 147.08; C_o = 123.55; C_m = 127.76; C_p = 122.07
2	Ph	N	149.71	124.17	150.12	124.17	149.71	40.30	128.0	C_i = 139.60; C_o = 128.94; C_m = 128.68; C_p = 126.45
		A[f]	147.68	106.03	145.09	114.75	145.22	83.65	146.4	C_i = 144.11; C_o = 120.06; C_m = 127.63; C_p = 112.41
3	CN	N	150.30	123.41	140.61	123.41	150.30	22.30	138.2	CN = 118.29
		A	146.76	110.60	153.93	111.71	147.24	39.47	165.0	CN = 130.79
4	SOPh	N	149.11	124.16	138.85	124.16	149.11	59.61	143.0	C_i = 142.61; C_o = 125.29; C_m = 128.89; C_p = 130.99
		A	147.15[g]	107.94[g]	151.32	112.57[g]	147.15[g]	77.01	166.2	C_i = 152.10; C_o = 125.10; C_m = 127.72; C_p = 127.29
5	SO_2Ph	N	149.51	125.75	137.56	125.75	149.51	59.93	142.0	C_i = 137.96; C_o = 127.97; C_m = 129.20; C_p = 134.07
		A[h]	147.12	111.72[g]	149.34[i]	111.72[g]	147.12	69.54	167.2	C_i = 150.46;[i] C_o = 124.27; C_m = 127.81; C_p = 128.61
6	CO_2Et	N	149.47	124.69	143.19	124.69	149.47	39.41	130.4	CO = 170.00; CH_2 = 60.47; CH_3 = 13.92
		A	147.01[g]	114.37[g]	151.95	114.37[g]	147.01[g]	69.75	153.7	CO = 166.66; CH_2 = 54.94; CH_3 = 15.53
7	COPh	N[j]	149.28	125.37	144.14	125.37	149.28	43.84	128.7	CO = 196.52; C_i = 136.13; C_o = 128.24; C_m = 128.74; C_p = 133.46
		A[j]	147.69	117.18	150.29[k]	117.18	147.69	87.76	149.3	CO = 173.36; C_i = 146.16;[k] C_o = 125.86; C_m = 127.08; C_p = 126.52

[a] Relative to Me_4Si (0.0 ppm). [b] 0.5 M solutions at 25 °C. [c] N for neutrals and A for anions. [d] Cis positions in respect to substituent X in anion isomers. [e] Relative to the benzylic methylene or methine group. [f] Reference 13. [g] Broad signals. [h] 50 °C. [i] Values can be exchanged. [j] 0.25 M solutions. [k] Values can be exchanged.

$$\delta^{13}C = 122.8 + A_X + A_{4\text{-Py}} - 160(1 - c_{4Py}^{4Py} - c_X^X) \quad (4)$$

Thanks to the possibility of C(3) and C(5) ^{13}C NMR anisochrony, we show that in ω-substituted 4-picolyl carbanions the pyridyl ring is a probe for delocalization which is efficient, experimental, and independent of any current model, and that it can qualitatively rank the resonance component of the electron-withdrawing capacity of various organic functionalities. We also show that the extent of charge partitioning (and thus the double-bond character of the bond between C(4) and the carbanionic carbon) is quantitatively dominated by the charge demand c_X of the substituent. The computed ^{13}C shifts of the carbanionic carbon, which are controlled by the charge demands c_X of the substituents, compare excellently with experimental values.

Results

Carbanions 1^-–7^- were generated in DMSO by deprotonation of the corresponding carbon acids with dimsylsodium. At the beginning of our investigations into carbanions, DMSO was chosen as a solvent because of its merits as a highly dissociating medium[25] and as a good coordinating system for the sodium cation.[26] Furthermore, we wanted to anchor our NMR results[27] to the equilibrium data obtained in this solvent by Bordwell.[19] We have already explained and documented[20,21,23] the reasons for our choice. However, the many merits of DMSO are offset by the instability of its conjugate base above 60 °C[28] and by the fact that its high melting point prevents low-temperature NMR studies.

