The Chemistry of n-$B_{18}H_{22}$ and i-$B_{18}H_{22}$

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Abstract: The isomeric hydrides n-$B_{18}H_{22}$ and i-$B_{18}H_{22}$ have been examined with regard to their chemical reactivities toward bases, nucleophiles, electrophiles, and electron addition. Both hydrides are strong diprotic acids with first and second pK_a's of approximately -1 and $+8$, respectively. Treatment of n-$B_{18}H_{22}$ with I_2 in ethanol apparently produced $B_{18}H_{21}I$. Reduction of n- and i-$B_{18}H_{22}$ with sodium amalgam afforded isomeric $B_{18}H_{22}{}^{2-}$ ions. Acid-catalyzed deuterium exchange of both $B_{18}H_{22}$ isomers led to the introduction of six deuterium atoms per mole. Base-catalyzed deuterium exchange resulted in the introduction of six deuterium atoms per mole of hydride with both isomers of $B_{18}H_{22}$. Prolonged treatment of n-$B_{18}H_{22}$ with aqueous base resulted in the formation of $B_{12}H_{12}{}^{2-}$ while similar treatment of i-$B_{18}H_{22}$ apparently produced borate salts. Reaction of n- and i-$B_{18}H_{22}$ with n-butyllithium produced the corresponding $B_{18}H_{20}{}^{2-}$ ions.

Several years ago, two isomeric $B_{18}H_{22}$ hydrides were prepared[1] and characterized by X-ray diffraction studies.[2,3] The two isomers of $B_{18}H_{22}$ (n- and i-) are formed simultaneously[1] during the hydrolysis of the hydronium ion salt of $B_{20}H_{18}{}^{2-}$. The chemistry of n- and i-$B_{18}H_{22}$ has not been described, although n-$B_{18}H_{22}$ was reported[1] to be a monoprotic acid in aqueous base titrations.

The two $B_{18}H_{22}$ hydrides are structurally related[2,3] to decaborane(14) and may be formally generated by fusion of two decaborane-like fragments with sharing of two common atoms in the fused structure. Figures 1–3 present the structures[2,3] and numbering systems of n- and i-$B_{18}H_{22}$ as well as $B_{10}H_{14}$. In n-$B_{18}H_{22}$ (C_i symmetry), the 5- and 6-boron atoms of one $B_{10}H_{14}$ fragment are, respectively, the 6- and 5-boron atoms of the second fragment. In the case of i-$B_{18}H_{22}$ (C_2 symmetry), the 5- and 6-boron atoms bear the same relationship to both $B_{10}H_{14}$ fragments.

Since the extremities of n- and i-$B_{18}H_{22}$ resemble $B_{10}H_{14}$, one might expect the chemistry of the two $B_{18}H_{22}$ hydrides and $B_{10}H_{14}$ to be similar. Indeed, the results of charge distribution calculations[4a] for the two $B_{18}H_{22}$ hydrides and $B_{10}H_{14}$ suggest that relative charge densities associated with the extremities of the two $B_{10}H_{14}$ fragments in the $B_{18}H_{22}$ hydrides roughly correspond to the relative charge densities at the corresponding boron atoms in $B_{10}H_{14}$ itself. Positions 4 and 4′ of the $B_{18}H_{22}$ isomers have the highest calculated negative charge density while positions 9 and 9′ correspond to the sites of lowest electron density. Experiments designed to test the chemical similarity of the $B_{18}H_{22}$ hydrides and $B_{10}H_{14}$ were undertaken and are reported herein.

Results

The isomeric $B_{18}H_{22}$ hydrides were prepared from the hydronium ion salt of $B_{20}H_{18}{}^{2-}$ as previously described[1] and separated by fractional crystallization. Table II (Experimental Section) presents the infrared spectra of n- and i-$B_{18}H_{22}$, respectively. Table I illustrates the ultraviolet spectrum of the isomeric $B_{18}H_{22}$ species determined in cyclohexane solution and Figures 4 and 5 present the 19.3-Mc/sec ^{11}B nmr spectra of n-$B_{18}H_{22}$ and i-$B_{18}H_{12}$, respectively.

Table I. Electronic Spectra of n- and i-$B_{18}H_{22}$ Derivatives

Compound	λ_{max}, mμ	ε
n-$B_{18}H_{22}{}^{a}$	329	6,280
	271	3,470
	218	13,600
n-$B_{18}H_{21}{}^{-\ b}$	375	4,230
	330	3,050
	256	2,635
	227	6,440
n-$B_{18}H_{20}{}^{2-\ b}$	350	7,680
	226	9,260
$B_{18}H_{21}I^{a}$	360	6,190
	275	3,490
	221	13,400
i-$B_{18}H_{22}{}^{a}$	307	10,300
	226	9,130
	212	8,500
i-$B_{18}H_{21}{}^{-\ b}$	358	3,630
	277	5,460
	236	7,110
	226	7,200
i-$B_{18}H_{20}{}^{2-}$	335	4,710
	289	5,440
	264	6,010
	226	8,640

[a] In cyclohexane solvent. [b] In acetonitrile solvent.

Acid–Base Reactions. Titration of both isomers in essentially aqueous media indicated that each isomer behaved as a diprotic acid. The first ionization constant of each isomer was immeasurably large and compared well with the similar ionization of strong acids. The second ionization constant was easily determined in both cases by determining the pH of partially neutralized solutions. The resulting pK_a values were 7.5 and 8.6 for n- and i-$B_{18}H_{22}$, respectively. The presence

$$n\text{- or } i\text{-}B_{18}H_{22} + H_2O \rightleftarrows n\text{- or } i\text{-}B_{18}H_{21}{}^{-} + H_3O^{+}$$

$$n\text{- or } i\text{-}B_{18}H_{21}{}^{-} + H_2O \rightleftarrows n\text{- or } i\text{-}B_{18}H_{20}{}^{2-} + H_3O^{+}$$

of a second ionization reaction was not previously observed.[1] The isomeric $B_{18}H_{20}{}^{2-}$ ions were also pro-

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[1] A. R. Pitochelli and M. F. Hawthorne, *J. Am. Chem. Soc.*, **84**, 2318 (1962).

