

High-Resolution ^1H and ^{11}B NMR Studies of 1,2- and 1,7- $\text{B}_{10}\text{C}_2\text{H}_{12}$

A. R. GARBER, G. M. BODNER, AND L. J. TODD

Department of Chemistry, Indiana University, Bloomington, Indiana 47401*

AND

A. R. SIEDLE†

Inorganic Chemistry Section, National Bureau of Standards, Washington, D.C. 20234

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The 70.6-MHz ^{11}B NMR spectrum of 1,2- $\text{B}_{10}\text{C}_2\text{H}_{12}$ has been assigned by use of labeled derivatives. The assignments are, in order of increasing field, B(9,12), B(8,10), B(4,5,7,11) and B(3,6). Resonances in 1,7- $\text{B}_{10}\text{C}_2\text{H}_{12}$ are due, in order of increasing field, to B(5,12), B(9,10), B(4,6,8,11) and B(2,3). The ^1H NMR spectrum of 1,2- D_2 -1,2- $\text{B}_{10}\text{C}_2\text{H}_{10}$ in C_6D_6 contains four quartets at -2.7 , -2.5 , -2.1 , and -1.7 ppm due to H(8,10), H(9,12), H(4,5,7,11) and H(3,6), respectively. Confirmation of the assignment was achieved by double-resonance experiments.

Because of the complexity of the ^{11}B nuclear magnetic resonance spectra of many large boron clusters, the interpretation and study of such spectra have been difficult. Eaton and Lipscomb (1) have reviewed progress in this area to date, and it appears that assignments of the ^{11}B NMR spectra of 1,2- (2a, 3) and 1,7- (2b, 3) dicarbocloso-dodecaborane (12) (hereinafter referred to as *o*- and *m*-carborane respectively) are not definitive, and occasionally have been done on a best-guess (1) basis.

Since the spectra of these icosahedral molecules have been used to help explain the nature of ^{11}B NMR chemical shifts, and in elucidating the topology of B-substituted carboranes, it was desirable to place extant assignments on a firmer basis. The study of the ^1H NMR spectra of boranes and carboranes has, in general, been unrewarding, owing to the presence of broad, overlapping lines separated by small chemical shifts. High-resolution spectra have, however, been obtained for (inter alia) B_2H_6 (4), B_5H_{11} (5, 6), B_4H_{10} , B_6H_{10} and B_6H_{12} (7), $\text{B}_{10}\text{H}_{14}$ (8), and B_3CH_8 (9).

EXPERIMENTAL¹

9,12- Br_2 -1,7- $\text{B}_{10}\text{C}_2\text{H}_{10}$, 9- Br -1,7- $\text{B}_{10}\text{C}_2\text{H}_{11}$, 9,12- Br_2 -1,2- $\text{B}_{10}\text{C}_2\text{H}_{10}$ (10), 3- C_6H_5 -1,2- $\text{B}_{10}\text{C}_2\text{H}_{11}$ (11), 3- F -1,2- $\text{B}_{10}\text{C}_2\text{H}_{11}$, and 2- F -1,7- $\text{B}_{10}\text{C}_2\text{H}_{11}$ (12) were prepared according to literature methods.

* Contribution No. 3031.

† To whom correspondence should be addressed.

¹ Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

Our experience with the bromination of carboranes was slightly different from that in the literature. In general, it was found preferable to slowly add a carbon disulfide solution of bromine to a mixture of carborane and aluminum in carbon disulfide. Small amounts of $B_{10}C_2Br_4H_8$, identified by mass spectroscopy, were formed along with the $B_{10}C_2Br_3H_9$. Preparations of 9,12- Br_2 -1,2- $B_{10}C_2H_{10}$ always contained traces of the tribromo derivative, which could be removed by recrystallization from hexane. The o - $B_{10}C_2D_4H_8$ was prepared from 1,2,3,4- $B_{10}D_4H_{10}$ (13) and 2-butyne-1,4-diol diacetate (14). The purity of this and other derivatives was confirmed by melting point, ^{11}B NMR, and mass spectroscopy.