The ^{13}C NMR data of precursor carbon acids and the corresponding carbanions are reported in Table II. The ^{13}C NMR spectra of anions 3^-, 6^-, and 7^- are shown in Figure 1a–c. The variable, substituent-dependent double-bond character between the carbanionic carbon and C(4) of the heterocycle is proved both by the data of Table II and by the spectra of Figure 1. Substituent charge demands increase along the series 1^-–7^-. Substituents with a weak charge demand (PhS, Ph, CN) give rise to sharp resonances for the anisochronous C(3) and C(5) of the pyridyl ring in the corresponding anions 1^-–3^-. The broadening of the two peaks due to C(3) and C(5) in 4^- clearly indicates that, in comparison with 1^-–3^-, rotation around the CH^-–C(4) bond is becoming faster on the NMR time scale. In carbanions 5^- and 6^- rotation is sufficiently fast to induce the merging of C(3) and C(5) resonances

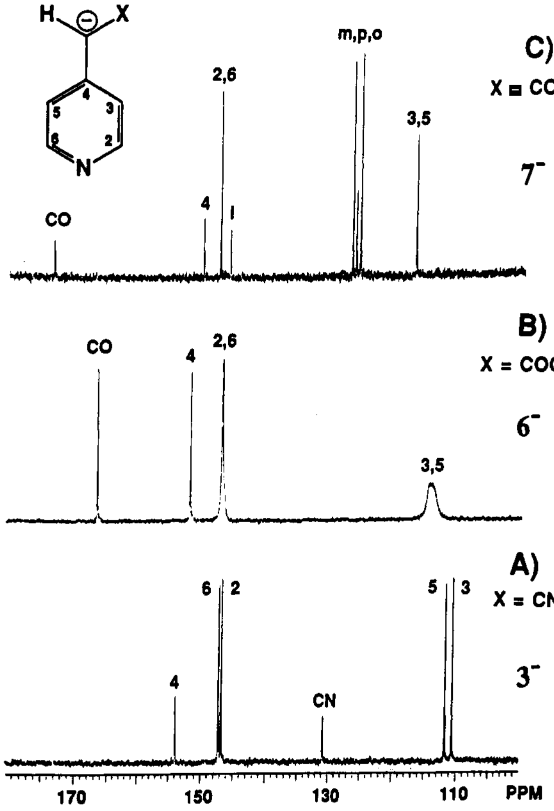

Figure 1. Aromatic region of the ^{13}C NMR spectra of ω-substituted picolyl carbanions in DMSO (T = 27 °C). When anisochrony of C(3) and C(5) and C(2) and C(6) occurs (case A: X = CN), the high-field peaks are assigned to carbon atoms cis to the substituent. i = ipso carbon of the PhCO group.

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into one broad peak. Finally, free rotation along this bond occurs in anion 7^-. Figure 1a–c shows the whole range of these different situations. The spectrum of 3^- is representative of the frozen situation A, while the spectrum of 6^- provides evidence for a slow exchange between the two structures A and C. The spectrum of 7^- shows that rotation around the 4-pyridyl carbon–carbanion carbon bond is rapid and, given the overwhelming evidence[8] that α-keto carbanions have an enolate structure, it seems reasonable to describe anion 7^- as one of the enolates 7C.

Assignments of C(3) and C(5) resonances in anion 2^- were based on well-founded stereochemical arguments.[13] The data agree with the compression effect[15,29] according to which the phenyl ring exerts a high-field displacement of the carbon atom of the pyridyl ring cis to it. Such a compression effect is also provoked by the cyano group. Indeed, the methyl ^{13}C resonance in (*Z*)-crotonitrile is at a higher field (17.5 ppm) than that in (*E*)-crotonitrile (19.1 ppm).[30] On the basis of these and our previous[13] results, we assume that the compression effect is also operative, and in the same direction, in carbanions 1^-, 3^-, and 4^-, thus giving rise to the anisochronous C(3) and C(5) ^{13}C resonances of the pyridyl ring.

