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An NMR Study of Icosahedral Heteroatom Borane Derivatives

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An extensive study of ^{13}C and ^{11}B shielding values of icosahedral heteroatom boranes is described. Shielding effects on polyhedral atoms due to variations (a) in directly bonded exopolyhedral groups, (b) in ortho cage groups, (c) in meta cage groups, and (d) in para cage groups are outlined. A linear relationship between ^{13}C and ^{11}B shielding values of isoelectronic and isostructural icosahedral molecules is demonstrated.

INTRODUCTION

To date only a limited amount of ^{13}C NMR information concerning carborane derivatives has appeared in the literature. Initially it was demonstrated that the ^{13}C signals of carbon atoms in the polyhedral borane surface could be measured without interference from ^{11}B–^{13}C coupling (*1*). Later it was demonstrated that for carboranes of the type $B_nC_2H_{n+2}$ ($n = 3$ to 10) polyhedral carbon atoms with the largest coordination number are the most shielded (*2*). There is approximately a 50 ppm difference between the carborane carbon signals of 1,5-$B_3C_2H_5$ and 1,2-$B_{10}H_{10}C_2H_2$ in which the carbon atoms change two units in coordination number. More recently ^{13}C shielding data of 9-Br-1,2-$B_{10}H_9C_2H_2$ and 9,12-Br_2-1,2-$B_{10}H_8C_2H_2$ have been used to show that there is an antipodal shielding effect caused by increasing the electron-withdrawing ability of a cage atom which is para to a polyhedral carbon atom (*3*). There have also been several reports where ^{13}C NMR data were used as one means of characterization of new carborane derivatives (*4*–*7*).

In this report we delineate some of the basic trends that occur for ^{13}C NMR shielding values of icosahedral carborane derivatives and the relationships between ^{13}C and ^{11}B NMR shielding trends in these systems.

EXPERIMENTAL

General Comments

Proton NMR spectra were obtained with either a Varian HA-100 or a Varian EM-360 spectrometer. Boron-11 NMR spectra were obtained at 70.6 MHz with a Varian HR-220 spectrometer. Carbon-13 NMR spectra were obtained either on a pulsed spectrometer operating at 15.1 MHz which was constructed in this department and previously described (*8*) or with a Varian XL-100-15 pulsed spectrometer operating at 25.2 MHz. The ^{13}C NMR chemical shift values were measured relative to

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an internal solvent resonance and are reported in ppm (*positive* values downfield) from TMS using the conversion, $\delta_{\text{TMS}} = \delta_{(\text{CH}_3)_2\text{CO}} + 30.43$ ppm. The ^{11}B NMR chemical shift values were measured relative to an external $BF_3.O(C_2H_5)_2$ reference (*negative* values downfield). The ^{1}H chemical shift values were measured relative to an internal TMS reference (positive values downfield). Elemental analyses were obtained from the University of Illinois Microanalytical Laboratory or from Schwarzkopf Microanalytical Laboratories, Woodside, New York.

Materials

The data presented below were used as a means of checking the identity and purity of the compounds employed in this study.

1-[Si(CH$_3$)$_3$]-1,2-B$_{10}$C$_2$H$_{11}$. Analysis: Calcd for $C_5H_{20}B_{10}Si$, C, 27.73, H, 9.31; found, C, 27.88, H, 9.39. ^{13}C NMR, –1.5 ppm (CH_3).

1-[CO$_2$CH$_3$]-1,2-B$_{10}$C$_2$H$_{11}$. Analysis: Calcd for $C_4H_{14}B_{10}O_2$, C, 23.73, H, 6.92; found, C, 23.83, H, 7.08. ^{13}C NMR, 161.3 ppm (carbonyl carbon), 55.5 ppm (CH_3).

1-[CO$_2$H]-1,2-B$_{10}$C$_2$H$_{11}$. ^{13}C NMR, 160.5 ppm (carbonyl carbon). ^{1}H NMR (acetone), 4.55 ppm (CH), 10.94 ppm (CO_2H). mp, 149–150° [lit. mp, 150–150.5° (*9*)].

1-CH$_3$-1,2-B$_{10}$C$_2$H$_{11}$. ^{13}C NMR, 25.4 ppm (CH_3). ^{1}H NMR (acetone), 4.63 ppm (CH), 4.34 ppm (CH_3). mp, 217–218° [lit. mp, 218–219° (*10*)].

