# The Sign of the ^{13}C–^{13}C Coupling Constant

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FEW measurements have been made of the signs of the coupling constants observed between directly bonded nuclei, particularly if neither of them is hydrogen. However, since the theoretical predictions of Pople and Santry[1] it has become desirable to determine more of these to verify the applicability of their molecular orbital theory. This experiment is particularly difficult to perform if the two nuclei concerned are ^{13}C, since the natural abundance of this isotope is only 1·1% making the natural abundance of a molecule containing two such nuclei about 0·01%. It was necessary therefore to use an enriched sample and some methyl cyanide, containing ca. 27% of ^{13}C enrichment of the methyl group leading to ca. 0·3% of the doubly substituted ^{13}C species, was obtained from Merck, Sharp, and Dohme.

The experiment was performed on a Varian spectrometer operating at 56·4 Mc./sec. in the proton region and employing field-frequency stabilisation by Anderson and Freeman's method.[2] The transmitter coil was tuned also to the ^{13}C resonant frequency of approximately 14·19 Mc./sec. Power could be supplied at this frequency from a Rohde and Schwarz frequency synthesiser via a tuned amplifier. It was decided to determine the relative signs of the directly-bonded ^{13}C–H and ^{13}C–^{13}C couplings by a spin decoupling[3] method and so it was first necessary to locate the ^{13}C resonances due to the ^{13}CN group of the doubly substituted species. In view of the low concentration of this the corresponding resonances of the $^{12}CH_3{}^{13}CN$ species were determined by a "tickling"[3] method involving observation of the satellites in the proton region, and the isotope shift between

(a)   (b)
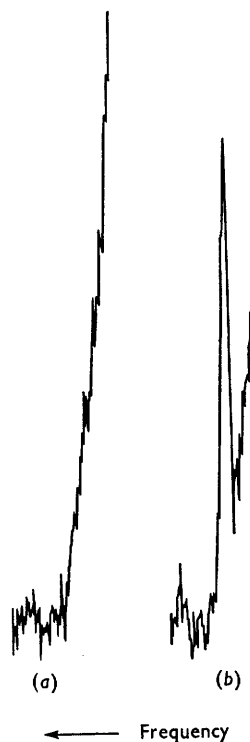
◀——————— Frequency

One half of the low-field doublet due to the $^{13}CH_3{}^{13}CN$ molecule (a) with irradiation of the high-frequency ^{13}CN quartet and (b) with irradiation of the low-frequency ^{13}CN quartet. The strong signal is due to $^{13}CH_3{}^{12}CN$.

this and the doubly substituted molecule was assumed to be negligible. The ^{13}C–^{12}C–H and

[1] J. A. Pople and D. W. Santry, Mol. Phys., 1964, **8**, 1.
[2] W. A. Anderson and R. Freeman, J. Chem. Phys., 1962, **37**, 2053.
[3] D. F. Evans and J. P. Maher, Proc. Chem. Soc., 1961, 208.

[13]C–[13]C couplings are known[4,5] to be 10.0 ± 0.2 c./sec. and 57.3 ± 0.3 c./sec., respectively, and so the spectrum in the [13]CN region due to the doubly substituted species consists of two discrete quartets, one corresponding to each of the methyl ^{13}C spin states. The corresponding proton spectrum consists of two pairs of lines each separated by the geminal [13]C–[12]C–H coupling and approximately equally spaced about each [13]CH$_3$[12]CN proton line. The normal spin decoupling experiment would consist of irradiating one of the [13]CN quartets and observing which pair of the proton lines coalesces. With so low a concentration, however, it proved more convenient to dephase the spectrum slightly so as to display one half of the proton spectrum of the doubly substituted molecule more clearly. The diagram shows the effect of irradiating the low- and high-frequency quartets in the [13]CN region whilst one of the low-field [13]CH$_3$[13]CN proton lines is observed and demonstrates that the proton line disappears when the high-frequency (i.e. low-field) [13]CN quartet is irradiated. This demonstrates that the [13]C–[13]C and ^{13}C–H couplings are of the same sign. The result was confirmed by observation of all the proton lines due to the doubly substituted molecule in turn and is in agreement with theoretical prediction.

[4] H. Dreeskamp and E. Sackmann, *Z. Phys. Chem.*, 1962, **34**, 18.
[5] H. J. Bernstein and K. Frei, *J. Chem. Phys.*, 1963, **38**, 1216.