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A High-Resolution Nuclear Magnetic Resonance Study of the Pentadecahydrodecaborate(1−) Ion

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The 70.6-MHz ^{11}B nmr spectrum of $B_{10}H_{15}^-$ consists of four doublets of relative intensities 4:2:2:2 reading upfield. The proposed assignment of these doublets is B(5,7,8,10), B(1,3 or 2,4), B(2,4 or 1,3), and B(6,9), respectively. The 220-MHz proton nmr spectrum of $B_{10}H_{15}^-$ consists of a low-field set of peaks and an upfield broad symmetrical peak with relative intensities 10:5. There appear to be five bridge-type hydrogen atoms in $B_{10}H_{15}^-$ which are probably undergoing rapid exchange in solution at room temperature.

Introduction

The pentadecahydrodecaborate(1−) ion, $B_{10}H_{15}^-$, can be generated by protonation of the tetradecahydrodecaborate(2−) ion,[2] by reaction of decaborane(14) with the borohydride ion,[3] and by electrolysis of decaborane(14) in aprotic solvents.[4] The best ^{11}B nmr spectrum of $B_{10}H_{15}^-$ reported thus far was obtained at 32 MHz in acetonitrile solution and consisted of two overlapping doublets.[5] As a continuation of our interest in nuclear magnetic resonance studies of complex boron hydride species, we undertook an investigation of the ^{1}H and ^{11}B nmr spectra of $B_{10}H_{15}^-$ using a high-resolution spectrometer.

Experimental Section

The ^{11}B nmr spectra were measured on equipment consisting of a pulsed nmr apparatus built in this department operating at 70.6 MHz, a Varian 51.7-kG superconducting magnet, a Fabri-Tek 1074 signal averager, and a Nicolet 1085 computer. Additional details have been reported elsewhere.[6]

The Na[$B_{10}H_{15}$] was prepared by the method of Schaeffer and Tebbe[3] and the ^{11}B spectra were measured immediately after preparation. 1,2,3,4-$B_{10}D_4H_{10}$ and μ_4,5,6,7,8,9,10-$B_{10}D_{10}H_4$ were prepared by literature methods[7] and converted to the corresponding $B_{10}H_{15}^-$ salt by the procedure indicated above.

Results and Discussion

At 70.6 MHz, the ^{11}B spectrum of Na[$B_{10}H_{15}$] in ethylene glycol dimethyl ether (monoglyme) (Figure 1A) consists basically of three readily apparent doublets, a, b, and d centered at +14.2, +19.8, and +21.8 ppm from $BF_3{\cdot}O(C_2H_5)_2$ having relative areas of 4:4:2, respectively.[8] We measured the spectrum of $CH_3(CH_2)_{15}N(CH_3)_3[B_{10}H_{15}]$ in toluene solution. This spectrum consists of two doublets at +13.9 and +19.0 ppm having relative areas of 4:6, respectively. The doublets corresponding to b and d in the spectrum of the sodium salt (Figure 1A) are more severely overlapped in the spectrum of the tetraalkylammonium salt. Thus, with less polar solvents and with tetraalkylammonium cations, the chemical shift pattern of the boron spectrum of this boron hydride ion is less well resolved but not drastically altered. Upon wide-band ^{1}H decoupling of the ^{11}B nmr spectrum of Na[$B_{10}H_{15}$], Figure 1D, the high-field member of doublet d shifts downfield approximately 60 Hz. If this peak were part of a 1:2:1 triplet, due to a BH_2 group, a shift of at least 100 Hz, corresponding to $J_{^{11}B-H}$ in a BH_2 group, would be expected. Both Figure 1A and 1D give some indication that the signal centered at +19.8 ppm is actually two closely overlapping doublets. Application of line narrowing[9] to the ^{11}B nmr spectrum of this anion is illustrated in Figure 2B. The possibility of overlapping doublets in the +19.8-ppm region is more clearly observed. A partially relaxed Fourier transform[10] and line-narrowed spectrum of the same sample with a magnetization decay time ($\tau = 24$ msec) such that the two doublets b and d (see Figure 1A) are nearly nulled is presented in Figure 2C. Figure 2D is the difference trace obtained by subtracting Figure 2C from Figure 2B. Use of these Fourier transform techniques provides further support for the contention that two doublets each of area 2 are present in the +19.8-ppm region of the spectrum.

