

half the intermetallic distance. Similarly, the interatomic distance in covalent compounds represents distance between ion cores with relatively high electron density between them.²⁴ In this case half the interatomic distance represents a portion of the total electron density and clearly will depend on the nature of the second ion core. Thus, it is reasonable to speak of ion cores and electrons in covalent compounds, but partition into radii has no clear meaning when electrons are delocalized.

Ionic radii for rare earth, actinide, d¹⁰, and transition metal cations will be given in part II of this series.

Registry No. Li⁺, 17341-24-1; Na⁺, 17341-25-2; K⁺, 24203-36-9; Rb⁺, 22537-38-8; Cs⁺, 18459-37-5; Be²⁺,

(24) K. Fajans, *Chimia*, 13, 349 (1959).

22537-20-8; Mg²⁺, 22537-22-0; Ca²⁺, 14127-61-8; Sr²⁺, 22537-39-9; Ba²⁺, 22541-12-4; B³⁺, 22537-21-9; Al³⁺, 22537-23-1; Sc³⁺, 22537-29-7; Y³⁺, 22537-40-2; Lu³⁺, 22541-24-8; Si⁴⁺, 22537-24-2; Ti⁴⁺, 16043-45-1; Zr⁴⁺, 15543-40-5; Hf⁴⁺, 22541-25-9; V⁵⁺, 22537-31-1; Nb⁵⁺, 22537-41-3; Ta⁵⁺, 22541-26-0; Cr⁶⁺, 18540-29-9; Mo⁶⁺, 16065-87-5; W⁶⁺, 22541-27-1; F⁻, 16984-48-8; Cl⁻, 16887-00-6; Br⁻, 24959-67-9; I⁻, 20461-54-5; O²⁻, 16833-27-5; S²⁻, 18496-25-8; Se²⁻, 22541-48-6; Te²⁻, 22541-49-7; ClO₄⁻, 14797-73-0; BF₄⁻, 14874-70-5; NO₃⁻, 14797-55-8; H⁻, 12184-88-2; CN⁻, 57-12-5; NH₂⁻, 32323-01-6; SH⁻, 15035-72-0; SeH⁻, 16661-43-1; BH₄⁻, 16971-29-2.

Acknowledgment. The author wishes to acknowledge many clarifying discussions concerning ionic radii with Professor Kasimir Fajans.

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Electrochemistry and Boron-11 Nuclear Magnetic Resonance Spectra of Monocarbon Carboranes

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The electrochemistry and 80.5-MHz ¹¹B nmr spectra of the monocarbon carboranes B₁₁CH₁₂⁻, B₁₀CH₁₁⁻, B₁₀CH₁₃⁻, and B₉CH₁₀⁻ have been investigated. It has been found that B₉CH₁₀⁻ undergoes a one-electron oxidation to yield the coupled product B₁₈C₂H₁₈²⁻ in high yield. The 80.5-MHz ¹¹B nmr spectrum of B₁₀CH₁₁⁻ has been found to exhibit doublets in the ratio of 1:5:4 which is incompatible with the previously proposed structure. An alternative structure for B₁₀CH₁₁⁻, based on the ¹¹B nmr spectrum, is proposed and a possible mechanism for facile rearrangements in 11-particle polyhedra is discussed.

Introduction

The polyhedral borane ions B₁₀H₁₀²⁻ and B₁₂H₁₂²⁻ have been found to undergo a variety of reactions with oxidizing agents. The aqueous chemical oxidation of B₁₀H₁₀²⁻ was found to produce B₂₀H₁₈²⁻, the result of a two-electron oxidation per B₁₀ unit.¹⁻⁵ Under milder conditions, it was also possible to isolate B₂₀H₁₉³⁻ in good yield, the result of a one-electron oxidation of B₁₀H₁₀²⁻.^{1,4,5} The electrochemical oxidation of B₁₀H₁₀²⁻ has been characterized as an initial one-electron transfer, followed by a homogeneous chemical reaction to yield B₂₀H₁₉³⁻. The B₂₀H₁₉³⁻ ion can undergo a further two-electron oxidation to give B₂₀H₁₈²⁻.⁶ The B₁₂H₁₂²⁻ ion undergoes a one-electron electrochemical oxidation in acetonitrile to yield B₂₄H₂₃³⁻.⁷

