Chemical and Structural Studies on the 2,4- and 2,3-Isomers of the Dicarba-*nido*-hexaborate(1−) Ion, $C_2B_4H_7^-$, and some Dipolar Derivatives

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The *closo*-carborane 1,6-$C_2B_4H_6$ reacts with trimethylamine to form 5-Me_3N^+-*nido*-2,4-$C_2B_4H_6^-$. The latter compound rearranges in chloroform, or thermally, to the 3-Me_3N^+ isomer. The parent 2,4-$C_2B_4H_7^-$ ion is obtained both from the action of NaH on either 3- or 5-Me_3N^+-2,4-$C_2B_4H_6^-$ and from the slow reaction of *closo*-1,6-$C_2B_4H_6$ with either NaH or LiH. The structures of 2,4-$C_2B_4H_7^-$ and 2,3-$C_2B_4H_7^-$ and the Me_3N^+-2,4-$C_2B_4H_6^-$ isomers are correlated with ^{11}B and ^1H n.m.r. data.

A STRONG Lewis base such as butyl-lithium will abstract the carbon-attached cage hydrogens from a *closo*-carborane, $C_2B_xH_{x+2}$, to give the anion $C_2B_xH_x^{2-}$,[1-5] in a reaction that is presumed to be irreversible. In all likelihood this involves a single proton abstraction to form the monoanion, $C_2B_xH_{x+1}^-$, two molecules of which disproportionate to give the dianion and a molecule of the starting material.

Should a base such as trimethylamine be allowed to react with the *closo*-carborane 1,6-$C_2B_4H_6$, two possibilities are considered both from the above observations and from the known chemistry of other boron compounds: (*a*) a measurable equilibrium between the unchanged carborane and the mono- and di-anions resulting from C–H proton abstraction may be observed; or (*b*) one or more of the cage borons may react to form a B–N adduct. It was with these possibilities in mind that the present study was undertaken.

EXPERIMENTAL

Materials.—Sodium hydride was obtained from Metal Hydrides Inc. as a 50·6% dispersion in mineral oil, the oil being removed before use by frequent washing with pentane. 1,2-Dimethoxyethane was dried by refluxing over calcium hydride and lithium aluminum hydride, and trimethylamine was dried over barium oxide. Both 1,6-dicarba-*closo*-hexaborane (6), and 2,3-dicarba-*nido*-hexaborane (8) were purified before use by passage through a 10 ft g.l.c. column of Apiezon on firebrick. All materials were handled in conventional high-vacuum equipment or in a dry-box under an atmosphere of dry nitrogen.

Nuclear Magnetic Resonance.—Both the ^1H and ^{11}B n.m.r. spectra were obtained on a Varian HA-100 n.m.r. spectrometer operating at 100 MHz and 32·1 MHz respectively. Decoupled ^1H spectra at 100 MHz were observed while irradiating at 32·1 MHz with a Nuclear Magnetic Resonance Specialties model HD-60A decoupling unit modified for use with the HA-100 instrument and Hewlett–Packard model 200CD wide-range audio oscillators. Conversely, decoupled ^{11}B spectra at 32·1 MHz were observed while irradiating with the heteronuclear decoupler equipped with 100 MHz modules. The radiation frequency was controlled by a Hewlett-Packard 200CD wide-range oscillator. Another 200CD oscillator drives a pseudo-random binary noise generator whose output is used to phase-shift the radiation frequency. This signal, amplified by an Electronic Navigation Industries 320L RF power amplifier, is then applied to the HA-100 probe which has been double-tuned for decoupling.

The proton chemical shift data (Table) were obtained by use of 1,2-dimethoxyethane, $\tau(CH_2) = 6{\cdot}57$, $\tau(CH_3) = 6{\cdot}73$ relative to tetramethylsilane ($\tau = 10{\cdot}00$), as an internal standard.[6] The boron-11 chemical shift data (Table; Figure 1) were obtained by use of boron trichloride, $\delta = -46{\cdot}8$ relative to boron trifluoride ethyl ether complex as an external standard.