C-Deutero carboranes were used for all 1H NMR work. These were obtained by treating the corresponding protio carborane with slightly more than two equivalents by butyllithium and quenching by slow addition of D_2O . The deuterated carboranes were purified by sublimation.

Preparation of 9,12- Br_2 -2- C_6H_5 -1,7- $B_{10}C_2H_9$. 9,12-Dibromo-*m*-carborane was degraded with potassium hydroxide in ethanol to form hygroscopic K^+ (3)-9, 12- Br_2 -1,7- $B_9C_2H_{10}^-$ by literature methods (11). Two mmole (0.66 g) of this salt was treated with 2 mmole of *n*-butyllithium in 15 ml of tetrahydrofuran. After stirring for 30 min at room temperature, the solution was frozen with liquid nitrogen and 2.0 mmole (0.31 g) of dichlorophenylborane was added in one portion. The mixture was allowed to warm to room temperature with stirring, stirred for 48 hr, and then refluxed for 1 hr. The solvent was removed under reduced pressure and the residue extracted by twice refluxing for 30 min with 15 ml of hexane. The hexane was evaporated and the residue chromatographed on a $3 \times \frac{1}{2}$ in. silica gel column. Elution with 3:1 hexane-benzene afforded a white solid which was recrystallized twice from hexane at $-80^\circ C$. The product, 0.01 g, melted at $122-123^\circ C$ *in vacuo*. The mass spectrum revealed a molecular ion peak at *m/e* 380, and an intense cluster of peaks due to loss of C_6H_5 . *Anal.* Calcd for $C_8H_{14}B_{10}Br_2$: C, 25.40; H, 3.70. Found: C, 26.14; H, 4.20.

Proton (220 MHz) and boron (70.6 MHz) spectra were obtained on a varian HR-220 spectrometer with a digitized frequency sweep. Boron-11 chemical shifts were measured relative to the reference to ± 0.1 ppm. Proton-decoupled spectra were obtained with a Varian probe modified by Professor A. O. Clouse. The ^{19}F spectra were obtained at 94.1 MHz on a Varian HA-100 spectrometer. Reference materials were external $BF_3 \cdot O(C_2H_5)_2$ (^{11}B), and internal $(CH_3)_4Si$ (1H). ^{19}F shifts were measured using internal C_6H_5F (113.7 ppm from CCl_3F) and are expressed relative to CCl_3F . Negative shifts are downfield of the reference.

RESULTS

The structures of *o*- and *m*-carborane and their respective numbering conventions are shown in Fig. 1. The ^{11}B NMR spectra of both species are slightly solvent dependent and the various resonances are better resolved in polar solvents such as acetone.

The spectrum of *m*- $B_{10}C_2H_{12}$ in acetone (Fig. 2A) consists of four doublets of relative intensities 2:2:4:2, each of which collapses to a sharp singlet upon irradiation at the proton frequency (Fig. 2B). The geometrically equivalent sets of boron nuclei also appear to be magnetically equivalent. The derivatives of *m*-carborane exhibit spectra shown in Figs. 2C-G can in most cases be readily interpreted in terms of the parent boron cluster, which experiences small perturbations due to the substituents.

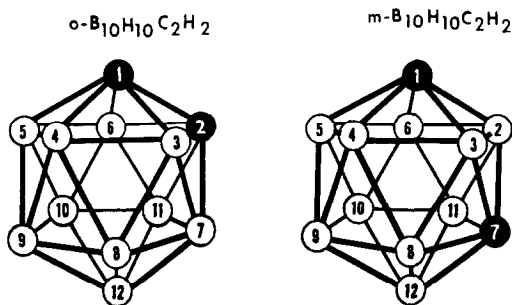


FIG. 1. Numbering system in 1,2- and 1,7- $\text{B}_{10}\text{C}_2\text{H}_{12}$.

