Reaction of (σ-2,4-$C_2B_4H_6$)-(π-2,4-$C_2B_4H_5$)Fe^{III}(π-C_5H_5) with Na/Hg and HCl. Under a nitrogen atmosphere a tenfold excess of sodium amalgam was added *via* a pressure-equalized addition funnel to 12 mg (0.04 mmol) of compound V in 10 ml of THF. Upon agitation the lime green solution turned light orange. After 30 min the THF layer was separated and reduced in volume to give a dull orange residue. Excess anhydrous gaseous HCl was then expanded into the reaction flask and the reaction was allowed to proceed for 30 min. After removal of HCl, the resulting crude product was extracted with pentane and solvent was removed at reduced pressure. The compounds IX and VI reported above were obtained from this residue by thin-layer chromatography. Compound VI eluted before compound IX in hexane. The relative yields of VI and IX were estimated as 4:1.

Reaction of 2,3-$C_2B_4H_8$ with $Fe(CO)_5$. Typically, 3.24 mmol of $Fe(CO)_5$ was distilled into an evacuated cylindrical Pyrex reactor which was 24 mm in diameter and connected to the vacuum line by a greaseless Teflon stopcock containing a Viton O-ring. While a liquid nitrogen trap was maintained on the reactor, 3.10 mmol of $C_2B_4H_8$ was added by distillation and the stopcock was closed. The reactor was warmed to room temperature, a heating tape controlled by a Variac was wrapped around the central portion of the reactor, and the reactor was clamped in a vertical position such that the bottom section containing a pool of liquid $Fe(CO)_5$ was immersed in a dewar flask of water at 25°. The heating tape was maintained at 215–245° for 24 hr during which substantial dark nonvolatile deposits, including metallic iron, were deposited on the reactor walls. Following the reaction the reactor was cooled to $-196°$; noncondensables ($\sim$3 mmol) were pumped off and the remaining volatiles were distilled through a $-45°$ trap which allowed $Fe(CO)_5$, $C_2B_5H_7$, and unreacted $C_2B_4H_8$ to pass through. The $-45°$ condensate consisted of two components which were separated by repeated fractionation through a $-23°$ trap. The condensate at $-23°$ consisted of (π-2,3-$C_2B_4H_6$)$Fe(CO)_3$ (X), a yellow-orange liquid, and the more volatile fraction was (π-2,3-$C_2B_3H_7$)$Fe(CO)_3$ (XI), a pale yellow liquid. Owing to the difficulties of separation by trap-to-trap fractionation, yields of the pure compounds have not been determined but are estimated to be 5–10% each.

Conversion of (π-2,3-$C_2B_4H_6$)$Fe(CO)_3$ to (π-2,3-$C_2B_3H_7$)$Fe(CO)_3$ in the Mass Spectrometer. In repeated experiments, nearly pure samples of X vapor (containing <2% XI) were introduced into the gas inlet section of the mass spectrometer, maintained at 250°. The first spectra produced immediately upon introduction of the sample contained a strong parent envelope of X (cutoff at *m/e* 214) with peaks of very weak intensity coresponding to XI (cutoff at *m/e* 204). Spectra taken over the next 10 min on the same gas sample showed a rapid buildup of XI and decline of X, with the last spectra indicting virtually pure XI.

Reaction of 2,4-$C_2B_5H_7$ with $Fe(CO)_5$. A hot–cold reactor of the type described above was charged with 3.2 mmol of $C_2B_5H_7$ and 5.2 mmol of $Fe(CO)_5$, and the central portion heated to 280° for 15 hr during which time the lower end was maintained at 25°. Following removal of noncondensables and unreacted starting materials, the two principal products, which were retained in a $-35°$ trap, were separated by repeated fractionation through a trap at $-23°$ to give 20 mg (0.10 mmol) of orange (π-2,4-$C_2B_4H_6$)-$Fe(CO)_3$ (XII) and 14 mg (0.063 mmol) of orange (π-(4)-1,8-$C_2B_4H_7$)$Fe(CO)_3$ (XIII). A total of 1.0 mmol of $C_2B_5H_7$ was recovered.

Acknowledgment. This work was supported by the Office of Naval Research.

Nuclear Magnetic Resonance Studies of the Stereochemically Nonrigid Molecules B_6H_{10}, 2-$CH_3B_6H_9$, and 2-BrB_6H_9. Tautomerism of Bridging Hydrogens and the Influence of Substituents on the Position of the Basal Boron–Boron Bond in the Static Structures Observed at Low Temperature

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Contribution from the Evans Laboratory of Chemistry, The Ohio State University, Columbus, Ohio 43210. Received November 10, 1972

Abstract: Variable-temperature pmr and boron-11 nmr spectra of hexaborane(10), 2-methylhexaborane(10), and 2-bromohexaborane(10) are presented. At sufficiently low temperatures, spectra are observed which establish the presence of structures in which bridge protons are static; furthermore, the hexaborane(10) spectra thus obtained are fully consistent with its known solid-state structure as determined by X-ray diffraction (C_s symmetry) and demonstrate that the chemical shift equivalence of the basal atoms at higher temperatures (consistent with C_{5v} symmetry) is the result of time averaging due to a rapid intramolecular migration of bridging hydrogens about the base of the pyramidal molecule. The structures of 2-$CH_3B_6H_9$ and 2-BrB_6H_9 have been deduced from their nmr spectra which are related to the spectra of B_6H_{10}. The tautomerism of bridging hydrogens is rapid on the nmr time scale at ambient temperature for each derivative and involves all bridging sites; however, at intermediate temperatures, not all sites are involved. At low temperature a static structure with no mirror plane of symmetry is inferred for each derivative. The position of the basal boron–boron bond in the static structure is apparently influenced by the inductive effect of the substituent.

