(b) J. P. Collman and W. R. Roper, *Adv. Organomet. Chem.*, **7**, 54 (1968); (c) J. P. Collman, *Acc. Chem. Res.*, **1**, 136 (1968).
(4) J. P. Collman, D. W. Murphy, and G. Dolcetti, *J. Am. Chem. Soc.*, **95**, 2687 (1973).
(5) J. P. Collman and M. R. MacLaury, *J. Am. Chem. Soc.*, **96**, 3019 (1974).
(6) M. R. MacLaury Ph.D. Thesis, Stanford University, 1974.
(7) All computations were done on a Digital PDP 11/45 computing system. The basic programs (supplied by Enraf-Nonius, Inc.) included a full-matrix least-squares program, Fourier programs, and a modified version of ORFFE (Busing and Levy's function and error program, and Johnson's ORTEP). A local program, ENXDR, was used for data collection.
(8) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.
(9) Supplementary material.
(10) J. P. Collman, E. B. Fleischer, D. Y. Jester, and D. W. Murphy, unpublished results.
(11) S. Bruckner, M. Calligaris, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta*, **3**, 278 (1969).
(12) P. C. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973), and references therein.
(13) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960.
(14) W. C. Hamilton and J. C. Ibers, "Hydrogen Bonding in Solids", W. A. Benjamin, New York, N.Y., 1968.
(15) (a) D. J. Sutor, *Nature (London)*, **195**, 68 (1962); (b) G. Palenick, *Acta Crystallogr.*, **19**, 47 (1965).
(16) J. P. Collman and D. D. Davis, unpublished results.
(17) (a) F. Vogtle and P. Neumann, *Tetrahedron*, **26**, 5299 (1970); (b) G. W. Gribble and J. R. Douglas, *J. Am. Chem. Soc.*, **92**, 5764 (1970).
(18) H. C. Clark and J. D. Ruddick, *Inorg. Chem.*, **9**, 2556 (1970).
(19) J. Hilton and L. H. Sutcliffe, *Prog. Nucl. Magn. Reson. Spectrosc.*, **10**, 27 (1975), and references therein.

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Studies of Boranes. XLV.[1] Crystal and Molecular Structure, Improved Synthesis, and Reactions of Tridecaborane(19)

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The crystal and molecular structure of $B_{13}H_{19}$ has been determined by a single-crystal X-ray diffraction study. The compound crystallizes in space group $P2_1/c$ with $a = 9.217$ (2) Å, $b = 6.498$ (3) Å, $c = 19.719$ (5) Å, and $\beta = 97.69$ (1)°. The calculated density for $Z = 4$ is 0.91 g/cm^3. The structure was solved by direct methods and refined to residuals $R_1 = 0.113$ and $R_2 = 0.055$. The structure can be described as an n-B_9H_{15} cage sharing two borons with a B_6H_{10} cage; however, the B_9 skeleton lacks the m symmetry present in n-B_9H_{15}. An improved synthesis of $B_{13}H_{19}$ has been obtained by the following reaction scheme: $KB_6H_8Br + {}^1/_2B_2H_6 \rightarrow KB_7H_{11}Br$; $KB_7H_{11}Br + B_6H_{10} \rightarrow B_{13}H_{19} + H_2 + KBr$. Reaction of $B_{13}H_{19}$ with potassium hydride yielded the relatively stable $KB_{13}H_{18}$, which regenerated $B_{13}H_{19}$ upon acidification. The ^{11}B NMR spectra of normal and isotopically labeled (^{10}B and ^2D) $B_{13}H_{19}$ and $KB_{13}H_{18}$ are discussed in relation to their structures.

Introduction

Tridecaborane(19) was first prepared in our laboratory in trace quantities from the pyrolysis of hexaborane(10) and subsequently was obtained in low yield by the generation of [B_7H_{11}] in the presence of hexaborane(10).[2] Structural studies were undertaken and a preliminary report of the X-ray crystal structure has appeared,[3] but reaction studies of tridecaborane(19) were hindered by the relatively small amounts of this material available.

In this work the complete analysis of the crystal and molecular structure of $B_{13}H_{19}$ is presented. We also wish to report an improved synthesis of $B_{13}H_{19}$ which involves the generation of the [B_7H_{11}] intermediate by KBr elimination from $KB_7H_{11}Br$ in the presence of hexaborane(10). The deprotonation of $B_{13}H_{19}$ to yield $KB_{13}H_{18}$ is described, along with attempts to generate a B_{14} species by borane addition to this anion. Studies involving ^{10}B and ^2D isotopic substitution are also presented.

Experimental Section

Crystallography—Crystal Data. A well-formed crystal of approximate dimensions 0.3 mm × 0.3 mm × 0.4 mm was utilized in the crystallographic study.[4] Preliminary precession photographs and a diffractometer search of the reciprocal lattice indicated $2/m$ Laue symmetry with conditions for nonextinction of $l = 2n$ for $h0l$ and $k = 2n$ for $0k0$, uniquely determining the space group to be $P2_1/c$ (No. 14, $C_{2h}{}^5$). A least-squares fit of angular data from 16 reflections centered in $\pm 2\theta$ yielded cell parameters of $a = 9.217$ (2) Å, $b = 6.498$ (3) Å, $c = 19.719$ (5) Å, and $\beta = 97.69$ (1)° (at ca. −130°). The calculated density of $d_{\text{calcd}} = 0.91$ g/cm^3 for $Z = 4$ is reasonable for compounds of this type.

Crystallography—Intensity Data Collection. Data were collected on a Picker FACS-1 diffractometer utilizing Mo Kα radiation (λ 0.71069 Å) monochromatized by a highly oriented graphite monochromator (002 plane, $2\theta_m = 12.06°$). Other diffractometer constants and data reduction formula are given elsewhere for the continuous θ–2θ scan technique used.[5]

Examination of ω and 2θ scans indicated a crystal of suitable mosaic character with no abnormalities. Three reflections chosen as standards were monitored after every 50 measurements and indicated no systematic changes in intensity. A total of 4023 reflections, including redundancies, were collected in the region $0° \leq 2\theta \leq 50°$ and reduced to 1763 unique intensities. The 729 reflections with $I \geq 2.33\sigma(I)$ were utilized in the solution and preliminary refinement of the structure, and all data were utilized in final refinement. No absorption corrections were made ($\mu = 0.36$ cm^{-1}). Preliminary scale and thermal parameters were determined by Wilson's method.[6]

Crystallography—Solution and Refinement of the Structure. Direct methods were used to assign phases to the 213 largest normalized structure factors, E_{hkl}, and an E map phased on these values located all 13 boron atoms in the structure. Isotropic least-squares refinement followed by a difference Fourier synthesis was used to locate all hydrogen atoms.[7] Full-matrix least squares were utilized to refine all positional parameters, anisotropic boron thermal parameters, isotropic hydrogen parameters, and an overall scale factor and isotropic extinction parameter. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 4I/(\sigma(I))^2$. A total of 1581 reflections were nonzero and thus had nonzero weight, giving a ratio of 8:1 for observations to parameters in the refinement. For the final cycle, the largest Δ/σ was 0.05, the goodness of fit was 1.16, and the extinction parameter was 1.8 (6) × 10^{-6}. The maximum extinction was 4.7% for the 004 reflection. The final residuals were $R_1 = 0.113$ and $R_2 = 0.055$ where $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o{}^2]^{1/2}$. The variance–covariance matrix was utilized to determine errors in bond distances and angles.