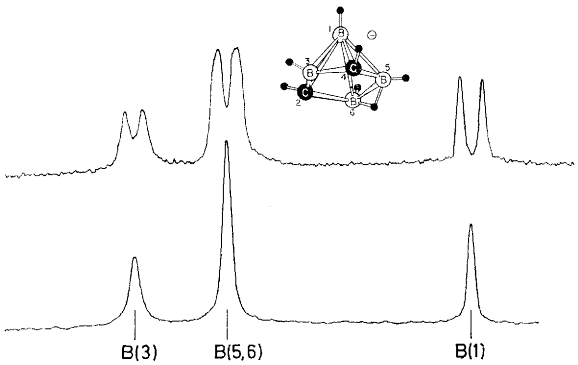

FIGURE 1 ^{11}B N.m.r. (32·1 MHz) of 2,4-$C_2B_4H_7^-$; upper spectrum, undecoupled; lower, proton decoupled

The chemical shift data obtained from the ^{11}B n.m.r. spectra were used to predict the relative double-irradiation frequencies used in obtaining boron-11 decoupled proton n.m.r. spectra. Each kind of boron could be separately irradiated with an acceptable minimum effect on neighbouring boron resonances so long as there was at least 5 p.p.m. separation between the resonances.

Preparation of 5-Me_3N^+-[2,4-$C_2B_4H_6^-$].—This was prepared from the reaction of 1,6-dicarba-*closo*-hexaborane (6) with trimethylamine by the method of Lockman and Onak.[7]

Preparation of 3-Me_3N^+-[2,4-$C_2B_4H_6^-$].—(a) *Chloroform-induced rearrangement of* 5-Me_3N^+-[2,4-$C_2B_4H_6^-$]. 5-Me_3N^+-[2,4-$C_2B_4H_6^-$] was dissolved in chloroform to give a saturated solution. A sample of this solution was decanted into an n.m.r. tube and the room-temperature rearrangement monitored by ^{11}B n.m.r. spectroscopy. After 1 day, the solution contained 30% 3-Me_3N^+-[2,4-$C_2B_4H_6^-$] and

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[1] R. E. Kesting, K. F. Jackson, E. B. Klusman, and J. F. Gerhart, *J. Appl. Polymer Sci.*, 1970, **14**, 2525.

[2] P. M. Garrett, J. C. Smart, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1969, **91**, 4707.

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[4] R. R. Olsen and R. N. Grimes, *Inorg. Chem.*, 1971, **10**, 1103.

[5] For original references concerning the abstraction of carbon-attached hydrogen from the three isomers of $C_2B_{10}H_{12}$ see R. N. Grimes, 'Carboranes,' Academic Press, New York, 1970.

[6] Sadtler Research Laboratories Inc., N.m.r. Spectra, No. 6235.

[7] B. Lockman and T. Onak, *J. Amer. Chem. Soc.*, 1972, **94**, 7923.

70% 5-Me_3N^+-[2,4-$C_2B_4H_6^-$]. After 10 days, the ratio was 60 : 40, after 25 days, 85 : 15, and after 36 days only the 3-Me_3N^+-[2,4-$C_2B_4H_6^-$] isomer was detected in the solution.

(b) *Thermal rearrangement of* 5-Me_3N^+-[2,4-$C_2B_4H_6^-$]. A Pyrex tube equipped with an n.m.r. tube side-arm and a greased stop-cock containing the white solid 5-Me_3N^+-[2,4-$C_2B_4H_6^-$] was heated carefully by means of an oil-bath. The vessel was attached to a vacuum line such that any volatile materials produced by the pyrolysis could be collected in two traps held at −78 °C and −196 °C. At 40—45 °C volatile material was evolved and collected in the −196 °C trap. An i.r. analysis showed this to be a mixture of trimethylamine [8] and 1,6-$C_2B_4H_6$.[9] At 80 °C a white substance was evolved and collected in the −78 °C trap. An ^{11}B n.m.r. analysis showed this to be trimethylamine–borane, Me_3N,BH_3.[10] Between 115 °C and 125 °C, more trimethylamine, 1,6-$C_2B_4H_6$, and Me_3N,BH_3 were collected in the respective cold traps. There was no further apparent change in the material being heated until 165 °C whereupon the solid started turning yellow and long, white, needle-like crystals appeared on the walls of the reaction vessel just above the oil level. At 169 °C, a further band of white solid appeared just below the oil level, leaving a tan residue at the bottom of the vessel. The last three components were transferred, under an atmosphere of dry nitrogen, to separate n.m.r. tubes and 1,2-dimethoxyethane added *via* the vacuum line. The first, most volatile solid dissolved readily in 1,2-dimethoxyethane and proved to be the rearranged isomer, 3-Me_3N^+-[2,4-$C_2B_4H_6^-$]. The tan residue was completely insoluble in 1,2-dimethoxyethane while the second white solid was reasonably soluble, but did not show any signals in the ^{11}B n.m.r. spectrum.

