A Method for Selective Enhancement of Carbon-13 Nuclear Magnetic Resonance Signals from Quaternary Carbon Atoms

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Summary Quaternary ^{13}C n.m.r. signals may be increased relative to those from hydrogen bearing carbon atoms, whose signals are vastly reduced or eliminated, by the use of very low powers for broad-band decoupling.

Carbon-13 F.t.n.m.r. spectra are normally obtained either by using high power (*ca.* 10 W) broad band (noise) proton decoupling,[1] in which case each carbon atom appears as a single resonance, or by using single frequency off-resonance proton decoupling at a somewhat lower power (2—5 W) in which case the residual couplings in the spectrum allow, in principle at least, the identification of methyl, methylene, methine, and quaternary carbon atoms. Due to reduced nuclear Overhauser enhancements and longer relaxation times the quaternary carbon atoms may give signals of reduced intensity and may not be readily identified in a complex off-resonance decoupled spectrum.

This report is concerned with a method by which the intensities of signals from quaternary carbon atoms may be relatively increased and the signals of the hydrogen bearing carbon atoms be considerably reduced or eliminated. This may be achieved by broad band (2 kHz) decoupling at a very low decoupling power level (0·05—0·25 W) applied at the proton resonances. The spectra of dihydrothebaine (I) shown in the Figure were obtained using a Varian XL-100-12-F.t.n.m.r. system operating at 25·2 MHz. All nineteen carbon resonances are visible on the high power noise decoupled spectrum (ii). Where no decoupling is employed (i), the signals from the majority of the carbon atoms, including the quaternaries are very weak or invisible. The low power noise decoupled spectrum (iii) shows strong sharp signals only from the quaternary carbon atoms and the solvent.

It appears that the use of a low power is insufficient to decouple completely the coupling of the proton bearing

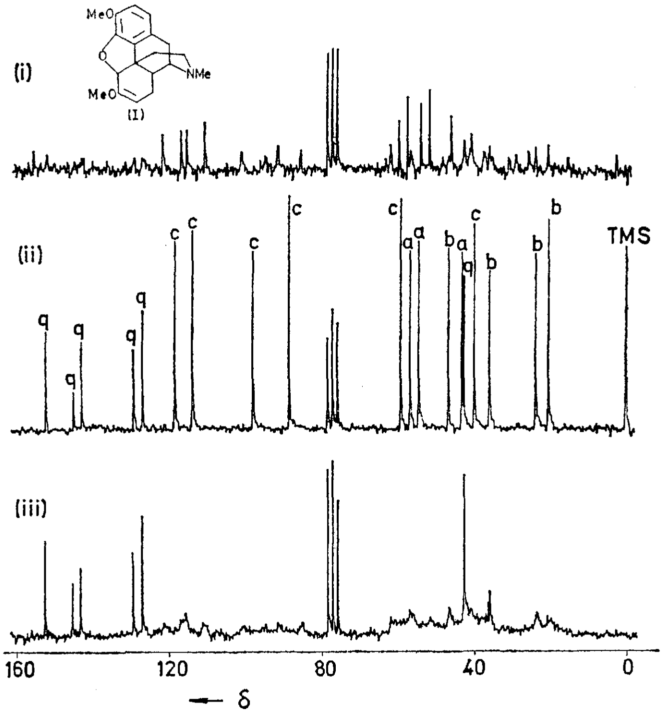

Figure. ^{13}C N.m.r. spectra at 25·2 MHz of dihydrothebaine (270 mg in 2 ml $CDCl_3$ + 0·1 ml $SiMe_4$). Spectral conditions: 6K pulses, 20° pulse, repetition rate 0·8 s. (i) Undecoupled spectrum; (ii) ^{1}H noise decoupled spectrum, H(I) power mode (10W), bandwidth = 2 kHz centred at τ5, a = methyl, b = methylene, c = methine and q = quaternary carbon atoms as deduced from off resonance decoupled spectrum (not shown); (iii) Very low power ^{1}H noise decoupled spectrum, LO power mode (103 dB), bandwidth and position as in (ii).

carbons which produce a complex pattern of low intensity lines or a coalescence effect, yet completely decouples the much smaller long range couplings of the quaternary carbon atoms. Satisfactory results have also been obtained with a variety of other compounds including codeine, quinoline, 4-t-butylacetophenone, 1,6-dimethylnaphthalene, and cholesterol. In some small molecules (*e.g.* ethylbenzene) a small but significant peak of a methylene carbon atom is observed. The best results have been obtained with large unsymmetrical molecules probably because in these cases the quaternary carbon atoms are completely relaxed *via* the dipolar mechanism and show significant Overhauser enhancements.[3] Optimum results may be obtained by the incorporation of a short delay (*ca.* 2 s) between consecutive pulses and careful adjustment of the decoupling power. Unlike off-resonance experiments, the instrument time is no greater than twice that for the conventional high power noise decoupling experiment.

A referee has pointed out that similar results have been obtained[4] *via* a different approach in which narrow band (*ca.* 300 Hz) proton decoupling at the more usual power levels is applied well upfield (6—8 p.p.m.) from the proton resonance of tetramethylsilane as in an off-resonance experiment.

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