A final list of observed and calculated structure factors is available (see paragraph at end of paper regarding supplementary data).

Apparatus and Materials. Standard high-vacuum techniques were used throughout this investigation. The 70.6-MHz ^{11}B NMR spectra were recorded on a Varian Associates HR-220 spectrometer equipped with a "home-built" pulse apparatus. Mass spectra were obtained with a Varian Associates CH-7 mass spectrometer. Only thoroughly dried reagent grade solvents were used in this study. Normal B_2H_6, $^{10}B_2H_6$ (92% ^{10}B), and B_2D_6 (>95% ^2D) were obtained from laboratory supplies. Hexaborane(10) was prepared by literature procedure.[8] Dimethyl ether, trimethylamine, and hydrogen chloride were obtained from the Matheson Co. and purified by low-temperature trap to trap distillation. Potassium hydride (35% in oil) was obtained from Alfa Inorganics; the oil was removed by repeated washings with *n*-hexane. The reaction of BCl_3 with excess D_2O was used to prepare DCl (~93% ^2D).

Preparation of $B_{13}H_{19}$. Potassium hydride (0.4 mmol) was transferred under a N_2 atmosphere to a reaction vessel equipped with a greaseless stopcock. The vessel was evacuated and 0.5 mmol of 2-BrB_6H_9[9] and 1 ml of dimethyl ethere were condensed on top of the KH at -196°. The reaction mixture was stirred at -78° for 1 hr to form a colorless solution of $KBrB_6H_8$ and H_2. The H_2 was removed, and 0.24 mmol of B_2H_6 was condensed into the vessel at -196°. After 1 hr of reaction at -78°, the excess B_2H_6 and ether distilled from the vessel and separated by reaction of the former with trimethylamine. The recovered trimethylamine–borane was weighed and 0.43 mmol of BH_3 was found to have reacted.[10] Hexaborane(10) (3.68 mmol) was condensed on top of the $KBrB_7H_{11}$ at -196°.[11] The vessel was placed in a -45° bath; the reaction solution yellowed immediately. The well-stirred solution was warmed to -20° over a period of 30 min and then placed in a 0° bath. After 30 min at 0°, the bath was removed, and the reaction was allowed to proceed at room temperature for 30–45 min. Only 0.05 mmol of H_2 was observed when the vessel was opened.[12] The volatile products of the reaction were pumped through a 0° trap and into a trap at -196° for a period of 3 hr. The yellow crystalline $B_{13}H_{19}$ in the 0° trap was contaminated with a trace of yellow liquid, but refractionation into another 0° trap yielded 0.13 mmol of pure $B_{13}H_{19}$. Purity was checked by ^{11}B NMR and mass spectral analysis. The yield based on initial potassium hydride was 32%.

The KBr left in the reaction flask was contaminated with traces of $B_{13}H_{19}$ and *n*-$B_{18}H_{22}$. The more volatile reaction products (originally passing through the 0° trap) were fractionated through a series of traps at -23, -63, -112, and -196°. The -23° trap contained a small amount of $B_{10}H_{14}$, while 2-BrB_6H_9 and a trace of B_6H_{10} stopped in the -63° trap. The -112° trap contained 2.54 mmol of B_6H_{10}, indicating that only 0.14 mmol was absorbed during the reaction. Dimethyl ether and 0.24 mmol of B_2H_6 were present in the -196° trap. These volatile fractions were characterized by mass spectral analysis.

Preparation of ^{10}B-Labeled $B_{13}H_{19}$. A dimethyl ether solution containing 0.38 mmol of $KBrB_6H_8$ was prepared as described above. To this solution was added 0.33 mmol of $^{10}B_2H_6$ (~92% ^{10}B). After 1 hr at -78°, the ether and excess $^{10}B_2H_6$ were distilled from the vessel and separated by reaction with trimethylamine. Mass spectral analysis of the 0.28 mmol of $^{10}BH_3 \cdot NMe_3$ recovered indicated that no isotopic dilution had occurred. The labeled $^*B_{13}H_{19}$ was then prepared in the same manner as above.

The 70.6-MHz ^{11}B NMR spectrum of this material in CH_2Cl_2 solvent is shown in Figure 1b. A comparison of this spectrum with that of normal $B_{13}H_{19}$ (Figure 1a) showed 73% ^{10}B content for resonance i and no observable decrease in the ^{11}B content for the other resonances. The recovered B_6H_{10} retained normal isotopic content as observed by mass spectral analysis, while the 0.07 mmol of recovered B_2H_6 contained 54% ^{10}B.

Attempted Exchange between B_2D_6 and $B_{13}H_{19}$. Approximately 0.8 mmol of B_2D_6 (>95% ^2D) was condensed into a vessel containing 0.11 mmol of $B_{13}H_{19}$ and 1 ml of CH_2Cl_2. The solution was warmed to room temperature and stirred for 1.5 hr. The vessel was cooled to -78°, and the B_2D_6 was fractionated from the CH_2Cl_2 and $B_{13}H_{19}$. A 70.6-MHz ^{11}B spectrum of this CH_2Cl_2 solution of $B_{13}H_{19}$ was identical with that of normal $B_{13}H_{19}$; suggesting that no exchange with B_2D_6 had occurred. A -131° trap was used to purify the recovered B_2D_6, and mass spectral analysis also indicated no decrease in ^2D content.

$KB_{13}H_{18}$. Tridecaborane(19) (0.14 mmol) and 3–4 ml of Et_2O were condensed at -196° into a vessel containing excess KH (~2 mmol). The yellow ether solution was then stirred at room temperature for 1 hr. The reaction was quenched at -196° and the H_2 was measured; 0.13 mmol was obtained. The ether solution of $KB_{13}H_{18}$ was filtered from the excess KH, and the solvent removed by pumping at room temperature for 1.5 hr. The resulting yellow solid was dissolved in acetonitrile, and the 70.6-MHz ^{11}B NMR spectrum shown in Figure 2A was obtained. Acidification of the solid anion with liquid HCl at -78° for 30 min resulted in the regeneration of $B_{13}H_{19}$ in 80–90% yield.