Bromination in the 9,10 positions (15) produces collapse and a downfield shift of the doublet centered at 10.4 ppm in the parent compound as shown in Fig. 2C, allowing an unambiguous assignment for B(9,10). The spectrum of 9-bromo-*m*-carborane (Fig. 2D) is more complex due to the lower symmetry, but it displays similar effects. The singlet

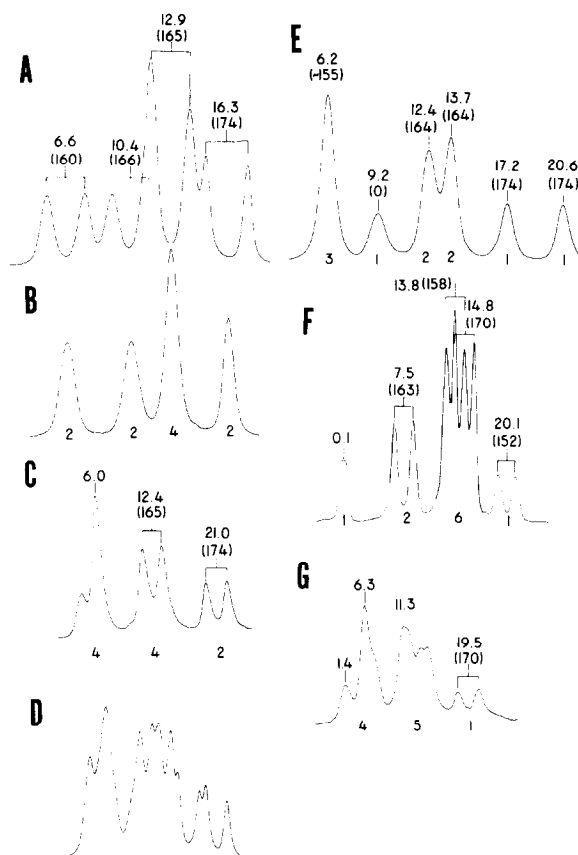


FIG. 2. The 70.6-MHz ^{11}B NMR spectra in acetone of (A) 1,7- $\text{B}_{10}\text{C}_2\text{H}_{12}$; (B) 1,7- $\text{B}_{10}\text{C}_2\text{H}_{12}$, ^1H decoupled; (C) 9,12- Br_2 -1,7- $\text{B}_{10}\text{C}_2\text{H}_{10}$; (D) 9-Br-1,7- $\text{B}_{10}\text{C}_2\text{H}_{11}$; (E) 9-Br-1,7- $\text{B}_{10}\text{C}_2\text{H}_{11}$, ^1H decoupled; (F) 2-F-1,7- $\text{B}_{10}\text{C}_2\text{H}_{11}$; (G) 9,12- Br_2 -2- C_6H_5 -1,7- $\text{B}_{10}\text{C}_2\text{H}_9$. Chemical shifts are in parts per million, coupling constants in hertz; areas are shown beneath each resonance.

due to B(9) appears at 6.2 ppm and partially overlaps a doublet of intensity 2 at this position. A doublet of intensity 1, presumably B(10), remains at 9.2 ppm. This becomes manifest in the proton-decoupled spectrum of this compound shown in Fig. 2E.

The spectrum of 2-fluoro-*m*-carborane is shown in Fig. 2F. Replacement of hydrogen by fluorine produces collapse and a large downfield shift of the B(2) resonance. The substituted boron appears as a broad singlet at 0.1 ppm, with unresolved coupling which, since it is unaffected by broad band proton irradiation, must be due to B-F spin coupling. The ^{19}F NMR spectrum of this compound in acetonitrile reveals a quartet centered at 91.9 ppm with $J_{\text{BF}} = 45$ Hz. The high-field doublet in the ^{11}B NMR spectrum of this derivative is of relative area 1, which would imply that this high-field doublet in the parent carborane must arise from B(2,3).

To confirm this interpretation of the spectrum of 2-fluoro-*m*-carborane, 2-phenyl-9,10-dibromo-*m*-carborane was prepared by boron insertion into $9,12\text{-Br}_2\text{-1,7-BgC}_2\text{H}_9^{2-}$, a reaction known (11) to be regiospecific. The ^{11}B NMR spectrum of this compound (Fig. 2G) reveals only one doublet of area 1 at high field. Reference to Fig. 2C shows that the effect of phenyl substitution at B(2) is, as expected, to reduce by one half the area of the highest-field resonance.

