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Carbon-13 and Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy: A Fourier N.m.r. Study of [^{15}N]Quinoline

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The carbon-13 and nitrogen-15 magnetic resonance spectra of [^{15}N]quinoline have been measured. A significant nitrogen lone pair effect was observed on the magnitude of $^2J[^{13}C(8)-^{15}N]$ as well as on the carbon chemical shift of C(8).

THE measurement of ^{13}C–^{15}N coupling constants has been hampered previously by the necessity for costly, time-consuming double enrichment experiments, caused by the low sensitivity and natural abundance of each of these nuclei. Thus the number of reports of such coupling is small. The most comprehensive compilation is by Binsch *et al.*[1]

The advent of noise decoupling and pulsed Fourier techniques now allows easier measurement of either ^{13}C or ^{15}N in natural abundance [2] and has thus reduced the difficulty involved in measuring ^{13}C–^{15}N couplings to the level of the single label experiment.

RESULTS AND DISCUSSION

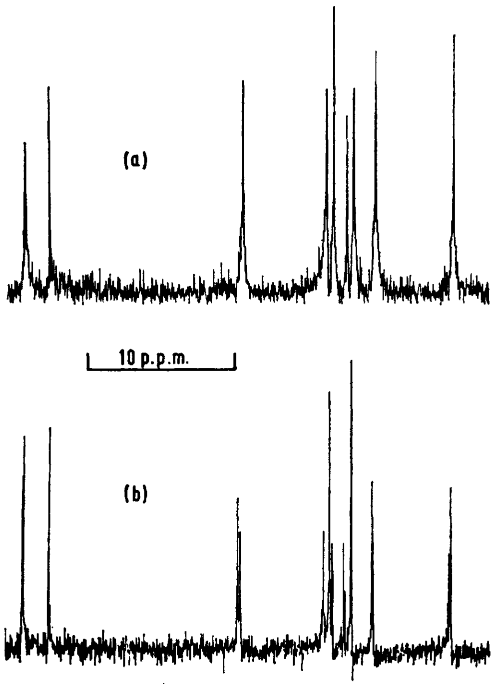
^{13}C–^{15}N *Coupling Constants*.—The natural abundance carbon-13 spectra of [^{14}N]- and [^{15}N]-quinoline are shown in the Figure. The carbon nitrogen couplings $J(^{13}C-^{15}N)$, clearly visible in the lower trace as splittings additional to those in the upper, are tabulated in Table 1.

TABLE 1

^{13}C–^{15}N Couplings in quinoline [a]

Carbon	Solvent CCl$_4$ [b]	MeOH [c]	H$_2$SO$_4$ [d]
2	1·4	2·4	15·9
3	2·7	2·6	~1·0
4	3·5	3·7	4·6
5	~0	~0	~0
6	0·9	~0	~0
7	3·9	3·9	2·7
8	9·3	8·4	~1·0
9	0·6	1·5	13·8
10	2·1	2·0	<1·0

[a] Values in Hz. [b] 50% Solution (v/v) (±0·15 Hz). [c] 50% Solution (v/v) (±0·15 Hz). [d] 30% Solution (v/v) (±0·25 Hz).



Natural abundance ^{13}C Fourier power spectrum of (a) [^{14}N]quinoline and (b) [^{15}N]quinoline in carbon tetrachloride. The spectra are the result of 512 pulses each of 40 μs duration spaced approximately 1·6 s apart

Binsch *et al* [1] have suggested an expression by which the one-bond coupling $^1J(^{13}C-^{15}N)$ may be related to the angular hybridization terms of the individual atoms. This relation [equation (1)], which is based on an

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[1] G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1964, **86**, 5564.

[2] J. M. Briggs, L. F. Farnell, and E. W. Randall, *Chem. Comm.*, 1971, 680.

average energy approximation with a constant value for ΔE, an excitation energy, gives a value of *ca.* 8·7 Hz for

$$80\,{}^{1}J({}^{13}\mathrm{C}\text{–}{}^{15}\mathrm{N}) = s_{\mathrm{C}}s_{\mathrm{N}} \qquad (1)$$

the case in which s_{C} and s_{N} (the percent s characters in the carbon and nitrogen hybrid orbitals respectively) are each 0·33. Clearly, the observed nitrogen-15 couplings for C(2) and C(9), in carbon tetrachloride, differ significantly from this value as has been observed for [^{15}N]pyridine.[3a,b] One explanation, which has been used in shift discussions (see below), is that the ΔE value is low for pyridine and quinoline.