The relative area of 4 found for doublet a in Figure 1A suggests that this resonance originates from B(5,7,8,10). This postulate is further confirmed by measurement of the ^{11}B nmr spectrum (Figure 1E) of the deuterated $B_{10}H_{15}^-$ ion obtained by reaction of μ_4,5,6,7,8,9,10-$B_{10}D_{10}H_4$ and $NaBD_4$. In Figure 1E there is apparent removal of ^{1}H–^{11}B spin coupling of doublet a and d.

The ^{11}B nmr spectrum of $B_{10}D_4H_{11}^-$ prepared by reaction of 1,2,3,4-$B_{10}D_4H_{10}$ with $NaBH_4$ is illustrated in Figure 1B. The two doublets b and c have apparently lost the ^{1}H–^{11}B spin coupling and on this basis can be assigned to B(2,4 and 1,3). All resonances except doublet d (Figure 1A) have been assigned and therefore this resonance must be due to B(6,9).

It has been reported that reaction of μ_4-$B_{10}H_{10}D_4$ with $NaBD_4$ followed by reaction of the product with DCl produced μ_4, 6,9-$B_{10}H_8D_6$.[11] We have found that reaction of $B_{10}H_{14}$ with $NaBD_4$ in monoglyme produced a $B_{10}H_{15}^-$ ion which has terminal deuterium atoms specifically attached at B(6,9) as indicated by the ^{11}B nmr spectrum given in Figure 1C. The deuterated $B_{10}H_{15}^-$ ion was converted back to decaborane by reaction with DCl. The ^{11}B nmr spectrum of the recovered decaborane showed some deuterium

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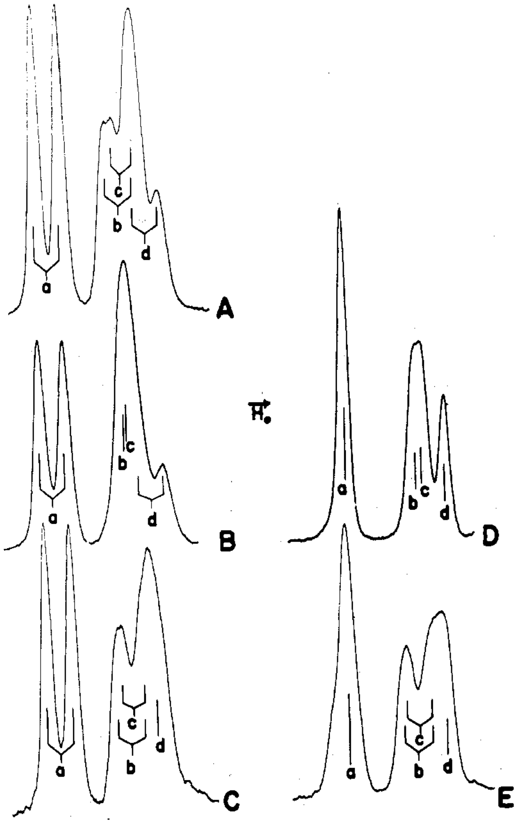

Figure 1. The 70.6-MHz ^{11}B nmr spectra of $Na[B_{10}H_{15}]$ in monoglyme: (A) normal spectrum; (B) spectrum of $B_{10}D_4H_{11}^-$ obtained from reaction of 1,2,3,4-$B_{10}D_4H_{10}$ with $NaBH_4$; (C) spectrum of deuterated $B_{10}H_{15}^-$ ion obtained from reaction of $B_{10}H_{14}$ with $NaBD_4$; (D) normal spectrum proton decoupled; (E) spectrum of $B_{10}H_4D_{11}^-$ obtained from reaction of μ_4,5,6,7,8,9,10-$B_{10}D_{10}H_4$ with $NaBD_4$.