[2] (a) P. G. Simpson and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **48**, 1490 (1962); (b) P. G. Simpson, K. Folting, R. D. Dobrott, and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 2339 (1963).

[3] (a) P. G. Simpson, K. Folting, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 1879 (1963); (b) P. G. Simpson and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 26 (1963).

[4] (a) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963; (b) M. F. Hawthorne in "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., John Wiley and Sons, Inc., New York, N. Y., 1967, Chapter V.

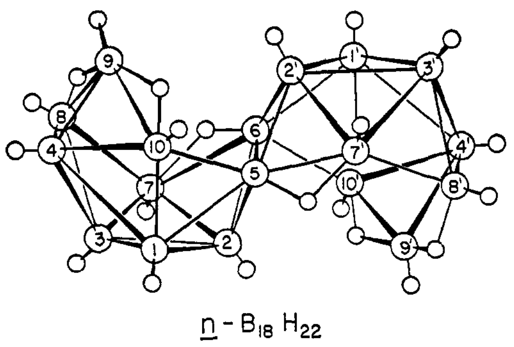

Figure 1. Structure and numbering system of n-$B_{18}H_{22}$.

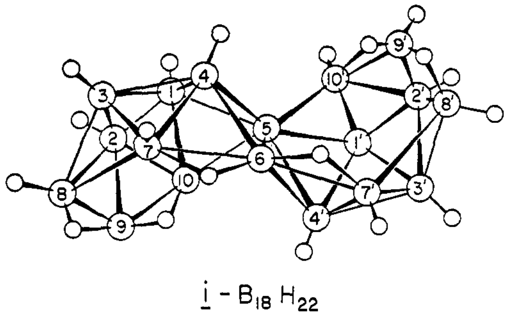

Figure 2. Structure and numbering system of i-$B_{18}H_{22}$.

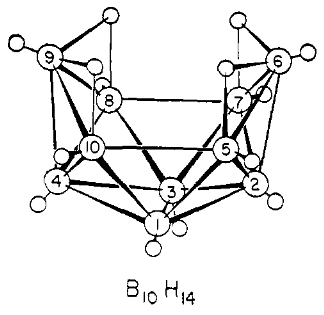

Figure 3. Structure and numbering system of $B_{10}H_{14}$.

duced from the reaction of sodium hydride with the parent hydrides in tetrahydrofuran solution. In each case 2.05–2.10 moles of H_2 was evolved per mole of hydride. The $B_{18}H_{20}^{2-}$ ions prepared by this route were identical (^{11}B nmr spectra) with those produced in aqueous solution. On a preparative scale, the two isomeric $B_{18}H_{21}^-$ and the two isomeric $B_{18}H_{20}^{2-}$ ions were isolated as their water-insoluble tetramethylammonium salts. The mono- and dianions were yellow in color, and Table I presents their electronic spectra determined in acetonitrile solution, and Figures 4 and 5 contain the 19.3-Mc/sec ^{11}B nmr spectra of n and i ions, respectively. Neutralization of the mono- and dianions with strong mineral acid regenerated the respective $B_{18}H_{22}$ in quantitative yield. The purification of $[(CH_3)_4N]_2$-i-$B_{18}H_{20}$ by recrystallization followed by regeneration of i-$B_{18}H_{22}$ served as the most convenient route to isomer-free i-$B_{18}H_{22}$.

While $B_{10}H_{14}$ is rapidly degraded[5] to $B_9H_{14}^-$ by strong, aqueous base, the $B_{18}H_{22}$ hydrides resist degradation in 3 N hydroxide ion solutions for 15–20 hr at room tempera-

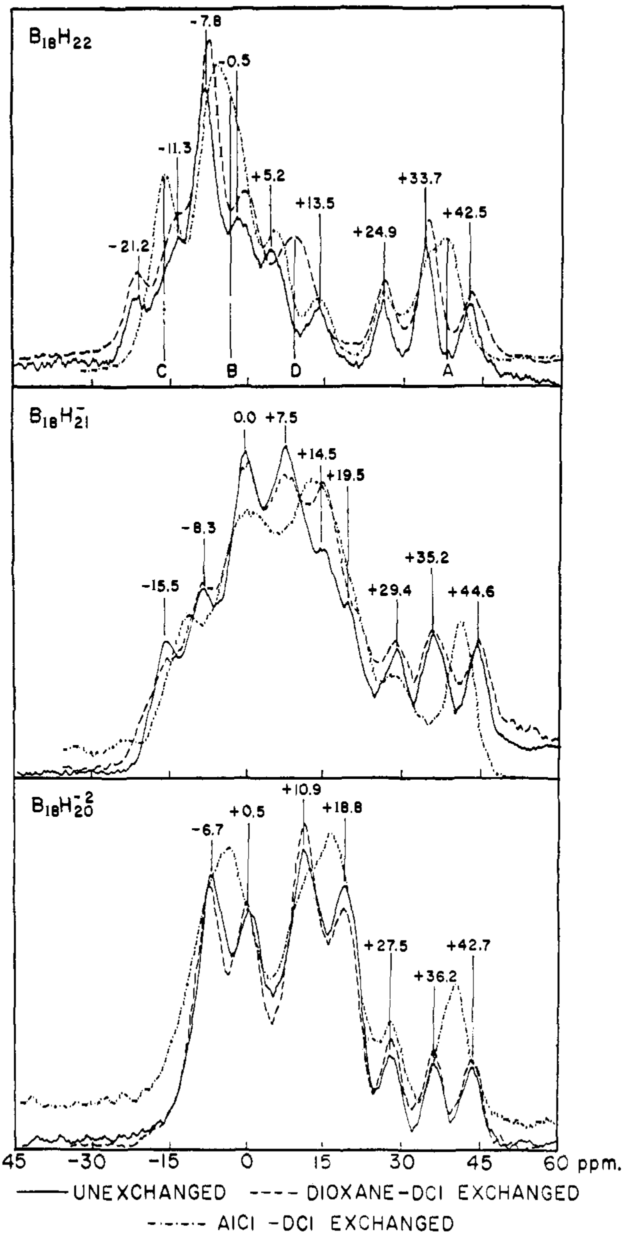

Figure 4. Collected 19.3-Mc/sec ^{11}B nmr spectra of n-$B_{18}H_{22}$, n-$B_{18}H_{21}^-$, and n-$B_{18}H_{20}^{2-}$.

ture. After 2–4 weeks, however, the $B_{18}H_{22}$ hydrides are completely degraded under these conditions. This slow degradation of n-$B_{18}H_{22}$ produced the icosahedral $B_{12}H_{12}^{2-}$ ion[6] in approximately 30% yield while similar degradation of i-$B_{18}H_{22}$ afforded no recognizable species save borate salts. Isolation of $B_{12}H_{12}^{2-}$, while perhaps surprising, is consistent with the finding of Muetterties and coworkers[7] that nearly all boron hydrides form $B_{12}H_{12}^{2-}$ when treated with amines at high temperatures in inert solvents.