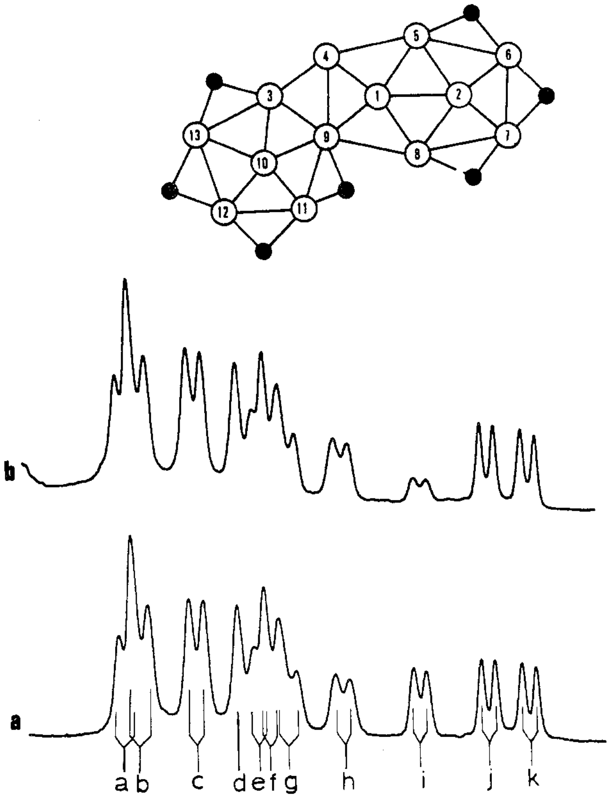

Figure 1. The structure and 70.6-MHz ^{11}B NMR spectra of (a) normal $B_{13}H_{19}$ and (b) $^*B_{13}H_{19}$ which contains 73% ^{10}B in position B (4).

A similarly prepared sample of $KB_{13}H_{18}$ (0.04 mmol) was treated with anhydrous liquid DCl at -78° for 30 min. The incorporation of deuterium in the recovered tridecaborane(19) was studied by both mass spectral and 70.6-MHz ^{11}B NMR analysis. The mass spectrum suggested the incorporation of seven or eight deuterium atoms per molecule. The ^{11}B NMR spectrum, however, was virtually identical with that of normal $B_{13}H_{19}$ (Figure 1a) except for loss of doublet ($J_{^{11}B-H_t}$) structure for resonance i; suggesting deuterium incorporation into this one terminal position. Extensive substitution of bridging hydrogens by deuterium had apparently taken place.

The previously described ^{10}B-labeled sample of $B_{13}H_{19}$, specifically labeled with 73% ^{10}B in one position, was allowed to react with KH, and an NMR sample in acetonitrile was prepared as above. The 70.6-MHz ^{11}B NMR spectrum of this $K^*B_{13}H_{18}$ sample is shown in Figure 2B. Comparison of this spectrum with that of normal $KB_{13}H_{18}$ (Figure 2A) indicates that the upfield resonance l has been reduced in intensity by an amount corresponding to 73% ^{10}B content for this position.

Reaction of B_2H_6, $^{10}B_2H_6$, and B_2D_6 with $KB_{13}H_{18}$. A clear yellow ether solution of 0.12 mmol of $KB_{13}H_{18}$ was prepared as previously described. Diborane(6) (0.49 mmol) was condensed into the vessel at -196°, and the reaction mixture was warmed to room temperature with stirring. The solution was cloudy initially, and more precipitate formed as the reaction continued for 30 min. The volatile products were pumped from the vessel, leaving a yellow pasty solid. The B_2H_6 was separated from the less volatile ether by fractionation through a -131° trap and 0.43 mmol was recovered.[13] An excess of liquid HCl was condensed on top of the yellow solid and allowed to react for 30 min at -78°. Fractionation of the products did not, however, yield a B_{14} hydride but only regenerated $B_{13}H_{19}$ in 90% yield.

Another sample of $KB_{13}H_{18}$ was prepared and allowed to react with B_2H_6 in the same manner, but instead of acidifying the anion, a 70.6-MHz ^{11}B NMR spectrum of the material in acetonitrile was obtained. The spectrum was identical with that of $KB_{13}H_{18}$ shown in Figure 2A except for the addition of an area 1 doublet that falls exactly under resonance g. When an excess of $^{10}B_2H_6$ was treated in a similar manner with $KB_{13}H_{18}$, resonance g again increased while the rest of the spectrum remained the same as that of $KB_{13}H_{19}$. The mass spectral analysis of the recovered $^{10}B_2H_6$ indicated that no appreciable boron exchange had taken place with the $KB_{13}H_{18}$. A

Table I. Positional and Isotropic Thermal Parameters

	x/a	y/b	Z/c	B, Å^2
B(1)	0.2877 (4)[a]	0.3484 (7)	0.3110 (2)	b
B(2)	0.1270 (5)	0.2352 (8)	0.3366 (2)	b
B(3)	0.5132 (5)	0.0449 (6)	0.3582 (2)	b
B(4)	0.4177 (4)	0.1788 (6)	0.2897 (6)	b
B(5)	0.2276 (4)	0.1081 (7)	0.2746 (2)	b
B(6)	0.1376 (6)	−0.0258 (9)	0.3367 (3)	b
B(7)	0.1675 (5)	0.1096 (8)	0.4135 (2)	b
B(8)	0.2662 (4)	0.3378 (8)	0.3992 (2)	b
B(9)	0.4455 (4)	0.3099 (6)	0.3650 (2)	b
B(10)	0.5930 (4)	0.2055 (6)	0.4302 (2)	b
B(11)	0.5966 (5)	0.4640 (7)	0.4077 (2)	b
B(12)	0.7562 (5)	0.3100 (8)	0.4131 (2)	b
B(13)	0.7066 (5)	0.0592 (7)	0.3867 (2)	b
H(1)	0.2692 (28)	0.4954 (42)	0.2843 (13)	2.64 (64)
H(2)	0.0302 (34)	0.3194 (50)	0.3225 (14)	5.07 (81)
H(3)	0.4653 (26)	−0.0956 (41)	0.3788 (12)	2.56 (61)
H(4)	0.4744 (26)	0.2087 (38)	0.2450 (12)	2.56 (58)
H(5)	0.1748 (28)	0.0962 (40)	0.2192 (13)	2.91 (61)
H(6)	0.0417 (32)	−0.1463 (48)	0.3239 (13)	4.14 (71)
H(7)	0.0998 (38)	0.0903 (54)	0.4561 (17)	6.40 (89)
H(8)	0.2558 (33)	0.4693 (47)	0.4323 (15)	4.25 (78)
H(10)	0.5788 (22)	0.1652 (35)	0.4829 (11)	1.36 (50)
H(11)	0.5964 (28)	0.5942 (43)	0.4429 (13)	3.11 (66)
H(12)	0.8534 (34)	0.3536 (47)	0.4502 (14)	4.55 (77)
H(13)	0.7659 (29)	−0.0676 (42)	0.4054 (13)	2.71 (66)
H(9-11)	0.5211 (31)	0.4858 (42)	0.3550 (15)	3.21 (64)
H(7-8)	0.2969 (39)	0.1750 (58)	0.4353 (16)	6.74 (90)
H(3-13)	0.6291 (32)	0.0169 (41)	0.3302 (14)	3.77 (68)
H(12-13)	0.7758 (30)	0.2096 (47)	0.3611 (14)	4.01 (70)
H(6-5)	0.2449 (35)	−0.0610 (52)	0.3010 (16)	5.15 (81)
H(6-7)	0.2079 (33)	−0.0700 (49)	0.3905 (16)	4.74 (76)
H(11-12)	0.7130 (34)	0.4610 (47)	0.3776 (15)	4.10 (72)

[a] Figures in parentheses throughout this paper refer to error in least significant digit. [b] Refined anisotropically.

