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A Complete Molecular Structure Determination of Pentaborane(9) by Rotational Spectroscopy

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The microwave spectra of 15 isotopic species of B_5H_9 were investigated. The complete molecular structure was determined from these data by assuming C_{4v} symmetry: B_r–B_r, 1.803 ± 0.002 Å; B_r–B_a, 1.690 ± 0.002 Å; B_r–H_t, 1.186 ± 0.002 Å; B_a–H_a, 1.181 ± 0.002 Å; B_r–H_μ, 1.352 ± 0.004 Å; B_a–B_rH_t, 128.72 ± 0.55°; $\angle\phi$, 193.10 ± 2.9°. Evidence is given of a large vibrational amplitude for the bridge hydrogens.

Introduction

Boron hydrides and carboranes form a very interesting class of compounds because of their electron deficiency and the three-center bridge hydrogen bonds. However, most structural studies by x-ray diffraction, electron diffraction, or microwave spectroscopy have not determined accurate positions for the bridge hydrogen atoms. In the course of other studies in this laboratory, it came to our attention that the structure determinations of pentaborane have not accurately located the hydrogen atoms. Since this is one of the most stable boron hydrides, we have undertaken a complete structure determination by rotational spectroscopy. In particular, we were interested in precisely locating the bridge hydrogen atoms.

The structure of pentaborane, B_5H_9, has been investigated previously by several authors: Dulmage and Lipscomb[2] determined the x-ray structure, Hedberg, Jones, and Schomaker[3] solved the electron diffraction structure, and Hrostowski and Myers[4] investigated the microwave spectra. However, in all these studies the hydrogen positions were obtained only with large uncertainties. The investigation of the rotational spectra of the deuterated isotopes provides the most accurate method to determine the bridge hydrogen structure.

The structure of B_5H_9 has been determined from the study of 15 isotopic species, and the results are compared to prior results. The structure of B_5H_9, the atom designation, and the orientation of the principal axis of the normal species are shown in Figure 1. Sometimes the boron and hydrogen atoms will be designated as apical, ring, terminal, or bridge by using the subscripts a, r, t, or μ, respectively. Some evidence of a large amplitude of the bridge hydrogen motion is also discussed. This is interesting since a much larger effect has been found in hexaborane(10), B_6H_{10}.[5] But this effect was not pursued in this work.

Experimental Section

The deuterated species of pentaborane were prepared by using the following H–D exchange reactions: the species 1-DB_5H_8 was obtained by repeated action of DCl upon B_5H_9 in the presence of aluminum chloride at 25 °C.[6] The species 2-DB_5H_8 was formed by the action of B_2D_6 upon B_5H_9 (1:2 ratio, to minimize double deuteration) during 5 days at 85 °C.[7] The presence of 1-DB_5H_8 in this sample was minimized by aluminum chloride catalyzed exchanges with HCl. The species μ-DB_5H_8 was prepared quite specifically by action of DCl upon LiB_5H_8.[8]

The estimated deuterium enrichments were 70% for 1-DB_5H_8 and 80% for both μ-DB_5H_8 and the 2-DB_5H_8 enriched samples. The spectra were taken with a Hewlett-Packard Model KII-8400B spectrometer at dry ice temperatures. Vapor pressures of 0.050–0.100 mm were used. No exchange of the deuterium in the terminal and bridge substituted isotopes was observed even after many weeks. The spectra were very dense.

Spectra and Assignment

As has been shown by previous investigations 2,3,4-pentaborane is a symmetric top molecule with a large dipole moment, 2.13 D,[4] in the direction of the symmetry axis. The complete structure is determined by only seven structural parameters. Therefore, the spectra of at least eight isotopic species have to be analyzed and used to calculate the structure. However, it is always desirable to have additional experimental data to allow for a more realistic error determination. Due to the abundance of the two boron atom isotopes—^{11}B:$^{10}B \approx$ 4:1—many singly and doubly substituted ^{10}B species could be studied in natural abundance. The spectra of 15 isotopic substituted molecules have been analyzed and used to calculate the structure. Table I gives a list of the measured species and abbreviations for the different species which will be used below. The estimated isotopic abundance in each sample is given.