While $B_{10}H_{14}$ undergoes the nucleophilic addition of alkyllithium reagents to eventually yield alkyl[8]-substituted decaborane(14) derivatives, n-butyllithium

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(5) L. E. Benjamin, S. F. Stofiej, and E. A. Tokacs, *J. Am. Chem. Soc.*, **85**, 2674 (1963).

(6) (a) M. F. Hawthorne and A. R. Pitochelli, *ibid.*, **82**, 3228 (1960); (b) H. C. Miller, N. E. Miller, and E. L. Muetterties, *ibid.*, **85**, 3885 (1963).

(7) H. C. Miller, N. E. Miller, and E. L. Muetterties, *Inorg. Chem.*, **3**, 1456 (1964).

(8) I. Dunstan, R. L. Williams, and N. J. Blay, *J. Chem. Soc.*, 5012 (1960).

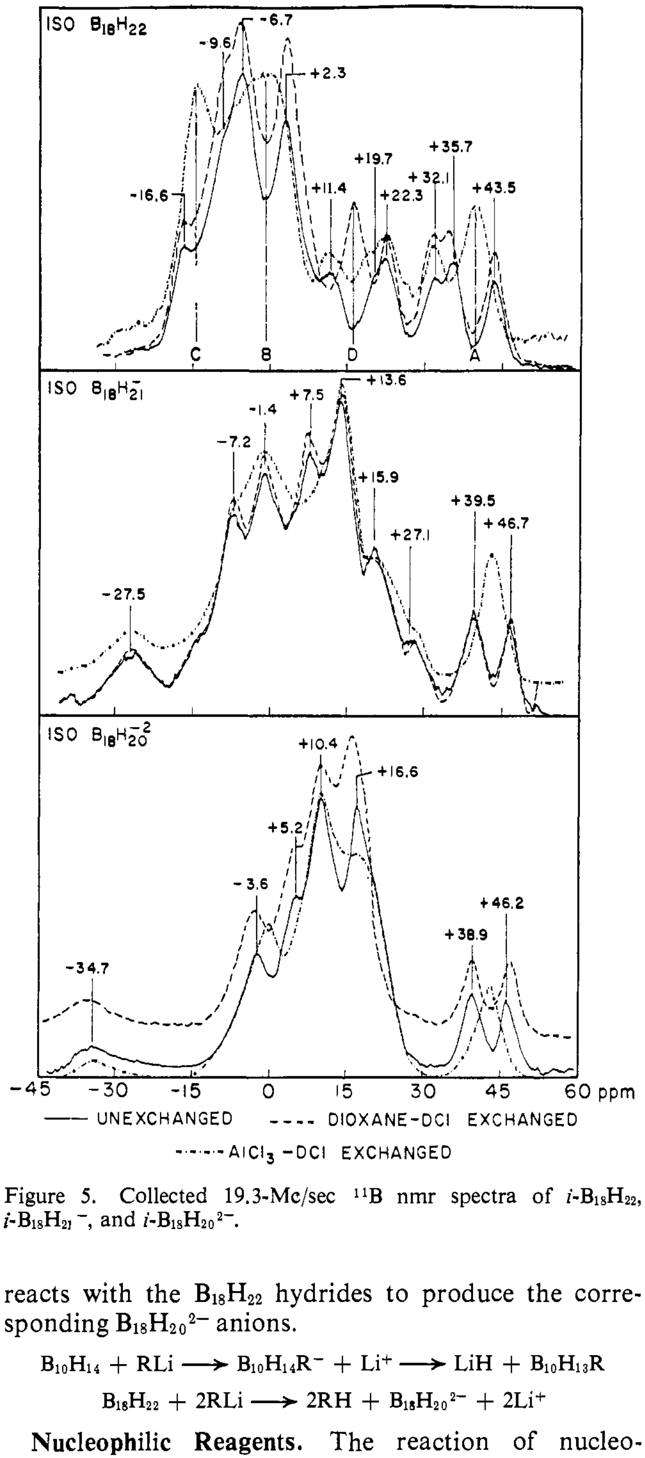

Figure 5. Collected 19.3-Mc/sec ^{11}B nmr spectra of i-$B_{18}H_{22}$, i-$B_{18}H_{21}^-$, and i-$B_{18}H_{20}^{2-}$.

reacts with the $B_{18}H_{22}$ hydrides to produce the corresponding $B_{18}H_{20}^{2-}$ anions.

$$B_{10}H_{14} + RLi \longrightarrow B_{10}H_{14}R^- + Li^+ \longrightarrow LiH + B_{10}H_{13}R$$

$$B_{18}H_{22} + 2RLi \longrightarrow 2RH + B_{18}H_{20}^{2-} + 2Li^+$$

Nucleophilic Reagents. The reaction of nucleophiles[4b,9] such as nitriles, dialkyl sulfides, phosphines, etc., with $B_{10}H_{14}$ to produce $B_{10}H_{12}$(ligand)$_2$ derivatives is a well-known reaction. The $B_{18}H_{22}$ hydrides were examined with respect to their possible reactivity with

$$B_{10}H_{14} + 2(\text{ligand}) \longrightarrow H_2 + B_{10}H_{12}(\text{ligand})_2$$

nucleophilic reagents such as acetonitrile. After 5 days at the reflux temperature in acetonitrile, both hydrides were recovered in high yield with no evidence of derivative formation.