Table II. Anisotropic[a] Thermal Parameters (× 10^4) for Borons

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
B(1)	104 (6)	198 (13)	15 (1)	25 (7)	3 (2)	13 (3)
B(2)	68 (6)	339 (23)	23 (1)	14 (8)	−6 (2)	20 (4)
B(3)	86 (6)	169 (12)	22 (1)	−9 (7)	15 (2)	2 (3)
B(4)	101 (6)	206 (12)	19 (1)	7 (7)	13 (2)	−7 (3)
B(5)	97 (6)	256 (15)	23 (1)	15 (8)	6 (2)	8 (4)
B(6)	106 (7)	410 (20)	34 (2)	−15 (10)	4 (3)	11 (5)
B(7)	77 (6)	390 (19)	26 (2)	24 (9)	10 (2)	27 (4)
B(8)	99 (6)	298 (15)	17 (1)	51 (8)	4 (2)	7 (4)
B(9)	95 (6)	137 (11)	20 (1)	8 (7)	15 (2)	9 (3)
B(10)	81 (6)	178 (12)	20 (1)	−12 (7)	4 (2)	16 (3)
B(11)	118 (7)	207 (14)	21 (1)	−8 (8)	−2 (3)	−3 (4)
B(12)	117 (7)	293 (16)	23 (1)	2 (9)	11 (3)	2 (4)
B(13)	99 (6)	218 (14)	24 (1)	23 (8)	4 (2)	4 (4)

[a] Anisotropic thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

similar reaction with B_2D_6 resulted in extensive deuterium exchange with the $KB_{13}H_{18}$, but the intensity of resonance g still increased as if superimposed on a doublet of relative area 1.

Table III. Bonded Distances (Å)

B(1)–B(2)	1.786 (6)	B(1)–H(1)	1.09 (3)
B(1)–B(4)	1.721 (5)	B(2)–H(2)	1.05 (3)
B(1)–B(5)	1.776 (6)	B(3)–H(3)	1.11 (3)
B(1)–B(8)	1.779 (5)	B(4)–H(4)	1.10 (2)
B(1)–B(9)	1.703 (5)	B(5)–H(5)	1.14 (2)
B(2)–B(5)	1.828 (6)	B(6)–H(6)	1.18 (3)
B(2)–B(6)	1.699 (7)	B(7)–H(7)	1.12 (3)
B(2)–B(7)	1.719 (6)	B(8)–H(8)	1.09 (3)
B(2)–B(8)	1.786 (6)	B(10)–H(10)	1.10 (2)
B(3)–B(4)	1.744 (6)	B(11)–H(11)	1.09 (3)
B(3)–B(9)	1.843 (5)	B(12)–H(12)	1.11 (3)
B(3)–B(10)	1.834 (6)	B(13)–H(13)	1.03 (3)
B(3)–B(13)	1.798 (6)	B(3)–H(3-13)	1.28 (3)
B(4)–B(5)	1.798 (6)	B(5)–H(6-5)	1.22 (3)
B(4)–B(9)	1.703 (5)	B(6)–H(6-5)	1.31 (3)
B(5)–B(6)	1.794 (7)	B(6)–H(6-7)	1.20 (3)
B(6)–B(7)	1.741 (7)	B(7)–H(7-8)	1.28 (3)
B(7)–B(8)	1.782 (7)	B(7)–H(6-7)	1.32 (3)
B(8)–B(9)	1.876 (5)	B(8)–H(7-8)	1.28 (4)
B(9)–B(10)	1.868 (5)	B(9)–H(9-11)	1.37 (3)
B(9)–B(11)	1.826 (6)	B(11)–H(9-11)	1.18 (3)
B(10)–B(11)	1.739 (6)	B(11)–H(11-12)	1.29 (3)
B(10)–B(12)	1.724 (6)	B(12)–H(12-13)	1.25 (3)
B(10)–B(13)	1.724 (6)	B(12)–H(11-12)	1.24 (3)
B(11)–B(12)	1.771 (6)	B(13)–H(3-13)	1.27 (3)
B(12)–B(13)	1.753 (7)	B(13)–H(12-13)	1.30 (3)

Table IV. Bonded Angles Involving Only Borons (deg)

