

A New Method for the Selective Observation of Proton-coupled ^{13}C N.M.R. Signals

Ian H. Sadler

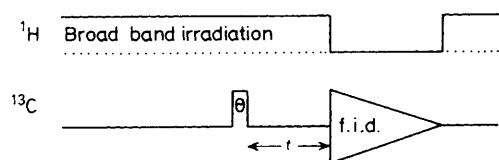
Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, U.K.

Individual proton-coupled ^{13}C multiplets are observed by using single pulses followed by an incremented delay period before data acquisition.

Selective excitation of carbon resonances by means of the DANTE sequence¹ to give the individual fully proton-coupled multiplets as separate spectra is of great value where extensive overlap of lines in the complete spectrum makes it impossible to distinguish these multiplets from each other. Similar results can be obtained by the two dimensional heteronuclear J -resolved technique² but this requires large amounts of computer storage to obtain high digital resolution.

This communication presents an alternative to the DANTE technique and relies on selective acquisition of the desired signals rather than selective excitation. Selectivity is obtained by making use of the phase variations that signals not coincident with the pulse frequency undergo during a delay period introduced between the excitation pulse and the data acquisition. The technique is carried out as shown in Scheme 1

1. A single hard excitation pulse is applied at the chemical shift frequency of the carbon resonance whose multiplet is to be selectively observed and after a short delay time t , the free induction decay (f.i.d.) is acquired. Broad-band proton decoupling is applied during the pre-excitation period, excita-



Scheme 1

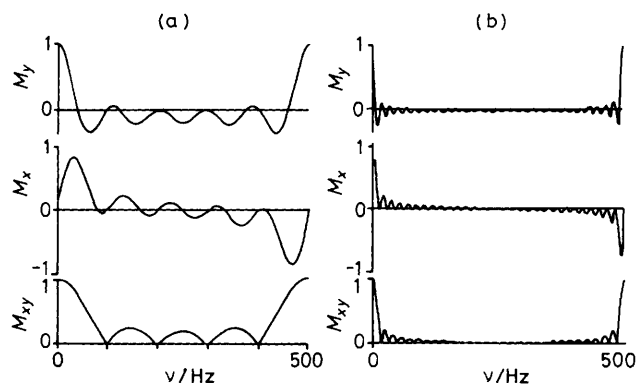


Figure 1. Selectivity of the technique shown in Scheme 1 for (a) 5 increments of 0.002 s; (b) 30 increments of 0.002 s normalised to $M_y(\nu = 0) = 1$.

tion, and delay t , but turned off during the data acquisition. During the total number of scans the delay t is incremented regularly by an amount δt from an initial value of δt to a final value t_f . Every time the delay is incremented the phase of any off-resonance signal, ν Hz from the pulse, alters by an amount $\phi = 2\pi\nu\delta t$, whereas the phase of the signal located at the pulse and at multiples of $(\delta t)^{-1}$ Hz from it remains unchanged. Provided enough short increments are employed, the signal phase alterations throughout the experiment result in a reduction of the final off-resonance signals to an insignificant level and only signals from a resonance located at the pulse frequency and at integral units of $1/\delta t$ Hz from it are observed. More formally, in a reference frame rotating at the pulse frequency the magnetisation vector M resulting from an off-resonance signal during the k th value of t precesses through an angle $k\phi$ during the delay and makes a contribution equal to $M\cos k\phi$ to the y -component (observed) of the total signal vector at the end of the experiment and a contribution $M\sin k\phi$ to the x -component. Thus the y and x components, M_y and M_x , of the final signal after n delays are given by equations (1) and (2).

$$M_y = \sum_{k=1}^n M\cos k\phi = M(\sin\{n\phi/2\})(\cos\{n+1\}\phi/2)/(\sin\phi/2) \quad (1)$$

$$M_x = \sum_{k=1}^n M\sin k\phi = M(\sin\{n\phi/2\})(\sin\{n+1\}\phi/2)/(\sin\phi/2) \quad (2)$$

The degree of selectivity is thus determined by the number and size of the increments. This is shown in Figure 1 where the signal components (M_y) and (M_x) and the absolute value signal ($M_{xy} = (M_y^2 + M_x^2)^{1/2}$) are plotted against the signal offset ν for an increment δ of 0.002 s and values of $n = 5$ and 30. Removal of the broad-band proton decoupling during the acquisition period restores the multiplet structure to the signal.