Decaborane(14) and amines react to produce the corresponding protonated amine salt of the $B_{10}H_{10}^{2-}$

$$B_{10}H_{14} + 2NR_3 \longrightarrow H_2 + [R_3N^+H]_2B_{10}H_{10}^{2-}$$

ion.[10] In contrast to these results, prolonged heating of the $B_{18}H_{22}$ hydrides with triethylamine in toluene at 100° for 20 hr gave no evidence of reaction except for the formation of the corresponding $B_{18}H_{21}^-$ ions.

Electron Addition. Decaborane(14) acquires two electrons[4b,11] when treated with sodium amalgam in tetrahydrofuran to produce a red intermediate followed by $B_{10}H_{14}^{2-}$. The red intermediate has been suggested to be the $B_{10}H_{13}\cdot^-$ radical ion. Titration of $B_{10}H_{14}^{2-}$ with aqueous acid leads to the formation of the $B_{10}H_{15}^-$ ion.[12]

In analogous reduction reactions, n- and i-$B_{18}H_{22}$ were found to react with sodium amalgam in tetrahydrofuran to produce the corresponding $B_{18}H_{22}^{2-}$ ions. The stoichiometry of these reactions was established by mea-

$$n\text{- or } i\text{-}B_{18}H_{22} + 2e^- \longrightarrow n\text{- or } i\text{-}B_{18}H_{22}^{2-}$$

suring the quantity of sodium consumed by each hydride. A transient green color was observed in these reductions which may be characteristic of the $B_{18}H_{22}\cdot^-$ radical ions. Further reactions of the two isomeric $B_{18}H_{22}^{2-}$ ions were not investigated.

Base-Catalyzed Deuterium Exchange. Decaborane(14) has been found to undergo base-catalyzed deuterium exchange in either aqueous[13] media (D_2O) or in dioxane–DCl solutions.[14] In these exchange processes the four bridge hydrogen atoms of $B_{10}H_{14}$ are rapidly exchanged followed by the slow exchange at the 5, 6, 7, 8, 9, and 10 positions. Base-catalyzed exchange does not occur at the 1, 2, 3, and 4 positions, and the $B_{10}H_{13}^-$ ion undoubtedly plays a major role in base-catalyzed exchange.

When n- and i-$B_{18}H_{22}$ were subjected to base-catalyzed exchange with DCl in dioxane solution, only six deuterium atoms per mole were incorporated. In both isomers, only two equivalent terminal B–H groups were exchanged as shown by collapse of one doublet of area 2 in the 19.3-Mc/sec ^{11}B nmr spectra (Figures 4 and 5). The remaining four deuterium atoms therefore entered bridge-hydrogen positions.

Electrophilic Deuterium Exchange. Electrophilic deuterium exchange has been found to occur[14] at the 1, 2, 3, and 4 positions of $B_{10}H_{14}$ when DCl–$AlCl_3$ was employed with carbon disulfide solvent. The rates of exchange at the four reaction sites were indistinguishable.

Treatment of n- and i-$B_{18}H_{22}$ with DCl–$AlCl_3$ in the presence of carbon disulfide solvent led to the ultimate exchange of six deuterium atoms per mole of $B_{18}H_{22}$. In the case of both isomers, the six deuterium atoms constituted three discrete pairs of equivalent positions. One such pair of positions was observed to exchange much more rapidly than the others. Figures 4 and 5 present the 19.3-Mc/sec spectra of the deuterated n- and i-$B_{18}H_{22}$ hydrides.

Miscellaneous Reactions. The base-catalyzed electrophilic deuterium-exchange reactions were employed

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(9) R. Schaeffer, *J. Am. Chem. Soc.*, **79**, 1006 (1957).

(10) (a) M. F. Hawthorne and A. R. Pitochelli, *ibid.*, **81**, 5519 (1959); (b) E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.*, **3**, 444 (1964).

(11) R. H. Toeniskoetter, Thesis, St. Louis University, St. Louis, Mo., 1956.

(12) J. A. Dupont and M. F. Hawthorne, *Chem. Ind.* (London), 405 (1962).

(13) I. Shapiro, M. Lustig, and R. E. Williams, *J. Am. Chem. Soc.*, **81**, 4998 (1959).

(14) J. A. Dupont and M. F. Hawthorne, *ibid.*, **84**, 1804 (1962).

to prepare significant quantities of the corresponding deuterated *n*- and *i*-$B_{18}H_{22}$ species. The labeled hydrides were then employed in the preparation of specifically deuterated (terminal positions only) isomeric sets of $B_{18}H_{21}^-$ and $B_{18}H_{20}^{2-}$ ions. The 19.3-Mc/sec ^{11}B nmr spectra of these deuterated anions are presented in Figures 4 and 5.

The reaction of *n*-$B_{18}H_{12}$ with iodine in ethanol was briefly examined, and the product of this reaction is tentatively formulated as $B_{18}H_{21}I$ on the basis of elemental analyses, molecular weight, and its 19.3-Mc/sec ^{11}B nmr spectrum (Figure 6). The ultraviolet spectrum of $B_{18}H_{21}I$ (cyclohexane solvent) is presented in Table I. As in the case of *n*- and *i*-$B_{18}H_{22}$, $B_{18}H_{21}I$ was a strong dibasic acid having a second ionization pK_a of 8.5. Equivalent weight values based upon the first and second ionization processes were as expected for the proposed empirical formula.

Discussion

Reactions. The chemistries of *n*- and *i*-$B_{18}H_{22}$ have paralleled each other and, in certain respects, that of $B_{10}H_{14}$. The major difference which separates $B_{18}H_{22}$ and $B_{10}H_{14}$ chemistry is the high reactivity of the latter compound toward nucleophiles and the complete lack of reactivity of the $B_{18}H_{22}$ hydrides toward these reagents. The lack of response of the $B_{18}H_{22}$ hydrides to nucleophilic attack by relatively nonbasic electron donors is probably a characteristic of the complex central portion of these molecules. Since the mechanism of the $B_{10}H_{14}^-$ ligand reaction is presently unknown,[4b,9] discussion of this point would not be profitable at this time.