Table I. Measured Isotopic Species of B_5H_9[a]

Species	Substituted atoms	Rel isotopic abundance
N	Normal isotope	0.35
B1	$^{10}B_1$	0.08
B2	$^{10}B_2$	0.33
B3	$^{10}B_2$ and $^{10}B_4$	0.16
D1	D_6	0.18
D2	$^{10}B_1$ and D_6	0.07
D3	$^{10}B_2$ and D_6	0.13
D4	$^{10}B_4$ and D_6	0.13
D5	D_6 and D_8	0.07
D6	$^{10}B_2$, D_6, and D_8	0.07
D7	D_1	0.28
D8	$^{10}B_2$ and D_1	0.26
D9	D_2	0.24
D10	$^{10}B_2$ and D_3	0.11
D11	$^{10}B_2$ and D_4	0.06

[a] Symmetry-equivalent forms are not listed. Dotted lines separate different samples. The relative abundance of enriched species in each sample is estimated.

The assignments of the spectra were made on the basis of their relative intensity and their consistency of fit. Because the different deuterated species could be prepared specifically, one sample contained only a few different ^{10}B isotopic species, thereby making the assignment easier.

Due to the nuclear quadrupole moment of the five boron atoms, the $J = 1 \leftarrow 0$ and $J = 2 \leftarrow 1$ transitions were broadened by unresolved hfs. The half-width of the $J = 1 \leftarrow 0$ transition was about 2 MHz. The unsymmetrically substituted species were sufficiently asymmetric to show Q-branch transitions which allowed a determination of the C rotational constants. However, only Q^c transitions with $J > 10$ were of sufficient intensity to be accurately measured. Because the high J lines are affected by centrifugal effects, the centrifugal distortion parameters were determined in terms of the Δ constants.[9] The centrifugal distortion constants were obtained by a fit of 28 transitions of the B2 species. Because Q transitions are independent of Δ_J this constant could not be determined and was not included in the fit. The centrifugal distortion parameters are listed in Table II.

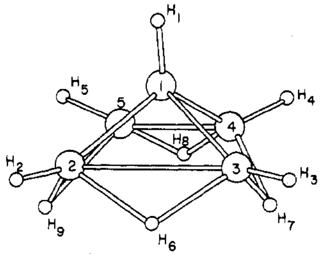

Figure 1. Molecular structure of B_5H_9.

Table II. Centrifugal Distortion Constants (kHz) of B2 Species[a]

Δ_J	0 fixed	δ_J	0.018 ± 0.001
Δ_{JK}	−1.86 ± 0.02	δ_K	0.40 ± 0.07
Δ_K	1.1 ± 0.4		

[a] Repr III^r was used. The errors represent the standard deviation obtained in the least-squares fit.

Table III. Transitions (MHz) and Rotational Constants (MHz) of Symmetric Top Species of B_5H_9

	$J = 1 \leftarrow 0$		$J = 2 \leftarrow 1$		
Species	ν_{exptl}	$\nu_{calcd} - \nu_{exptl}$	ν_{exptl}	$\nu_{calcd} - \nu_{exptl}$	B
N	14 005.90	−0.14	28 011.36	0.16	7002.88 ± 0.07
B1	14 179.69	0.03	28 359.45	−0.01	7089.86 ± 0.02
D1	13 194.14	−0.18	26 387.75	0.17	6596.98 ± 0.09

Table IV. Rotational Constants (MHz) of Asymmetric Top Species of B_5H_9[a]

