Applications and Limitations of Second-order Effects in Off-resonance Proton-decoupled ^{13}C Nuclear Magnetic Resonance Spectra

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Summary Broadening and additional splitting due to second-order effects in off-resonance proton-decoupled ^{13}C n.m.r. spectra provide evidence that carbon atoms are adjacent to one another.

RECENTLY it was shown[1] that additional broadening occurs in single-frequency off-resonance proton-decoupled carbon-13 n.m.r. spectra when a vicinal AB proton pair is irradiated. Newmark and Hill[2] have demonstrated that additional peaks may appear in the off-resonance carbon spectra when the protons being irradiated form a tightly coupled set, and similar phenomena have been noted by Emsley *et al.*[3] Here we generalise our original observation,[1] and show that these 'troublesome' additional peaks[3] and broadening[4] contain useful information for the assignment of ^{13}C n.m.r. spectra. The off-resonance spectrum of 2-methylnorbornan-2-ol (Figure) is an example.

For the present discussion, it is important to note that C-5 and C-6 show additional broadening, while the other methylene carbons C-3 and C-7 appear as simple triplets. The protons attached to each of these methylene carbons exist as AB pairs. This, then, is not a sufficient condition to observe additional broadening in the carbon spectrum. Consideration of the appropriate formulae[5] reveals that a simple triplet will result in the X part of an ABX spectrum if $J_{AX} = J_{BX}$. In off-resonance spectra the apparent couplings[6,7] are usually reduced by a factor of three or more from the true carbon–hydrogen coupling constants. Thus for the apparent J_{AX} and J_{BX} to differ by an amount sufficient to generate observable broadening or splitting, either the AB chemical shift difference must be several p.p.m. or the true couplings must differ by 10 Hz or more. These are very rare occurrences and almost all isolated methylene carbons give clean triplets in off-resonance spectra.

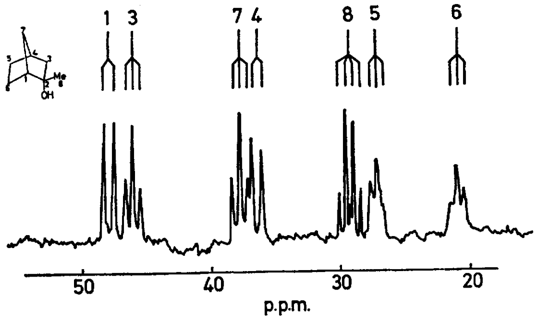

FIGURE. Off-resonance proton-decoupled 25·2 MHz ^{13}C spectrum of 2-methylnorbornan-2-ol. Chemical shifts are in p.p.m. from Me_4Si. Decoupler offset 200 Hz above Me_4Si with power equivalent to 2100 Hz.

The apparent couplings, J_{AX} and J_{BX}, will differ appreciably if protons A and B are on adjacent carbon atoms. Thus the necessary condition for broadening or additional multiplicity in off-resonance spectra is that at least one proton directly bonded to carbon and the proton (or protons) on the adjacent carbon atom must exist as a tightly coupled set. It follows that such multiplet distortion must be present for at least two carbon atoms which must be bonded to one another.† These second-order effects will appear for a methyl carbon in an A_3BX system, a methylene carbon in an A_2BX system, and a methine carbon in an ABX system. In each case the B proton is not bonded to the carbon under study and the examples represent the minimum requirement. Quaternary carbons will not show the effect. In the norbornanol example, C-3 and C-7 are distinguished from C-5 and C-6 using this criterion.

Noise off-resonance decoupling[6] has also been suggested as a technique for assigning methylene carbons[8] and quaternary carbons.[9] The use of this method for methylene carbons breaks down for the norbornyl system. This is a general problem when the methylene protons are non-equivalent, because pure antisymmetric spin states no longer exist. This has been strikingly illustrated in the noise off-resonance spectrum of cedrol.[9]

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† For practical purposes, a tightly coupled system is defined as a pair of protons for which $\Delta\nu/J \leqslant 3$. This generalization will break down in a few cases which should be readily recognizable from the proton spectrum. When protons form a tightly coupled set *via* long-range coupling, the carbon atoms to which they are attached will be broadened even though they are not directly bonded. For example, such a situation might occur for *meta*-carbon atoms on an aromatic ring.

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