N.m.r. data on $C_2B_4H_7^-$ compounds

Compound	Groups	δ(^{11}B) BF_3,Et_2O (*J*/Hz)	Pattern	Rel. area	τ(^1H) Me_4Si = 10·00 (*J*/Hz)	Pattern	Rel. area
3-Me_3N^+-2,4-$C_2B_4H_6^-$	B(1)–H	+53·4 (165)	Doublet	1	11·11 (157)	Quartet [a]	1
	B(3)–NMe	−27·0 (—)	Singlet	1	7·03	Singlet	(9)
	B(5,6)–H	+0·6 (146)	Doublet	2	6·88	*b*	2
	C–H	—	—		6·45—6·85 [c]	*c*	(2) [c]
	Hμ	—	—		14·46	Very broad singlet	1
5-Me_3N^+-2,4-$C_2B_4H_6^-$	B(1)–H	+50·5 (160)	Doublet	1	10·91 (160)	Quartet [a]	1
	B(3)–H	−20·4 (134)	Doublet	1	5·56	*b*	1
	B(5)–NMe_3	−13·5 (50 ± 5) [d]	Doublet	1	6·99	Singlet	(9)
	B(6)–H	+0·6 (141)	Doublet	1	5·77	*b*	1
	C–H	—	—		6·45—6·85 [c]	*c*	(2)
	Hμ	—	—		12·74	Very broad singlet	1
2,4-$C_2B_4H_7^-$	B(1)–H	+51·9 (157)	Doublet	1	11·60 (158)	Quartet	1
	B(3)–H	−21·2 (123)	Doublet	1	5·69	*b*	1
	B(5,6)–H	−1·3 (135)	Doublet	2	6·90	*b*	2
	C–H	—	—		6·45—6·85 [c]	*c*	(2)
	Hμ	—	—		14·66	Very broad singlet	1
2,3-$C_2B_4H_7^-$	B(1)–H	+55·0 (158)	Doublet	1	12·19 (157)	Quartet	1
	B(5)–H	+5·5 (134)	Doublet	1	7·84	*b*	1
	B(4,6)–H	−7·1 (135)	Doublet	2	6·45—6·85 [c]	Singlet	2
	C–H	—	—		5·24	Singlet	2
	Hμ	—	—		15·11	Very broad singlet	1

[a] All observed quartets are 1 : 1 : 1 : 1 relative area due to ^{11}B ($I = \frac{3}{2}$) coupling. [b] The quartets of the basal terminal hydrogens were not well defined. This is attributed to partial lattice relaxation of the attached borons. The decoupled peaks, however, were reasonably sharp and these were used for the area comparison. [c] Overlaps with solvent peaks; exact chemical shift therefore cannot be accurately determined. [d] Coupling is to Hμ.

Preparation of the 2,3-$C_2B_4H_7^-$ *Ion*.—The reaction vessel, a Pyrex tube equipped with two n.m.r. tube side-arms and a greased stop-cock, was charged with lithium hydride (24·2 mmol), 2,3-dicarba-*nido*-hexaborane (8) (5·35 mmol), and 1,2-dimethoxyethane (5 ml) and the mixture was stirred at room temperature for four days. A non-condensable (−196 °C) gas, presumably hydrogen, was removed at the end of this period. A little reaction mixture was decanted into one of the n.m.r. tube side-arms and the tube sealed off. Only signals due to the 2,3-$C_2B_4H_7^-$ ion and, in trace, the BH_4^- ion [10] were observed in the ^{11}B n.m.r. spectrum indicating that all the 2,3-$C_2B_4H_8$ had been consumed.