The pmr[1] and boron-11 nmr[2] spectra of B_6H_{10} are consistent with a pentagonal pyramidal structure of C_{5v} symmetry in solution while the solid-state structure I, determined by X-ray diffraction,[3] exhibits only C_s symmetry. Resolving this apparent discrep-

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(1) J. Leach, T. Onak, J. Spielman, R. R. Rietz, R. Schaeffer, and L. G. Sneddon, *Inorg. Chem.*, **9**, 2170 (1970).

(2) R. E. Williams, S. G. Gibbons, and I. Shapiro, *J. Chem. Phys.*, **30**, 333 (1959).

(3) K. Eriks, W. N. Lipscomb, and R. Schaeffer, *J. Chem. Phys.*, **22**, 754 (1954); F. L. Hirshfeld, K. Eriks, R. E. Dickerson, E. L. Lippert, and W. N. Lipscomb, *ibid.*, **23**, 56 (1958); M. G. Rossman, R. A. Jacobson, F. L. Hirshfeld, and W. N. Lipscomb, *Acta Crystallogr.*, **12**, 530 (1959).

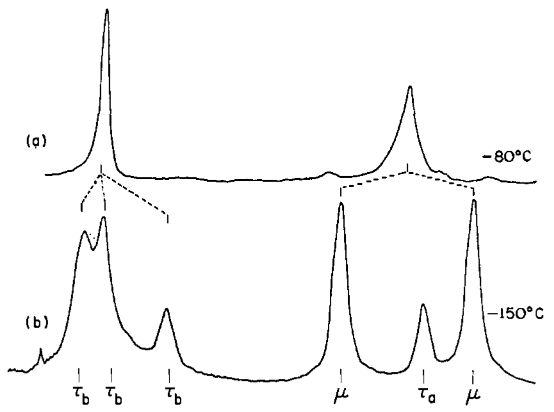
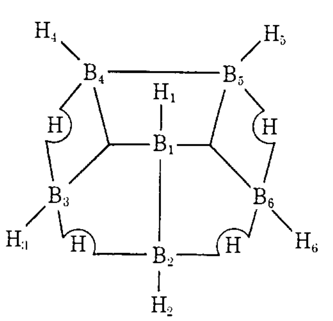


Figure 1. The 100-MHz pmr spectra of B_6H_{10} in $CHClF_2$: τ_b = basal terminal hydrogen, τ_a = apical terminal hydrogen, μ = bridge hydrogen; (a) basal boron atoms spin decoupled, (b) all boron atoms spin decoupled.



I

ancy has been a problem of long standing. One rationale assumes coincidental overlap of basal resonances,[4] while in another,[5] a rapid tautomerism[6–8] is proposed involving only bridging protons and basal borons, thereby time averaging the magnetic environment of the basal atoms. We demonstrate herein by means of low-temperature pmr and boron-11 nmr studies that the latter rationale is in fact correct. In addition, we present variable-temperature nmr spectra of the hexaborane(10) derivatives 2-$CH_3B_6H_9$ and 2-BrB_6H_9 which show that the tautomerism of bridge hydrogens is rapid on the nmr time scale at ambient temperature, that the slowing of the rate of tautomerism occurs in two discrete steps, and that, at low temperature, spectra are observed which correspond to static structures which do not have a mirror plane of symmetry. Furthermore, the position of the basal boron–boron bond is apparently influenced by the inductive effect of the substituent, being adjacent to to the electron-withdrawing bromine and away from the electron releasing methyl group.

Results and Discussion

Pmr Spectra of B_6H_{10}. In the solid-state structure of B_6H_{10} (I) there are three types of terminal basal hydrogens and two types of bridging protons in the ratio of 2:2:1 (terminal) and 2:2 (bridge). In contrast, the pmr spectrum with basal borons spin decoupled (Figure 1a) shows only one resonance for the five basal terminal hydrogens (τ 5.82) and one resonance for the four bridging protons (τ 11.10) in the temperature range ambient[1] to approximately −80°. However, as spectra are recorded at progressively lower temperatures (below −80°) the bridge proton resonance broadens and at −95° resolves into two distinct peaks of equal area.[9] On further cooling, the bridge proton peaks sharpen and the basal terminal hydrogen peak first broadens and then splits into three peaks below −130°.[10] The pmr spectrum at −150° of B_6H_{10} (Figure 1b) with all boron-11 nuclei spin decoupled is thus fully consistent with the solid-state structure determined by X-ray diffraction. Furthermore, the appropriate weighted averages of the chemical shifts of the nonequivalent basal terminal hydrogens and the nonequivalent bridge protons observed below −130° are equal within experimental error to the values recorded above −80° for the equivalent basal terminal hydrogens and bridge protons, respectively. It is clear that the apparent C_{5v} symmetry exhibited in the pmr spectra of B_6H_{10} (and boron-11 nmr spectra discussed below) is the result of a rapid migration of bridging protons about the base of the pyramidal boron framework and that this tautomerism is slow on the nmr time scale at −150°; *i.e.*, the spectrum of the static structure of B_6H_{10} is observed. While the spectral data presented herein do not differentiate between intermolecular and intramolecular exchange, we believe that intermolecular exchange is unimportant[11,12] since bridge proton exchange in the systems $B_6H_9^-$–B_6H_{10}[13] and $B_6H_{11}^+$–B_6H_{10}[14] is slow on the nmr time scale below 0°.

