Improved Resolution of Low Field Quaternary Carbon Resonances in ^{13}C N.M.R. Spectroscopy

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Summary An improved method of simplifying the low field region of ^{13}C n.m.r. spectra, termed Spin Echo Broad Band Off-Resonance Decoupling (SEBBORD), allows immediate distinction to be made between quaternary C and CH carbon resonances, even in cases of extreme spectral complexity.

ASSIGNMENT of multiplicity in ^{13}C n.m.r. spectroscopy is usually sought using the Single Frequency Off-Resonance Decoupling (SFORD) technique.[1] In the low field region of the spectrum this amounts to distinguishing between quaternary carbon singlets and CH carbon doublets. Since the SFORD technique results in the observation of reduced one-bond C–H splittings[1] and is often associated with some line broadening, assignment of multiplicity can be difficult in congested spectral regions. The present method (Spin Echo Broad Band Off-Resonance Decoupling, or SEBBORD) uses the spin echo sequence: [relaxation delay] 90–τ–180–τ–[data acquisition], with off-resonance broad band decoupling of protons being applied during the period 2τ and continued during data acquisition (Figure 1). Anthracene oil, a distillation product from coal tar, containing a mixture of polynuclear aromatic compounds with a moderate hetero-atom content (3·9% by weight for this sample), is used to illustrate the method in Figure 2.

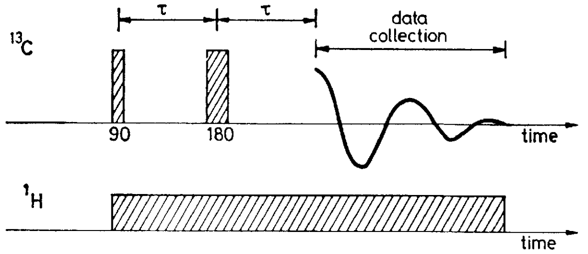

FIGURE 1. Pulse sequence for the spin echo broad band off-resonance decoupling technique described in the text.

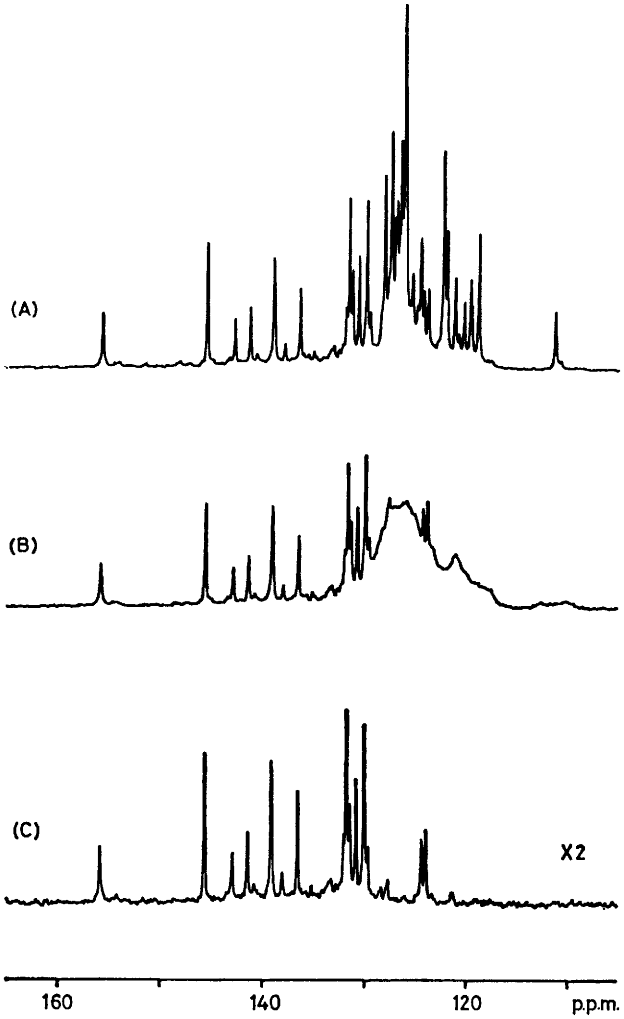

FIGURE 2. The low field region of the 50·3 MHz ^{13}C n.m.r. spectrum of anthracene oil in $CDCl_3$. The sample contains 0·7 weight % of tris(acetylacetonato)chromium(III). (A) Conventional 'on-resonance' broad band decoupled spectrum, (B) conventional off-resonance broad band decoupled spectrum with the ^{1}H decoupling frequency shifted 6 kHz from that in (A), (C) Spin Echo Broad Band Off-Resonance Decoupled (SEBBORD) spectrum, with decoupler set as in (B). Phase alternation was applied to the ^{13}C 180° pulse (see the text) resulting in improved spectral phase characteristics.

A conventional ^{13}C n.m.r. experiment, with strong broad band 'on-resonance' decoupling during data acquisition, yields the spectrum shown in Figure 2(A). By comparison, broad band off-resonance decoupling during data acquisition results[1,2] in selective broadening of CH carbon resonances as shown in Figure 2(B). With suitable choice of decoupler power and off-resonance frequency, line widths of *ca.* 80 Hz can be achieved. For the SEBBORD experiment, in addition to this selective line broadening, transverse relaxation during the period 2τ causes a marked decrease in the CH carbon magnetization relative to the quaternary carbon magnetization. The decrease in relative intensity is given by the factor $\exp[-2\tau(a - b)]$ where a and b are the transverse relaxation times of CH and quaternary carbons, respectively, in the presence of off-resonance broad band decoupling. A value of τ 20 ms was used to obtain the SEBBORD spectrum given in Figure 2(C). This shows excellent resolution of quaternary carbon resonances, to the extent that even the very weak sharp resonances observed can be confidently identified as due to quaternary carbons. The resolution achieved is a clear improvement on that obtainable by methods such as SFORD,[1] conventional broad band off-resonance decoupling [Figure 2(B)] and partially relaxed Fourier transform spectra.[3] Nuclear Overhauser enhancement can be achieved in the sequence by 'on resonance' broad band decoupling during the relaxation delay period. All spectra in Figure 2 were obtained with the decoupler gated off during this period.

N.m.r. spectroscopy is a major method of analysis for hydrocarbon fuels deriving from coal and petroleum sources. For ^{13}C n.m.r. spectra, a number of authors attempt to distinguish between aromatic quaternary and aromatic non-quaternary carbon,[4] usually by assuming a cut-off point for these two types of carbon, in the vicinity of 129—130 p.p.m. The SEBBORD method provides a means of direct observation of quaternary carbon intensity distribution and hence avoids errors inherent (Figure 2) in the assumption of a cut-off point. Both over-estimates (by up to *ca.* 15%) and under-estimates (by up to *ca.* 30%) of the quaternary aromatic carbon content of various products from fossil fuels have been noted so far.

We thank The Broken Hill Proprietary Co. Ltd., for permission to publish this work. The Bruker WP-200 n.m.r. spectrometer used in this work was obtained with funding by the Australian Government, *via* the National Energy Research Development and Demonstration Council.

(*Received, 5th September* 1980; *Com.* 967.)

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