The application of the method to the ^{13}C n.m.r. spectrum of β -pinene is shown in Figure 2. The fully proton-coupled spectra Figure 2(a) of the methyl and aliphatic methylene carbons overlap heavily even at 90 MHz and yield little useful information. The spectra in Figure 2(b)–(f) were obtained by placing the pulse frequency at the appropriate resonance position from the proton noise-decoupled spectrum, Figure 2(g). A total of 33 values of t were used incrementing by 0.003 s every 160 scans. The power of the method is illustrated by the multiplets obtained for the two methylene carbons whose centres lie only 10 Hz apart.

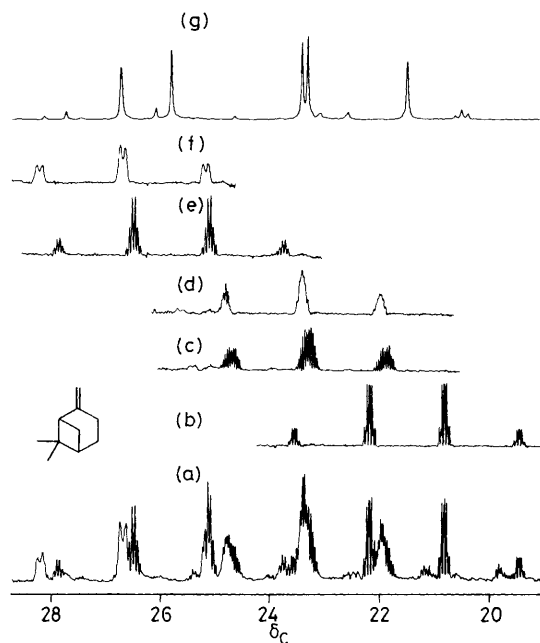


Figure 2. ^{13}C N.m.r. spectra of β -pinene at 90 MHz (obtained using a Bruker WH-360 spectrometer). (a) Fully proton coupled spectrum; (b)–(f) selective multiplet acquisition. Conditions: 5280 pulses, 22° pulse, pre-excitation delay 0.23 s, acquisition time 1.0 s, f.i.d. weighted by exponential and Gaussian multiplication (line broadening = -0.8 Hz, Gaussian broadening = 0.3). (g) ^1H Broad-band decoupled spectrum, 320 pulses.

As a guide for general usage, good selectivity is achieved if not less than 25 increments are used and the increment size is set such that the final delay is not less than $0.8/\Delta f$, where Δf is the separation between the closest pair of carbon resonances in the proton-decoupled spectrum. This is shown by plots of the type shown in Figure 1 for a whole range of values of n and has been confirmed experimentally. The final delay should be made as short as possible consistent with the desired selectivity since if it is too long the final signal is reduced by relaxation. A suitable choice of the delay increment equal to the reciprocal of the separation of the centres of multiplets which do not overlap with each other *e.g.* Figure 2(b,f) allow both multiplets to be observed simultaneously, with consequent time saving. The excitation pulse may be set at the value normally used to obtain fully proton-coupled ^{13}C n.m.r. spectra with an appropriate pre-excitation delay. It is not necessary to attenuate the power of excitation pulse from its usual level, as is normally required by DANTE. This might make it easier to apply on some spectrometers. Clearly the technique can also be applied to the observation of proton-coupled multiplets of other nuclei. It is not suitable as an alternative to DANTE for relaxation and exchange experiments since all the lines in the spectrum are excited.

Received, 18th September 1986; Com 1341

References

- G. Bodenhausen, R. Freeman, and G. Morris, *J. Magn. Reson.*, 1976, **23**, 171; G. A. Morris and R. Freeman, *ibid.*, 1978, **29**, 433.
- A. Bax, 'Two-Dimensional Nuclear Magnetic Resonance in Liquids,' Reidel, Amsterdam, 1982, p. 127.