The structures of the isomeric sets of $B_{18}H_{21}^-$ and $B_{18}H_{20}^{2-}$ ions are quite likely related to that of the $B_{10}H_{13}^-$ ion. Unfortunately, the structure of the latter ion has not been conclusively demonstrated by X-ray diffraction studies. However, the bulk of ^{11}B nmr data available suggests that the structure[4a,15] resembles a $B_{10}H_{14}$ molecule with the 5–6 and 6–7 B–H–B bridges removed and a BH_2^- group at position 6. If this proposed structure of $B_{10}H_{13}^-$ is indeed correct, then the reasonable assumption may be made that the position-9 boron atoms of *n*- and *i*-$B_{18}H_{22}$ play the role of boron atom 6 in $B_{10}H_{14}$ when the $B_{18}H_{21}^-$ ions are formed. Further extension of this same concept would easily explain the formation of the $B_{18}H_{20}^{2-}$ ions by allowing ionization to occur at both the 9 and 9′ B–H–B bridge systems in *n*- and *i*-$B_{18}H_{22}$ and the introduction of four B–D–B bridges during base-catalyzed deuterium exchange. The fact that base-catalyzed deuterium exchange of *n*- and *i*-$B_{18}H_{22}$ introduced deuterium at only two equivalent terminal B–H positions suggests that these positions are 9 and 9′ in both isomers of $B_{18}H_{22}$. Further exchange of terminal positions 7, 8, 10, 7′, 8′, and 10′ must be prevented by the nature of the bonding at the center of the hydrides. Again, conclusions are limited by the lack of knowledge associated with the mechanism of base-catalyzed exchange at all hydrogen positions about the open face of $B_{10}H_{14}$ itself.

^{11}B Nmr Spectra. The 19.3-Mc/sec ^{11}B nmr spectra of *n*-$B_{18}H_{22}$, *i*-$B_{18}H_{22}$, and their derived ions are presented in Figures 4 and 5 and the similar spectrum of $B_{18}H_{21}I$ is shown in Figure 6. The general appearances of the ^{11}B nmr spectra of all neutral species are similar. Both *n*- and *i*-$B_{18}H_{22}$ have two sets of doublets, representing two boron atoms per set, isolated at high field. These resonances are centered at +30 and +38 ppm[16] for *n*-$B_{18}H_{22}$ and +27 and +40 ppm[16] for *i*-$B_{18}H_{22}$. In $B_{18}H_{21}I$ an additional singlet representing one boron atom appears in this high-field array. This singlet may well represent the boron atom which bears the iodine substituent. Closer comparison of the ^{11}B nmr spectra of *n*-$B_{18}H_{22}$ and $B_{18}H_{21}I$ reveals that a doublet in the spectrum of *n*-$B_{18}H_{22}$ is missing in the spectrum of $B_{18}H_{21}I$. The missing doublet in the $B_{18}H_{21}^-$ spectrum is located just above the highest peak (+7.8 ppm[16]) in the *n*-$B_{18}H_{22}$ spectrum.

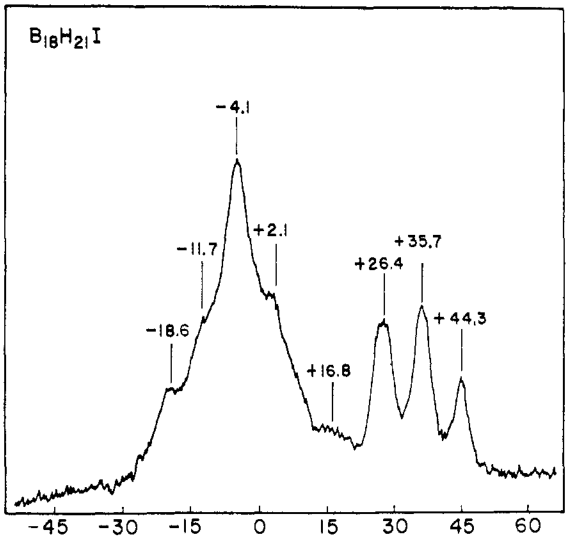

Figure 6. The 19.3-Mc/sec ^{11}B nmr spectrum of $B_{18}H_{21}I$.

The ^{11}B nmr spectrum of *i*-$B_{18}H_{22}$ contains a third doublet (two B atoms) which partly overlaps the high-field doublets and the low-field envelope.

The changes which occur in the ^{11}B nmr spectra when *n*-$B_{18}H_{22}$ and *i*-$B_{18}H_{22}$ are converted to their corresponding $B_{18}H_{21}^-$ and $B_{18}H_{20}^{2-}$ ions are relatively simple. The resonances of *n*-$B_{18}H_{22}$ and *i*-$B_{18}H_{22}$ which occur at low field are slightly shifted to higher field. In the case of *i*-$B_{18}H_{21}^-$ and $B_{18}H_{20}^{2-}$, a new singlet appears at low field.

Deuterium Labeling and ^{11}B Nmr Assignments. The acid-catalyzed deuterium-exchange reaction introduced six deuterium atoms per mole of *n*-$B_{18}H_{22}$ or *i*-$B_{18}H_{22}$. Examination of the ^{11}B nmr spectra of the acid-catalyzed exchange products (Figures 4 and 5) proves that these six deuterium exchange sites are terminal positions since three doublets of weight two each (A, B, and C in Figures 4 and 5) collapse to singlets upon deuteration. The high-field doublet (A) was found to collapse most rapidly in both *n*-$B_{18}H_{22}$ and *i*-$B_{18}H_{22}$, indicating more rapid exchange at these sites. Charge-distribution calculations[4a] coupled with the known results[14] of the acid-catalyzed deuterium exchange of $B_{10}H_{14}$ suggest that the three exchanged terminal hydrogens reside at the 4,4′, 2,2′, and either 1,1′ or 3,3′ positions. The 4,4′ and 2,2′ positions bear the greatest negative charge in the ground-state *n*- and *i*-$B_{18}H_{22}$ molecules,[4a] and electrophilic exchange must certainly involve these

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(15) W. N. Lipscomb, *Advan. Inorg. Nucl. Chem.*, **1**, 117 (1959).