The doublet at 12.9 ppm in *m*-carborane can be assigned to B(4,6,8,11) on the basis of intensity and the low-field doublet at 6.6 ppm, otherwise unassigned, must be due to B(5,12). This yields an unambiguous assignment of the spectrum in agreement with that previously postulated (2b), i.e., in order of increasing magnetic field, B(5,12), B(9,10), B(4,6,8,11), and B(2,3).

The spectrum of *o*-carborane in acetone is shown in Fig. 3A. The two doublets of area 2 at 3.1 and 9.6 ppm collapse upon deuteration at the 8,9,10,12 positions as shown in Fig. 3B. Bromination at the 9,12 positions produces collapse and a downfield shift of the lowest-field resonance by 3.2 ppm with respect to the parent carborane (Fig. 3C). These two low-field doublets may therefore be assigned in order of increasing magnetic field to B(9,12) and B(8,10) respectively. The doublet of intensity 4 at 13.7 ppm is assigned to B(4,5,7,11) (vide infra) and the remaining doublet at ca. 14 ppm is assigned to B(3,6).

The spectrum of 3-fluoro-*o*-carborane is shown in Fig. 3D. Fluorination in this position has evidently halved the intensity of the high-field doublet and shifted the B(3) resonance approximately 14 ppm downfield. The asymmetry of substitution in this derivative has drastically reduced the degeneracy of chemical shifts, leading to a non-equivalence of the boron resonances due to B(8) and B(10) and resonances due to B(4,7) and B(5,11). Incompletely resolved B-F coupling again is apparent at B(3). The ^{19}F NMR spectrum in acetonitrile showed a quartet centered at $\delta = 75.2$ ppm, $J_{\text{BF}} = 52$ Hz.

The spectrum of 3-phenyl-*o*-carborane, shown in Fig. 3E, illustrates that caution must be exercised in the analysis of derivative spectra on the basis of small perturbations of the parent compound. The overlapping singlet and doublet at lowest field are readily assigned to B(3) and B(1,12), respectively. The doublet at 8.7 ppm in this spectrum, however, has a relative intensity of 1. The only plausible explanation of this behavior consistent with the above data is that B(8,10) are now nonequivalent and that one of these borons is now contained within the doublet of intensity 6 at 12.7 ppm. (This nonequivalence of B(8,10) is also to be seen in the spectrum 3-fluoro-*o*-carborane shown in Fig. 3D.)

The ^1H spectrum of *o*-carborane is sensitive to both solvent and concentration. Spectra were recorded under different conditions in an attempt to optimize these variables with respect to resolution. The concentration dependence was examined to ensure that the various resonances were not shifting in opposite directions and crossing over as the concentration was changed. The ^1H spectrum of *m*-carborane was too poorly resolved for further, detailed study.