Preparation of the 2,4-$C_2B_4H_7^-$ *Ion*. (a) *From* LiH *and* 1,6-$C_2B_4H_6$. An n.m.r. tube was charged with lithium hydride (2·29 mmol), 1,6-dicarba-*closo*-hexaborane (6) (1·06 mmol), and sufficient 1,2-dimethoxyethane to render the resulting solution 1·6M in 1,6-$C_2B_4H_6$. The reaction was monitored by ^{11}B n.m.r. spectroscopy. There was no reaction after several days at room temperature. After 10 days in an oven at 80 °C, *ca.* 50% of the 1,6-$C_2B_4H_6$ had been converted into the 2,4-$C_2B_4H_7^-$ ion and a trace of the BH_4^- ion, the solution assuming a yellowish tinge. After 17 days' heating at 80 °C, 70% of the 1,6-$C_2B_4H_6$ had been converted and after 27 days 93% of the 1,6-$C_2B_4H_6$ had been converted into the 2,4-$C_2B_4H_7^-$ ion, along with a trace of the BH_4^- ion and a trace of compound(s) giving rise to a broad hump, 20—40 p.p.m., in the ^{11}B n.m.r. spectrum. The solution was at this time golden yellow.

(b) *From* 5-Me_3N^+-[2,4-$C_2B_4H_6^-$] *and* NaH. 5-Me_3N^+-[2,4-$C_2B_4H_6^-$] (*ca.* 2 mmol) was prepared [7] and used *in situ*. Sodium hydride (3 mmol) was added, under dry nitrogen, to

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[9] R. W. Jotham and D. J. Reynolds, *J. Chem. Soc.* (*A*), 1971, 3181.

[10] G. R. Eaton and W. N. Lipscomb, ' N.m.r. Studies of Boron Hydrides and Related Compounds,' Benjamin, New York, 1969.

the reaction flask, a Pyrex tube fitted with an n.m.r. tube side-arm and a Teflon stop-cock. 1,2-Dimethoxyethane (10 ml) was then added *via* the vacuum line and the mixture stirred for 8 days. At the end of this period the volatile materials were removed and examined. No non-condensable gas was found, but trimethylamine (*ca.* 1·2 mmol) was identified by its i.r. spectrum.[8] The ^{11}B n.m.r. spectrum showed the sample to consist of a 1 : 1 mixture of the 2,4-$C_2B_4H_7^-$ ion and unchanged 5-Me_3N^+-[2,4-$C_2B_4H_6^-$] with a trace of an unknown compound giving a very broad resonance between 0·4 and 50 p.p.m. 12 Days after the sample had been sealed off, the ^{11}B n.m.r. spectrum was re-run and only signals due to the 2,4-$C_2B_4H_7^-$ ion and the trace of unknown compound were observed.

(c) *From* 3-Me_3N^+-[2,4-$C_2B_4H_6^-$] *and* NaH. A 100 ml round-bottomed flask fitted with a greased stop-cock and an n.m.r. tube side-arm was charged with sodium hydride (2·94 mmol), and 3-Me_3N^+-[2,4-$C_2B_4H_6^-$] (*ca.* 2 mmol), and 1,2-dimethoxyethane (5 ml). The mixture was stirred for 10 days, then the volatile material was removed and shown by i.r. and n.m.r. spectroscopy to consist of trimethylamine [8] and 1,2-dimethoxyethane.[6] A little non-condensable (−196 °C) gas was also detected. The solid remaining in the reaction flask was dissolved in 1,2-dimethoxyethane and the resulting solution decanted into the n.m.r. tube side-arm, which was sealed off. The ^{11}B and ^1H n.m.r. spectra of this solution showed that the 2,4-$C_2B_4H_7^-$ ion, some borate (presumably from ether cleavage), and other unidentified impurities were produced.