By spin decoupling at specific boron-11 resonance frequencies singly and in all possible combinations while observing the pmr spectra of B_6H_{10} at low temperature, we find that the highest field basal terminal hydrogen (τ 6.85) and the lower field set of bridge protons (τ 9.86) are apparently spin coupled to the highest field basal boron atom (δ 6.5 ppm) which is the boron opposite the B–B bond (see I above). The higher field bridge resonance is therefore due to the bridge protons adjacent to the B–B bond. The resonances at τ 5.76 and 5.42 are due to hydrogens terminally bonded to the borons which resonate at −18 ppm in the boron-11

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(4) R. Schaeffer, "Progress in Boron Chemistry," Vol. 1, H. Steinberg and A. L. McCloskey, Ed., Macmillan, New York, N. Y., 1964.

(5) R. E. Williams, *J. Inorg. Nucl. Chem.*, 20, 198 (1961); W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

(6) Common chemical use of the term tautomerism is restricted to a dynamic equilibrium existing among *isomers* differing only in the placement of hydrogen atoms. When *equivalent* structures are involved, the behavior is said to be fluxional.[7] The process which simplifies the nmr spectra of hexaborane(10) and its 2-substituted derivatives would thus be tautomerism only for the latter not the former. All these species may be described as being stereochemically nonrigid,[8] but the phrase is not sufficiently specific. Extension of the term tautomerism to include the rapid interconversion of equivalent structures is logical from a chemical point of view, is consistent with the etymology of the word (Gk. *tauto-*, the same), and is convenient in discussing the compounds in the present investigation. We therefore use the term tautomerism to imply the migration of bridge hydrogens in hexaborane(10) as well as in the 2-substituted derivatives. Furthermore, we believe this term should be applied to all cases of stereochemical nonrigidity arising from the migration of hydrogen atoms.

(7) F. A. Cotton, *Accounts Chem. Res.*, 1, 257 (1968).

(8) E. L. Muetterties, *ibid.*, 3, 266 (1970).

(9) The splitting of the bridge resonance of B_6H_{10} was first observed by J. C. Carter and N. L. H. Mock, private communication.

(10) V. T. Brice, H. D. Johnson, II, and S. G. Shore, *J. Chem. Soc., Chem. Commun.*, 1128 (1972).

(11) Carter and Mock have reached the same conclusion[12] on the basis of unpublished results.

(12) J. C. Carter and N. L. H. Mock, *J. Amer. Chem. Soc.*, 91, 5891 (1969).

(13) H. D. Johnson, II, R. A. Geanangel, and S. G. Shore, *Inorg. Chem.*, 9, 908 (1970).

(14) H. D. Johnson, II, V. T. Brice, G. L. Brubaker, and S. G. Shore, *J. Amer. Chem. Soc.*, 94, 6711 (1972).

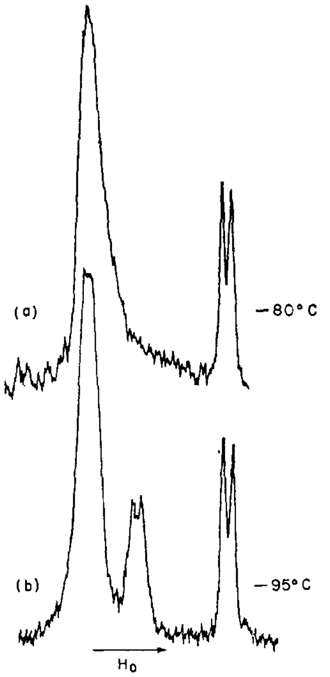

Figure 2. The 32.1-MHz boron-11 nmr spectra of B_6H_{10} in CH-ClF$_2$, no spin decoupling.

Table I. Nmr Data for B_6H_{10}

100-MHz $^1H^a$			32.1-MHz $^{11}B^c$	
Ambient temp	−150°	Assignments^b	Ambient temp	−95°
11.10	12.14	$\mu_{3,4}$; $\mu_{5,6}$		
	(11.00)^d	all μ		
	9.86	$\mu_{2,3}$; $\mu_{2,6}$		
5.82	6.85	2	−14.1	6.5
	(5.84)	2, 3, 4, 5, 6		(−13.8)
	5.76	4,5 or 3,6		−18.6
	5.42	3,6 or 4,5		
11.22	11.27	1	51.8	51.8

^{a} Chemical shifts expressed in ppm relative to tetramethylsilane equals 10.00. ^{b} The number, n, denotes B_n or the terminal hydrogen attached to B_n. The symbol $\mu_{y,x}$ denotes a proton bridging B_x and B_y. ^{c} Chemical shifts expressed in ppm relative to $BF_3 \cdot O(C_2H_5)_2$ = 0.0. ^{d} Values in parentheses are appropriately weighted averages.

nmr spectrum (see Table I). We cannot unambiguously assign the resonances at τ 5.76 and 5.42 which are due to hydrogens 4,5 and 3,6.

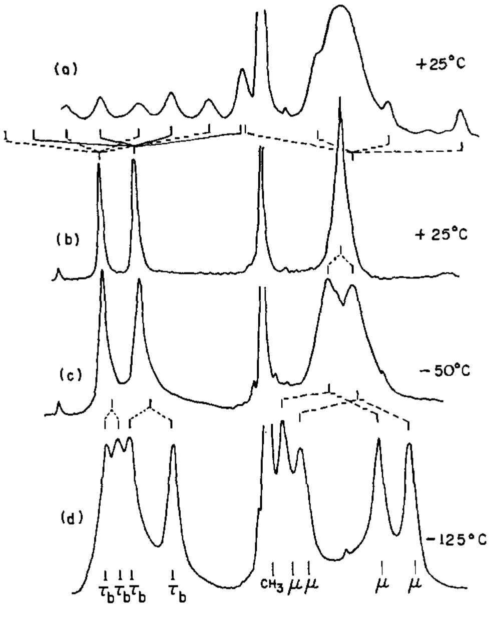

Figure 3. The 100-MHz pmr spectra of 2-$CH_3B_6H_9$ in CD_2Cl_2–$CHCl_3$: τ_b = basal terminal hydrogen, μ = bridge hydrogen; (a) no spin decoupling; (b), (c), and (d) all basal boron atoms spin decoupled, apical hydrogen not visible under these conditions.