(16) Relative to external trimethyl borate standard at zero ppm.

sites. The third pair of exchange sites are most likely the 3,3′ positions since these are farther removed from the center of the $B_{18}H_{22}$ hydrides and should be closer akin to the exchangeable 3 (1) sites of $B_{10}H_{14}$. The electrophilic exchange sites (resonances A, B, and C) can apparently be easily traced in the ^{11}B nmr spectra of the n-$B_{18}H_{21}^{-}$ and n-$B_{18}H_{20}^{2-}$ ions and the corresponding i-$B_{18}H_{22}$ derivatives. However, such an assignment technique is not unequivocal because of the possibility of gross chemical shifts which might occur upon ionization of the $B_{18}H_{22}$ hydrides.

The base-catalyzed deuterium-exchange reaction introduced two equivalent deuterium atoms, which for reasons discussed above most likely represent the 9,9′ positions of the $B_{18}H_{22}$ hydrides. The ^{11}B nmr resonances associated with these exchange sites are labeled D in Figures 4 and 5. No attempt was made to unequivocally assign the 9,9′-boron resonances in the isomeric sets of $B_{18}H_{21}^{-}$ or $B_{18}H_{20}^{2-}$ ions. The low-field singlet seen in the ^{11}B nmr spectrum of the i-$B_{18}H_{21}^{-}$ and i-$B_{18}H_{20}^{2-}$ ions may be assigned to the boron atoms at position 5 or 6.

Experimental Section

Preparation of Mixed Hydrides. The triethylammonium salt of $B_{20}H_{18}^{2-}$ was prepared as previously described[17] and recrystallized from hot water. A solution of 30 g (0.079 mole) of this salt was prepared in 1500 ml of a 90% absolute ethanol–10% acetonitrile solution and passed through a 500-g acid ion-exchange column. The resulting solution was divided into two equal portions, and the two halves were separately concentrated at room temperature in 1-l. flasks on a vacuum line. As the last traces of solvent were removed, the yellow solution underwent an exothermic reaction in which appreciable quantities of hydrogen were evolved. After 20 min, the evolution of hydrogen had ceased and the solutions became quite viscous. After 12 additional hr on the vacuum line, 150 ml of cyclohexane followed by 200 ml of water were added to each flask. The resulting mixtures were stirred at room temperature for 3 hr, whereupon the cyclohexane layer was separated and concentrated to dryness at room temperature under vacuum. A mixture (approximately 2:1) of n-$B_{18}H_{22}$ and i-$B_{18}H_{22}$ was obtained as a pale yellow solid. The yield of mixed hydrides from the combined work-up was 9.2 g (53%).

Separation of Hydrides. Pure n-$B_{18}H_{22}$, mp 179–180°, was obtained as the least soluble component after several recrystallizations of the mixed hydrides from cyclohexane. Evaporation of the filtrates gave enriched i-$B_{18}H_{22}$ which could be obtained free of n-$B_{18}H_{22}$ only after many recrystallizations from 2,3-dimethylbutane. Alternatively, separation could be carried out by recrystallization of a mixture of n-$B_{18}H_{20}^{2-}$ and i-$B_{18}H_{20}^{2-}$ as their tetramethylammonium salts (*vide infra*) from an acetonitrile–benzene mixture followed by regeneration of the pure hydrides and a final recrystallization from 2,3-dimethylbutane. When pure, i-$B_{18}H_{22}$ melted at 128–129°. Recrystallization of the hydrides is most convenient for the preparation of pure n-$B_{18}H_{22}$.

Preparation of n-$B_{18}H_{21}^{-}$ and i-$B_{18}H_{21}^{-}$. Pure n-$B_{18}H_{22}$ (308 mg, 1.42 mmoles) was dissolved in 5 ml of toluene, and 1 ml of triethylamine was added slowly with stirring. A waxy, deep yellow salt precipitated. The precipitated salt was dissolved in aqueous acetonitrile and the anion precipitated with aqueous tetramethylammonium chloride. Recrystallization from aqueous acetonitrile afforded deep yellow n-$B_{18}H_{21}^{-}N^{+}(CH_3)_4$ in 95% yield. *Anal.* Calcd for $C_4H_{33}NB_{18}$: C, 16.6; H, 11.4; N, 4.8; B, 67.2; equiv wt, 289.5. Found: C, 15.5; H, 11.7; N, 4.2; B, 66.8; equiv wt,[18] 292.

Pure i-$B_{18}H_{22}$ when treated in an identical manner, gave bright yellow i-$B_{18}H_{21}^{-}$ as its tetramethylammonium salt in 95% yield. *Anal.* Found: C, 17.3; H, 12.4; N, 4.8; B, 65.9; equiv wt,[18] 291.

Preparation of n-$B_{18}H_{20}^{2-}$ and i-$B_{18}H_{20}^{2-}$. Pure n-$B_{18}H_{22}$ (320 mg, 1.48 mmoles) was dissolved in 3 ml of methanol containing 0.3 g of potassium hydroxide. This solution was added to 20 ml of water containing 1.0 g of potassium hydroxide. Addition of aqueous tetramethylammonium chloride precipitated the bis(tetramethylammonium) salt of n-$B_{18}H_{20}^{2-}$ in 76% yield. Recrystallization from acetonitrile gave a pale yellow analytical sample. *Anal.* Calcd for $C_8H_{44}N_2B_{18}$: C, 26.5; H, 12.1; N, 7.7; B, 53.7; equiv wt, 362.5. Found: C, 26.1; H, 11.8; N, 7.7; B, 53.5; equiv wt,[18] 358. Pure i-$B_{18}H_{22}$, when treated in the same manner, gave the bis(tetramethylammonium) salt of i-$B_{18}H_{20}^{2-}$ in 64% yield. Recrystallization was accomplished using an acetonitrile–benzene mixture. *Anal.* Found: C, 26.0; H, 11.5; N, 7.6; B, 53.6; equiv wt,[18] 360.