Attempted Conversion of 2,3-$C_2B_4H_7^-$ *into* 2,4-$C_2B_4H_7^-$.—Because it has been shown that carboranes with carbon atoms separated by one or more boron atoms are more stable than isomers with carbon atoms bonded together, we have attempted thermally to rearrange the 2,3-$C_2B_4H_7^-$ to the 2,4-isomer. The 2,3-$C_2B_4H_7^-$ in glyme [11] was prepared by allowing 2,3-$C_2B_4H_8$ to react with an excess of LiH. The resulting ion showed the characteristic ^{11}B n.m.r. pattern of the 2,3-$C_2B_4H_7^-$ ion. After the sample had been heated for a day at 160 °C a yellow colour developed and the n.m.r. spectrum indicated that an appreciable amount of borohydride ion, BH_4^-, had formed. There was no evidence for the 2,4-$C_2B_4H_7^-$ ion. Apparently, the 2,3-ion decomposes before rearrangement is possible.

DISCUSSION

A polar solid is slowly formed between trimethylamine and *closo*-1,6-$C_2B_4H_6$. As suggested,[7] the ^{11}B and ^1H n.m.r. spectra of this compound are consistent with that of a dipolar *nido*-carborane, 5-Me_3N^+-2,4-$C_2B_4H_6^-$, rather than an ammonium salt of the 1,6-$C_2B_4H_6$ conjugate base. This dipolar compound is a derivative of the previously unknown parent *nido*-2,4-$C_2B_4H_7^-$, into which it can be converted by the action of NaH in monoglyme. Alternatively, the parent *nido*-ion can be formed directly from *closo*-1,6-$C_2B_4H_6$ and the metal hydride, or from the action of hydride on 3-Me_3N^+-2,4-$C_2B_4H_6^-$ (Figure 2). The formation of the substituted *nido*-carborane 5-Me_3N^+-2,4-$C_2B_4H_6^-$ from the reaction of trimethylamine with the *closo*-1,6-$C_2B_4H_6$ is consistent with bonding systems [12–14] developed for the carboranes. The pair of electrons from the nitrogen of the amine, upon terminally bonding to one of the four equivalent borons of the closed polyhedral carborane, serves to shift the boron-attached terminal hydrogen with its electron-pair into a bridge position.[7] The net effect is to add a pair of electrons to the *closo*-cage which moves the six skeletal atoms to six of the seven vertices of the next higher polyhedron.[12] Mechanistically, the 5-substituted isomer of the 2,4-$C_2B_4H_7^-$ ion is rationalized more satisfactorily in this reaction than other structurally related compounds (*i.e.*, 3-Me_3N^+-2,4-, 4-, or 5-Me_3N^+-2,3-$C_2B_4H_6^-$).[7] But it is clear from the present study that the 3-Me_3N^+-2,4-$C_2B_4H_6^-$ is thermodynamically more stable than the 5-isomer, for the latter can be quantitatively rearranged to the former compound by standing in $CHCl_3$ at room temperature for 2—4 weeks. There are many mechanistic possibilities for this rearrangement, all of them too elaborate to warrant discussion before additional experimental work is conducted.

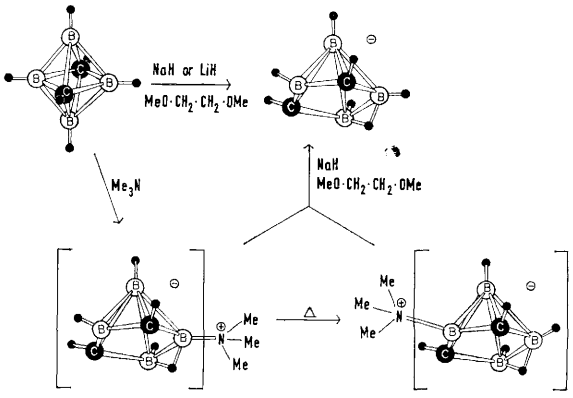

FIGURE 2 Reaction diagram

It is rather likely that 3-Me_3N^+-2,4-$C_2B_4H_6^-$ is the most stable of the substituted *nido*-carborane series which includes the two (as yet unknown) B-Me_3N^+ isomers of 2,3-$C_2B_4H_7^-$. This is based on the principle that carboranes with non-adjacent carbon atoms are more stable than their counterparts with neighbouring carbon atoms.[13,15] Accordingly, it was thought that the parent 2,3-$C_2B_4H_7^-$ ion [11] might rearrange thermally to the presumably more stable 2,4-isomer. However, unlike the *closo*-carboranes, which survive reasonably high temperatures (400—700 °C) and will undergo skeletal rearrangements in this temperature range, the *nido*-2,3-$C_2B_4H_7^-$ ion decomposed extensively around 160 °C with no indication of the formation of the 2,4-isomer.