1-CH$_2$Br-1,2-B$_{10}$C$_2$H$_{11}$. ^{13}C NMR, 32.3 ppm (CH_2Br). mp, 46–49° [lit. mp, 47–49° (*11*)].

1-vinyl-1,2-B$_{10}$C$_2$H$_{11}$. ^{13}C NMR, 132.7 and 122.4 (vinyl carbons). ^{1}H NMR (acetone), 4.59 ppm (CH), 5.2–6.5 ppm, multiplet (vinyl protons). mp, 78–79° [lit. mp, 78–79° (*12*)].

1-[COC$_6$H$_5$]-1,2-B$_{10}$C$_2$H$_{11}$. ^{13}C NMR, 185.6 ppm (carbonyl carbon), 134.5, 133.6, 130.3, and 129.0 ppm (C_6H_5). ^{1}H NMR (acetone), 4.26 ppm (CH), 7.5–8.2 ppm, multiplet (C_6H_5). mp, 57–58° [lit. mp, 57.8–58° (*13*)].

1-C$_6$H$_5$-1,2-B$_{10}$C$_2$H$_{11}$. ^{13}C NMR, 133.9, 130.4, 129.3, 127.8 ppm (C_6H_5). ^{1}H NMR (acetone), 5.02 ppm (CH), 7.3–7.8 ppm, multiplet (C_6H_5).

3-C$_6$H$_5$-1,2-B$_{10}$C$_2$H$_{11}$. mp, 98–101° [lit. mp, 109–110° (*14*)]. The mass spectrum cutoff at *m/e 222*, which corresponds to the $^{12}C_8H_{16}{}^{11}B_{10}$ parent ion.

1-[CO$_2$CH$_3$]-1,7-B$_{10}$C$_2$H$_{11}$. Analysis: Calcd for $C_4H_{14}B_{10}O_2$, C, 23.73, H, 6.92; found, C, 23.92, H, 7.15. ^{13}C NMR, 162.3 ppm (carbonyl carbon), 54.7 ppm (CH_3). ^{1}H NMR (CCl_4), 2.95 ppm, 1H (CH), 3.32 ppm, 3H (CH_3).

1-CH$_3$-*1,7-B$_{10}$C$_2$H$_{11}$*. mp, 208–210° [lit. mp, 208–210° (*15*)]. ^{13}C NMR, 24.5 ppm (CH_3).

1-[COCH$_3$]-1,7-B$_{19}$C$_2$H$_{11}$. Analysis: Calcd for $C_4H_{14}B_{10}O$, C, 25.81, H, 7.53; found, C, 26.08, H, 7.67. ^{13}C NMR, 192.2 ppm (carbonyl carbon), 27.9 ppm (CH_3). ^{1}H NMR (CCl_4), 2.18 ppm (CH_3), 2.95 ppm (CH).

1-[OCOCH$_3$]-1,7-B$_{10}$C$_2$H$_{11}$. mp, 50–55° [lit. mp, 58–59° (*16*)]. ^{13}C NMR, 166.3 ppm (carbonyl carbon), 20.8 ppm (CH_3).

1-[Si(CH$_3$)$_3$]-1,7-B$_{10}$C$_2$H$_{11}$. mp, 68.5–71° [lit. mp, 67–68° (*17*)]. Analysis: Calcd for $C_5H_{20}B_{10}Si$, C, 27.78, H, 9.26; found, C, 27.99, H, 9.51. ^{13}C NMR, –0.6 ppm (CH_3).

1,2-[SCH$_3$]$_2$-1,2-B$_{10}$C$_2$H$_{10}$. mp, 101–102° [lit. mp, 101–102° (*18*)]. ^{13}C NMR, 19.4 ppm (CH_3).

1,2-[CH$_3$]$_2$-1,2-B$_{10}$C$_2$H$_{10}$. mp, 262–263° [lit. mp, 262–263° (*19*)]. ^{13}C NMR, 23.2 ppm (CH_3).

$1,2\text{-}[Si(CH_3)_3]_2\text{-}1,2\text{-}B_{10}C_2H_{10}$. mp, 136–139° [lit. mp, 141–142° (*20*)]. ^{13}C NMR, 1.7 ppm (CH_3).