Species	A	B	C
B2	7169.18 ± 0.02	7005.81 ± 0.02	4968.29 ± 0.02
B3	7338.30 ± 0.02	7008.56 ± 0.02	5047.21 ± 0.02
B4	7260.01 ± 0.03	7092.44 ± 0.03	4968.13 ± 0.03
D1	6901.83 ± 0.04	6724.52 ± 0.04	4805.01 ± 0.05
D2	6989.16 ± 0.02	6807.78 ± 0.02	4804.89 ± 0.04
D3	7009.31 ± 0.03	6771.08 ± 0.03	4879.50 ± 0.11
D4	7014.25 ± 0.03	6776.09 ± 0.03	4881.71 ± 0.10
D5	6794.45 ± 0.02	6465.61 ± 0.02	4726.65 ± 0.03
D6	6887.97 ± 0.03	6521.50 ± 0.03	4800.35 ± 0.04
D8	6745.53 ± 0.04	6600.80 ± 0.04	4968.13 ± 0.04
D9	7002.55 ± 0.04	6471.90 ± 0.04	4624.69 ± 0.05
D10	7168.78 ± 0.06	6474.40 ± 0.06	4694.86 ± 0.16
D11	7005.82 ± 0.04	6622.36 ± 0.04	4699.55 ± 0.05

[a] Errors are standard deviations obtained from least-squares fits.

The rotational constants of all the other isotopic species were obtained by using the same Δ constants. These were held fixed at the values of Table II in the fitting process. For all species only Q transitions out of the set of transitions of the B2 species have been included in the fit.

Although the centrifugal distortion is very small its inclusion decreased the standard deviations of the rotational constants of all measured species, showing the significance of the Δ constants. Deuterating the bridge position caused a 3° tilt of the molecule with respect to the principal axis system, thus generating a small dipole moment component in the *a* direction. The small asymmetry splitting of many K doublets led to a drastic change of the Stark effect pattern of some higher *J* lines.

Table III gives the transitions and rotational constants of the symmetric top species; Table IV shows the rotational constants obtained from the transitions given in Table V[10] for all the asymmetric isotopic species.

Structure

First, the positions of the atoms were obtained in terms of Cartesian coordinates in the principal axis system of the isotopes used as reference species. Then the coordinates were transformed to the principal axis coordinate system of the normal species.

By applying standard formulas for the calculation of the atomic positions of a symmetric top molecule,[11] the first set of coordinates of all atoms was obtained in the principal axis system of the species by using the monosubstituted species. A second set of coordinates was determined by application of Kraitchman's method to the asymmetric species using the B2 species as the reference molecule together with all doubly substituted species. However, the coordinates obtained by this method refer to the principal axis system of the B2 species and had to be transformed back to the N species before they could be compared directly with the set of coordinates determined previously. The transformation, consisting of a rotation as well as a translation of the axis system is dependent on the relative signs of the coordinates. The signs given in Table VI and Table VII are those which led to the best agreement of the two sets of coordinates. This procedure for determining relative signs, known as the *isotopic pulling method*,[12] has been successfully applied to carboranes.[13] The two sets of coordinates were averaged before calculating bond distances and bond angles.

The values for the coordinates of the bridge hydrogens show a large scatter of about ±0.06 Å which is much more than

Table VI. Atomic Coordinates of B_5H_9 Except μ-Hydrogens[a]

	Reference species			
	B2 species		N species	
Atom	In principal axis system of isotope B_2	After transformation to normal isotope	In principal axis system of normal isotope	Av
B_1	0.0	0.0	0.0	0.0
	0.0000 ± 0.0400	0.0	0.0	0.0
	0.9341 ± 0.0001	0.9367 ± 0.0001	0.9353 ± 0.0005	0.9360 ± 0.0005
B_4	0.0	0.0	0.0	0.0
	1.2563 ± 0.0000	1.2751 ± 0.0000	1.2751 ± 0.0006	1.2751 ± 0.0004
	−0.1707 ± 0.0003	−0.1773 ± 0.0003	−0.1681 ± 0.0026	−0.1727 ± 0.0065
H_1	0.0	0.0	0.0	0.0
	−0.0437 ± 0.0047	0.0	0.0	0.0
	2.1138 ± 0.00	2.1167 ± 0.0001	2.1170 ± 0.0004	2.1169 ± 0.0002
H_3	2.4421 ± 0.0110	2.4421 ± 0.0110	2.4438 ± 0.0002	2.4425 ± 0.0006
	−0.1303 ± 0.0353	0.0	0.0	0.0
	0.0000 ± 0.0200	0.0036 ± 0.0230	0.0639 ± 0.0139	0.0382 ± 0.0180
H_4	0.0	0.0	0.0	0.0
	2.4210 ± 0.0005	2.4415 ± 0.0006	2.4438 ± 0.0002	2.4425 ± 0.0007
	0.0621 ± 0.0022	0.0470 ± 0.0018	0.0639 ± 0.0139	0.0382 ± 0.0180

[a] Conversion factor 505 375 MHz amu A^2 used throughout in this paper. Symmetry equivalent atoms in B2-system not listed. The errors listed indicate only the dependence of the coordinates on the accuracy of the rotational constants given in Tables III and IV.