Boron-11 Nmr Spectra of B_6H_{10}. The boron-11 nmr spectrum of B_6H_{10} at room temperature exhibits two doublets with the area ratio 5:1.[2] The larger doublet at low field is due to the five equivalent basal boron atoms and the smaller doublet at higher field is due to the apical boron atom. At −80° (Figure 2a) the basal resonance is collapsed to a single peak with no resolvable spin coupling[15,16] and it has shifted to lower field by about 2 ppm. At −95° (Figure 2b) this peak has shifted further downfield and a doublet has appeared upfield of it.[17] The doublet nature of this basal peak was confirmed by proton spin decoupling. The relative areas of the three resonances at −95° are 4:1:1 reading from low to high field. At lower temperatures (to approximately −125°), the resonances, especially the basal resonances, are severely broadened, but no further change in chemical shifts is evident.

A consideration of the static structure of B_6H_{10} leads one to expect three basal boron resonances with relative areas of 2:2:1 as is observed in the pmr spectrum for the corresponding basal terminal hydrogens. In order to rationalize the appearance of only one peak for these two sets of nonequivalent boron atoms, it is only necessary to propose that the reciprocal of the frequency difference in these boron chemical shifts is small relative to the bridge proton exchange rate at −100°, thus producing a single time-averaged peak. In a recent publication concerning LCAO–SCF calculations on B_6H_{10},[18] it was suggested that the three types of basal boron atoms should have similar chemical shifts. The observed difference in chemical shifts, 25.1 ppm, is clearly not in accord with this suggestion.

Pmr Spectra of 2-$CH_3B_6H_9$. The pmr spectrum of 2-$CH_3B_6H_9$ at room temperature with no boron-11 spin decoupling (Figure 3a) exhibits two quartets at low field due to basal terminal hydrogens (τ_b), a quartet at higher field due to the apical hydrogen (τ_a), a broad proton resonance at higher field (μ), and a sharp methyl peak. The identification of these resonances is made in a straightforward manner by comparison with the spectrum of B_6H_{10} at room temperature. Methyl substitution in the base of B_6H_{10} has shifted the bridge resonance to lower field and split the τ_b resonance into two resonances of equal area, one of which is

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(15) Collapse of the basal resonance was first reported by Odom and Schaeffer[16] who observed the spectrum from ambient temperature to −70°.

(16) J. D. Odom and R. Schaeffer, *Inorg. Chem.*, **9**, 2157 (1970).

(17) The splitting of the basal resonance into two peaks exhibiting no spin coupling has been observed by Carter and Mock, private communication.

(18) I. R. Epstein, J. A. Tossell, E. Switkes, R. M. Stevens, and W. N. Lipscomb, *Inorg. Chem.*, **10**, 171 (1971).

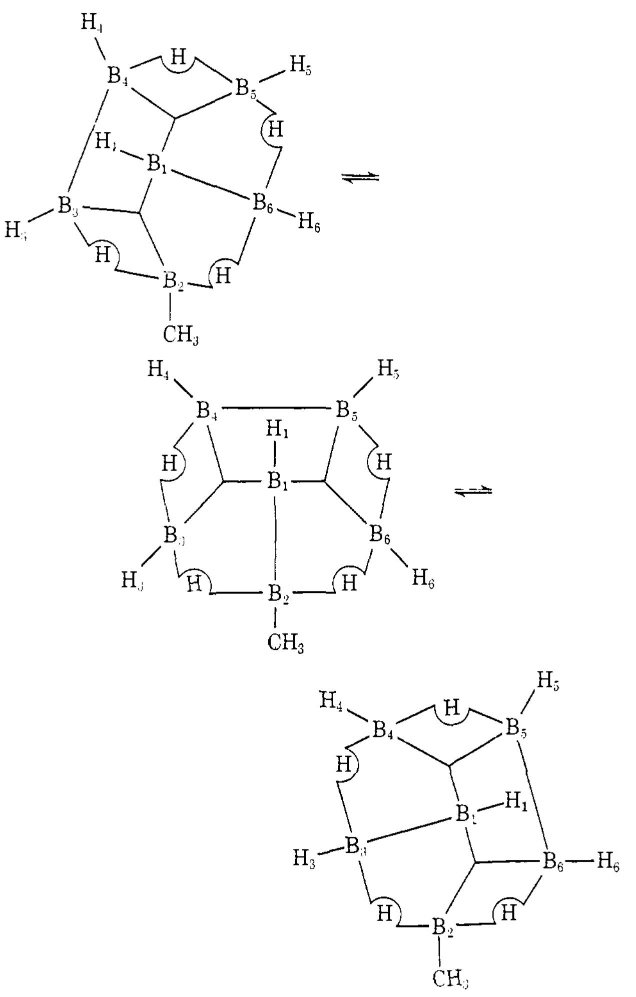
shifted substantially upfield while the other is at slightly lower field. Furthermore, narrow line boron-11 spin-decoupling frequencies show that the τ_b hydrogens at higher field are bonded to the higher field basal boron atoms. From the boron-11 nmr spectrum of 2,3-$(CH_3)_2B_6H_8$[19] it is apparent that the methyl substituent causes adjacent basal boron atoms to resonate at higher field This allows assignment of the higher field τ_b resonance in the pmr spectrum of 2-$CH_3B_6H_9$ to H_3 and H_6 and the lower field τ_b resonance to H_4 and H_5. In Figure 3b, all basal boron atoms are spin decoupled (the apical quartet is not visible at this substantially lower rf power level) and one bridge resonance is observed from room temperature to about −20° indicating the rapid exchange of all bridge protons in this temperature range; a static structure would require at least two types of bridge protons.