In the recent past, carboranes which contain only one carbon atom in the polyhedral structure have been reported. They can be considered to be members of the B_nCH_{n+2} or

the B_nCH_{n+4} series, or anions derived therefrom by H⁺ removal. The former series includes B₅CH₇^{8,9} and its ion B₅CH₆⁻⁹ and the ions B₉CH₁₀⁻¹⁰, B₁₀CH₁₁⁻¹¹ and B₁₁CH₁₂⁻¹⁰. The latter series includes B₅CH₉¹² and the ions B₁₀CH₁₃⁻¹⁰ and B₁₀CH₁₁^{3-,13,14}.

We have undertaken a study of the nature of the electrochemical behavior of the monocarbon carboranes B₉CH₁₀⁻, B₁₀CH₁₁⁻, B₁₀CH₁₃⁻, and B₁₁CH₁₂⁻ to determine whether the redox chemistry of the polyhedral borane ions could be extended to the monocarbon carborane species.

Results and Discussion

B₁₁CH₁₂⁻. The 80-MHz ¹¹B nmr spectrum of CsB₁₁CH₁₂ in acetonitrile exhibited three doublets at +7.0, +13.1, and +16.0 ppm (vs. BF₃·Et₂O) in the ratio of 1:5:5, which clearly supports an icosahedral geometry as previously proposed.¹⁰ The cyclic voltammetry of CsB₁₁CH₁₂ in acetonitrile indicated no oxidation waves to the anodic limit of the solvent system (see Table I).

B₁₀CH₁₃⁻. The 80.5-MHz ¹¹B nmr spectrum of Cs[7-

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Table I. Cyclic Voltammetry of Monocarbon Carboranes

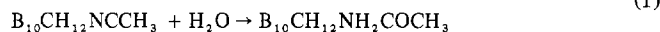
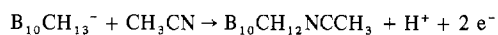
Compound ^a	$E_{p/2}$, ^a V vs. sce	n^b
CsB ₁₁ CH ₁₂ (B ₁₂ H ₁₂ ²⁻)	>+2.4 (+1.4)	
CsB ₁₀ CH ₁₃ (B ₁₁ H ₁₃ ²⁻)	+1.65 (-0.45)	2.0
(Et ₄ N)B ₁₀ CH ₁₁ (B ₁₁ H ₁₁ ²⁻)	+1.45 (+0.05)	1.0
(Et ₄ N)B ₉ CH ₁₀ (B ₁₀ H ₁₀ ²⁻)	+1.85 (+0.4)	1.0
(Et ₄ N) ₂ B ₁₈ C ₂ H ₁₈ (B ₂₀ H ₁₉ ³⁻)	+2.35 (+0.7)	

^a Anodic oxidation wave determined with a stationary Pt electrode in acetonitrile (0.1 M in tetraethylammonium perchlorate). Scan rate 6 V/min. The values in parentheses are those for the isoelectronic borane analogs which have been previously reported: R. L. Middaugh and R. J. Wiersema, *Inorg. Chem.*, **10**, 432 (1971).

^b Determined by exhaustive controlled-potential coulometry using a Pt gauze electrode in acetonitrile (0.1 M in tetraethylammonium perchlorate).

B₁₀CH₁₃] exhibited doublets at +0.9, +12.4, +23.4, +26.9, and +31.6 ppm in the ratio of 1:4:2:1:2 which is consistent with the proposed geometry of an 11-vertex icosahedral fragment having a carbon atom in the periphery of the open face and possessing C_s symmetry.