Table VII. Position of the Bridge Hydrogens in B_5H_9 (Å)[a]

	Reference species					
Atom	N	B2	B1	D5	D6	Av
a. In Principal Axis Systems of Different Isotopes						
H_6	0.9699 ± 0.0003	0.9726 ± 0.0001	0.9702 ± 0.0002	1.3412 ± 0.0003	1.3168 ± 0.0006	
	−0.9699 ± 0.0003	−0.9238 ± 0.0014	0.9702 ± 0.0002	$(-0.0289)^{1/2}$	−0.2231 ± 0.0016	
	−1.0640 ± 0.0005	−1.0995 ± 0.0005	−1.0485 ± 0.0003	−1.0594 ± 0.0002	−1.0702 ± 0.0005	
H_7	0.9699 ± 0.0003	0.9727 ± 0.0001	0.9702 ± 0.0002			
	0.9699 ± 0.0003	0.8997 ± 0.0013	0.9702 ± 0.0002			
	−1.0640 ± 0.0005	−1.0842 ± 0.0005	−1.0485 ± 0.0003			
H_8	−0.9699 ± 0.0003		−0.9702 ± 0.0002		−1.3027 ± 0.0006	
	0.9699 ± 0.0003		0.9702 ± 0.0002		0.1930 ± 0.0018	
	−1.0640 ± 0.0005		−1.0485 ± 0.0003		−1.0582 ± 0.0005	
b. After Transformation to Principal Axis System of Normal Species						
H_6	0.9699 ± 0.0003	0.9728 ± 0.0001	0.9702 ± 0.0002	0.9484 ± 0.0002	0.9858 ± 0.0005	0.9495 ± 0.009
	−0.9699 ± 0.0003	−0.9121 ± 0.0014	−0.9702 ± 0.0002	−0.9484 ± 0.0002	−0.9782 ± 0.0005	−0.9495 ± 0.009
	−1.0640 ± 0.0005	−1.0881 ± 0.0005	−1.0630 ± 0.0003	−1.0917 ± 0.0003	−1.0631 ± 0.0005	−1.0744 ± 0.006
H_7	0.9699 ± 0.0003	0.9723 ± 0.0001	0.9702 ± 0.0002	0.9484 ± 0.0002		0.9495 ± 0.009
	0.9699 ± 0.0003	0.9120 ± 0.0013	0.9702 ± 0.0002	0.9484 ± 0.0002		0.9495 ± 0.009
	−1.0640 ± 0.0005	−1.0900 ± 0.0005	−1.0630 ± 0.0003	−1.0917 ± 0.0003		−1.0744 ± 0.006
H_8	−0.9699 ± 0.0003		−0.9702 ± 0.0002	−0.9484 ± 0.0002	−0.9837 ± 0.0005	−0.9495 ± 0.009
	0.9699 ± 0.0003		0.9702 ± 0.0002	0.9484 ± 0.0002	0.8891 ± 0.0005	0.9495 ± 0.009
	−1.0640 ± 0.0005		−1.0630 ± 0.0003	−1.0917 ± 0.0003	−1.0610 ± 0.0005	−1.0744 ± 0.006

[a] Symmetry equivalent atoms in the B2 system not listed. The errors listed indicate only the dependence of the coordinates on the accuracy of the rotational constants given in Tables III and IV.