B(2)–B(1)–B(4)	115.9 (3)	B(2)–B(7)–B(8)	61.3 (3)
B(2)–B(1)–B(5)	61.7 (2)	B(6)–B(7)–B(8)	107.9 (3)
B(2)–B(1)–B(8)	60.1 (2)	B(1)–B(8)–B(2)	60.1 (2)
B(2)–B(1)–B(9)	115.7 (3)	B(1)–B(8)–B(7)	108.2 (3)
B(4)–B(1)–B(5)	61.8 (2)	B(1)–B(8)–B(9)	55.5 (2)
B(4)–B(1)–B(8)	112.8 (3)	B(2)–B(8)–B(7)	57.6 (3)
B(4)–B(1)–B(9)	59.6 (2)	B(2)–B(8)–B(9)	107.5 (3)
B(5)–B(1)–B(8)	107.0 (3)	B(7)–B(8)–B(9)	118.0 (3)
B(5)–B(1)–B(9)	108.6 (3)	B(1)–B(9)–B(3)	111.1 (3)
B(8)–B(1)–B(9)	65.2 (2)	B(1)–B(9)–B(4)	60.7 (2)
B(1)–B(2)–B(5)	58.9 (2)	B(1)–B(9)–B(8)	59.4 (2)
B(1)–B(2)–B(6)	111.2 (3)	B(1)–B(9)–B(10)	164.9 (3)
B(1)–B(2)–B(7)	110.8 (3)	B(1)–B(9)–B(11)	137.9 (3)
B(1)–B(2)–B(8)	59.7 (2)	B(3)–B(9)–B(4)	58.8 (2)
B(5)–B(2)–B(6)	61.0 (3)	B(3)–B(9)–B(8)	116.1 (3)
B(5)–B(2)–B(7)	107.8 (3)	B(3)–B(9)–B(10)	59.2 (2)
B(5)–B(2)–B(8)	104.5 (3)	B(3)–B(9)–B(11)	107.5 (3)
B(6)–B(2)–B(7)	61.2 (3)	B(4)–B(9)–B(8)	109.0 (3)
B(6)–B(2)–B(8)	109.6 (3)	B(4)–B(9)–B(10)	115.4 (3)
B(7)–B(2)–B(8)	61.1 (3)	B(4)–B(9)–B(11)	133.8 (3)
B(4)–B(3)–B(9)	56.6 (2)	B(8)–B(9)–B(10)	112.5 (2)
B(4)–B(3)–B(10)	115.1 (3)	B(8)–B(9)–B(11)	115.8 (3)
B(4)–B(3)–B(13)	126.3 (3)	B(10)–B(9)–B(11)	56.2 (2)
B(9)–B(3)–B(10)	61.1 (2)	B(3)–B(10)–B(9)	59.7 (2)
B(9)–B(3)–B(13)	105.1 (3)	B(3)–B(10)–B(11)	111.8 (3)
B(10)–B(3)–B(13)	56.7 (2)	B(3)–B(10)–B(12)	110.1 (3)
B(1)–B(4)–B(3)	115.2 (3)	B(3)–B(10)–B(13)	60.6 (2)
B(1)–B(4)–B(5)	60.6 (2)	B(9)–B(10)–B(11)	60.7 (2)
B(1)–B(4)–B(9)	59.6 (2)	B(9)–B(10)–B(12)	107.2 (3)
B(3)–B(4)–B(5)	112.4 (3)	B(9)–B(10)–B(13)	107.0 (3)
B(3)–B(4)–B(9)	64.6 (2)	B(11)–B(10)–B(12)	61.5 (3)
B(5)–B(4)–B(9)	107.6 (3)	B(11)–B(10)–B(13)	111.9 (3)
B(1)–B(5)–B(2)	59.4 (2)	B(12)–B(10)–B(13)	61.1 (3)
B(1)–B(5)–B(4)	57.6 (2)	B(9)–B(11)–B(10)	63.2 (2)
B(1)–B(5)–B(6)	107.3 (3)	B(9)–B(11)–B(12)	107.1 (3)
B(2)–B(5)–B(4)	110.1 (3)	B(10)–B(11)–B(12)	58.8 (2)
B(2)–B(5)–B(6)	56.0 (3)	B(10)–B(12)–B(11)	59.7 (2)
B(4)–B(5)–B(6)	122.7 (3)	B(10)–B(12)–B(13)	59.5 (2)
B(2)–B(6)–B(5)	63.0 (3)	B(11)–B(12)–B(13)	109.0 (3)
B(2)–B(6)–B(7)	59.9 (3)	B(3)–B(13)–B(10)	62.7 (2)
B(5)–B(6)–B(7)	108.4 (4)	B(3)–B(13)–B(12)	110.5 (3)
B(2)–B(7)–B(6)	58.8 (3)	B(10)–B(13)–B(12)	59.5 (2)

Results and Discussion

Description of the Structure. Tridecaborane(19) is a conjuncto borane consisting of a hexaborane and a nonaborane fragment sharing two boron positions. Final positional and thermal parameters are given in Tables I and II, and bonded distances and angles, in Tables III and IV. The molecule is shown in Figure 3, and the unit cell packing in Figure 4. All hydrogen positions were refined isotropically; the thermal parameters, estimated errors based on the variance–covariance matrix, and consistency of B–H$_t$ distances indicate they were accurately determined. One can visualize the structure as containing B_6, B_7, B_8, and B_9 fragments. One B_6 fragment (B(3)–B(13)–B(12)–B(11)–B(9)–B(10)) is structurally identical with B_6H_{10} with four bridging hydrogens on the exterior face, and the two borons corresponding to the two-center two-electron bond of B_6H_{10} are also part of a B_9 fragment (B(3)–B(4)–B(5)–B(6)–B(7)–B(8)–B(9)–B(1)–B(2)). The latter fragment is similar to *n*-B_9H_{15} with the exception of the hydrogen arrangement around the boron which is a –BH_2 group in *n*-B_9H_{15}.[14] The seven-coordinate B(9) of $B_{13}H_{19}$ has no terminal hydrogen, as is the case of

