Natural-abundance Carbon-13 Nuclear Magnetic Resonance Spectra of Some Carborane Derivatives

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WE and others have made unsuccessful attempts to measure ^{13}C–^{1}H spin coupling constants of 1,2-$B_{10}H_{10}C_2H_2$ and related carboranes from high-resolution ^{1}H n.m.r. spectra. Determination of these coupling constants as well as the chemical shifts of the ^{13}C nuclei should prove to be valuable probes of the electronic structure of these unusual electron-deficient polyhedral molecules. Natural-abundance ^{13}C n.m.r. spectra have now been determined at 15·086 MHz. using an externally locked fixed-field spectrometer. The r.f. frequency was provided by a frequency synthesizer swept with a linear digitized programmer. A Varian (C-1024) time-averaging computer was used for accumulating all spectra. The accumulation of 100 scans of the ^{13}C spectrum of a 3·8 M-solution of 1,2-$B_{10}H_{10}C_2H_2$ in acetone gave the trace shown in Figure 1. The peak on the right-hand side of the Figure is the lowest-field portion of the acetone methyl quartet. The spectrum in Figure 2 was obtained after 249 sweeps of a 2·5 M-solution of $(CH_3)_3NH$ [7,9-$B_9C_2H_{12}$].† In this case the entire acetone methyl

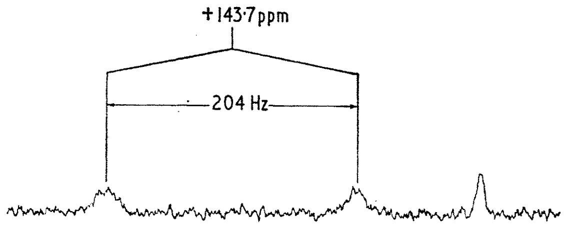

FIGURE 1. *Carbon-13 n.m.r. spectrum of* 1,2-$B_{10}H_{10}C_2H_2$ *relative to carbon disulphide as reference.*

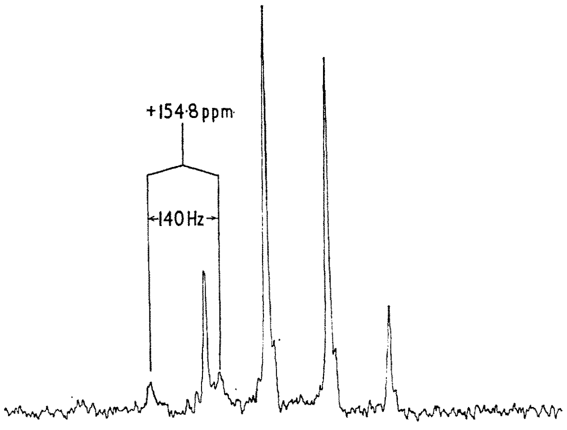

FIGURE 2. *Carbon-13 n.m.r. spectrum of* $(CH_3)_3NH$[7,9-$B_9C_2H_{12}$] *relative to carbon disulphide as reference.*

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† The numbering system employed follows the new nomenclature rules which recently appeared in *Inorg. Chem.*, 1968, 7, 1945.

quartet is shown. The ^{13}C n.m.r. parameters of these carborane derivatives and others are given in the Table.

TABLE

Compound	δ_C[a]	J_{C-H}(Hz.)[b]
1,2-$B_{10}H_{10}C_2H_2$	143·7	204
1,7-$B_{10}H_{10}C_2H_2$	143·8	184
Cs[$B_{11}H_{11}CH$]	147·5	163
$(CH_3)_3NH[7,8\text{-}B_9C_2H_{12}]$	154·8	142
$(CH_3)_3NH[7,9\text{-}B_9C_2H_{12}]$	154·8	140

[a] Chemical shifts were measured from internal acetone as reference and converted to the carbon disulphide reference scale, $\delta(CS_2) = \delta(Me_2CO) + 169{\cdot}6$ p.p.m.

[b] The error in these one-bond carborane C–H coupling constants is believed to be no greater than ±5 Hz.

Considering only the twelve-atom closed-cage carboranes, one observes an increase in the ^{13}C–H directly bonded coupling constant which parallels the expected increase in effective nuclear charge on the carbon atom toward the 2*s*-electrons. The 1,2-$B_{10}H_{10}C_2H_2$ molecule with adjacent higher-charge carbon nuclei should have a larger effective nuclear charge than 1,7-$B_{10}H_{10}C_2H_2$ which has nonadjacent carbon atoms. The one-carbon carborane anion, $B_{11}H_{11}$-CH^- should have an even lower effective nuclear charge. Since the "*s*" character of the C–H bond in the icosahedral molecules should not change significantly, the effective nuclear charge dependence of the ^{13}C–H coupling constant first suggested by Grant and Litchman may be the important factor here.[1] No boron–carbon coupling has yet been observed in the measurements.

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[1] D. M. Grant and W. M. Litchman, *J. Amer. Chem. Soc.*, **1965**, **87**, 3994.