The cyclic voltammetry of Cs[7-B₁₀CH₁₃] in acetonitrile exhibited an irreversible oxidation wave with $E_{p/2}$ = +1.65 V vs. sce. The 1-B₁₀CH₁₃⁻¹⁵ isomer was not studied. Controlled-potential electrolysis of Cs[7-B₁₀CH₁₃] at +1.80 V indicated a 2 e oxidation to yield B₁₀CH₁₂NHCOCH₃⁻. This product is derived from the "oxidative substitution"¹⁶ of acetonitrile followed by hydrolysis of the nitrile ligand to amide¹⁷ (eq 1).



The 80-MHz ¹¹B nmr spectrum of (Et₄N)B₁₀CH₁₂NHCOCH₃ in acetonitrile consisted of a singlet at +3.0 and nine overlapping doublets at +3.5, +12.0, +12.7 (area 2), +23.0, +24.3, +27.3, +31.3, and +34.9 ppm. The asymmetric ¹¹B nmr spectrum is consistent with substitution on a boron in the open face.

B₁₀CH₁₁⁻. The ¹¹B nmr spectrum of Cs⁺- or Et₄N⁺-B₁₀CH₁₁⁻ in acetone solution shown in Figure 1 exhibited three doublets in the ratio of 1:5:4 at +4.3, +12.0, and +16.2 ppm, respectively. Previously,^{11,18} the 32-MHz ¹¹B nmr spectrum had been interpreted on the basis of three doublets of area 2:4:4 and "rationalized in terms of a "closo" octadecahedral structure of C_{2v} symmetry (Figure 2) if it is assumed that the two pairs of boron atoms B8-B9 and B10-B11 are accidentally equivalent."¹¹ The proposed structure places a carbon atom in the unique seven-coordinate apex (position 1).

The 80-MHz spectrum of B₁₀CH₁₁⁻ clearly rules out such a proposed structure. It has been shown, however, that 2,3-B₉C₂H₁₁ does possess a static closo-C_{2v} structure based on the 60-MHz ¹¹B nmr spectrum, which exhibits boron atoms in the ratio of 4:2:2:1, and an X-ray structure determination.¹⁹ However, the isoelectronic B₁₁H₁₁²⁻ ion exhibits only a single doublet at 32 MHz,²⁰ which was interpreted

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(17) H. C. Miller, W. R. Hertler, E. L. Muettterties, W. H. Knoth, and N. E. Miller, *Inorg. Chem.*, **4**, 1216 (1965).

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(20) R. L. Middaugh and R. J. Wiersema, *Inorg. Chem.*, **10**, 432 (1971).

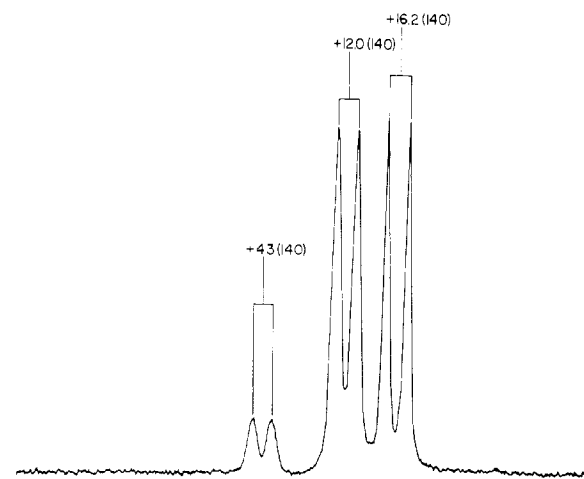


Figure 1. The 80.5-MHz ¹¹B nmr spectrum of (Et₄N)B₁₀CH₁₁ in acetone solution.