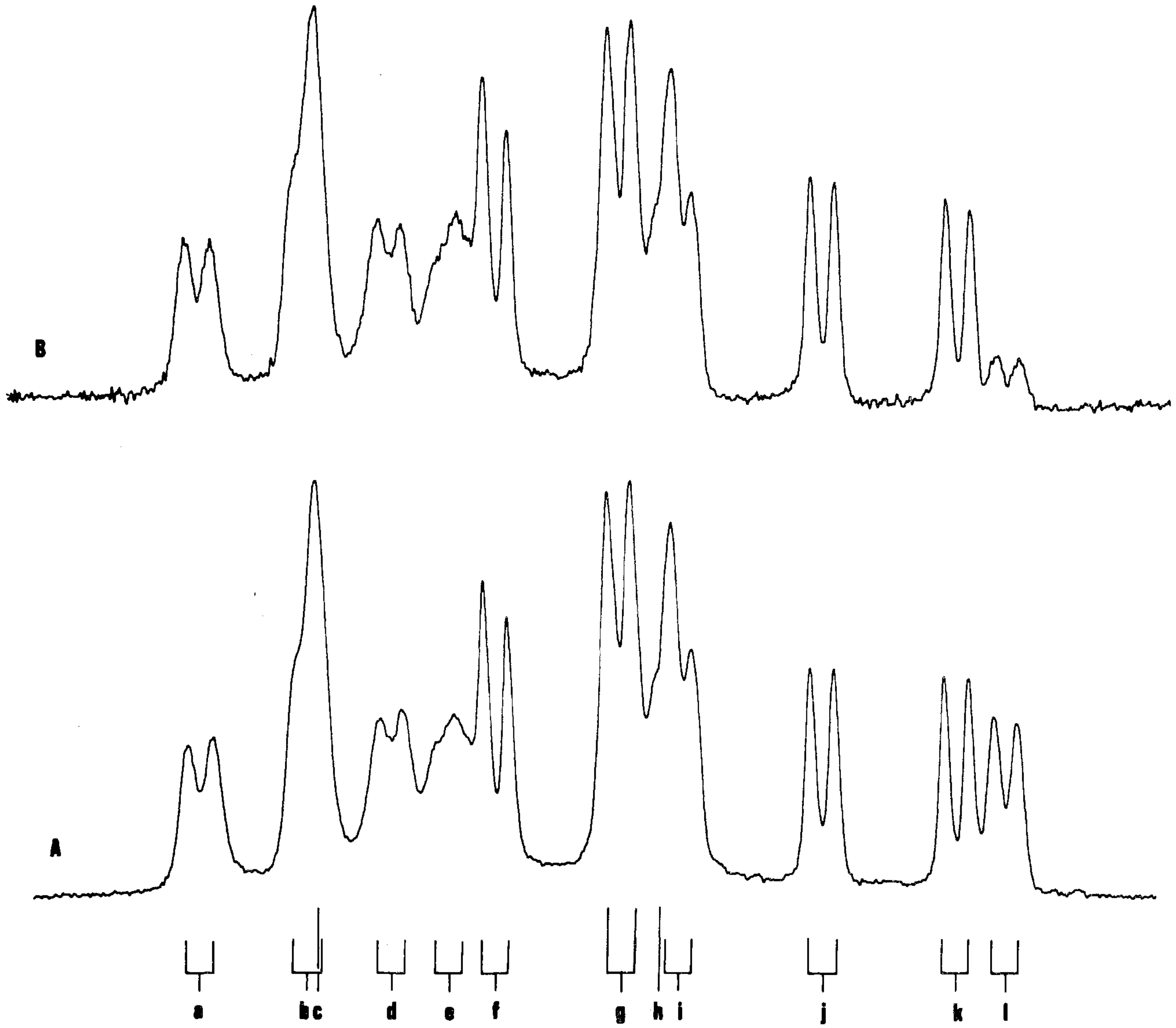

Figure 2. The 70.6-MHz ^{11}B NMR spectra of (A) normal $KB_{13}H_{18}$ and (B) specifically ^{10}B-labeled $K^*B_{13}H_{18}$. Chemical shifts (ppm relative to external $BF_3 \cdot OEt_2$) and $J_{^{11}B-H_t}$ coupling constants (±10 Hz) are as follows: a (−20.3, 160),b (−11.0, 160), c (−10.2), d (−4.0, 150), e (+1.1, ~150), f (+5.1, 150), g (+15.9, 150), h (+19.3), i (+20.7, 150), j (+33.1, 150), k (+44.6, 150), and l (+49.0, 150).

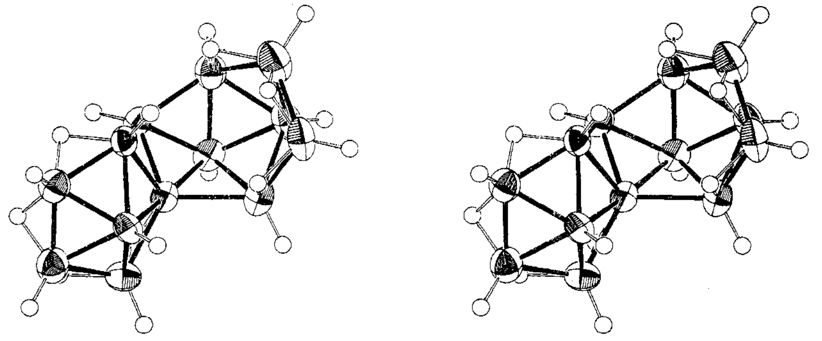

Figure 3. Stereoscopic view of $B_{13}H_{19}$. The hydrogens have been given artificial *B*'s of 1.0 Å^2 for artistic purposes. The thermal ellipsoids for borons are drawn at the 50% probability level.

other seven-coordinate borons in conjuncto boranes.[15]

One interesting structural feature of the molecule is the geometry of the B_9 fragment. Instead of resembling *n*-B_9H_{15}, a model of the molecule indicates that the B_9 fragment appears more closely to approximate a $B_{10}H_{14}$ fragment with the B(5) position of the latter removed.[16] In fact, there are rather large deviations in what could be "equivalent" B–B bond distances (i.e., B(1)–B(8), B(1)–B(5); B(4)–B(5), B(8)–B(9); etc.) in a B_9 fragment of *m* symmetry as is present in *n*-B_9H_{15}. The average deviation in the present structure is 0.04 Å, while the average deviation in *n*-B_9H_{15} is only 0.005 Å.[17] In an attempt to see if the B_9 portion was better described as a decaborane fragment, a least-squares fit[18] of the nine related boron positions in $B_{10}H_{14}$, *n*-B_9H_{15}, and $B_{13}H_{19}$ was determined, and the results are given in Table V. These data indicate that the B_9 fragment of $B_{13}H_{19}$ can best be described as being

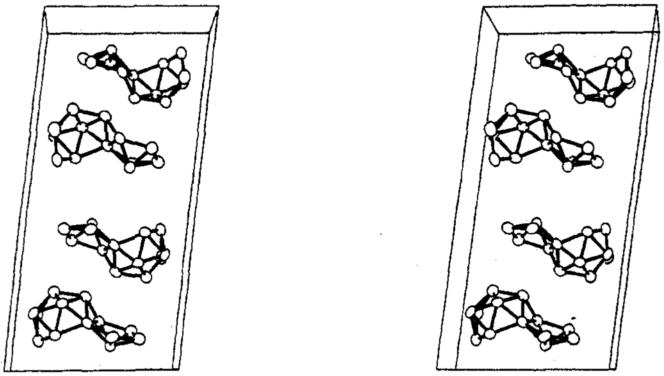

Figure 4. Stereoscopic view of the molecular packing of $B_{13}H_{19}$, viewed down the *b* axis. Hydrogens have been omitted for clarity.

Table V

	Comparison compounds		
	n-B_9H_{15}-$B_{13}H_{19}$	$B_{10}H_{14}$-$B_{13}H_{19}$	*n*-B_9H_{15}-$B_{10}H_{14}$
$\Sigma(\Delta d)^2$	0.071	0.087	0.185
$\Sigma\Delta d/n$	0.08 (4)	0.08 (5)	0.12 (8)
$\Sigma\Delta d_{BB}/n^a$	0.04 (3)	0.04 (3)	0.04 (4)

[a] $\Sigma\Delta d_{BB}/n$ represents the average of differences in the 17 boron–boron bonds in the B_9 fragment.

intermediate in geometry between the two.[19]

Another structural feature of interest is the asymmetric hydrogen bridge between B(9) and B(11). The B(11)–H(9-11) distance, 1.18 Å, is quite short for a bridging hydrogen and, in fact, is close to a B–H_t distance. Nonbonded contact distances and the topological approach of Lipscomb and Epstein[20] have been applied successfully[17] in the simpler boranes to explain hydrogen character; therefore, they were employed in this study. In general the hydrogen atoms on the "exterior" edge of the cage tend to rearrange in such a manner as to give the structure with the most allowed valence forms, consistent with geometric constraints imposed by nonbonded hydrogen–hydrogen and hydrogen–boron contacts. It is in fact these nonbonded constraints which usually explain asymmetric bridges in the boranes.

