Linear Free Energy Relationships for Carbon-13 Chemical Shifts in *N*-Phenacylpyridinium Bromides

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Summary Quantitative relationships between the carbon-13 chemical shift of the carbonyl and methylene carbon atoms of *N*-phenacylpyridinium bromides and σ^+ values for 3- and 4-substituents on the pyridine ring have been found.

Recently several reports have appeared which established linear free energy relationships (L.F.E.R.) between Hammett substituent constants and carbon-13 chemical shifts for carbonyl or carbonyl-related carbon atoms in benzylidenanilines,[1] benzoic acids,[2] and benzonitriles.[3] These reports are in contrast to those by early investigators which indicated that the carbonyl carbon chemical shift in acetophenones,[4] benzaldehydes,[5] and methyl benzoates[6] was insensitive to substituent effects. We report here a correlation with Hammett substituent constants of the carbon-13 chemical shifts for the ketone carbonyl and methylene carbon atoms of *N*-phenacylpyridinium bromides.

Table 1. ^{13}C chemical shifts for the *N*-phenacylpyridinium bromides $XC_5H_4\overset{+}{N}CH_2COPhBr^-$ (0·3 mol % in water)[a,b]

X	$\delta(CH_2)$	$\delta(CO)$	X	$\delta(CH_2)$	$\delta(CO)$
4-CN	67·27	190·82	3-Me	66·16	192·20
3-CN	67·01	190·82	3-NH_2[b]	66·23	192·32
4-CO_2Me[b]	66·75	191·34	4-Bu^t	65·32	192·32
3-Cl	66·62	191·34	4-Et	65·52	192·46
3-Br	66·42	191·34	4-Me	65·52	192·38
4-Cl[b]	65·90	191·68	4-MeO[b]	64·41	192·97
H	66·42	192·12	4-Me_2N	62·53	194·53

[a] The natural abundance proton decoupled carbon-13 spectra were recorded on a JEOL-FX-60 spectrometer operating at 15·04 MHz at 38 °C, in H_2O (rapid deuterium exchange of the methylene protons prevents the convenient use of D_2O) using acetone as internal standard (that the observed L.F.E.R. results were independent of the internal standard was demonstrated by a comparative study using acetone as an external standard); the values reported have been adjusted to the Me_4Si scale. The resolution of the instrument under typical operating conditions was 0·06 p.p.m.; the chemical shifts were reproducible to values within the resolution of the instrument. The carbonyl carbon chemical shifts are concentration dependent (0·7 p.p.m. over the range 0·1—0·9 mole %); however, measurements on all compounds were made at a constant concentration of $0·3 \pm 0·02\%$.
[b] New compounds gave C and H analysis within ±0·3% of the theoretical values; all other compounds gave physical data in accordance with literature values.

Table 1 contains the carbon-13 chemical shift data for the methylene and the carbonyl carbon atoms for a series of *N*-phenacyl 3- and 4-substituted pyridinium bromides obtained from their proton-decoupled spectra determined in water. It can readily be seen that substituents on the pyridine ring affect the chemical shift of the carbonyl and methylene carbon atoms in a regular manner. The direction of the shift for the methylene signal is the same as that for the methyl carbon signal in a series of substituted *N*-methylpyridinium compounds.[7] The change in the carbonyl shift with substituents is in the opposite direction, which is as expected when it is recognized that electron donors increase the polarization of the carbonyl π bond toward oxygen. The possibility that the effect of substituents on the chemical shift reported here could arise from the presence of a rapidly established equilibrium between the phenacyl salt and its corresponding ylide was eliminated by studying the effect of pH on the chemical shift. The carbonyl chemical shift of the 4-cyano compound, which has the lowest $\mathrm{p}K_a$[8] of the compounds studied, was examined over the pH range 1·0—4·4. The chemical shifts changed by only 0·05 p.p.m. over that range.†

Table 2

Correlation results[a]

Carbon	σ-Constant	n[b]	p[c]	c[d]	s.d.[e]	r[f]
CH_2	σ	14	2·7102	65·52	0·526	0·898
CH_2	σ°	13	2·8479	65·71	0·766	0·792
CH_2	σ^+	14	1·9084	66·00	0·266	0·972
C=O	σ	14	−2·3344	192·18	0·198	0·974
C=O	σ°	13	−2·5876	192·35	0·404	0·907
C=O	σ^+	14	−1·5318	191·94	0·129	0·986

[a] The results of least squares fit of the data by the expression $\delta = p\sigma + c$. [b] n = number of data points; for σ° correlation, Et was omitted from treatment owing to absence of a σ° value. [c] Slope of the line. [d] Calculated intercept. [e] Standard deviation. [f] Correlation coefficient.

The ^{13}C n.m.r. shift data were correlated with σ, σ°, and σ^+ and the results of the statistical treatment are recorded in Table 2.[9] Both the methyl and carbonyl carbon signals are correlated best with σ^+. It is also interesting to note that the data for the 3-substituted compounds fall on the same line as those for the 4-substituted compounds. Although we have studied a limited number (five) of 3-substituted compounds, this observation is of interest because of the continuing quandary concerning correlation of *meta*-substituent chemical shifts.[10] It can be seen that the β-carbon (carbonyl carbon) in this system is less sensitive to substituents than the α-carbon (methylene carbon) and this is in contrast to the reported greater sensitivity for the β-carbon in comparison with the α carbon atoms in series of substituted 1-phenylpropenes,[11] 1-phenylpropynes,[11] and benzylidenemalononitriles.[12] The sensitivity of the carbonyl carbon atom to substituent

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† At pH > 4·4, the ylide precipitated from the water solution.

effects is comparable to that of the carbonyl or carbonyl related carbon atoms of the benzylidenanilines,[1] benzoic acids,[2] and benzonitriles,[3] although the carbonyl carbon in the system reported here is a β-carbon.

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