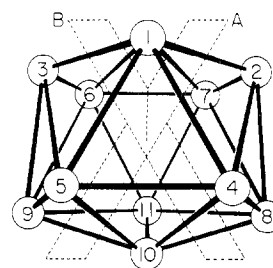


Figure 2. Idealized structure of a "closo" 11-particle polyhedron exhibiting C_{2v} symmetry.

as either accidental equivalence of five-, six-, and seven-coordinate borons in a closo-C_{2v} structure or a rapid polyhedral rearrangement such as to render all borons equivalent on the nmr time scale. On the basis of the 80-MHz ¹¹B nmr spectrum the isoelectronic B₁₀CH₁₁⁻ ion would have a structure (see Figure 2) with a carbon atom at position 2. The symmetry of 1:5:4 obtained from the ¹¹B nmr spectrum can then be obtained by conceptually "splitting" the molecule along the B plane and allowing the halves of the molecule to rotate. Such an operation renders positions 1, 4, 7, and 8 equivalent, positions 3, 5, 6, 10, and 11 equivalent, and position 9 unique.

The conceptual rotation of the halves of the molecule can be viewed mechanistically as a sequence of "dsd" type rearrangements,^{21,22} as shown in Figure 3. In the case of 11-particle polyhedra, only *one* "bond" is broken to generate the square face, whereas in 12-particle polyhedra the "dsd" mechanism requires the simultaneous formation of six square faces in the cuboctahedral intermediate. In B₁₀CH₁₁⁻, the bond between B(1) and B(6) is broken, B(1), B(4), B(7), and B(8) undergo a slight rotation, and a bond is formed between B(3) and B(7). The net result of this type of formal rotation is that the "seven-coordinate" position has moved from position 1 to position 7. By continuing this process, it generates the equivalency observed in the ¹¹B nmr spectrum.

The same kind of mechanism, *i.e.*, formal "rotation" of belts of boron atoms by consecutive dsd rearrangements, can be applied to B₁₁H₁₁²⁻. In this case of B₁₁H₁₁²⁻, the molecule can be conceptually "split" along either the A or B plane (Figure 2) which would then account for the observed magnetic equivalence of all the boron atoms.

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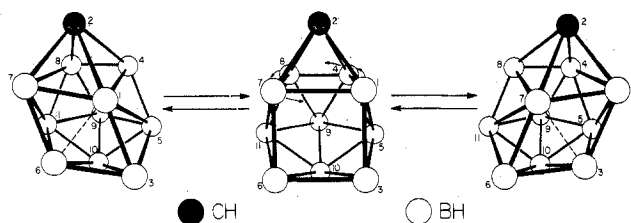


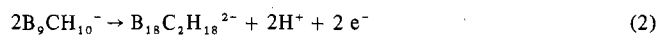
Figure 3. Sequence of "dsd" type rearrangements resulting in rotation of belts in an 11-particle polyhedron.

The concept of rotation of planes of five atoms has been postulated previously.²³ If the mutual rotation of a pair of belts of five boron atoms is actually operative in icosahedral rearrangements, such rearrangements must be associated with a high activation energy ($\Delta H^\ddagger = 40\text{--}60$ kcal/mol).²⁴ However, the proposed mutual "rotation" of belts of four boron atoms and five boron atoms is apparently facile and must therefore have a low activation energy. The driving force for this rearrangement is possibly the relief of high coordination (seven-coordinate) imposed on the boron atoms in a static C_{2v} system. In $B_{10}CH_{11}^-$, this type of rearrangement "spreads" the high coordination over four atoms, whereas in $B_{11}H_{11}^{2-}$ all the atoms are involved.

The $B_{10}CH_{11}^-$ ion was found to undergo a 1 e oxidation in acetonitrile at +1.45 V (see Table I). The oxidation product was not isolated.