The principal nonbonded distances for $B_{13}H_{19}$ are given in Table VI. The contention that these intramolecular distances help determine the structure is seen by their consistency and by the fact that the shortest *inter*molecular contact is nearly 0.5 Å larger.[21] Using the information above, one would predict that H(9-11) should in fact be asymmetric in the opposite sense; i.e., the contacts with H(11) and H(11-12) would tend to make B(11)–H(9-11) > B(9)–H(9-11). In fact the 1.77-Å H(9-11)–H(11-12) distance is the shortest nonbonded distance present, and there are no significant opposing nonbonded contacts. This discrepancy, however, is consistent with results which we have obtained using Lipscomb and Epstein's topological approach. Allowing the external hydrogens to "float" around the face of the borane cage, assuming bridging and $-BH_2$ character, one finds that there are eight geometrically allowed structures for which acceptable valence forms can be formulated. Of these structures, the one with no $-BH_2$ groups has 30 allowed valence forms,[17] and the only other structure with over 10 valence forms is that with H(9-11) shifted to a $-BH_2$ group on B(11). This structure consists of 20 allowed valence forms, suggesting that H(9-11) may in fact have significant terminal character.

Table VI

A. Intramolecular Nonbonded H-H Distances (Å)			
H(3)-H(3-13)	2.03 (4)	H(12)-H(12-13)	2.03 (4)
H(5)-H(6-5)	1.95 (4)	H(12)-H(11-12)	1.93 (4)
H(6)-H(6-5)	2.06 (4)	H(13)-H(3-13)	1.89 (4)
H(6)-H(6-7)	1.94 (4)	H(13)-H(12-13)	2.01 (4)
H(7)-H(7-8)	1.99 (5)	H(9-11)-H(11-12)	1.77 (4)
H(7)-H(6-7)	2.02 (4)	H(7-8)-H(6-7)	1.95 (4)
H(8)-H(7-8)	1.95 (4)	H(3-13)-H(12-13)	1.88 (4)
H(11)-H(9-11)	1.91 (4)	H(12-13)-H(11-12)	1.78 (4)
H(11)-H(11-12)	1.98 (4)	H(6-5)-H(6-7)	1.84 (4)
B. Intermolecular Nonbonded H-H Distances (Å)			
H(4)-H(9-11)	2.45 (5)	H(4)-H(3-13)	2.60 (5)
H(5)-H(11-12)	2.45 (5)	H(2)-H(5)	2.66 (5)
H(1)-H(3-13)	2.56 (5)	H(2)-H(12-13)	2.66 (5)
H(3)-H(11)	2.59 (5)	H(6)-H(5)	2.66 (5)

The asymmetry of H(9-11) toward B(11) in the presence of strong nonbonded H–H interactions with H(11) and H(11-12) appears to be the only experimental evidence suggesting partial terminal character for this bridge hydrogen. No triplets due to $-BH_2$ groups are observed in the ^{11}B NMR spectrum (see Figure 1a); however, this is not uncommon for cases where "unique terminals" ("pseudo bridges") are present.[22] The 220-MHz ^1H NMR spectrum of $B_{13}H_{19}$ is not sufficiently resolved to enable the location of a resonance for a "unique terminal", if present, nor can a ratio of terminal to bridge hydrogens be obtained.[23] Thus with the theoretical and experimental data available, we conclude the H(9-11) probably contains appreciable terminal hydrogen character (toward B(11)), but at this time we cannot unequivocally prove this supposition.

Synthesis and Reactions. We had previously established the importance of the $[B_7H_{11}]$ intermediate in the synthesis of $B_{13}H_{19}$.[2] However, the $BF_3{\cdot}OEt_2$ formed in generating this intermediate from $B_7H_{11}{\cdot}OEt_2$ appeared to interfere with the subsequent reaction with B_6H_{10}. As an alternative procedure, we chose the reaction scheme of eq 1–3. We suggest that

$$2\text{-}BrB_6H_9 + KH \xrightarrow{Me_2O} KB_6H_8Br + H_2 \tag{1}$$

$$KB_6H_8Br + {}^1/_2B_2H_6 \xrightarrow{Me_2O} KB_7H_{11}Br \tag{2}$$

$$KB_7H_{11}Br + B_6H_{10} \rightarrow B_{13}H_{19} + H_2 + KBr \tag{3}$$

$[B_7H_{11}]$ was formed by KBr elimination from $KB_7H_{11}Br$ at −45°. The $[B_7H_{11}]$ was then trapped by reaction with the large excess of B_6H_{10}. The resultant acid–base adduct, $B_7H_{11}{\cdot}B_6H_{10}$ ($B_{13}H_{21}$), slowly lost hydrogen to yield $B_{13}H_{19}$ in good yield.

In an attempt to relate the structure of $B_{13}H_{19}$ (Figure 1) to its B_7 and B_6 fragments, we undertook a ^{10}B-labeling study. The utilization of $^{10}B_2H_6$ in reaction 2 resulted in the formation of a B_7 framework containing one ^{10}B label. Reaction with B_6H_{10} resulted in a labeled $^*B_{13}H_{19}$. A comparison of the ^{11}B NMR spectrum of this material with that of normal $B_{13}H_{19}$ (Figure 1) revealed that only resonance i had been reduced in area corresponding to a 73% ^{10}B label in this position. The retention of the label in a specific position leads us to believe that gross boron-cage structural rearrangements are probably not involved in the joining of the B_7 and B_6 fragments. If one examines the structure of $B_{13}H_{19}$ in Figure 1, a B_6H_{10} type fragment (B(3)–B(13)–B(12)–B(11)–B(9)–B(10)) can be envisioned as fused with a B_7 fragment (B(4)–B(5)–B(6)–B(7)–B(8)–B(1)–B(2)). On further examination, the B_7 fragment resembles a B_6H_{10} type pentagonal pyramid with B(4) bridging B(1) and B(5). We suggest that the B_6 framework remains intact in the $[B_7H_{11}]$ intermediate and that the seventh boron occupies a position which was vacated by a bridging hydrogen in the formation of the initial B_6 anion. The reaction of B_6H_{10} with KH has previously been shown to result in the loss of a bridging hydrogen.[24] Thus, B(4) becomes the most probable position for the ^{10}B enrichment, and resonance i in the ^{11}B NMR spectrum (Figure 1) is tentatively assigned to B(4).

It was not too surprising that $B_{13}H_{19}$ failed to react or even exchange hydrogens with B_2D_6, but we felt that it was likely that a B_{13} anion would absorb borane to lead eventually to a B_{14} hydride. Reaction of $B_{13}H_{19}$ with excess potassium hydride, in diethyl ether solution, did indeed yield the $KB_{13}H_{18}$ salt, presumably by loss of an acidic bridge hydrogen. The ^{11}B NMR spectrum of this anion in acetonitrile is shown in Figure 2A. Reacidification with anhydrous HCl resulted in the regeneration of $B_{13}H_{19}$. Reaction of the $KB_{13}H_{18}$ with DCl, however, resulted in extensive deuterium incorporation into bridge hydrogen positions. The ^{11}B NMR spectrum of this deuterated $B_{13}H_{19}$ showed loss of doublet ($J_{^{11}B-H_t}$) structure for resonance i (Figure 1), previously suggested to correspond to the B(4) position. The terminal hydrogen on B(4) thus also appears to have been exchanged with deuterium.