A comparison of both the short and long range couplings in the heterocyclic rings of [^{15}N]quinoline and [^{15}N]pyridine (Table 2) gives good agreement for the two molecules. The magnitudes of these couplings (signs were not determined) increase with the number of bonds intervening between the two nuclei.

TABLE 2

Comparison of the $J(^{13}\mathrm{C}\text{–}^{15}\mathrm{N})$ values in the heterocyclic rings of [^{15}N]pyridine and [^{15}N]quinoline

[^{15}N]Pyridine [a]		[^{15}N]Quinoline (CCl$_4$)	
Carbon	$J(^{13}\mathrm{C}\text{–}^{15}\mathrm{N})$	Carbon	$J(^{13}\mathrm{C}\text{–}^{15}\mathrm{N})$ [b]
2	0·45	2	1·4
3	2·4	3	2·7
4	3·6	4	3·5
		9	0·6
		10	2·1

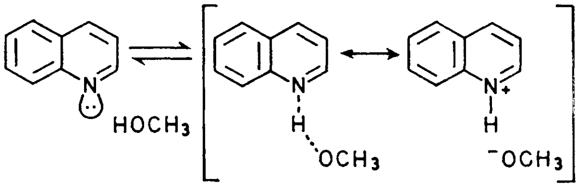
[a] Data from ref. 3a. [b] Values in Hz.

A different trend is observed for carbons C(5) through to C(8) in the second ring of quinoline with the couplings at C(6) (0·9 Hz) and C(8) (9·3 Hz) being of especial interest. The former represents the first reported four-bond carbon–nitrogen coupling, while the latter appears unusually large compared with the other two bond couplings, *viz.* $^{2}J[^{13}\mathrm{C}(3)\text{–}^{15}\mathrm{N}]$, in the heterocyclic ring.

Although the calculated charge densities and bond orders[4] for the quinoline molecule give no indication that C(8) is in a special environment, previous studies have shown that both the proton and carbon chemical shifts[4] at this position appear at appreciably lower field than do the corresponding shifts for nuclei at positions 5—7. The value for $^{2}J[^{13}\mathrm{C}(8)\text{–}^{15}\mathrm{N}]$ can be explained, however, by assuming that this centre is under the influence of the nitrogen lone pair and that we are observing a geometrical dependence of $^{2}J(^{13}\mathrm{C}\text{–}^{15}\mathrm{N})$ on the orientation of the non-bonded electrons on nitrogen.

The solvent dependence of the carbon–nitrogen couplings in [^{15}N]quinoline agrees well with the results of similar studies on [^{15}N]pyridine:[3a] protonation at nitrogen causes a large increase in the magnitude of $^{1}J[^{13}\mathrm{C}(2)\text{–}^{15}\mathrm{N}]$ and $^{1}J[^{13}(9)\text{–}^{15}\mathrm{N}]$ as well as a substantial increase in $^{3}J[^{13}\mathrm{C}(4)\text{–}^{15}\mathrm{N}]$. The presence of these large one-bond carbon–nitrogen couplings in the protonated species markedly facilitates the assignment of the carbon spectrum. A similar approach has been used for the identification of the carbon resonances in the [^{15}N]anilinium and [^{15}N]toluidinium ions.[5]

Solvation of the nitrogen by methanol produces relatively large increases in $^{1}J(^{13}\mathrm{C}\text{–}^{15}\mathrm{N})$ at carbons 2 and 9 and only minor changes at the other carbon atoms with the exception of C(8). The changes at C(2) and C(9) are in keeping with the idea of partial protonation of nitrogen, *via* hydrogen bonding. This may be represented by equilibrium (2) in which the structures in square brackets are two possible cannonical forms. This type of argument has been advanced previously to account for the solvent dependence of the ^{14}N shift in pyridine.[6]



(2)

The solvent dependence of the coupling at C(8) supports the suggestion of a lone pair effect. Bonding of the lone pair by complete protonation decreases the magnitude of $^{2}J[^{13}\mathrm{C}(8)\text{–}^{15}\mathrm{N}]$ to the value found for C(3) a position not subject to the lone pair influence. Partial protonation in methanol solution produces a smaller decrease, *viz.* 0·9 Hz.