On cooling below −20°, the bridge resonance broadens then splits into two peaks of equal area which have a weighted average chemical shift equal to that of the single peak observed at higher temperature (see Table II). In this intermediate temperature region, −25 to −50°, the pmr spectrum (see Figure 3c) is consistent with a molecule of C_s symmetry. While a symmetrical static structure is of C_s symmetry, it is not consistent with the low-temperature spectra discussed below which require an unsymmetrical static structure below −80°. We believe that the two bridging protons adjacent to the methyl boron, $\mu_{2,6}$ and $\mu_{2,3}$, are fixed while the other two bridging protons are exchanging rapidly on the nmr time scale among the remaining three bridging sites.

Table II. Nmr Data for 2-$CH_3B_6H_9$

100-MHz ^1H[a]			Assignments[b]	32.1-MHz ^{11}B[c]	
−5°	−50°	−115°		Room temp	−80°
		12.20	$\mu_{4,5}$		
	11.09	(11.04)[d]	$\mu_{4,5}$; $\mu_{5,6}$		
		9.87	$\mu_{5,6}$		
10.83	(10.83)	(10.78)	all-μ		
		11.54	$\mu_{2,3}$		
	10.57	(10.52)	$\mu_{2,3}$; $\mu_{2,6}$		
		9.51	$\mu_{2,6}$		
		7.10	6		5.8
6.44	6.52	(6.64)	3, 6	−6.5	(−6.0)
		6.19	3		−18
		5.95	4 or 5		
5.69	5.72	(5.81)	4, 5	−17.6	−18
		5.67	5 or 4		
11.04	11.13	11.23	1	49.4	49.4
9.16	9.17	9.19	CH_3, 2	−29.4	−29.8

[a] Chemical shifts expressed in ppm relative to tetramethylsilane equals 10.00. [b] The number, n, denotes B_n or the terminal hydrogen attached to B_n; the symbol $\mu_{x,y}$ denotes a proton bridging B_x and B_y. [c] Chemical shifts expressed in ppm relative to $BF_3 \cdot O(C_2H_5)_2$ = 0.0. [d] Values in parentheses are appropriately weighted averages.



This structural model has C_s symmetry and is consistent with the static structure deduced from the low-temperature spectra in which the B–B bond is not adjacent to the methyl group.

At progressively lower temperatures, each of the two bridge resonances splits into two resonances (*ca.* −80°) and each basal terminal resonance also splits into two peaks (*ca.* −100°). In each case the weighted average chemical shift of each set of resonances observed at low temperature agrees within experimental error with the chemical shift of the corresponding single resonance observed at higher temperature (see Table II). Four bridge resonances and four terminal basal resonances are evident in Figure 3d, and a structure with a mirror plane is clearly excluded. In the two possible structures, the basal B–B bond is between B_3 and B_4, II, or between B_2 and B_3, III.

A consideration of the pmr spectra from which we have inferred static structures for B_6H_{10} (Figure 1b) and 2-$CH_3B_6H_9$ (Figure 3d) reveals clear similarities which show that the effect of the B–B bond on the chemical shifts of the basal hydrogen atoms is greater than the effect of the methyl group. Thus, the resonance at τ 6.85 in the spectrum of B_6H_{10} which is due to the unique τ_b hydrogen (H_2) opposite the B–B bond occurs at much higher field than the remaining τ_b hydrogens. Therefore, since the resonance at τ 7.10 in the spectrum of 2-$CH_3B_6H_9$ occurs at much higher field than the remaining τ_b hydrogen it must be due to the hydrogen opposite the B–B bond. Recalling

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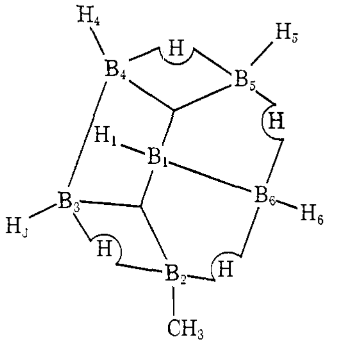
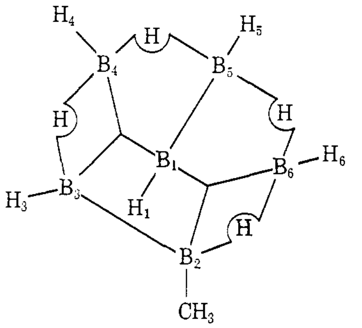
[19] D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, 92, 4571 (1970).



II



III

that the resonance at τ 7.10 and that at 6.19 are time averaged at higher temperatures and that this time-averaged peak was assigned to the τ_b hydrogens adjacent to the substituent, we now conclude that the B–B bond is one position removed from the methyl-substituted boron as in structure II above. Returning now to the comparison of the low-temperature spectra of B_6H_{10} and $2\text{-}CH_3B_6H_9$, we conclude, in like manner, that the two bridge resonances at higher field in the $2\text{-}CH_3B_6H_9$ spectrum are adjacent to the B–B bond as is the case for B_6H_{10}. This conclusion is supported by selective decoupling of boron-11 nuclei. In spectra recorded while spin decoupling B_3, B_4, and B_5 (δ -18 ppm) the higher field bridge resonances (τ 12.20 and 11.54) are much sharper than when only B_6 (δ $+5.8$ ppm) is decoupled. Assuming that the bridges adjacent to the methyl-substituted boron are shifted downfield relative to the parent compound as is the case for B_5H_9 and its derivatives,[20] the bridge resonances may be confidently assigned as shown in Table II.