$B_9CH_{10}^-$. The 80-MHz ^{11}B nmr spectrum of the $B_9CH_{10}^-$ ion in acetonitrile exhibited three doublets in the ratio of 1:4:4 at -28.4 , $+20.0$, and $+25.1$ ppm. This spectrum is consistent with the proposed bicapped Archimedean anti-prism geometry with a carbon at the apex.¹⁰

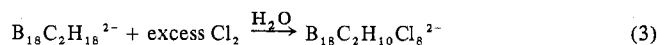
Controlled-potential electrolysis of $Et_4NB_9CH_{10}$ in acetonitrile at +1.95 V vs. sce indicated a one-electron oxidation to yield $(Et_4N)_2B_{18}C_2H_{18}$ in 90% yield (eq 2).



The 80-MHz ^{11}B nmr spectrum of the Et_4N^+ or Bu_4N^+ salt of $B_{18}C_2H_{18}^{2-}$ in acetonitrile consisted of a singlet of area 1 at -44.5 ppm and two doublets each of area 4 at $+18.3$ and $+23.6$ ppm. The proposed structure, shown in Figure 4, consists of two B_9C moieties linked through the apex boron atoms. A similar structure is observed in the "a²" isomer of the isoelectronic $B_{20}H_{18}^{4-}$ ion.¹

The $B_{18}C_2H_{18}^{2-}$ ion is considerably less basic than the $B_{20}H_{18}^{4-}$ ion and exhibits no protonation to form $B_{18}C_2H_{19}^-$ in aqueous solutions. Attempts to oxidize further the $B_{18}C_2H_{18}^{2-}$ to $B_{18}C_2H_{18}$ (isoelectronic with $B_{20}H_{18}^{2-}$) either electrochemically or chemically with Ce^{4+} have led to degradation.

The $B_{18}C_2H_{18}^{2-}$ ion can be recovered unchanged from $Na-NH_3(l)$ solutions, which demonstrated its stability toward reducing agents. The $B_{18}C_2H_{18}^{2-}$ ion can be chlorinated without cleavage of the B-B bond to yield $B_{18}C_2H_{10}Cl_8^{2-}$ (eq 3). The ^{11}B nmr spectrum of $B_{18}C_2H_{10}Cl_8^{2-}$ consisted



of a singlet of area 1 at -24.0 ppm, a singlet of area 4 at $+5.7$ ppm, and a doublet of area 4 at $+9.4$ ppm. The carborane CH was observed at τ 5.42. Presumably the eight equivalent equatorial boron atoms adjacent to the B-B bond

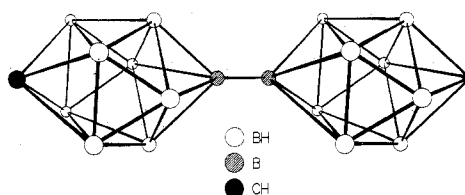


Figure 4. Proposed structure of the $B_{18}C_2H_{18}^{2-}$ ion.

are chlorinated in $B_{18}C_2H_{10}Cl_8^{2-}$ which accounts for the observed ^{11}B and 1H nmr spectra. Under similar conditions the $B_9CH_{10}^-$ ion chlorinates to yield $B_9CH_5Cl_5^-$. The ^{11}B nmr spectrum of $B_9CH_5Cl_5^-$ exhibits a singlet of area 1 at -23.1 ppm, a singlet of area 4 at $+7.3$, and a doublet of area 4 at $+12.6$. The ^{11}B nmr spectrum indicates that the $B_9CH_{10}^-$ ion undergoes halogenation at the apex boron atom and the four boron atoms furthest from the apex carbon atom.

Conclusions

The electrochemical behavior of the monocarbon carboranes $B_9CH_{10}^-$, $B_{10}CH_{11}^-$, $B_{10}CH_{13}^-$, and $B_{11}CH_{12}^-$ appears to parallel closely the behavior of the isoelectronic polyhedral borane ions. The monocarbon carboranes do exhibit a drastic increase in the potentials for oxidation ($+0.4$ V for $B_{10}H_{10}^{2-}$ vs. $+1.85$ V for $B_9CH_{10}^-$) which probably accounts for the inability of $B_{11}CH_{12}^-$ to undergo oxidation ($+1.4$ V for $B_{12}H_{12}^{2-}$ vs. $>+2.4$ V for $B_{11}CH_{12}^-$) in acetonitrile. The observed increase in the potential for oxidation with incorporation of a second carbon atom into the polyhedral framework is possibly the reason that the isoelectronic $B_8C_2H_{10}$ and $B_{10}C_2H_{12}$ carboranes fail to undergo any electrochemical oxidation.