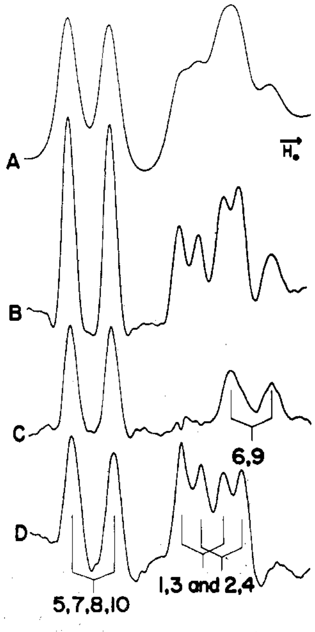

Figure 2. The 70.6-MHz Fourier transform ^{11}B nmr spectra of $Na[B_{10}H_{15}]$ in monoglyme: (A) normal spectrum; (B) line-narrowed spectrum; (C) partially relaxed Fourier transform and line-narrowed spectrum; (D) difference spectrum obtained by subtracting 2C from 2B.

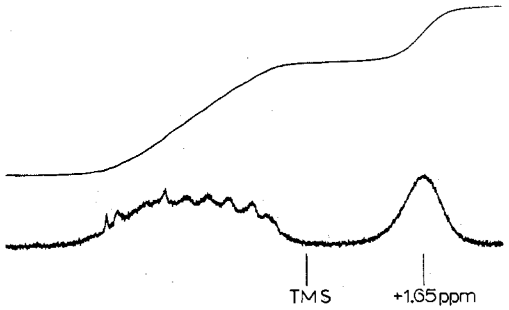

Figure 3. The 220-MHz proton nmr spectrum and integral of $Ph_4As[B_{10}H_{15}]$ at room temperature. The phenyl protons are at low field and are not included in the spectrum.

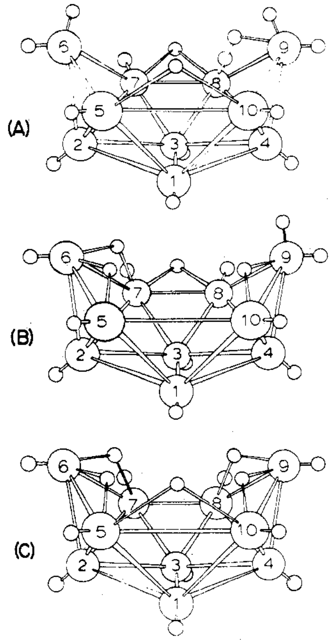

Figure 4. Possible structures for the $B_{10}H_{15}^-$ ion in solution. The structures are based on the (A) 3622, (B) 4531, and (C) 5440 semitopological models for the $B_{10}H_{15}^-$ ion.

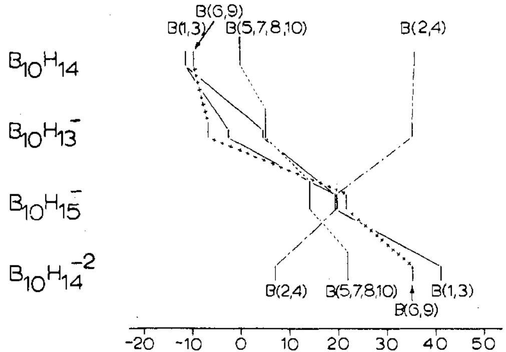

Figure 5. Correlation diagram of the 70.6-MHz ^{11}B nmr spectra of $B_{10}H_{14}$, $B_{10}H_{13}^-$, $B_{10}H_{15}^-$, and $B_{10}H_{14}^{2-}$ ($BF_3 \cdot O(C_2H_5)_2$ = 0 ppm).

labeling at B(6,9). However there is also some scrambling of deuterium into B(5,7,9,10) and B(2,4) as is also evident upon close examination of Figure 1A of ref 11.

The 220-MHz proton nmr spectrum of $Ph_4As[B_{10}H_{15}]$ in acetone-d_6 at room temperature consists of a complex set of peaks at low field and a very broad symmetrical peak at high field (+1.65 ppm) relative to tetramethylsilane (Figure 3). The area ratio of the complex set of peaks and broad singlet is 10:5, respectively. Under the conditions of these nmr measurements there appears to be rapid exchange of five bridge-type hydrogen atoms in the $B_{10}H_{15}^-$ ion. The upfield resonance in the proton nmr spectrum at −80° is also a symmetrical peak which is somewhat sharper than the peak which was observed at room temperature.