The discussion presented above is consistent with the conclusions derived from the variable-temperature nmr spectra of $2\text{-}CH_3B_5H_7^-$ [21a] and $1\text{-}CH_3B_4H_8^-$.[21b]

Boron-11 Nmr of $2\text{-}CH_3B_6H_9$. The boron-11 nmr spectrum of $2\text{-}CH_3B_6H_9$ at room temperature (Figure 4a) displays a high field doublet (area 1) due to the apical boron (B_1), two basal doublets (areas 2 each), and at lowest field a singlet (area 1) due to the methyl substituted boron (B_2). From the boron-11 nmr spectrum of $2,3\text{-}(CH_3)_2B_6H_8$[19] it is evident that in this molecule the two basal boron atoms (B_4 and B_6) adjacent to the two methyl-substituted boron atoms (B_2 and B_3) resonate at higher field than the basal boron atom (B_5) which is not adjacent. Therefore, in the spectrum of $2\text{-}CH_3B_6H_9$, the higher field basal doublet is assigned to B_3 and B_6 adjacent to the methyl-substituted boron, B_2, and the lower field doublet is assigned to B_4 and B_5.

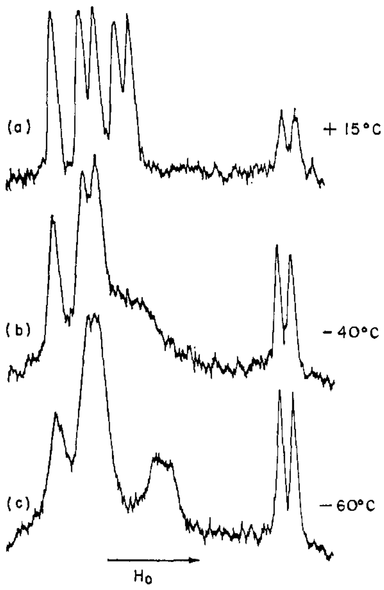


Figure 4. The 32.1-MHz boron-11 nmr spectra of $2\text{-}CH_3B_6H_9$ in $CD_2Cl_2\text{-}CHCl_3$, no spin decoupling.

On cooling the sample to $-40°$, the higher field basal doublet broadens, but the spectrum is otherwise unchanged at this intermediate temperature. At $-60°$ the higher field basal doublet has split into two peaks, one (δ $+5.8$) has shifted upfield and the other (δ -18) shifted downfield by approximately the same amount and it then overlaps the lower field doublet which has not shifted appreciably. The relative areas at this temperature (Figure 4c) are 1:3:1:1 from low to high field. By comparison to the boron-11 nmr spectrum of B_6H_{10} at low temperature (Figure 2b) and following the discussion presented in the previous section, the highest field basal resonance (δ $+5.8$) is assigned to B_6, the boron opposite the B–B bond. The peak of intensity 3 at -18 ppm is thus due to B_3, B_4, and B_5.

Pmr Spectra of $2\text{-}BrB_6H_9$. The pmr spectrum of $2\text{-}BrB_6H_9$ at ambient temperature consists of two quartets at low field due to the basal hydrogens, a quartet at higher field due to the apical hydrogen, and a broad bridge proton resonance at high field. Figure 5a shows the spectrum with basal borons decoupled. The single resonance observed for the bridge protons at ambient temperature indicates a rapid tautomerism involving all bridge sites. Spin decoupling at known boron-11 nmr frequencies one at a time demonstrates that at ambient temperature and the intermediate temperature range, the higher field basal terminal hydrogens are coupled to (and therefore bonded to) the higher field basal borons. At $-60°$ with basal borons decoupled (Figure 5b), the higher field basal terminal resonance, τ 6.07, is broadened and the bridge resonance is split into two peaks of equal intensity which have an average chemical shift equal to that of the single bridge resonance observed at higher temperature (see Table III). Although at intermediate temperatures the spectrum of $2\text{-}BrB_6H_9$ is similar to that of $2\text{-}CH_3B_6H_9$, we believe for two reasons that a

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[20] P. M. Tucker, T. Onak, and J. B. Leach, *Inorg. Chem.*, 9, 1430 (1970).

[21] (a) V. T. Brice and S. G. Shore, *ibid.*, 12 309 (1973); (b) I. Jaworiwsky and S. G. Shore, unpublished results.