Abstraction of a bridge hydrogen atom from the

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[11] T. Onak and G. B. Dunks, *Inorg. Chem.*, 1966, **5**, 439.

[12] R. E. Williams, *Inorg. Chem.*, 1971, **10**, 210.

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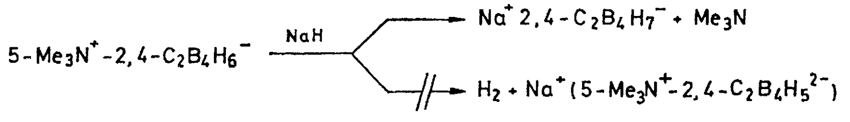
[14] K. Wade, *Chem. Comm.*, 1971, 792.

[15] R. E. Williams, 'Progress in Boron Chemistry,' vol. 2, chap. 2, Pergamon, Oxford, 1969.

nido-series $C_nB_{6-n}H_{10-n}$ ($n = 1$—3) is readily accomplished with an alkali-metal hydride or with butyllithium.[11,16–18] In contrast, the structurally related $5\text{-}Me_3N^+\text{-}2,4\text{-}C_2B_4H_6^-$ undergoes amine displacement rather than loss of a bridge hydrogen with NaH, as shown in the Scheme. Apparently, the unit negative charge associated with the *nido*-cage of this reactant sufficiently diminishes the acidity of the bridge hydrogen to make the production of H_2 unlikely. Also, the expected product from proton abstraction concentrates two unit charges on the cage, a situation obviously less favourable than the amine displacement pathway in which the cage in the carborane product contains no more negative charge than the starting compound.



SCHEME

Nuclear Magnetic Resonance.—The high-field $B\text{–}H_t$ resonances in both the ^{11}B and ^1H n.m.r. spectra of the compounds listed in the Table are unique to apically situated nuclei within a pyramidal framework of atoms.[10] The remaining boron and terminal hydrogen chemical shifts for each molecule are not unusual for basally located nuclei of the pyramid.[10] Each of the suggested pentagonal pyramidal structures (Figures 1 and 2) contains a bridge hydrogen and this is easily observed as a broad singlet in the proton n.m.r. at exceptionally high field, *ca.* τ 12—15.

Comparisons of chemical shifts within the present series of compounds are in agreement with structural changes and substituent effects. It is well known that cage carbons in *nido*-carboranes can shift neighbouring boron and hydrogen resonances to lower field,[19–23] and, of course, the field effect of the Me_3N^+ group should operate in the same direction. In accord with the data in the Table, the B(3) in $2,4\text{-}C_2B_4H_7^-$ and B(3) in $5\text{-}Me_3N^+\text{-}2,4\text{-}C_2B_4H_6^-$ (both of which are surrounded by two cage carbon atoms) are found at relatively low field, $\delta = -20$ to -21; and the B(3) of $3\text{-}Me_3N^+\text{-}2,4\text{-}C_2B_4H_6^-$, where both effects are operating, is found at lowest field, $\delta = -27$. Also, B(5) of $5\text{-}Me_3N^+\text{-}2,4\text{-}C_2B_4H_6^-$ is at lower field, $\delta = -13{\cdot}5$, than the same boron, $\delta = -1{\cdot}3$, in the parent $2,4\text{-}C_2B_4H_7^-$. Downfield shifts are also observed for the terminal hydrogens attached to borons with neighbouring cage carbons, and/or with a neighbouring $Me_3N^+\text{–}B$ group (by comparison with other boron-attached hydrogens). Also, the Me_3N^+–neighbouring bridge hydrogen of the 5-substituted 2,4-isomer is almost 2·0 p.p.m. to lower field than the parent compound. The presence of this positively charged nitrogen even affects the bridge hydrogen when located on the opposite side of the basal plane; thus the bridge hydrogen of the 3-substituted 2,4-isomer is 0·2 p.p.m. to lower field than that of the parent compound. Additionally, the apical terminal hydrogens of the nitrogen compounds are shifted to lower field than the apical hydrogen in the parent $2,4\text{-}C_2B_4H_7^-$ ion.

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