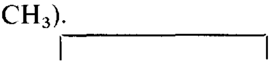
$1,7\text{-}[Sn(CH_3)_3]_2\text{-}1,7\text{-}B_{10}C_2H_{10}$. The sample was obtained from Olin Mathieson Co. and vacuum distilled before use. ^{11}B NMR (acetone) doublet signals at 2.47 (2B), 6.00 (2B), 8.34 (4B) and 12.87 ppm (2B). ^{13}C NMR, –8.0 ppm (CH_3).

$1,7\text{-}[Ge(CH_3)_3]_2\text{-}1,7\text{-}B_{10}C_2H_{10}$. Analysis: Calcd for $C_8H_{28}B_{10}Ge_2$, C, 25.39, H, 7.40; found, C, 25.38, H, 7.34. ^{13}C NMR, –1.2 ppm (CH_3).

$1,7\text{-}[Si(CH_3)_3]_2\text{-}1,7\text{-}B_{10}C_2H_{10}$. Analysis: Calcd for $C_8H_{28}B_{10}Si_2$, C, 33.33, H, 9.72; found, C, 32.95, H, 9.89. ^{11}B NMR (acetone) doublet signals at 2.45 (2B), 7.12 (2B), 9.18 (4B), and 13.22 ppm (2B). ^{13}C NMR, –0.8 ppm (CH_3).

$1,7\text{-}(CH_3)_2\text{-}1,7\text{-}B_{10}C_2H_{10}$. ^{13}C NMR, 36.4 ppm (CH_3).

$1,7\text{-}[CO_2CH_3]_2\text{-}1,7\text{-}B_{10}C_2H_{10}$. ^{13}C NMR, 161.8 ppm (carbonyl carbons), 55.2 ppm (CH_3).



$1,2\text{-}[(CH_2\text{–})_4]\text{-}CB_{10}H_{10}C$

Treatment of $1,2\text{-}B_{10}H_{10}C_2H_2$, 2.48 g with 2.1 equivalents of butyl lithium in 40 ml of ether formed C,C′-dilithiocarborane. This lithio derivative was refluxed for 6 hr, with 1.1 equivalents (5.88 g) of 1,4-diiodobutane. The resulting deep red mixture was treated with water and the ether soluble fraction washed several times more with water and then chromatographed on silica gel with cyclohexane as eluent. Three recrystallizations from absolute methanol gave 0.9 g (27% yield) of $1,2\text{-}[(\text{–}CH_2)_4]\text{-}1,2\text{-}B_{10}H_{10}C_2$. mp, 132–134°C [lit. mp, 122–123° (*21*)]. Analysis: Calcd for $C_6H_{18}B_{10}$, C, 36.32, H, 9.14; found, C, 36.53, H, 9.07. ^1H NMR ($CDCl_3$) contains two broad multiplets at 1.57 (4H) and 2.42 ppm (4H).

RESULTS AND DISCUSSION

Solvent effects

The ^{13}C NMR data for most but not all the compounds used in this study were obtained in acetone solution. Due to solubility problems, a few of the NMR samples were run in other solvents. Since we knew from our previous work (*22*) that the proton signal of the polyhedral CH groups, particularly in the case of $1,2\text{-}B_{10}H_{10}C_2H_2$,

TABLE 1

CARBON-13 SHIELDING VALUES OF CARBORANES IN VARIOUS SOLVENTS

Solvent	δ_C (ppm)		
	$1,2\text{-}B_{10}C_2H_{12}$	$1,7\text{-}B_{10}C_2H_{12}$	$1,12\text{-}B_{10}C_2H_{12}$
DMSO	(56.5)[a]	(56.5)	(64.1)
Acetone	56.9 (56.6)	56.5 (56.8)	64.0 (64.6)
CH_2Cl_2	(55.1)	(56.1)	(64.3)
THF	(55.8)	(56.2)	(64.2)
C_6H_6	54.2	54.8	
CCl_4	53.5	54.3	62.9

[a] Values in parentheses are from Ref. (*31*).

was strongly solvent dependent, we measured the ^{13}C shielding values of the $B_{10}H_{10}C_2H_2$ isomers in various solvents (see Table 1). An increase in the polarity of the solvent results in a deshielding of the carbon signal with the largest change (3 ppm) occurring with the most polar molecule 1,2-$B_{10}H_{10}C_2H_2$.