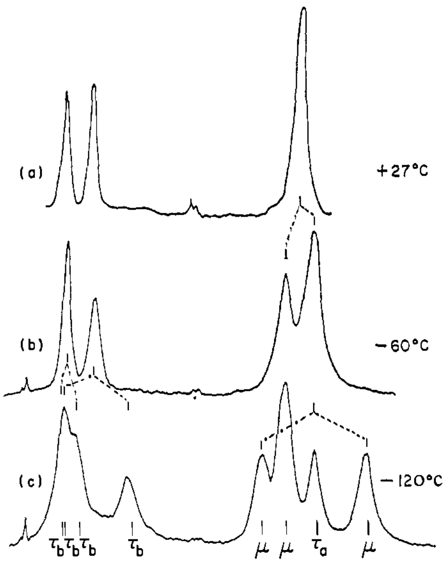


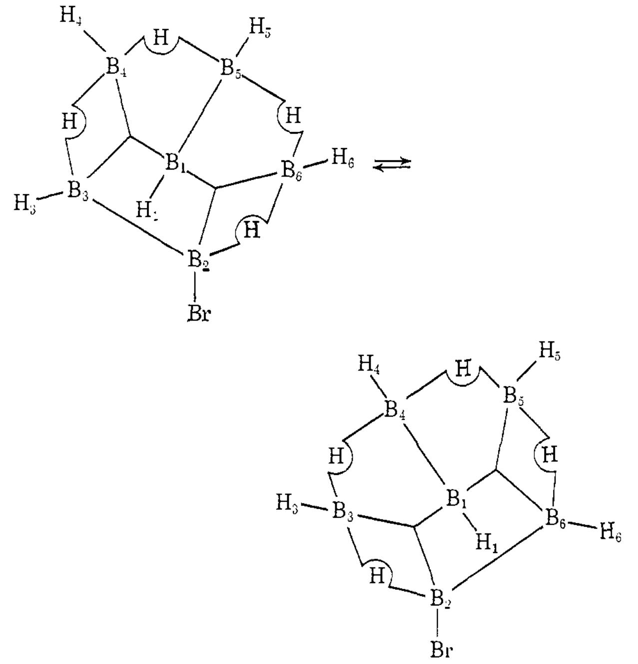
Figure 5. The 100-MHz pmr spectra of 2-BrB_6H_9: τ_b = basal terminal hydrogen, τ_a = apical terminal hydrogen, μ = bridge hydrogen; (a) in CD_2Cl_2–$CHCl_3$ with basal boron atoms spin decoupled; (b) and (c), in $CHClF_2$–CD_2Cl_2 with all boron atoms spin decoupled.

Table III. Nmr Data for 2-BrB_6H_9

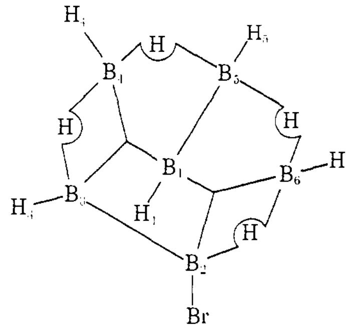
100-MHz $^1H^a$ Room temp	100-MHz $^1H^a$ −60°	100-MHz $^1H^a$ −130°	Assignments^b	32.1-MHz $^{11}B^c$ Room temp	32.1-MHz $^{11}B^c$ −100°
		11.64	$\mu_{3,4}$		
	10.55	(10.58)^d	$\mu_{3,4}$; $\mu_{5,6}$		
		9.51	$\mu_{5,6}$		
10.23	(10.28)	(10.29)	all-μ		
	10.02	10.00	$\mu_{2,6}$; $\mu_{4,5}$		
		6.80	5^d		5.9
6.02	6.07	(6.14)	4, 5	−6.2	(−6)
		5.49	4		−18
		5.73	3 or 6		
5.48	5.54		3, 6	−18.1	−18
		5.35 (est.)	6 or 3		
10.42		10.61	1	48.3	49.9
			2		18 ± 1

[a] Chemical shifts expressed in ppm relative to tetramethylsilane equals 10.00. [b] The number, n, denotes B_n or the terminal hydrogen attached to it; the symbol $\mu_{x,y}$ denotes a proton bridging B_x and B_y. [c] Chemical shifts expressed in ppm relative to $BF_3 \cdot O(C_2H_5)_2$ = 0.0. [d] Values in parentheses are appropriately weighted averages.

different structural model (still involving limited tautomerism) is necessary to fit the 2-BrB_6H_9 spectra at −60°. First, the lower field bridge resonance of relative area two at τ 10.0 is present in the spectrum at −120° unchanged. Second, we deduce from spectra at −120° (see discussion below) a static structure for 2-BrB_6H_9 in which the B–B bond is adjacent to the bromo-substituted boron. Neither of the foregoing points is consistent with the model proposed to fit the spectra of 2-$CH_3B_6H_9$ at intermediate temperature. A rapid equilibration of the two tautomers of 2-BrB_6H_9 shown below fits the spectrum at −60°,



with the proviso that the resonance due to the proton bridging B_4 and B_5 accidentally coincides at τ 10.0 with the resonance due to the exchanging bridge proton ($\mu_{2,6} \rightleftarrows \mu_{2,3}$). Then the bridge peak at τ 10.55 is assigned to $\mu_{3,4}$ and $\mu_{5,6}$ which are symmetrically equivalent on the nmr time scale. On cooling to −120° this limited tautomerism becomes slow on the nmr time scale and the latter bridge resonance splits into two peaks of equal area. Note that $\mu_{2,6}$ in the first tautomer above is magnetically equivalent to $\mu_{2,3}$ in the second tautomer; therefore, the chemical shift of this proton is the same when static (see structure IV) as when exchanging rapidly as described above. Of course, the $\mu_{4,5}$ resonance is unaffected as well. Placement of the B–B bond adjacent to the bromo-substituted boron is necessary to the analysis present immediately above; however, this static structure is also the one most consistent with the chemical shifts observed for the bridge protons of 2-BrB_6H_9 compared to the shifts observed for the bridge protons in the static structure of B_6H_{10}. The effect of substituting bromine for hydrogen in derivatives of B_5H_9 is to shift the bridge protons adjacent to the bromine downfield by 1.6 ppm.[20] No two bridge protons in the static structure of 2-BrB_6H_9 are shifted by that much compared to bridge protons in equivalent positions relative to B–B bond in B_6H_{10}. Therefore, we conclude that bromo-boron has only one adjacent bridge as in structure IV below.