The results of this and previous studies²⁰ indicate that 11-particle polyhedra with one carbon or less probably do not exhibit the static $closo-C_{2v}$ geometry of $B_9C_2H_{11}$ in solution, which reflects a very low barrier for interconversion in 11-particle systems.

Experimental Section

Physical Measurements. Infrared spectra were obtained using a Perkin-Elmer Model 137 infrared spectrophotometer. The 1H nmr spectra were obtained using a Varian Associates HA-100 spectrometer. The ^{11}B nmr spectra at 80.5 MHz were obtained using the superconducting spectrometer designed and constructed by Professor F. A. L. Anet of this department. The ^{11}B chemical shifts are reports vs. $BF_3 \cdot Et_2O$. The electrochemical apparatus used in this study has been described previously.²⁴ Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Equivalent weights were determined by titration of the eluent with standardized NaOH solutions after the salts were passed through an acid ion-exchange column.

Reagents. CsB_9CH_{10} and $CsB_{11}CH_{12}$ were prepared by pyrolysis of $CsB_{10}CH_{13}$ according to the literature procedure.³ $CsB_{10}CH_{11}$ was prepared by oxidation of $Na_3B_{10}CH_{11}$ with iodine as reported previously.⁴ All other chemicals were reagent grade and used as received.

$B_{18}C_2H_{18}^{2-}$. In a typical experiment, 1.67 g (6.64 mmol) of $Cs(1-B_9CH_{10})$ was dissolved in 50 ml of acetonitrile which was 0.1 M in tetraethylammonium perchlorate. This solution was subjected to exhaustive controlled-potential electrolysis at +1.95 V vs. sce. The current was monitored with an electronic integrator²⁴ and gave a value of $n = 1.06$ equiv/mol. The acetonitrile solution was added to 500 ml of distilled water containing excess Et_4NBr , precipitating a white solid which was recrystallized from hot aqueous acetonitrile. The yield of $(Et_4N)_2B_{18}C_2H_{18}$ was 1.5 g (90%). Titration of the filtrate from the precipitation of $(Et_4N)_2B_{18}C_2H_{18}$ with standardized NaOH used 5.82 mmol of base (87.5% based on eq 2). Owing to the limited solubility of the Et_4N^+ salt, the $(n-Bu)_4N^+$ salt was prepared by passing an aqueous acetonitrile solution of $(Et_4N)_2B_{18}C_2H_{18}$ through an acid ion-exchange column. The eluent was neutralized with aqueous NaOH. Addition of excess Bu_4NBr precipitated $(Bu_4N)_2B_{18}C_2H_{18}$ which was recrystallized from aqueous acetone.

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(24) T. E. Paxson, M. K. Kaloustian, G. M. Tom, R. J. Wiersema, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **94**, 4882 (1972).

^1H and ^{11}B nmr spectra were obtained using the Bu_4N^+ salt.

Anal. Calcd for $[\text{Et}_4\text{N}]_2\text{B}_{18}\text{C}_2\text{H}_{18}$: B, 39.12; C, 43.47; H, 11.77; N, 5.64; equiv wt 248.6. Found: B, 38.51; C, 42.85; H, 11.88; N, 6.28; equiv wt 256.

The ^{11}B nmr spectrum of the Bu_4N^+ salt in acetonitrile consisted of a singlet of area 1 at -44.5 ppm and two doublets of area 4 at $+18.3$ and $+23.6$ ppm, respectively. The carborane CH in the ^1H nmr spectrum was observed at τ 5.68.