The Substituted Carbon

In general when the hydrogen atom of a polyhedral CH group of a carborane is substituted by a group containing a carbon, nitrogen, or oxygen central atom, the carborane carbon resonance is deshielded. This is clearly shown in the NMR data of the carbon-substituted derivatives of ortho- and meta-carborane presented in Tables 2–4. Upon changing substituents from hydrogen to other groups it is interesting

TABLE 2

^{13}C SHIELDINGS OF THE POLYHEDRAL CARBON ATOMS OF 1-R-1,2-$C_2B_{10}H_{11}$ DERIVATIVES

R Group	δ_C (ppm) CR	δ_C (ppm) CH
H	56.9	56.9
$Si(CH_3)_3$	65.0	60.9
CO_2CH_3	69.9	58.8
CO_2H	70.7	59.0
CH_3	71.5	62.9
CH_2Br	72.8	62.9
$CH{=}CH_2$	74.6	61.4
COC_6H_5	77.0	60.3
C_6H_5	77.7	61.4
NH_2	92.3	69.5

TABLE 3

^{13}C SHIELDINGS OF THE POLYHEDRAL CARBON ATOMS OF 1-R-1,7-$C_2B_{10}H_{11}$ DERIVATIVES

R Group	δ_C (ppm) CR	δ_C (ppm) CH
H	56.5	56.5
$Si(CH_3)_3$	66.3	59.2
CO_2CH_3	72.7	56.1
CO_2H	73.4	55.8
SCH_3	72.9	57.3
CH_3	71.9	57.3
C_6H_5	78.9	56.6
$COCO_3$	81.1	56.6
SO_2CH_3	86.9	57.2
$OCOCH_3$	97.2	53.0

TABLE 4

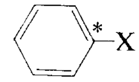
^{13}C SHIELDINGS OF THE POLYHEDRAL CARBON ATOMS OF 1,2- AND 1,7-$B_{10}H_{10}C_2R_2$ DERIVATIVES

Substituent	δ_C (ppm)
1,2-$B_{10}H_{10}C_2R_2$ Derivatives	
SCH_3	73.9
CH_3	74.6
$Si(CH_3)_3$	76.3
C_6H_5	86.5
1,7-$B_{10}H_{10}C_2R_2$ Derivatives	
$Sn(CH_3)_3$	52.6
$Ge(CH_3)_3$	68.5
$Si(CH_3)_3$	68.6
CH_3	72.1
CO_2CH_3	73.0
SCH_3	73.6
C_6H_5	79.3

to compare the variations in shielding of aliphatic, aromatic and carborane systems as illustrated in Table 5. It is seen for carbon-, nitrogen- and oxygen-containing substituents that the $\Delta\delta_C$ values more closely resemble the aliphatic model systems. Previously it had been shown by a Taft treatment of *m*- and *p*-fluorophenyl ^{19}F chemical shifts of C-substituted carboranes that the phenyl group interacts with the carborane cage mainly by an inductive mechanism (*23*). Comparison of our ^{13}C shielding results with those of related aliphatic and aromatic molecules suggest that other carbon-,

TABLE 5

VARIATION IN SHIELDING OF SUBSTITUTED CARBON ATOMS IN ALIPHATIC, AROMATIC, AND CARBORANE SYSTEMS

	$\Delta\delta_C$ (ppm)[a] [b]				
X Group	$CH_3\overset{*}{C}H_2X$	$\overset{*}{C}H_3X$		1,2-X$\overset{*}{C}B_{10}H_{10}CH$	1,7-X$\overset{*}{C}B_{10}H_{10}CH$
-H	0	0	0	0	0
$-CH_3$	−10.2	−8.0	−9.1	−15.3	−14.7
-Ph	−31.4	−23.4	−13.0	−21.1	−22.0
$-NH_2$	−39.0	−30.4	−19.2	−35.6	
$-O\overset{\overset{O}{\|}}{C}CH_3$	−54.2	−53.1	−23.0		−41.5

[a] (δ_C of hydrogen-substituted compound) − (δ_C of X-substituted compound) = $\Delta\delta_C$.