IV

In the spectrum of 2-BrB_6H_9 at −120°, only three basal terminal resonances are visible. However, a consideration of their chemical shifts in comparison with the shifts for the two pairs of basal terminal hydrogens recorded at −60° shows that there must in fact be four unique basal terminal hydrogen resonances. The resonance at τ 6.80 is (by analogy to the spectra of the static structures of B_6H_{10} and 2-$CH_3B_6H_9$) assigned to the terminal hydrogen opposite the B–B bond, H_5, which must arise from the splitting of the higher field basal terminal set.

The peak at τ 5.49 is therefore due to the second member of that set, H_4. The resonance at τ 5.73 arises from a splitting of the lower field terminal pair and a resonance at τ 5.35 ± 0.05 is thus implied.

Boron-11 Nmr of 2-BrB_6H_9. The spectra of 2-BrB_6H_9 at ambient temperature, Figure 6a and b, show that the bromine substituent is in a basal position. In the spectrum with all hydrogens spin decoupled, Figure 6a, four boron resonances are present in the area ratio 1:2:2:1. These are assigned to B_2 (bonded to Br), $B_{3,6}$, $B_{4,5}$, and B_1 reading from low to high field. In Figure 6b (no spin decoupling) it is seen that the singlet owing to B_2 overlaps the lower arm of the doublet at −18.1 ppm. In the intermediate temperature region, −40 to −70°, the highest field basal doublet is broadened, but the spectrum is otherwise the same as at ambient temperature. At −110° this resonance has split into two peaks. One peak is upfield at δ 5.9 ppm, assigned by analogy with the spectra discussed previously to B_5 opposite to the B–B bond. The other peak has merged with the resonance at −18 ppm. The bromo-substituted boron, B_2, has apparently shifted upfield to about −18 ppm as well.

Experimental Section

Materials. All solvents were dried over $LiAlH_4$. The $(CD_3)_2O$ was prepared from CD_3I and $KOCD_3$ in tetrahydrofuran. CD_3I and CD_3OD were purchased from Stohler Isotopes Co. $CHClF_2$ was obtained from the Matheson Co. and used directly from the cylinder. Hexaborane(10) and 2-methylhexaborane(10) were prepared from 1-BrB_5H_8 and 1-Br-2-$CH_3B_5H_7$, respectively.[22]

Instrumentation. Pmr and boron-11 nmr studies were carried out using a Varian HA-100 high-resolution spectrometer at 100 MHz in the HA mode and at 32.1 MHz in the HR mode, respectively. All pmr chemical shifts are given in τ units relative to $(CH_3)_4Si$ = τ 10.00 using $CHCl_3$ = τ 2.75 or $CHClF_2$ = τ 2.76. Boron-11 nmr shifts are obtained by tube interchange using BCl_3 (δ −46.8[23]) and are reported referenced to $BF_3\cdot(CH_3CH_2)_2O$ (δ 0). Decoupling experiments were carried out using an Electronic Navigation Laboratories 320 L power amplifier, a Hewlett Packard 3722 A noise generator, and a General Radio frequency synthesizer. Sample temperatures were determined with a thermocouple placed in the probe *ca.* 1 cm from the bottom of the nmr tube. The error is estimated as ±5°.

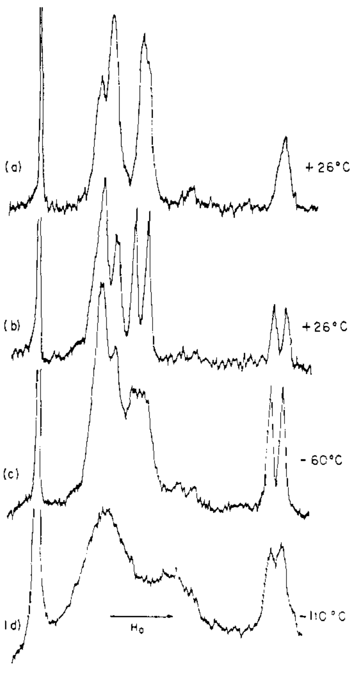


Figure 6. The 32.1-MHz boron-11 nmr spectra of 2-BrB_6H_9 in CD_2Cl_2–$CHCl_3$, BCl_3 standard at extreme left: (a) all hydrogens spin decoupled; (b), (c), and (d) no spin decoupling.

Preparation of 2-BrB_6H_9. A 100-ml reaction bulb was attached to the vacuum line and 11 mmol of 2,6-lutidine, 11 mmol of Br_2, and about 30 ml of CH_2Cl_2 were distilled in at −196°. The vessel was warmed to room temperature and stirred, then cooled to −196°. Hexaborane(10), 11 mmol, was condensed in just above the solution and the mixture was warmed to −97° (CH_2Cl_2 slush bath). When the solution had melted, stirring was started and the B_6H_{10} was washed into the solution. In a matter of minutes, the solution was clear and pale yellow. The CH_2Cl_2 was removed from the vessel at −78°. The desired product, 2-BrB_6H_9, was recovered by allowing the reaction vessel to warm to room temperature from −78° over 2–3 hr while open to the vacuum pump through U-traps maintained at 0, −35, and −196°. About 1 mmol of 2-BrB_6H_9 was collected in the −35° trap. The vapor pressure at 25° is too low to measure with a mercury manometer; the melting point is −33 to −34°. The mass spectrum obtained on the AEI MS-9 exhibits a parent peak at *m/e* = 156.04253; calculated for $^{81}Br^{11}B_6{}^1H_9{}^+$, 156.04268. *Anal.* Calcd B, 42.16; hydridic hydrogen, 0.0846 mmol/mg. Found: B, 40.7; hydridic hydrogen, 0.0829 mmol/mg.

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[22] H. D. Johnson, II, V. T. Brice, and S. G. Shore, *Inorg. Chem.*, **12**, 689 (1973).

[23] T. Onak and J. Spielman, *J. Magn. Resonance*, **3**, 122 (1970).