To compute the ^{13}C chemical shifts of the carbanionic carbon in 1^-–7^-, we need to know the charge demands c_X of the pyridyl ring and of the various substituents X. The charge demands for the pyridyl substituents have been reported[20] only as c_{Py}^{Ph} for the benzyl carbanions series. We obtained the c_{Py}^{Py} values for the 2- and 4-pyridyl groups (0.278 and 0.277, respectively) from eq 3 using[20] $c_{2Py}^{Ph} = 0.411$ and $c_{4Py}^{Ph} = 0.408$. We used the c_X^X values of Table I for the substituents X in 2^-–7^-. Shift computation in the case of carbanion 1^- is somewhat different because the charge demand c_X^X of the PhS substituent is not experimentally available. Equation 5 can be obtained from eq 1 by substituting q_C with eq 2 where $c_X = c_{PhS}^{PhS}$. Applied

$$\delta^{13}C = 122.8 + 2A_{PhS} - 160(1 - 2c_{PhS}^{PhS}) \qquad (5)$$

to $(PhS)_2CH^-$, this should have provided us with c_{PhS}^{PhS}. However, both eqs 1 and 5 require the carbanionic carbon to be trigonal, whereas NMR evidence shows that the carbanion center in $(PhS)_2CH^-$ is tetrahedral.[31] Various theoretical reports[32] indicate that the considerable increase in the acidity of carbon acids due to the presence of arylthio and alkylthio groups[33] is not primarily associated with charge delocalization onto the sulfur atom but rather to polarizability effects of the sulfur atom. In deference to these theoretical indications, we assigned a zero charge demand value for the PhS group ($c_X^X = 0$) in anion 1^-, thus ensuring that the PhS group could not compete with the pyridyl ring in delocalizing the charge. Consequently, the "saturated" value $c_{4Py}^{4Py} = 0.277$ for the charge demand of the pyridyl group was unsuitable and we used the "full" value $c_{4Py}^{Ph} = 0.408$, as obtained from the benzyl anion series $PhCH^-X$. The computed ^{13}C chemical shifts of the carbanionic carbon in 1^-–7^- are reported in Table III, together with the π electron densities q_C on the carbanionic carbons. Figure 2 shows the calculated shifts plotted against the experimental shifts ($\delta^{13}C_{calcd} = (0.947 \pm 0.045)\delta^{13}C_{exp} + (2.123 \pm 0.731)$, $r = 0.994$, $n = 7$).

Table III. Comparison of Experimental and Computed ^{13}C NMR Shifts of the Carbanionic Carbon in ω-Substituted 4-Picolyl Anions and Computed π Electron Densities q_C on the Carbanionic Carbon

X	computed	exptl	q_C
SPh	50.50[a]	51.44	1.584
Ph	79.22	83.65	1.405
CN	38.34	39.47	1.509
SOPh	77.28	77.01	1.492
SO_2Ph	70.24	69.54	1.521
CO_2Et	68.70	69.75	1.448
COPh	83.68	87.76	1.356

[a] Using the full value of $c_{4Py}^{Ph} = 0.408$.