The previously described sample of $^*B_{13}H_{19}$, 73% ^{10}B in position B(4), was also treated with potassium hydride and the correspondingly labeled $K^*B_{13}H_{18}$ was prepared. The ^{11}B NMR spectrum of this material (Figure 2B) shows the label to reside in the position corresponding to resonance l. Assuming that no boron skeletal rearrangement has taken place in the formation of the anion, resonance l in the ^{11}B NMR spectrum of $KB_{13}H_{18}$ can tentatively be assigned to a corresponding B(4) position of the anion cage.

The initial results of the reaction of diborane(6) with the $KB_{13}H_{18}$ salt were encouraging in that BH_3 appeared to be absorbed in an approximate 1:1 ratio. However, an exact 1:1 stoichiometry could not be established for this reaction and acidification of what we hoped was the B_{14} anion resulted only in the regeneration of $B_{13}H_{19}$ in high yield. The ^{11}B NMR spectra of samples of $KB_{13}H_{18}$ which had been treated with either B_2H_6 or $^{10}B_2H_6$ proved to be identical.[25] These spectra also differed from that of $KB_{13}H_{18}$ (Figure 2A) only in that the relative intensity of resonance g had increased as if this doublet resonance were superimposed on a new doublet resonance of relative area 1. Reaction of $KB_{13}H_{18}$ with B_2D_6 yielded a material whose ^{11}B NMR spectrum indicated that extensive deuterium–hydrogen exchange had taken place, but resonance g still increased as if superimposed on a doublet of area 1. These data suggest that the B_{14} anion, if formed, is too unstable to be of synthetic utility and that the increase in intensity of resonance g is probably due to a small amount of decomposition product.

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Registry No. $B_{13}H_{19}$, 43093-20-5; 2-BrB_6H_9, 50545-82-9; B_2H_6, 19287-45-7; B_6H_{10}, 23777-80-2; $KB_{13}H_{18}$, 56363-22-5; ^{11}B, 14798-13-1; KH, 7693-26-7.

Supplementary Material Available: Table VII, a listing of structure factor amplitudes, and Table VIII, which contains angles involving hydrogen atoms (18 pages). Ordering information is given on any current masthead page. Crystallographic data, for this paper only, are also available in microfiche for $2.00 from the Chemistry Library, Indiana University, Bloomington, Ind. 47401. Request Molecular Structure Center Report No. 7503.

References and Notes

(1) Part XLIV: J. C. Huffman, D. C. Moody, and R. Schaeffer, *J. Am. Chem. Soc.*, **97**, 1621 (1975).
(2) J. Rathke, D. C. Moody, and R. Schaeffer, *Inorg. Chem.*, **13**, 3040 (1974).
(3) (a) J. C. Huffman, D. C. Moody, J. W. Rathke, and R. Schaeffer, *J. Chem. Soc., Chem. Commun.*, 308 (1973). (b) The previously reported abnormally long B(7)–B(8) distance of 2.08 Å was found to be in error due to a transcription error for one positional parameter of B(7). The correct distance is 1.78 Å.
(4) The crystal used in this structure determination was a product of the pyrolysis of hexaborane(10) and was supplied by Jerome Rathke.
(5) M. O. Visscher, J. C. Huffman, and W. E. Streib, *Inorg. Chem.*, **13**, 792 (1974).
(6) A. J. C. Wilson, *Nature (London)*, **150**, 152 (1942).
(7) All computations were performed on a CDC 6600 computer. For phase determination a local version of Long's program was used. Least squares, Fourier summations, and error analyses were performed by A. C. Larson's programs, and figures were produced by Johnson's ORTEP. Scattering factors were the nine-parameter form in "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, p 99.
(8) H. D. Johnson, II, V. T. Brice, and S. G. Shore, *Inorg. Chem.*, **12**, 689 (1973).
(9) Prepared by reaction of BBr_3 with B_6H_{10}: (a) P. J. Dolan, Ph.D. Thesis, Indiana University, 1974; (b) P. J. Dolan, D. C. Moody, and R. Schaeffer, to be submitted for publication.
(10) The procedure presented here for the preparation of $KB_7H_{11}Br$ is analogous to the literature procedure for KB_7H_{12} (see ref 2).
(11) Care should be taken that all of the $KB_7H_{11}Br$ is covered with B_6H_{10} before removing the −196° bath.
(12) It appears that the [$B_{13}H_{21}$] intermediate is partially stabilized in the presence of excess B_6H_{10}, but more H_2 loss must occur during the lengthy fractionation procedure, since only $B_{13}H_{19}$ is isolated in the product material.
(13) The amount of BH_3 absorbed varied for different experiments but only in the range of 80–100% of what would be expected for a 1:1 stoichiometry.
(14) R. E. Dickerson, P. J. Wheatley, P. A. Howell, and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 200 (1957).
(15) (a) P. G. Simpson and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 26 (1963); (b) P. G. Simpson, K. Folting, R. D. Dobrott, and W. N. Lipscomb, *ibid.*, **39**, 2339 (1963); (c) R. D. Dobrott, L. B. Friedman, and W. N. Lipscomb, *ibid.*, **40**, 866 (1964).
(16) Using standard IUPAC nomenclature.
(17) J. C. Huffman, Ph.D. Thesis, Indiana University, 1974.
(18) Program BMFIT: S. C. Nyburg, University of Toronto.
(19) The localized molecular orbitals for $B_{13}H_{19}$ are currently being examined by Professor W. N. Lipscomb, and it is indeed possible that the results of this study will clarify the nature of the B_9 fragment.
(20) I. R. Epstein and W. N. Lipscomb, *Inorg. Chem.*, **10**, 1921 (1971).
(21) There is, of course, an appreciable B–H shortening effect in borane crystal structures similar to that observed for C–H distances. This effect will tend to shorten intermolecular distances and lengthen intramolecular distances. We consider the 0.5 Å to be significant nevertheless.
(22) A. O. Clouse, D. C. Moody, R. R. Rietz, T. Roseberry, and R. Schaeffer, *J. Am. Chem. Soc.*, **95**, 2496 (1973).
(23) J. W. Rathke and D. C. Moody, unpublished results.
(24) H. D. Johnson, II, R. A. Geanangel, and S. G. Shore, *Inorg. Chem.*, **9**, 908 (1970).
(25) Digital subtraction of these two spectra revealed no hidden resonances.