Chemical Shifts.—The factors contributing to the chemical shift of second row elements have been reviewed previously[7] and will not be discussed here. The dominance of the paramagnetic term, σ_{p} [equation (3)] in the equation for the total screening is assumed. A diamagnetic correction has not been included although this approach has been advocated.[8]

$$\sigma_{\mathrm{p}} \propto \frac{1}{r^{3}}\,\frac{1}{\Delta E}\,\Sigma Q_{\mathrm{AB}} \qquad (3)$$

Nitrogen-15. The undecoupled nitrogen-15 resonance of [^{15}N]quinoline is a doublet (1 : 1) of triplets (1 : 2 : 1) resulting from a large two-bond coupling to H(2) (11·8 ± 0·5 Hz) and two approximately equal three-bond couplings to protons 3 and 8 (*ca.* 1·5 ± 0·5 Hz).[9] Under conditions of complete proton decoupling a single absorption, 288·5 p.p.m. downfield from the nitrogen signal of $^{15}\mathrm{NH_4Cl}$, is observed. This value is in good agreement with the value of 281 p.p.m. reported by Herbison-

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[3] (*a*) R. L. Lichter and J. D. Roberts, personal communication; (*b*) P. S. Pregosin, E. W. Randall, and A. I. White, unpublished results.

[4] R. J. Pugmire, D. M. Grant, M. J. Robins, and R. K. Robins, *J. Amer. Chem. Soc.*, 1969, **91**, 6381.

[5] P. S. Pregosin, A. I. White, and E. W. Randall, unpublished results.

[6] H. Saito, K. Nukada, H. Kato, T. Yonezawa, and K. Fukui, *Tetrahedron Letters*, 1965, 111.

[7] D. G. Gillies and E. W. Randall, *Progr. N.M.R. Spectroscopy*, 1971, **6**, 119; E. F. Mooney and P. H. Winson, 'Annual Review of N.M.R. Spectroscopy,' vol. 2, ed. E. F. Mooney, Academic Press, London, 1969, p. 153.

[8] R. Grinter and J. Mason, *J. Chem. Soc.* (*A*), 1970, 2196.

[9] The coupling $^{3}J[^{15}\mathrm{N}\text{–}\mathrm{H}(8)]$ has been observed previously, R. Price, Ph.D. thesis, University of London, 1969; no measurement was possible due to the complexity of the spectrum of H(8).

Evans and Richards[10] for the nitrogen chemical shift of [^{14}N]quinoline. The low field position of the quinoline nitrogen is probably due, in part, to the contribution of the relatively low lying $n \longrightarrow \pi^*$ transition available for this molecule. This effect would be expected to decrease ΔE and thus increase σ_p, with a concomitant low field shift. A similar explanation has been advanced to account for the nitrogen-shift of [^{14}N]pyridine,[11] and is consistent with the coupling constant discussion.

The solvent dependences of the nitrogen resonances in [^{15}N]pyridine and [^{15}N]quinoline are shown in Table 3.

Table 3

Nitrogen-15 chemical shifts

Compound	$\delta(^{15}N)$ [a]	Compound	$\delta(^{15}N)$
Quinoline (CCl_4)	288·5 [b]	Pyridine (neat)	291·6 [e]
Quinoline (MeOH)	273·7 [c]		
Quinolinium (H_2SO_4)	159·4 [d]	Pyridinium (CF_3CO_2H)	181·1 [e]

[a] Relative to a 5M solution of $^{15}NH_4Cl$ in 2N-HCl. Values correct to ±0·5 p.p.m. A positive value denotes a shift to higher frequency (*i.e.* to lower field). [b] 50% Solution (v/v). [c] 50% Solution (v/v). [d] 30% Solution (v/v). [e] Obtained by double resonance. Data from R. Price, Ph.D. thesis, University of London, 1969.

In methanol solution hydrogen bonding to nitrogen induces a 14·8 p.p.m. upfield shift. The direction of this shift is consistent with the idea of partial protonation and its effect on the ΔE term. Complete protonation, by solution in sulphuric acid, gives a quinolinium nitrogen resonance at 159·4 p.p.m., 129·1 p.p.m., upfield from the conjugate base. Assuming a linear dependence of the nitrogen shift on degree of protonation, one may estimate the percentage contribution of the ionic structure in equation (2) utilizing the three values for the quinoline nitrogen resonances shown in Table 3. The calculated value of 9% in methanol solution agrees well both with the values calculated using the solvent dependences of $^1J[^{13}C(2)-^{15}N]$ and $^1J[^{13}C(9)-^{15}N]$ (which yield estimates of *ca.* 7%) and the value of 12% estimated for pyridine in methanol solution.[3a]

Carbon-13. The positions of the carbon-13 absorptions of quinoline, relative to external Me_4Si, as well as their solvent dependences are shown in Table 4. We find our values in CCl_4 agree well with literature values.[4] Assignment of the carbon resonances in methanol were made utilizing known solvent effects[12] in combination with $^{13}C-^{15}N$ couplings. The assignments in sulphuric acid were made by employing off resonance techniques [C(9), C(10)], $^{13}C-^{15}N$ couplings [C(2), C(4)] and the observed methyl substituent effects in 6- and 8-methylquinoline and their protonated species.*