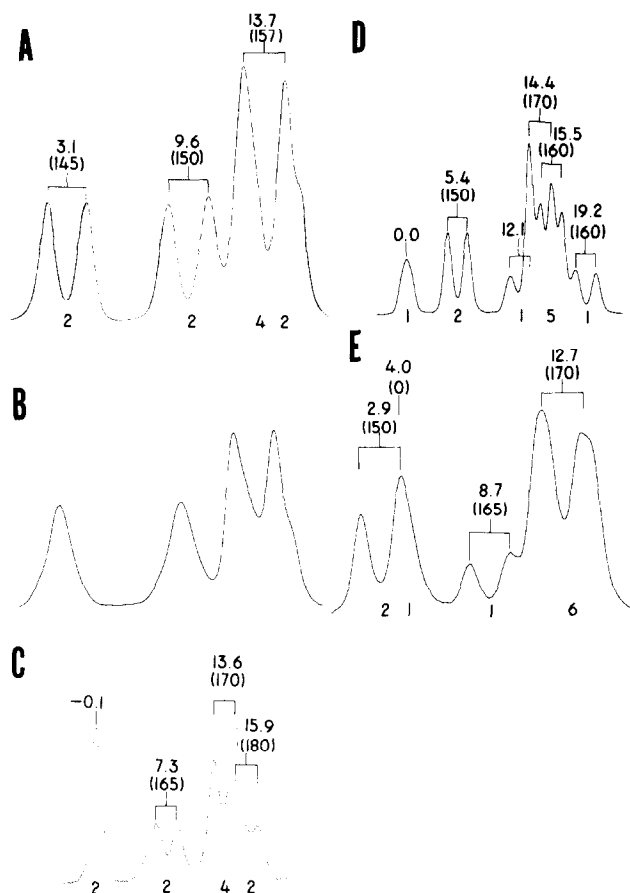


FIG. 3. The 70.6-MHz ^{11}B NMR spectra in acetone of (A) 1,2- $\text{B}_{10}\text{C}_2\text{H}_{12}$; (B) 8,9,10,14- D_4 -1,2- $\text{B}_{10}\text{C}_2\text{H}_8$; (C) 9,10- Br_2 -1,2- $\text{B}_{10}\text{C}_2\text{H}_{10}$; (D) 3-F-1,2- $\text{B}_{10}\text{C}_2\text{H}_{11}$; (E) 3- C_6H_5 -1,2- $\text{B}_{10}\text{C}_2\text{H}_{11}$.

As in the case of the ^{11}B spectra, symmetry arguments require the presence of four magnetically distinct B-H proton environments in *o*-carborane. The 220-MHz ^1H spectrum of a 0.33 *M* solution in benzene- d_6 does indeed contain four overlapping quartets centered at -2.7 , -2.5 , -2.1 , and -1.7 ppm in the expected intensity ratio of 2:2:4:2 (Fig. 4A). The two quartets at lowest field are greatly decreased in intensity in the spectrum of the 8,9,10,12 tetradeutero derivative (Fig. 4B). The resonance centered at -2.5 ppm has disappeared in the spectrum of the 9,12 dibromo derivative (Fig. 4C). This allows assignment of the signals at -2.5 and -2.7 ppm to H(9,12) and H(8,10), respectively.

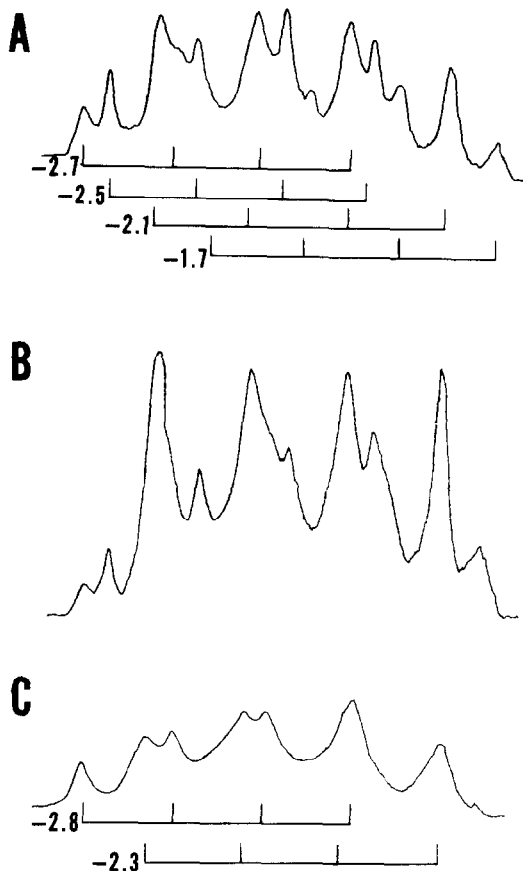


FIG. 4. The 220-MHz ^1H NMR spectra in benzene- d_6 of (A) 1,2- D_2 -1,2- $\text{B}_{10}\text{C}_2\text{H}_{10}$; (B) 1,2,8,9,10,12- D_6 -1,2- $\text{B}_{10}\text{C}_2\text{H}_6$; (C) 1,2- D_2 -9,12- Br_2 -1,2- $\text{B}_{10}\text{C}_2\text{H}_6$.