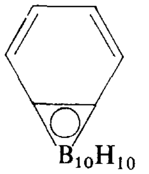
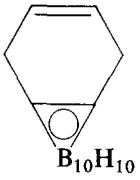
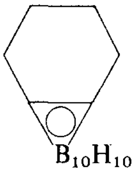
[b] Shielding values for aliphatic and aromatic systems were obtained from Ref. (*32*).

nitrogen-, and oxygen-containing substituents may also interact with the icosahedral carborane cage mainly by an inductive mechanism.

Matteson and co-workers have synthesized benzocarborane and concluded that the six-member carbon ring was only slightly aromatic in character (*24*). The ^{13}C shielding data of this and related compounds are presented in Table 6. The carborane carbon atom shieldings show little change in the series and are approximately 50 ppm upfield of typical aromatic resonances. These results support the contention of Matteson about the lack of ring-cage π bonding in benzocarborane and further illustrate our suggestion that carbon substituents interact mainly in an inductive manner with the carborane cage.

TABLE 6

CARBON-13 SHIELDING DATA OF BENZOCARBORANE AND RELATED DERIVATIVES[a]

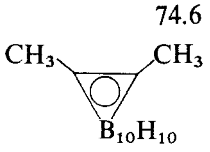
Compound	δ_C (ppm)
	123.9 129.2 73.5
	120.3 33.5 71.4
	20.0 33.2 74.5

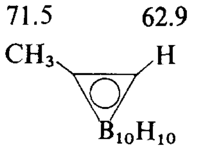
[a] The shielding value of each type of carbon atom is given to the right of that atom in the structure.

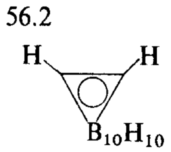
The Ortho Effect

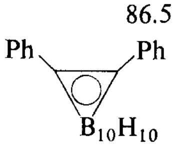
The shielding data of monosubstituted ortho-carborane derivatives in Table 2 clearly show that replacement of hydrogen with groups containing a central carbon, nitrogen, or oxygen atom results in a deshielding of the adjacent (ortho) polyhedral carbon signal. Comparison of the derivatives in the following scheme further illustrates this trend.

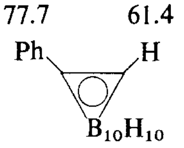
The ^{13}C chemical shift of each type of polyhedral carbon is noted directly above the respective position. The polyhedral carbons of 1,2-$(CH_3)_2$-1,2-$B_{10}H_{10}C_2$ are deshielded (relative to 1,2-$B_{10}H_{10}C_2H_2$) by the directly bonded methyl group as well as the methyl group on the adjacent carbon. The methyl-substituted polyhedral carbon atom of 1-CH_3-1,2-$B_{10}H_{10}C_2H$ is less deshielded because the adjacent carbon has a hydrogen

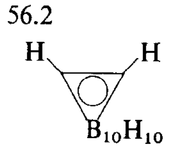












substituent. The same trend is seen in the ^{13}C spectral data of other C-substituted ortho-carborane derivatives which are presented in Tables 2 and 4. Phenyl substitution on an adjacent polyhedral *boron* atom also results in a deshielding of the carbon signal. The carborane resonance of 3-Ph-1,2-$B_{10}C_2H_{11}$ was observed at 58.3 ppm.

This ortho trend is also observed in the ^{11}B NMR spectra of the ortho-, meta- and *p*-carboranes, as illustrated in Table 7. The specific boron position-to-^{11}B resonance assignments shown in Table 7 were made with the aid of the X-ray structure determinations of bromo-substituted ortho- and meta-carboranes (*25*, *26*) and the assumption that the BH resonance position changes would be small (0–4 ppm) upon bromine

TABLE 7

^{11}B NMR DATA OF ORTHO- AND META-CARBORANE DERIVATIVES

Compound	Atom	δ_B (ppm)
1,2-$B_{10}H_{10}C_2H_2$	B(9,12)	3.1
	B(8,10)	9.6
	B(4,5,7,11)	13.9
	B(3,6)	~15
9,12-Br_2-1,2-$B_{10}H_8C_2H_2$	B(9,12)	−0.1
	B(8,10)	8.0
	B(4,5,7,11)	13.6
	B(3,6)	15.9
1,7-$B_{10}H_{10}C_2H_2$	B(5,12)	6.6
	B(9,10)	10.4
	B(4,6,8,11)	12.9
	B(2,3)	16.2
1,7-$(CH_3)_2$-1,7-$B_{10}H_{10}C_2$	B(5,12)	7.2
	B(9,10)	9.9
	B(4,6,8,11)	9.9
	B(2,3)	11.7
1,12-$B_{10}C_2H_{12}$		15.0
1,12-$(CH_3)_2$-1,12-$B_{10}H_{10}C_2$		11.0