From the available evidence we propose that the $B_{10}H_{15}^-$

ion in solution maintains the structure of a 10-atom icosahedral fragment. Bridge hydrogen tautomerism may involve rapid interconversion between structures like those presented in Figure 4. Similar mechanisms have been proposed for bridge hydrogen tautomerism in B_6H_{10} and $B_{11}H_{14}^-$.[12,13]

The relative chemical shifts of the different types of boron-11 nuclei in the spectra of four decaborane species have now been determined.[14-16] The interrelationships of this chemical shift information are illustrated in Figure 5. It is observed that the weighted average of the boron chemical shifts for each molecule is found at higher field in the order $B_{10}H_{14} < B_{10}H_{13}^- < B_{10}H_{15}^- < B_{10}H_{14}^{2-}$. From left to right in this series is the most probable order for increasing electron density available for bonding in the decaborane cage framework. It is also observed that the B(1,3), B(5,7,8,10), and B(6,9) resonances gradually change to higher field while the B(2,4) resonance changes to lower field as one looks at the spectra in the order $B_{10}H_{14}$, $B_{10}H_{13}^-$, $B_{10}H_{15}^-$, and $B_{10}H_{14}^{2-}$, respectively.

Registry No. $Na[B_{10}H_{15}]$, 12008-67-2; $Ph_4As[B_{10}H_{15}]$, 39301-43-4.

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Preparation of Bis(*B*-hydroxy) Derivatives of 1,8-Dimethyl-*closo*-dicarbaundecaborane(11). Their Properties and Derivative Chemistry[1]

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In the reaction of 1,8-$(CH_3)_2C_2B_9H_9$ with chromic acid in benzene at 0° a bis(hydroxy) derivative [1,8-(3,7)-$(CH_3)_2C_2B_9H_7(OH)_2$] is formed. Spectral, structural, and chemical evidence indicates the two hydroxy groups are on adjacent B(3,7) positions. In addition, the bis(hydroxy)carborane on pyrolysis dimerizes to give two carborane polyhedra linked *via* two bridging oxygen atoms at the B(3,3′,7,7′) positions of 1,8-$(CH_3)_2C_2B_9H_9$. Pyrolysis in the presence of an organic diol such as *pyrocatechol* produces a carborane polyhedron linked *via* two oxygen bridges to the organic ligand, *i.e.*, phenyl ring.

Introduction

A large body of literature exists, in which C-substituted derivatives of the carborane series $C_2B_nH_{n+2}$ have been prepared. The derivative chemistry of the carborane series has been the subject of extensive reviews.[2,3] By comparison there are only a few B-substituted derivatives reported, in which the substituent is other than a halogen atom. The majority of these are derivatives of the icosahedral carborane $C_2B_{10}H_{12}$ and include *B*-alkyl, alkylamino, and alkoxy derivatives.[4]

We wish to report the first class of B-substituted derivatives of the 1,8-$(CH_3)_2C_2B_9H_9$ carborane. In the preparation of the *nido*-$(CH_3)_2C_2B_7H_{11}$ carborane *via* the sequence of degradation reactions of the $(CH_3)_2C_2B_{10}H_{10}$ outlined by Hawthorne[5] one of the intermediate steps involved the reaction of 1,8-$(CH_3)_2C_2B_9H_9$ with chromic acid in toluene. From this reaction sequence we have isolated a bis(hydroxy) derivative (I), $(CH_3)_2C_2B_9H_7(OH)_2$, 1,8-dimethyl-3,7-dihydroxy-1,8-dicarba-*closo*-undecaborane(11).[6] The only prior reports in the literature of *B*-hydroxy derivatives were the synthesis of 1-methyl-*B*-hydroxy-1,2-carborane and the *B*-hydroxy-1,2-carborane by reaction of nitric acid with the respective 1,2-$B_{10}C_2H_{12}$ at 20°.[7,8] There are no reported B-substituted derivatives of the 1,8-dicarba-*closo*-undecaborane(11) family.

Experimental Section

Methods and Materials. 1,8-Dimethyl-1,8-dicarba-*closo*-undecaborane(11) was prepared by literature method.[9] All solvents were reagent grade and used without further purification. Pyrocatechol was obtained from Eastman Kodak and 2,3-butanediol from Aldrich Chemical; both were used as received. Deuterium chloride was prepared by a standard reaction using D_2O and benzoyl chloride.

Infrared spectra were obtained on either a Perkin-Elmer 337 or a

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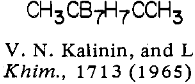
[6] We have adopted the following formula to indicate the structure of 1,8-(3,7)-$(CH_3)_2C_2B_9H_7(OH)_2$



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