Preparation of n-$B_{18}H_{21}I$. Pure n-$B_{18}H_{22}$ (302 mg, 1.40 mmoles) was dissolved in 10 ml of absolute ethanol, and 1.42 g (11.1 mmoles) of iodine dissolved in 30 ml of ethanol was slowly added with stirring. The yellow color of the iodine was rapidly discharged. The solvent was removed under high vacuum at room temperature, and recrystallization of the residue from 2,3-dimethylbutane afforded $B_{18}H_{21}I$ (278 mg, 58%) as pale yellow plates, mp 184–185°. *Anal.* Calcd for $B_{18}H_{21}I$: B, 56.8; H, 6.1; I, 37.1; equiv wt, 342; mol wt, 342. Found: B, 56.9; H, 6.1; I, 36.0; equiv wt,[18] 344; mol wt,[19] 355.

Preparation of n-$B_{18}H_{22}^{2-}$ and i-$B_{18}H_{22}^{2-}$. Pure n-$B_{18}H_{22}$ (214 mg, 0.99 mmole) was weighed into one compartment of a two-compartment vessel. Excess sodium amalgam was placed in the second compartment and pure anhydrous tetrahydrofuran condensed in the system at low temperature. The reaction vessel was sealed and its contents mixed in the cold. The solution rapidly became intensely green and then slowly turned yellow. After stirring at room temperature for 24 hr the flask was cooled in liquid nitrogen and the reaction products examined for hydrogen. Less than 0.01 mmole of hydrogen was present. If the reactants were warmed to room temperature prior to mixing, the same color changes were noted, but 0.05 g (0.01 mmole) of hydrogen was evolved in the reaction.

In a separate experiment, 142 mg (0.66 mmole) of pure n-$B_{18}H_{22}$ was allowed to react in the cold with 7.60 g of sodium amalgam containing 0.294 mequiv of sodium/g. After the solution became yellow, the excess sodium amalgam was separated, washed with anhydrous tetrahydrofuran, and decomposed in 30 ml of 0.100 *N* hydrochloric acid. The excess acid was then titrated with 0.0853 *N* potassium hydroxide and required 24.30 ml for neutralization. The hydride sample had therefore consumed 1.31 mequiv of Na (theory requires 1.32 mequiv for n-$B_{18}H_{22}^{2-}$).

Pure i-$B_{18}H_{22}$ was subjected to the two experiments described above and gave identical results. A transient green color, indistinguishable from that formed from n-$B_{18}H_{22}$, was observed in the first experiment, and less than 0.01 mmole of H_2 was liberated from 216 mg (1.00 mmole) of i-$B_{18}H_{22}$. In the second experiment, using standardized sodium amalgam, 0.913 mequiv of i-$B_{18}H_{22}$ consumed 1.91 mequiv of sodium (theory for i-$B_{18}H_{22}^{2-}$, 1.82 mequiv).

Deuterium Exchange. Pure n-$B_{18}H_{22}$ (98.6 mg, 0.456 mmole), 200 mg (1.52 mmoles) of $AlCl_3$, 5 ml of carbon disulfide, and 2.1 l. (93.8 mmoles) of pure deuterium chloride were sealed in an evacuated 500-ml flask equipped with an nmr tube appendage containing a glass wool plug. The reactants were stirred at room temperature and occasionally tipped into the nmr tube for examination of the ^{11}B nmr spectrum. After 75 hr no further change occurred in the ^{11}B nmr spectrum; deuterated n-$B_{18}H_{22}$ was recovered and analyzed as described below. Six deuterium atoms per mole of n-$B_{18}H_{22}$ were introduced. This material was dissolved in benzene and converted to the deuterated $B_{18}H_{21}^{-}$ ion by the addition of triethylamine. The salt obtained in this fashion was dissolved in acetonitrile and its ^{11}B nmr spectrum recorded. The deuterated n-$B_{18}H_{22}$ was dissolved in aqueous base and precipitated as the deuterated $B_{18}H_{20}^{2-}$ ion by addition of tetramethylammonium chloride. The ^{11}B nmr spectrum of this deuterated ion was then examined in acetonitrile solution at 19.3 Mc/sec.

In a separate experiment 98.0 mg (0.456 mmole) of pure n-$B_{18}H_{22}$ and 5 ml of purified dioxane were sealed along with 2.1 l. (93.8 mmoles) of pure DCl in a system bearing an nmr tube appendage (*vide supra*) and its ^{11}B nmr spectrum was examined periodically. After 400 hr, no further changes were noted in the ^{11}B nmr spectrum and the material was recovered. The material contained 6 g-atoms of deuterium per mole of hydride when analyzed as de-

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(17) M. F. Hawthorne, R. L. Pilling, and P. F. Stokely, *J. Am. Chem. Soc.*, **87**, 1893 (1965).

(18) Cation exchange of weighed sample of salt in aqueous acetonitrile followed by potentiometric titration of liberated $B_{18}H_{22}$ with standardized base.

(19) Osmometric determination in benzene solvent.

scribed below. Conversion to the 1− and 2− ions was accomplished as in the case of the deuterated n-$B_{18}H_{22}$ except that D_2O was employed as solvent in the formation of the latter ion. The ^{11}B nmr spectra of these materials were examined in acetonitrile solution at 19.3 Mc/sec.

Pure i-$B_{18}H_{22}$ was subjected to acid- and base-catalyzed deuterium-exchange reactions in similar experiments. In $AlCl_3$-catalyzed exchange, six atoms of deuterium per mole of hydride were incorporated as in the case of dioxane-catalyzed exchange.

Determination of H/D Ratios in Deuterated $B_{18}H_{22}$ Samples. Small samples of partially deuterated n- and i-$B_{18}H_{22}$ (~5–10 mg) were placed in a heavy-walled tube (100-ml volume), cooled to −78°, evacuated, and sealed off on the vacuum line. Each reaction tube carried a break-seal and associated standard taper joint for introducing the H_2–HD–D_2 gas mixture into a vacuum line and thence into a small gas-sample bulb fitted for the mass spectrometer (Hitachi Perkin-Elmer RMU-6). The sealed reaction tubes were heated for 12 hr at 575° in a sealed furnace, cooled, and opened in the vacuum line. The released gas was compressed into the gas-sampling bulb with a Toepler pump. The mass spectrum of the product gases was examined and the H_2, HD, and D_2 peaks measured. Each run was analyzed in triplicate and the results were averaged. In all cases, 5.6 to 6.0 atoms/mole of hydride of deuterium were found to be present assuming complete decomposition of the $B_{18}H_{22}$ samples to boron metal and H_2, HD, and D_2.