substitution (*27*). It is observed that the B (8, 10) resonance is deshielded by 1.6 ppm in 9,12-Br_2-1,2-$B_{10}H_8C_2H_2$ relative to the parent carborane and the B (2,3) resonance is deshielded by 4.5 ppm in 1,7-$(CH_3)_2$-1,7-$B_{10}H_{10}C_2$ relative to the parent carborane (*27*). Likewise it is observed that the ^{11}B resonance of 1,12-$(CH_3)_2$-1,12-$B_{10}H_{10}C_2$ is deshielded by 4 ppm relative to *p*-carborane. These data further illustrate the observation that for icosahedral carboranes an increase in the electron-withdrawing ability of a polyhedral atom results in a deshielding perturbation of ^{11}B and ^{13}C resonances of polyhedral atoms ortho to them.

The Meta Effect

The ^{13}C data of Table 3 show that the polyhedral CH resonances of monosubstituted meta-carborane derivatives are deshielded slightly with a variety of substituents. The following scheme further illustrates this observation.

$$\begin{array}{ccc} \qquad\qquad 72.1 & 71.9 \qquad 57.3 & 56.5 \qquad \\ CH_3B_{10}H_{10}CCH_3 & CH_3CB_{10}H_{10}CH & HCB_{10}H_{10}CH \\ \qquad\qquad 79.3 & 78.9 \qquad 56.6 & 56.5 \qquad \\ PhCB_{10}H_{10}CPh & PhCB_{10}H_{10}CH & HCB_{10}H_{10}CH \end{array}$$

The chemical shift of each type of polyhedral carbon is noted directly above the respective position. The chemical shift of a polyhedron carbon atom does not change very much regardless of whether the polyhedral carbon atom in the meta position is carbon substituted or proton substituted.

Antipodal (Para) Effect

We have previously reported that halogen substitution of an icosahedral atom in carboranes and metallocarboranes results in a shielding of the antipodal polyhedral atom (*3*). We now observe more generally for icosahedral systems that an increase in the electron-withdrawing ability of a cage atom causes an increase in the shielding of the antipodal polyhedral nucleus, all other things being equal. For example, the ^{13}C signals of the 1,12-$CHB_{10}H_{10}E$ derivatives have the values 64.0 ppm (E = CH), 83.1 ppm (E = P), and 84.0 ppm (E = As). As the polyhedral atom E becomes more electronegative, the antipodal CH signal is more shielded. The para-carborane derivatives in the following scheme further illustrate this trend.

$$\begin{array}{ccc} \qquad\qquad\qquad 72.9 & 79.9 \qquad 57.4 & 64 \qquad \\ CH_3CBH_{10}H_{10}CCH_3 & CH_3CB_{10}H_{10}CH & HCB_{10}H_{10}CH \end{array}$$

The polyhedral CH of 1,12-$CH_3CB_{10}H_{10}CH$ is more shielded than the CH of 1,12-$HCB_{10}H_{10}CH$. Also, the cage carbon of 1,12-$CH_3CB_{10}H_{10}CCH_3$ is more shielded than the methyl-substituted cage carbon of 1,12-$CH_3CB_{10}H_{10}CH$. In both of these examples the more shielded nucleus is antipodal to the more electron-withdrawing group.

This same trend is also observed in the ^{11}B shieldings of icosahedral molecules. The boron atoms antipodal to the polyhedral heteroatoms in $B_{11}H_{11}CH^-$ and $B_{11}H_{11}As^-$ have the shielding values +6.5 and −7.9 ppm, respectively. The more electronegative CH unit results in a greater shielding of the antipodal boron signal.