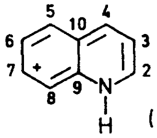
The changes in chemical shift on protonation of carbons 2, 3, and 4 (−6·0, +1·1, and +13·3 p.p.m., respectively) are similar to those observed by Pugmire and Grant[12] for the pyridine–pyridinium set (−7·8, +5·0, and +12·4). Interestingly the resonances of carbons 5—7 move to low field by relatively large quantities (+3·2, +3·2, and +7·0) whereas the resonance of C(8) moves to high field by 9·6 p.p.m.

Table 4

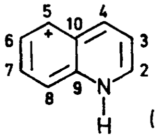
Carbon-13 chemical shifts [a] in quinoline

	Solvent		
Carbon	CCl_4 [b]	MeOH [c]	H_2SO_4 [d]
2	+150·89	+150·46	+144·94
3	+121·67	+121·77	+122·75
4	+136·12	+136·98	+149·39
5	+128·46	+128·37	+130·19
6	+126·95	+126·85	+131·64
7	+129·86	+130·18	+136·88
8	+130·50	+129·11	+120·92
9	+149·28	+148·12	+137·74
10	+128·89	+128·78	+129·76

[a] In p.p.m. downfield from external Me_4Si, a positive value denotes a shift to higher frequency. Values correct to ±0·1 p.p.m. [b] 50% Solution (v/v). [c] 50% Solution (v/v). [d] 30% Solution (v/v).



(I)



(II)

Transmission of the positive charge *via* the π system [(I) and (II)] might be expected to induce low field shifts at carbons 5 and 7; thus explaining the observed shifts at these centres. The shift at C(6), however, cannot be explained in this way.

The peculiar behaviour at C(8) is quite consistent with our previous observations at this centre. In this instance protonation removes the deshielding influence of the nitrogen lone pair and results in an upfield shift. The deshielding influence of an oriented nitrogen lone pair is not novel. Recently a dependence of the carbon chemical shift of a series of nitrosamines on the orientation of the nitroso-nitrogen lone pair has been reported;[13] a low field shift of about 10 p.p.m. has been observed. Thus both the magnitude and direction of the shift at C(8) are quite reasonable.

EXPERIMENTAL

Spectra were recorded on a Bruker HFX multinuclear spectrometer operating at 22·63 and 9·12 MHz for ^{13}C and ^{15}N respectively under conditions of complete proton decoupling. All solutions were contained inside 5-mm tubes inserted concentrically within a 10-mm tube containing neat hexafluorobenzene, the fluorine resonance of which was used to provide a field-frequency lock.

Carbon line positions were measured relative to the carbon resonance of external Me_4Si, while nitrogen shifts were

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* Off-resonance techniques readily allow the identification of C(6) in 6-methylquinoline and its quinoline ion, and of C(8) in the 8-methyl compounds. These assignments provide a qualitative estimate of the movement of the corresponding carbon resonances on protonation of quinoline itself.

[10] D. Herbison-Evans and R. E. Richards, *Mol. Phys.*, 1964, **8**, 19.

[11] J. D. Baldeschwieler and E. W. Randall, *Proc. Chem. Soc.*, 1961, 303; V. M. S. Gil and J. N. M. Murrell, *Trans. Faraday Soc.*, 1964, **60**, 248.

[12] R. J. Pugmire and D. M. Grant, *J. Amer. Chem. Soc.*, 1968, **90**, 697.

[13] P. S. Pregosin and E. W. Randall, *Chem. Comm.*, 1971, 399.

measured relative to external ^{15}N-enriched ammonium chloride in acid solution (5M in 2N-HCl).

The spectra were obtained by storing the free-induction decays produced by a series of 40 μs r.f. pulses in a Fabritek 1074 computer of average transients. The interferograms which result were then Fourier transformed utilizing a Digital PDP 8I computer. Coupling constants were measured from the carbon spectra and are estimated to be correct to ±0·15 Hz at an effective spectral width of 125 Hz.

[^{15}N]Quinoline was measured as 50% (v/v) solutions in CCl_4 and in methanol, and as a 30% (v/v) solution in H_2SO_4.

8-Methylquinoline and 6-methylquinoline were obtained from Koch–Light Laboratories and were used without further purification.

[^{15}N]Quinoline (98·5% enriched) was obtained from Merck, Sharpe, and Dohme of Canada.

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