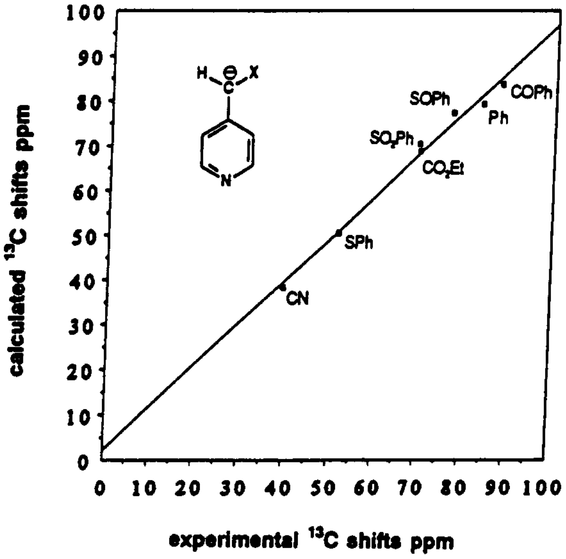

Figure 2. Plot of experimental vs calculated ^{13}C shifts of the carbanionic carbon in ω-substituted picolyl carbanions $4\text{-}PyCH^-X$. [$\delta^{13}C_{calcd} = (0.947 \pm 0.045)\delta^{13}C_{exp} + (2.123 \pm 0.731)$, $r = 0.994$, $n = 7$].

Discussion

Our results clearly indicate that delocalization of the negative charge in ω-substituted 4-picolyl carbanions 1^-–6^- is associated with a variable degree of double-bond character between the carbanionic carbon and the C(4) of the pyridyl ring. This behavior is shown not only by those substituents which are commonly recognized as poor resonance acceptor (PhS, Ph, PhSO, $PhSO_2$) but also by those which are reasonably good (CO_2Et, CN). The resonance hybrid structure of the enolate 7C is preferred because the negative charge is predominantly delocalized onto the oxygen atom of the strong electron-withdrawing benzoyl group.

NMR revealed that geometric isomerism is consistent with the trend of the charge demands previously assigned to the functionalities present on the carbanionic center. This agreement is quantitative, since the incorporation of

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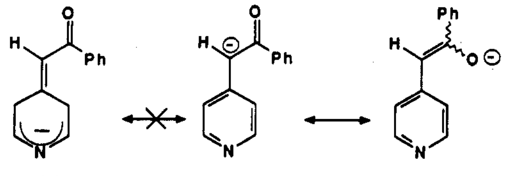


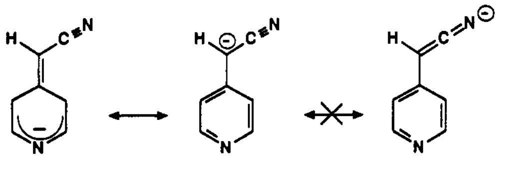
7A 7B 7C

these values into eq 4 reproduces the experimental ^{13}C shifts of anions 1^-–7^- with a high degree of precision (Table III). In this regard, a number of considerations appear appropriate.

Firstly, it is rewarding to find that theoretical suggestions[32] that the phenylthio group is unable to delocalize the negative charge resident on an adjacent carbanionic carbon by resonance mechanisms are experimentally confirmed by the correct prediction of the ^{13}C NMR shift of the CH^- group of anion 1^-, made by using a zero charge demand for the PhS group.

Secondly, the good fit of computed and experimental ^{13}C carbanionic shifts includes the 4-benzylpyridine anion (2^-) as a diactivated carbanion ^-CHXY. In such systems, the negative charge is more or less evenly partitioned between the X and Y groups. This is not true in anion 2^-, where experimental charge mapping[20] requires for the phenyl ring $c_{\mathrm{Ph}}^{\mathrm{Ph}} = 0.175$ and $c_{4\mathrm{Py}}^{\mathrm{Ph}} = 0.408$. Because of the internal compensation of $c_{\mathrm{Ph}}^{\mathrm{Ph}} = 0.29$, obtained from diphenylmethyl carbanion, with $c_{4\mathrm{Py}}^{4\mathrm{Py}} = 0.277$, eq 4 predicts the carbanionic ^{13}C shift of 2^- equally well.

Thirdly, anion 3^- cannot be described as a ketene imine nitranion **3C** since the ^{13}C NMR spectrum indicates the predominant contribution of structure **3A**.