For ortho-carborane derivatives, the signal of the boron atoms antipodal to the

TABLE 8

^{11}B ANTIPODAL EFFECTS OF SOME ORTHO-HETEROATOM-BORANES

Compound	δ_B (ppm) B(9,12)
$1,2[(CH_2)_4\text{-}CB_{10}H_{10}C]$	+5.7
$1,2\text{-}(CH_3)_2\text{-}B_{10}H_{10}C_2$	+5.1
$1,2\text{-}B_{10}H_{10}C_2H_2$	+2.2
$1,2\text{-}[(CH_3)_3Si]_2\text{-}B_{10}H_{10}C_2$	−2.2
$1,2\text{-}B_{10}H_{10}P_2$	−17.7

carbon atoms, B(9, 12), is the lowest field resonance. The shielding data in Table 8 further illustrate the antipodal shielding trend. For $1,2\text{-}B_{10}H_{10}P_2$ it is assumed that the lowest field signal is due to B(9,12), as is the case with the isoelectronic carboranes.

Correlation of ^{11}B and ^{13}C Shielding Values in Icosahedral Molecules

Previous work has shown that there is a linear correlation between ^{11}B and ^{13}C shileding values of tetracoordinate (*28*) (i.e., $R_3B:NR_3$ vs $R_3C\text{–}CR_3$) and tricoordinate compounds (*29, 30*) (i.e., R_3B vs R_3C^+). We have found that a similar linear relationship exists in icosahedral heteroatom-borane systems if one is careful to pick *isoelectronic* and *isostructural* molecules for the ^{11}B and ^{13}C shielding values. Available shielding data are presented in Table 9 and presented as a graph in Fig. 1.

TABLE 9

CARBON-13 AND BORON-11 SHIELDING DATA FOR SOME CARBORANES AND THEIR ICOSAHEDRAL BORON ANALOGS

No.	Carborane	δ_C (ppm)	Boron analog	δ_B (ppm)
1	$1,12\text{-}B_{10}H_{10}CHAs$	86.0	$B_{11}H_{11}As^-$	−8.0
2	$1,2\text{-}B_{10}H_{10}CHAs$	70.0	$B_{11}H_{11}As^-$	7.5
3	$1,12\text{-}B_{10}C_2H_{12}$	64.0	$B_{11}H_{11}CH^-$	6.3
4	$1,7\text{-}B_{10}H_{10}CHAs$	63.0	$B_{11}H_{11}As^-$	8.5
5	$1,2\text{-}B_{10}C_2H_{12}$	56.9	$B_{11}H_{11}CH^-$	12.6
6	$1,7\text{-}B_{10}C_2H_{12}$	56.5	$B_{11}H_{11}CH^-$	15.5
7	$B_{11}H_{11}CH^-$	54.6	$B_{12}H_{12}^{-2}$	16.9

The assignments of the two area-five resonances in the ^{11}B NMR spectra of $B_{11}H_{11}CH^-$ and of $B_{11}H_{11}As^-$ are not known with certainty. On the basis of our findings concerning ortho and meta shielding effects in icosahedral molecules (vide supra), we assume that the resonance at lowest field is ortho to the heteroatom in both molecules. Least-squares analysis of the data leads to the equation $\delta_B = 0.74\delta_C - 56.2$. We do not believe that comparison of the slope obtained above with those reported

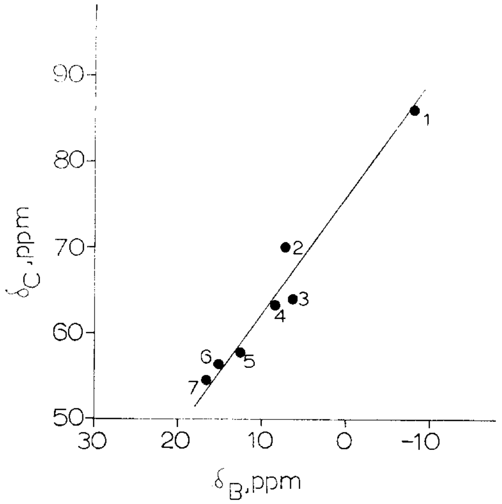


FIG. 1. A plot of ^{13}C shielding values in carboboranes versus ^{11}B shielding values in analogous icosahedral boron compounds. Numbers refer to entries in Table 9.

previously (*28–30*) will be useful until the solvent effects upon shielding values in these different systems are understood and can be interrelated.

