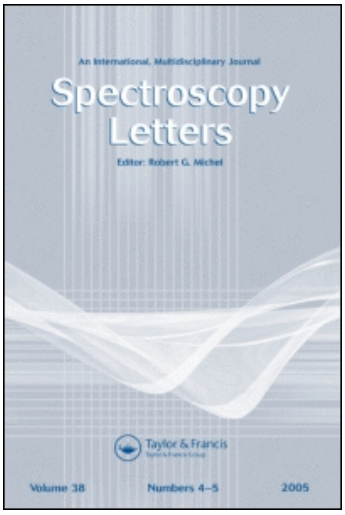

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Carbon-13 Magnetic Resonance Spectral Studies of Quinoline Derivatives. Assignments of Bridgehead Carbons

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CARBON-13 MAGNETIC RESONANCE SPECTRAL STUDIES OF QUINOLINE DERIVATIVES. ASSIGNMENTS OF BRIDGEHEAD CARBONS

KEY WORDS : CMR, chemical shifts, quinoline, shielding effects

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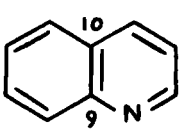
Abstract : Evidence is presented to confirm the assignments of the bridgehead carbon atoms of quinoline. The chemical shifts of C-9 and C-10 in a series of methylquinoline derivatives were determined and their respective assignments deduced from a consideration of shielding effects. The selection of suitable reference compounds is discussed.

The Carbon-13 magnetic resonance spectrum of quinoline (I) has been determined and analysed by Pugmire et al.[1] Assignments of the bridgehead carbons C-9 and C-10 were made by comparison with the respective pyridine shieldings. There was a 20.3 p.p.m. difference

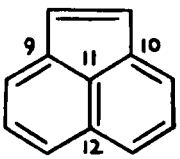


(I)

between these carbons and the lower field signal was assigned to C-9, since it was α to the nitrogen. No other evidence was presented to confirm the assignments. Subsequent workers[2,3] have referred to these assignments but have not presented any experimental evidence to support

them. We now wish to report such experimental evidence which confirms the respective assignments for the bridgehead carbons C-9 and C-10 as originally reported by Pugmire et al.[1]

Quaternary carbons may readily be distinguished from ring carbons by the use of off-resonance techniques,[4a] however, distinction between quaternary carbons, except on the basis of intensity (e.g. C-9/C-10 from C-11 and from C-12 in acenaphthylene (II))[5] is more difficult.



(II)

Such distinction between magnetically non-equivalent carbons of similar intensity has been achieved through use of the relative amplitude of the Nuclear Overhauser Effect,[5,6] and also from theoretical calculation of their chemical shifts.[5] Recently the use of deuterium isotope upfield shifts and deuterium-carbon coupling has been introduced.[7] Although each of these techniques has been applied to the assignment of quaternary carbons in hydrocarbons[5-7] as far as we are aware none of these techniques have yet been applied to the quinoline nucleus.

It is well known[4b] that introduction of a methyl group into an aryl ring causes variations in the ring carbon shieldings. From the chemical shifts obtained it is possible to compile a table of additivity parameters for use in predicting the chemical shifts of multiply substituted methyl derivatives.

The same data may also be used in an alternate manner to assign bridgehead carbon chemical shifts, by consideration of shielding effects. Since the para effect is much larger than those for the ortho and meta positions[8] the latter two effects may be ignored in the consideration of bridgehead carbon assignments.

We have determined the ^{13}C chemical shifts for the bridgehead carbon atoms of a series of methylquinoline derivatives and the results are shown in Table 1.

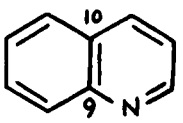
It is seen that substitution of a methyl group at the *para* positions to C-9 (i.e. at positions 3 and 6) causes an upfield shift of that carbon. The extent of the shielding effect is smaller than the 3.1 p.p.m. obtained with toluene[8] but is nevertheless very characteristic ; the extent of the effect produced at the quaternary carbon is also similar when substitution occurs in either ring. Similar effects are obtained for substitution at the *para* positions to C-10 (i.e. at positions 2 and 7). These results therefore confirm the respective assignments of C-9 and C-10 as originally proposed by Pugmire *et al.*[1]

In addition to the *para* shielding effects; *ortho* disubstitution (as in 2,3- and 3,4-dimethyl- and 2,3,4-trimethylquinoline) caused a slightly smaller effect than monomethyl substitution (see note b in Table 1). 2,3,4-Trisubstitution also caused a greater effect than would be expected for the central singly substituted position (see note c in Table 1). Parallel effects for *ortho* disubstituted and for 1,2,3-trisubstituted methylbenzene derivatives have been reported previously.[4b,8] Hence, for unequivocal assignments of bridgehead carbon atoms, monomethyl substituted derivatives should ideally be used.

In order to assess the respective upfield shifts it was found expedient not to use quinoline itself as the standard but to use instead, 4-methylquinoline and 8-methylquinoline as the reference compounds for the heterocyclic and carbocyclic rings respectively. In each of these compounds the overall effect of substitution of a methyl group on the shielding of the bridgehead carbons is present, but there is no additional *para* shielding effect. That these compounds serve as reasonable standards is shown by their respective chemical shifts for C-9 and C-10 which are very similar;

Table 1

^{13}C Chemical shifts for C-9 and C-10 in some methylquinoline derivatives



Substituted quinoline	Chemical Shift (δ) C-9	C-10	Shielding Effect (p.p.m.)(a) C-9	C-10
quinoline (ref. 1)	149.1	128.9		
quinoline (ref. 2)	149.3	128.9		
2-Me	147.8	126.3*	+0.1	-1.7
3-Me	146.5*	128.0	-1.2	0.0
4-Me	147.7	128.0	—	—
2,3-Me_2	146.4*	127.3*	-1.3	-0.7 (b)
2,4-Me_2	147.5	126.3*	-0.2	-1.7
3,4-Me_2	146.7*	128.2	-1.0 (b)	+0.2
2,3,4-Me_3	145.7*	126.9*	-2.0 (c)	-1.1 (b)
8-Me	147.3	128.1	—	—
6,8-Me_2	146.0*	128.3	-1.3	+0.2
7,8-Me_2	147.3	126.5*	0.0	-1.6

NOTES Starred results represent a para shielding effect

(a) Compared to 4-methylquinoline for heterocyclic ring substitution and to 8-methylquinoline for carbocyclic ring substitution

(b) Smaller effect due to ortho disubstitution

(c) Larger effect due to central atom of diortho trisubstitution

these shifts are also similar to the chemical shifts of either C-9 or C-10 in other methyl substituted compounds in which there is no para effect for one particular bridgehead carbon atom. (e.g. C-9 in 2-methylquinoline or C-10 in 3-methylquinoline) It is also of interest to note that the chemical shifts of the bridgehead carbons in the two reference compounds show a greater deviation from quinoline for C-9 which is the atom closest to the nitrogen.

The technique described above may also be used to assign bridgehead carbon atoms in other six-membered polycyclic molecules. Thus the data reported by Parker and Roberts[9] for the chemical shifts of methylindoles could be employed to confirm the assignment of the bridghead carbons in the indole molecule.

Spectra were determined, for samples dissolved in $CDCl_3$ in the presence of TMS, on a Bruker HX90E spectrometer operated in the Fourier Transform mode at 22.63 MHz, with broad band proton decoupling. Spectra were determined by the Physico Chemical Measurements Unit, Harwell to whom we are indebted.

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