Reaction of $B_{18}H_{22}$ Hydrides with Aqueous Base. Pure n-$B_{18}H_{22}$ (300 mg, 1.39 mmoles) was dissolved in 25 ml of 20% potassium hydroxide and stirred at room temperature for 2 weeks during which time the yellow color gradually faded. The solution was then acidified and no precipitation was observed. Addition of aqueous triethylammonium chloride solution gave 151 mg (31 mole %) of the triethylammonium salt of $B_{12}H_{12}^{2-}$ identified by its infrared and ^{11}B nmr spectra. Treatment of 285 mg (1.32 mmoles) of i-$B_{18}H_{22}$ in the same manner required 4.5 weeks for the yellow color to be discharged. Acidification of the resulting solution gave no neutral hydride precipitate. Addition of aqueous triethylammonium chloride or tetramethylammonium chloride did not precipitate the corresponding $B_{12}H_{12}^{2-}$ salts as in the case of the n-$B_{18}H_{22}$ reaction.

Reaction with n-Butyllithium. Excess n-butyllithium in hexane was added to a solution of pure n-$B_{18}H_{22}$ dissolved in hexane. The solution very rapidly turned deep yellow, then pale yellow, and deposited a pale yellow precipitate which was shown to be dilithium $B_{18}H_{20}^{2-}$ by its ^{11}B nmr spectrum. When only 1 equiv of n-butyllithium was added, one-half the n-$B_{18}H_{22}$ present was converted to insoluble dilithium $B_{18}H_{20}^{2-}$ and the remainder of the hydride remained unreacted. Pure i-$B_{18}H_{22}$ gave identical results under the same conditions.

Spectra. All electronic spectra were recorded on a Beckman Model DB spectrometer equipped with a Sargent recorder. The ^{11}B nmr spectra were obtained relative to external $B(OCH_3)_3$ at 19.3 Mc/sec on a Varian Model HR-60 spectrometer. Spectra of ionic species were obtained in acetonitrile solution, and the spectra of neutral compounds were obtained in cyclohexane solution. Infrared spectra (Table II) were obtained with a Beckman IR-5 spectrophotometer.

Determination of pK_a of n- and i-$B_{18}H_{22}$ and $B_{18}H_{21}I$. The pK_a's of the second ionization of n- and i-$B_{18}H_{22}$ were determined by direct titration at 25° in water. Small samples of the neutral hydride were dissolved in 2 ml of methanol and added to a rapidly stirred aqueous base solution (100 ml) which contained about 90–95% of the base required for the conversion of the hydride to the corresponding $B_{18}H_{21}^-$ ion. The resulting solutions were titrated potentiometrically using a glass electrode *vs.* sce. The first break in the titration curve corresponded nicely to the expected equivalent weight value for one ionizable proton. Continued titration of the second proton afforded a titration curve from which the pH values at 0.25, 0.50, and 0.75 neutralization were calculated from these data by the usual procedure.

Table II. Some Characteristic Infrared Bands (cm^{-1}) of n- and i-$B_{18}H_{22}$ Derivatives (Nujol Mulls)

n-$B_{18}H_{22}$		i-$B_{18}H_{22}$	
2550 (s)	1940 (w)	2550 (s)	1940 (w)
1080 (m)	1390 (w)	1220 (w)	1152 (w)
1200 (w)	990 (s)	1080 (w)	1030 (w)
945 (m)	925 (s)	1030 (w)	1000 (s)
910 (s)	878 (w)	970 (w)	950 (m)
950 (sh)	835 (s)	935 (w)	920 (w)
805 (w)	782 (m)	910 (w)	860 (m)
760 (m)	738 (m)	833 (m)	792 (w)
725 (m)	712 (m)	780 (w)	769 (w)
695 (m)	668 (w)	743 (m)	728 (w)
		711 (w)	695 (w)
		660 (m)	638 (w)
n-$B_{18}H_{21}^-$ [a]		i-$B_{18}H_{21}^-$ [a]	
−2530 (s)	1940 (w)	2530 (s)	1940 (w)
1085 (w)	1040 (w)	1315 (w)	1163 (w)
1025 (w)	995 (m)	1060 (m)	1018 (s)
952 (s)	921 (m)	998 (w)	971 (w)
895 (w)	863 (w)	948 (s)	912 (w)
835 (m)	784 (w)	870 (w)	850 (m)
752 (w)	745 (w)	835 (m)	794 (w)
725 (w)	715 (w)	780 (w)	748 (w)
684 (w)		734 (w)	726 (w)
		708 (w)	678 (w)
n-$B_{18}H_{20}^{2-}$ [a]		i-$B_{18}H_{20}^{2-}$ [a]	
−2600 (s)	2500 (s)	−2600 (s)	2500 (s)
2410 (s)	1930 (w)	2410 (s)	1930 (w)
1290 (m)	1175 (w)	1285 (m)	1175 (w)
1076 (m)	1040 (w)	1150 (w)	1076 (m)
1021 (m)	982 (s)	1035 (m)	1020 (m)
952 (s)	921 (s)	995 (m)	978 (s)
895 (w)	878 (w)	950 (s)	855 (s)
958 (m)	883 (w)	795 (w)	775 (w)
800 (m)	785 (w)	752 (w)	730 (w)
741 (m)	725 (m)	705 (w)	680 (s)
688 (w)	672 (w)	645 (w)	
642 (w)			
$B_{18}H_{21}I$			
2650 (s)	1950 (w)		
1300 (m)	1075 (w)		
1035 (w)	1011 (w)		
983 (s)	945 (w)		
919 (s)	889 (w)		
850 (w)	848 (m)		
832 (s)	807 (w)		
782 (m)	767 (m)		
752 (m)	725 (s)		
711 (w)	698 (w)		
689 (w)	661 (w)		
642 (w)			

[a] As $(CH_3)_4N^+$ salt.

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