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REFERENCES

1. A. O. Clouse, D. Doddrell, S. B. Kahl, and L. J. Todd, *Chem. Commun.* 729 (1969).
2. L. J. Todd, *Pure Appl. Chem.* **30**, 587 (1972).
3. A. R. Siedle, G. M. Bodner, A. R. Garber, D. C. Beer, and L. J. Todd, *Inorg. Chem.* **13**, 2321 (1974).
4. F. Sato, T. Yamamoto, J. R. Wilkinson, and L. J. Todd, *J. Organometal. Chem.* **86**, 243 (1975).
5. A. R. Siedle, G. M. Bodner, and L. J. Todd, *J. Organometal. Chem.* **33**, 137 (1971).
6. G. S. Wikholm and L. J. Todd, *J. Organometal. Chem.* **71**, 219 (1974).
7. D. V. Howe, C. J. Jones, R. J. Wiersema, and M. F. Hawthorne, *Inorg. Chem.* **10**, 2516 (1971).
8. D. Doddrell and A. Allerhand, *Proc. Nat. Acad. Sci. U.S.A.* **68**, 1083 (1971).
9. T. L. Heying, J. W. Ager, S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *Inorg. Chem.* **2**, 1097 (1963).
10. D. Grafstein, J. Bobinski, J. Dvorak, H. F. Smith, N. N. Schwartz, M. S. Cohen, and M. M. Fein, *Inorg. Chem.* **2**, 1120 (1963).
11. M. M. Fein, J. Bobinski, N. Mayes, N. N. Schwartz, and M. S. Cohen, *Inorg. Chem.* **2**, 1111 (1963).
12. T. L. Heying, J. W. Ager, S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.* **2**, 1089 (1963).
13. V. I. Stanko, A. I. Klimova, Yu, A. Chapovskii, and T. P. Klimova, *Zh. Obsch. Khim.* **36**, 1779 (1966).
14. M. F. Hawthorne and P. A. Wegner, *J. Amer. Chem. Soc.* **90**, 896 (1968).
15. D. Grafstein and J. Dvorak, *Inorg. Chem.* **2**, 1128 (1963).
16. L. I. Zakharkin and G. G. Zhigareva, *Izv. Akad. Nauk. SSSR Ser. Khim.* 2290 (1970).

17. L. P. Dorofeenko, A. L. Klebanskii, V. F. Gridina, N. E. Norden, I. I. Ermachlova, and V. N. Churmaeva, *Zh. Obshch. Khim.* **41,** 595 (1971).
18. H. D. Smith, C. O. Obenland, and S. Papetti, *Inorg. Chem.,* **5,** 1013 (1966).
19. L. I. Zakharkin, V. A. Brattsev, and Yu. A. Chapovskii, *Zh. Obshch. Khim.* **35,** 2160 (1965).
20. R. M. Salinger and C. L. Frye, *Inorg. Chem.* **4,** 1815 (1965).
21. L. I. Zakharkin, *Izv. Akad. Nauk SSSR Ser. Khim.* **1114** (1965).
22. L. J. Todd and A. R. Garber, unpublished results.
23. R. G. Adler and M. F. Hawthorne, *J. Amer. Chem. Soc.* **92,** 6174 (1970).
24. D. S. Matteson and N. K. Hota, *J. Amer. Chem. Soc.* **93,** 2893 (1971).
25. J. A. Potenza and W. N. Lipscomb, *Inorg. Chem.* **5,** 1471, 1478 (1966).
26. H. Beall and W. N. Lipscomb, *Inorg. Chem.* **6,** 874 (1967).
27. A. R. Siedle and L. J. Todd, unpublished results: T. E. Fielding, Ph.D. Thesis, University of Pittsburgh, 1971.
28. B. F. Spielvogel and J. M. Purser, *J. Amer. Chem. Soc.* **89,** 5294 (1967).
29. B. F. Spielvogel, W. R. Nutt, and R. A. Izydore, *J. Amer. Chem. Soc.* **97,** 1609 (1975).
30. H. Nöth and B. Wrackmeyer, *Chem. Ber.* **107,** 3089 (1974).
31. E. I. Fedin, V. A. Antonovich, E. G. Rys, V. N. Kalinin, and L. I. Zakharkin, *Izv, Akad. Nauk SSSR Ser. Khim.* 801 (1975).
32. J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, 1972.