$\text{B}_{18}\text{C}_2\text{H}_{10}\text{Cl}_8^{2-}$. $(\text{Et}_4\text{N})_2\text{B}_{18}\text{C}_2\text{H}_{18}$ (200 mg, 0.4 mmol) was dissolved in 50 ml of aqueous acetonitrile and passed through an acid ion-exchange column. The eluent was neutralized with NaOH and evaporated to a volume of 75 ml. Chlorine was bubbled through the solution for 2 hr at room temperature. The solution was neutralized with NaOH and treated with excess Et_4NBr . The white solid was collected by filtration and recrystallized from aqueous acetone. The yield of $(\text{Et}_4\text{N})_2\text{B}_{18}\text{C}_2\text{H}_{10}\text{Cl}_8$ was 250 mg (81%).

Anal. Calcd for $[\text{Et}_4\text{N}]_2\text{B}_{18}\text{C}_2\text{H}_{10}\text{Cl}_8$: B, 25.11; C, 27.90; H, 6.76; Cl, 36.60; N, 3.63; equiv wt 387.4. Found: B, 24.81; C, 27.87; H, 6.49; Cl, 36.71; N, 3.53; equiv wt 383.

The ^{11}B nmr spectrum consisted of a singlet of area 1 at -24.0 ppm, a singlet of area 4 at $+5.7$ ppm, and a doublet of area 4 at $+9.4$ ppm. The carborane CH was observed at τ 5.42.

$\text{B}_9\text{CH}_5\text{Cl}_5^-$. $(\text{Et}_4\text{N})\text{B}_9\text{CH}_{10}$ (250 mg, 1 mmol) was converted to the Na^+ salt by passage through an acid ion-exchange column with aqueous acetonitrile and neutralization of the eluent with NaOH. The solution was evaporated to about 75 ml and treated as described above for the halogenation of $\text{B}_{18}\text{C}_2\text{H}_{18}^{2-}$. The yield of $(\text{Et}_4\text{N})\text{B}_9\text{CH}_5\text{Cl}_5$ was 0.35 g (83%). The ^{11}B nmr exhibited a singlet of area 1 at -23.1 ppm, a singlet of area 4 at $+7.3$ ppm, and a doublet of area 4 at $+12.6$ ppm. The equivalent weight was found to be 423, which compares well with that calculated for the $(\text{Et}_4\text{N})\text{B}_9\text{CH}_5\text{Cl}_5$ of 421.9.

$\text{B}_{10}\text{CH}_{12}\text{NHCOCH}_3^-$. In a typical experiment $\text{CsB}_{10}\text{CH}_{13}$ (2.49 g, 9.37 mmol) was exhaustively electrolyzed at $+1.75$ V vs. sce. Integration of the current indicated $n = 2.14$ equiv/mol. The electrolysis solution was added to 200 ml of H_2O containing excess Et_4NBr and neutralized with NaOH. The aqueous solution was extracted with two 100-ml portions of CH_2Cl_2 . The CH_2Cl_2 solution was washed with three 100-ml portions of H_2O , dried with MgSO_4 , and evaporated to dryness. The oily residue was dissolved in EtOH, filtered, and diluted with Et_2O . A white flocculent precipitate formed which was collected by filtration. The yield of $(\text{Et}_4\text{N})\text{B}_{10}\text{CH}_{12}\text{NHCOCH}_3 \cdot \text{H}_2\text{O}$ was 2.8 g (88%).

Anal. Calcd for $[\text{Et}_4\text{N}]\text{B}_{10}\text{CH}_{12}\text{NHCOCH}_3 \cdot \text{H}_2\text{O}$: B, 31.93; C, 39.03; H, 11.31; N, 8.27; equiv wt 338.5. Found: B, 31.32; C, 38.48; H, 10.86; N, 7.41; equiv wt 347.