The quartet centered at -2.1 ppm has a relative area of 4 and so must be due to H(4,5,7,11). The highest-field quartet, otherwise unassigned, must then be due to H(2,3). These assignments were confirmed by $\{^1\text{H}\}^{11}\text{B}$ spectra (Fig. 5), in which irradiation at the appropriate ^1H frequency resulted in the collapse of the previously assigned ^{11}B doublets. Because of the width of the decoupling signal employed, this technique, while useful in confirming spectral assignments, does not provide accurate ^1H chemical shifts.

DISCUSSION

The ^{11}B assignments presented here confirm those previously suggested (2a, b), although the earliest postulated assignment for *m*-carborane (3) has been shown to be in error.

The availability of unambiguous assignments of these spectra led us to attempt a correlation of the ^{11}B NMR data with the molecular orbital calculations offered to date. Cheung *et al.* (16) have attempted CNDO/2 calculations on the carboranes, and Koetzle and Lipscomb (17) have recently reported nonempirical results parameterized from a minimum basis set SCF calculation for $\text{B}_4\text{C}_2\text{H}_6$ (18). The most interesting

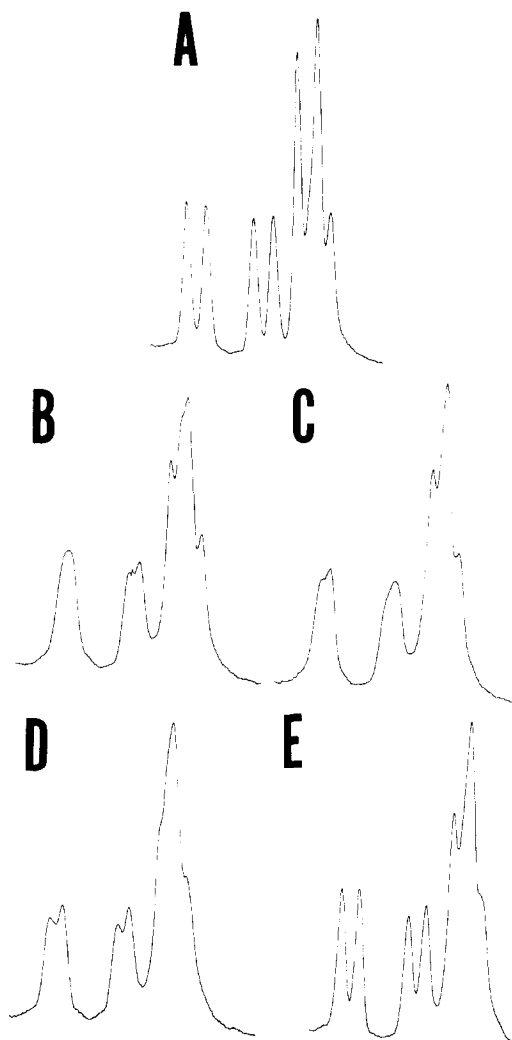


FIG. 5. The 70.6-MHz ^{11}B NMR spectrum of $1,2\text{-B}_{10}\text{C}_2\text{H}_{12}$ irradiated at a ^1H frequency corresponding to (A) no irradiation; (B) -2.5 ppm; (C) -2.7 ppm; (D) -2.1 ppm; (E) -1.7 ppm.

observation was that neither method predicts the order of chemical shifts in the meta isomer from a simple correlation of ^{11}B chemical shift and the net atomic charge. Attempts at a prediction of relative order imply that the B(9,10) resonance should be downfield of the B(5,12) resonance, and not the opposite, as is observed. This would suggest either that the theoretical procedures are in error, or, more probably, that there is an additional contribution to the ^{11}B chemical shift, not arising simply from a charge distribution effect.

It is of interest to note that the ^{19}F chemical shifts for $2\text{-F-1,7-B}_{10}\text{C}_2\text{H}_{11}$ and $3\text{-F-1,2-B}_{10}\text{C}_{11}$ are in the range typical of aliphatic rather than aromatic fluorines (19) and that $J(^{11}\text{B}\text{-}^{19}\text{F})$ values are similar to those in the trigonal mixed halide BF_2Br ($J_{\text{BF}} = 56$ Hz) (20, 21).

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