Table VIII. Final Structure of B_5H_9

	Present work	MW, ref 4	ED, ref 3	XR, ref 2
B(2)-B(3), Å	1.803 ± 0.002[a]	1.800 ± 0.003	1.805 ± 0.014	1.77 ± 0.02
B(2)-B(1), Å	1.690 ± 0.002[a]	1.687 ± 0.005	1.700 ± 0.017	1.66 ± 0.02
B(2)-H(2), Å	1.186 ± 0.002[a]		1.234 ± 0.066	1.20 ± 0.07
B(1)-H(1), Å	1.181 ± 0.002[a]		1.234 ± 0.066	1.21 ± 0.05
B(2)-H(μ), Å	1.352 ± 0.004[a]		1.359 ± 0.077	1.35 ± 0.04
∠B(1)B(2)H(2), deg	128.72 ± 0.55		120 ± 20	115 ± 5
∠ϕ,[b] deg	193.10 ± 2.9		187 ± 10	190 ± 5

[a] This value is calculated by the method explained in the discussion. [b] ϕ is the dihedral angle between the B(1)B(2)B(3) and the B(2)B(3)-H_μ planes.

the errors obtained from each individual set of coordinates. For this reason, more bridge-substituted molecules have been measured, including doubly bridge substituted species and a triply substituted species. The coordinates of the bridge hydrogens calculated from Kraitchman's equation are listed in Table VII where part a gives the coordinates in the principal axis system of the different isotopes and part b their corresponding values after transformation to the principal axis system of the N species.

The average was calculated by assuming the bridge hydrogen is in a symmetric position and by weighting the individual *a* and *b* coordinates by the number of spectra from which they were derived. Their coordinates, together with those of Table VI, result in the structure of pentaborane given in Table VIII. The values obtained from earlier investigations have been listed for comparison. The boron–boron distances derived from the microwave (MW) and electron diffraction (ED) studies agree very well but show a significant deviation from the values obtained from the x-ray (XR) investigation. This shrinkage of about 2% in the solid phase has been observed for several carboranes[12,13] and might be caused by crystal packing forces. The accuracy of the B–H bond lengths is much higher than those for the diffraction methods. Diborane, B_2H_6, is the only other boron hydride whose structure has been measured in the gas phase[14] and the structure parameters obtained are given for comparison: B–B = 1.775 ± 0.004 Å, B–H_t = 1.196 ± 0.008 Å, B–H_μ = 1.339 ± 0.006 Å.

Discussion

The positions of the bridge hydrogens were calculated from numerous spectra, but the standard deviation of their coordinates is anomalously large, even though there is no close-to-the-axis-atom involved. The error within each subset of coordinates is an order of magnitude smaller than the scatter among the sets. Furthermore, the coordinates obtained for H_6, H_7, and H_8 with one reference species agree amazingly well (cf. Table VIIb). Inspection of the sensitivity of the coordinates on changes in the rotational constants indicates that the deviations from the mean values were biggest in those cases where the coordinates had a large dependence on the *C* rotational constants. This behavior indicates a different zero point vibrational contribution to the *C* rotational constants for the bridge-substituted isotopes.

For a rigid symmetric molecule, the moment of inertia along the symmetry axis, I_z, is related to the moment of inertia of the asymmetric singly substituted species by the expression[9]

$$I_z = I_z' + I_x' - I_y' \tag{1}$$

where the primed quantities refer to the asymmetric molecule. This relation also holds for symmetrically doubly substituted species. Table IX shows the results obtained from calculations of the *C* rotational constant of the N species by using eight different sets of isotopes. The values obtained from the singly bridge hydrogen substituted species D1 and D2 lie about 5.5 MHz above the value derived from the other isotopes. The doubly bridge substituted species gives a deviation twice this amount. The latter fact indicates that the motions of the bridge hydrogens are responsible for this large deviation.