The infrared spectrum of $(\text{Et}_4\text{N})\text{B}_{10}\text{CH}_{12}\text{NHCOCH}_3 \cdot \text{H}_2\text{O}$ included absorptions at 3500 (H_2O), 3250 (NH), 2550 (BH) and 1620 cm^{-1} (CO) which is consistent with the above formulation. The ^{11}B nmr exhibited a singlet at $+3.0$ ppm for the substituted boron and nine additional doublets, each of area 1, which is expected for an asymmetrically substituted open 11-particle polyhedral structure.

Registry No. Cs(1- B_9CH_{10}), 38192-38-0; $(\text{Et}_4\text{N})_2\text{B}_{18}\text{C}_2\text{H}_{18}$, 38192-39-1; $(\text{Bu}_4\text{N})_2\text{B}_{18}\text{C}_2\text{H}_{18}$, 38192-40-4; $(\text{Et}_4\text{N})_2\text{B}_{18}\text{C}_2\text{H}_{10}\text{Cl}_8$, 38192-41-5; $(\text{Et}_4\text{N})\text{B}_9\text{CH}_{10}$, 38192-43-7; $(\text{Et}_4\text{N})\text{B}_9\text{CH}_5\text{Cl}_5$, 38192-42-6; $\text{CsB}_{10}\text{CH}_{13}$, 38192-44-8; $(\text{Et}_4\text{N})\text{B}_{10}\text{CH}_{12}\text{NHCOCH}_3$, 37-239-397; $\text{CsB}_{11}\text{CH}_{12}$, 38192-46-0; $(\text{Et}_4\text{N})\text{B}_{10}\text{CH}_{11}$, 38192-45-9.

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Unsymmetrically B-Substituted Borazines. Nuclear Magnetic Resonance Characterization

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The proton nmr spectra of ten B-substituted *N*-trimethylborazines were determined in noninteracting (CCl_4) and interacting (C_6H_6 or C_6D_6) solvents. The differences in the spectra are attributed to the association of anisotropic benzene molecules with molecular dipoles of the borazines. The spectra obtained on CCl_4 solution have been analyzed on the basis of characteristic group contributions to the chemical shift of the probe substituents. A discussion of the effect of substituents on the electronic environment of the borazine nucleus is presented.

Introduction

In the course of preparing a series of unsymmetrically B-substituted *N*-trimethylborazines for other purposes, we have also investigated the ^1H nmr spectra of these substances in an attempt to provide a simpler basis for their characterization and a method for identifying these substances in reaction mixtures.

Experimental Section

All spectra were recorded at ambient temperature on a Varian A-60 spectrometer at 60-MHz frequency. The chemical shifts are reported in cycles per second downfield from an internal standard of tetramethylsilane in benzene and in carbon tetrachloride as solvents. Preliminary studies showed that concentration-dependent chemical shifts of about 2 cps occurred at concentrations greater than 15%; consequently all subsequent spectra were recorded in the concentration range 8–5% and were comparable with those obtained at infinite dilution. Instrumental error was less than 1.0 cps over a 500-cps sweep and less than 0.5 cps over the range 0–250 cps on a 500-cps sweep. The chemical shifts (± 0.2 cps) are average values

obtained from several spectra recorded for each compound. All samples were pure borazines except 2,6-dimethyl-4-chloro-1,3,5-trimethylborazine which contained approximately 10% hexamethylborazine. Deuterated benzene (99.5%) was used as solvent for the phenyl derivatives and benzene was used for the other samples. An independent study indicated that a solvent isotope effect was not present in these systems, an observation that is in agreement with other observations.¹ The proton chemical shifts are given in Tables I–III.

The details of the preparation and purification of the unsymmetrically B-substituted borazines are described in a previous paper.²

Discussion

As a matter of convenience, the ^1H nmr spectra of the unsymmetrically B-substituted *N*-trimethylborazines are discussed with reference to the numbering system shown in I.

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