3A 3B 3C

In the accompanying paper,[34] we shall discuss in detail the problem of charge delocalization in α-cyano carbanions. However, it should be pointed out here that the charge demand of the cyano group is considerably smaller than that of the 4-pyridyl ring, although the cyano group provides the phenylacetonitrile anion ($pK_a = 21.9$)[19] with a stabilization that is 6.2 kcal/mol larger than that which the pyridyl ring provides the 4-benzylpyridine anion ($pK_a = 26.7$).[19] Since the sensitivity of the DMSO acidity of diactivated cyanocarbon acids XCH_2CN to polar-inductive effects is about 0.81 times smaller than their sensitivity to resonance effects,[21] it is unlikely that the high polar-inductive effect of the cyano group accounts for the greater increase in the acidity of phenylacetonitrile in comparison with that of 4-benzylpyridine. Despite various reports[20,22,35] supporting the weak resonance electron-withdrawing power of the cyano functionality in α-cyano carbanions, this problem has so far been overlooked. The data and reasoning described above suggest that an alternative mechanistic explanation is needed to account for the stabilization that the cyano group provides adjacent carbanionic centers. Neither resonance nor polar-inductive field effects alone are enough.[34]

Conclusion

We provide evidence that, in ω-substituted picolyl carbanions, the 4-pyridyl ring acts as a probe for the partitioning of the negative charge between the heterocycle and the substituent. This distribution is quantified by the charge demands c_X of the groups bonded to the carbanionic center. π Charge–^{13}C shift relationships, which incorporate charge demands into the charge-dependent term contributing to the shift, efficiently predict the shift of trigonal carbanionic carbons. The results are consistent with the assumption that the phenylthio PhS group stabilizes adjacent carbanion centers without involving charge delocalization onto the sulfur atom. Experimental evidence is offered for the small contribution that ketene imine nitranion structures make to the description of α-cyano carbanions, such as the 4-pyridylacetonitrile anion.

Experimental Section

^1H and ^{13}C NMR shifts were recorded at 25 °C on a Varian XL-300 spectrometer, operating at, respectively, 300 and 75.47 MHz and measured relative to Me_4Si as external standard; ^{13}C NMR shifts were recorded using 0.50 M solutions in DMSO. The DMSO-d_6 solvent provided the internal deuterium lock; anion solutions in DMSO (10-mm o.d. tubes) were provided with an internal 5-mm coaxial tube containing neat DMSO-d_6. Elemental analyses were performed using a Perkin-Elmer 240 instrument in our department's microanalysis laboratory. Melting points are uncorrected. Extracts were dried over Na_2SO_4. Anions were prepared following a previously described procedure.[13,20–23]

Materials. 4-Benzylpyridine and 4-pyridylacetonitrile hydrochloride were purchased from Aldrich. Ethyl (4-pyridyl)acetate,[36] 4-phenacylpyridine,[37] phenyl 4-picolyl sulfide,[38] and phenyl 4-picolyl sulfone[39] were prepared according to known procedures.

(±)-Phenyl 4-Picolyl Sulfoxide. A solution of 70% *m*-chloroperbenzoic acid (8.82 g, 35.8 mmol) in CH_2Cl_2 was added dropwise to a solution of phenyl 4-picolyl sulfide (6.00 g, 29.8 mmol) in CH_2Cl_2 (50 mL), with stirring and maintaining the temperature below 0 °C. The reaction mixture was then brought to room temperature and stirred overnight. The mixture was subsequently washed with aqueous sodium metabisulfite and aqueous sodium hydrogen carbonate, the solvent being removed from the dried solution to leave the product as a white solid (2.91 g, 13.4 mmol, 45%), mp 173 °C (benzene): $\delta_H(CDCl_3)$ 8.47 (2 H, AA′BB′ system, d, $J_{2,3} = 6.01$ Hz, 2-H and 6-H of pyridine ring), 7.51–7.33 (5 H, m, phenyl ring protons), 6.86 (2 H, d, 3-H and 5-H), 4.04 (1 H, AB system, d, $J_{gem} = 12.5$ Hz, methylene proton), 3.92 (1 H, d, methylene proton). Found: C, 66.04; H, 5.00; N, 6.25. $C_{12}H_{11}NOS$ requires: C, 66.32, H, 5.11; N, 6.45.

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