Assuming that any motion of the bridge hydrogens would be reduced in the deuterated species, we recalculated the bridge positions by assuming a linear correction δ for the C constants. Hence, 4δ, 3δ, or 2δ has been added to the *C* constants of the

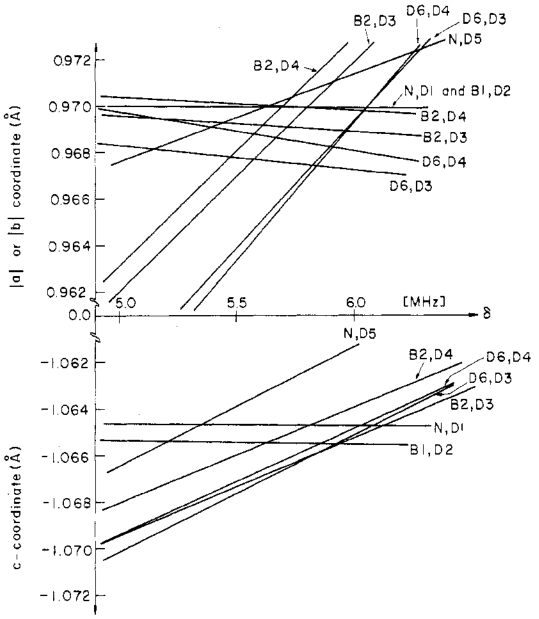

Figure 2. Large amplitude vibrational effect in B_5H_9.

B_5H_9, all the μ-DB_5H_8, and all the μ-$D_2B_5H_7$ species, respectively. In Figure 2, the $|a|$ and $|b|$ and c coordinates of the bridge hydrogen determined from the various isotopes are plotted as a function of the value of δ. Only a small portion of the total curve is depicted. The values of $|a|$ and $|b|$ can be plotted on the same graph since $|a| = |b|$ in the equilibrium positions for C_{4v} symmetry. Each line is labeled by the species used to determine the coordinates. A clear convergence of the coordinates occurs for $\delta = 5.8$ MHz, giving $|a| = |b| = 0.9688 \pm 0.004$ Å and $c = -1.0653 \pm 0.005$ Å. Because the values given in Table VI are much less sensitive to an equal shift of all C constants, these coordinates have been used together with the H_μ coordinates above to give $B-H_\mu = 1.352 \pm 0.004$ Å.

As has been pointed out by Poynter and Beaudet[15] and later by Kuczkowski, Gillies, and Gallaher[16] a large error of the calculated structure can arise when Kraitchman's equations are applied to near symmetric top molecules and when large rotations of the principal axes occur upon substitution. Small vibrational contributions which do not completely cancel in the structural calculation can be "amplified" by the Kraitchman procedure thus leading to large deviations in the r_s values. However, in the case of pentaborane the inconsistency of the calculated coordinates originates not from an amplification of normal size vibrational contributions. In fact, the errors given in Table VII are proportional to this "amplification" effect. To obtain the effect on the b coordinate originating from uncancelled vibrational effects of ± 0.005 μÅ^2, the errors given must be multiplied by about 20. Also, the substitution "defect" of $\delta \sim 5.8$ MHz obtained from Figure 2 (where of course any amplification would be included) is much bigger than usually observed. This is also supported by the results of Table IX.

Table IX. Calculation of the C Rotational Constant of the Normal Species

Species	C, MHz	Dev from av of B2, D9, B4, D8, B3 value (MHz)
B2	4889.28 ± 0.02	0.12
D1	4894.87 ± 0.05	5.71
D9	4889.23 ± 0.05	0.07
B4	4889.08 ± 0.03	−0.08
D8	4889.18 ± 0.04	0.02
D2	4894.54 ± 0.04	5.38
B3	4889.01 ± 0.02	−0.15
D5	4900.02 ± 0.03	10.86

Hence, the very large H–D substitution effect of several megahertz cannot originate from a normal vibration and suggests the existence of a large amplitude motion for the bridge hydrogens. In that case, a precise location of these hydrogens might be more problematic. A systematic investigation of vibrational satellites, which has not yet been done, should help clarify this question. However to reduce the complexity of the spectrum an all ^{10}B or all ^{11}B sample is necessary.

Supplementary Material Available: Table V, measured transitions of asymmetric species (3 pages). Ordering information is given on any current masthead page.

Registry No. B_5H_9, 19624-22-7.

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$$|a_s^*| - |a_s| = \frac{a_s}{2}\left\{\frac{\delta a}{P_a' - P_a} + \frac{\delta b}{P_b' - P_a} + \frac{\delta c}{P_c' - P_a}\right\}$$