We have made a calculation on the reduced complex with parameters comparable to set IV; the charge distributions for oxidized and reduced species are given in Table VII. The observed trends are qualitatively in agreement with this model. Donation from the ligands to the iron dσ orbitals decreases by about 0.35 electron upon reduction, while π back donation onto the ligand increases by 0.37 electron (see Table VII; if the extra electron had gone entirely into an iron dπ orbital, the Fe(t_{2g}) population would have been 6.08. The difference between this and the actual value of 5.71 represents the increase in π back-donation). The net increase in charge assigned to iron is 0.21 electron. This is in general agreement with the small difference in Mössbauer isomer shift between the oxidized and reduced complex.[41] We plan to analyze the calculated charge densities at iron for a variety of iron complexes in a separate publication. Qualitatively, our results are in agreement with earlier Xα calculations in predicting the difference in Mössbauer isomer shift for this pair to be much less than is usual for comparisons of (formally) Fe(II) and Fe(III) species.

This comparison and the other results of the present work suggest that the Xα multiple-scattering method is quite successful in predicting the nature of the bonding and spin distributions in transition-metal complexes and that more work will be required to achieve reliable predictions of charge-transfer excited states. The errors in the latter arise not only from the use of a muffin-tin potential but also from intrinsic errors in the Xα exchange-correlation potential.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research and to the National Resource for Computation in Chemistry, administered by NSF and the Basic Energy Sciences Division of DOE, for a grant of computer time.

Registry No. $Fe(CN)_6^{3-}$, 13408-62-3; $Li_3[Fe(CN)_6]$, 13601-17-7; $Fe(CN)_6^{4-}$, 13408-63-4.

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Microwave Spectrum, Structure, and Dipole Moment of Tetraborane(10), B_4H_{10}

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The microwave spectrum of B_4H_{10} has been detected and assigned between 26.5 and 40 GHz. Transitions observed are consistent with a nearly prolate rotor of C_{2v} symmetry in which the molecular dipole moment is oriented along the c axis. Rotational constants have been determined for four isotopic species from which the following structural parameters have been derived: B_1–B_2 = 1.854 ± 0.002, B_1–B_3 = 1.718 ± 0.002, B_2–B_4 = 2.806 ± 0.001, B_1–H_μ = 1.428 ± 0.02, and B_2–H_μ = 1.425 ± 0.02 Å. The large uncertainties in the B–H_μ bond lengths arise from a poorly determined r_c coordinate for the bridge hydrogen atoms. There is evidence that these hydrogen atoms may undergo large amplitude vibrational motions. The dipole moment has been determined as μ = 0.486 ± 0.002 D from Stark shift measurements.

Introduction

First produced and characterized by Stock and Massenez[1] in 1912 tetraborane(10), B_4H_{10}, is the simplest known example of an arachno borane, yet no accurate determination of the gas-phase structure has been made. X-ray crystallographic studies by Nordman and Lipscomb[2] showed that its structure was based on a "folded-diamond" framework of boron atoms (see Figure 1) and not a butane-like arrangement as had been previously proposed.[3] This result was also confirmed by Jones, Hedberg, and Schomaker in a contemporary study using electron diffraction techniques.[4] In both studies, however, the bridge hydrogen atom positions were not accurately determined.

Recently in this laboratory we have been interested in the nature and properties of multicentered bonds in which hydrogen atoms take up bridging positions and have used microwave spectroscopy to study them. Because of the key position of tetraborane in the borane family, together with the knowledge that significant differences in structure have been found between solid and gaseous states of a few carboranes,[5,6] we have undertaken an accurate determination of the gas-phase structure by microwave spectroscopy.

Little change was found in the structure of the boron atom framework in going from solid to gas phase, showing that the basic shape of the molecule is not greatly affected by crystal packing forces. In contrast the four hydrogen atoms which bridge the edges of the boron frame seem to undergo large vibrational motions. The X-ray and microwave B–H_μ bond lengths are quite different; however, it was the difficulty in determining the c coordinate of the hydrogen atoms that suggested unusual behavior of the bridge structure.

Experimental Section

Tetraborane(10), B_4H_{10}, was obtained from diborane(6), B_2H_6, stored in a steel cylinder at 25 °C and 5–10 atm pressure. Under such conditions tetraborane is formed in about 4 mol % steady-state concentration, while the pentaboranes are virtually absent.[7] Purification was accomplished by fractional condensation under high vacuum. Isotopically labeled μ-B_4H_9D was prepared by cleavage of pentaborane(11) with D_2O.[8] This reaction is very specific in placing a deuterium atom in only one of the bridge positions of tetraborane, although care must be taken to prevent subsequent *intramolecular* scrambling to terminal positions[9] by keeping the samples at low temperatures. All samples of tetraborane (both deuterated and nondeuterated) were stored at liquid-nitrogen temperatures when not in use.

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Table I. Measured Transition Frequencies (MHz) of Tetraborane

transition	normal		$^{10}B_1$		$^{10}B_2$		D_u	
	ν_{obsd}	$\nu_{obsd} - \nu_{calcd}$	ν_{obsd}	$\nu_{obsd} - \nu_{calcd}$	ν_{obsd}	$\nu_{obsd} - \nu_{calcd}$	ν_{obsd}	$\nu_{obsd} - \nu_{calcd}$
$2_{11} \leftarrow 1_{01}$	29 609.35	0.05	29 894.70	0.08	30 160.43	0.01	28 858.02	0.03
$2_{20} \leftarrow 1_{10}$	38 686.59	0.07	39 430.31	0.00	38 949.41	−0.07	37 327.23	−0.78
$2_{21} \leftarrow 1_{11}$	39 238.56	−0.12	39 960.38	−0.08	39 536.00	0.06	37 944.21	0.75
$4_{40} \leftarrow 4_{32}$	35 732.58	0.02					34 079.22	−0.04
$4_{41} \leftarrow 4_{31}$	35 711.71	0.08					34 045.69	−0.01
$5_{41} \leftarrow 5_{33}$	35 697.90	−0.06	37 137.64	0.01	34 944.83	0.01	34 039.88	0.04
$5_{42} \leftarrow 5_{32}$	35 614.35	0.03	37 070.80	0.05	34 837.57	−0.02	33 905.98	0.03
$6_{42} \leftarrow 6_{34}$	35 665.28	−0.06	37 103.67	−0.04	34 914.80	0.00	34 014.53	−0.02
$6_{43} \leftarrow 6_{33}$					34 595.59	0.02	33 617.00	0.06
$7_{43} \leftarrow 7_{35}$	35 662.42	−0.02	37 089.39	−0.01	34 928.91	0.01	34 050.51	0.00
$7_{44} \leftarrow 7_{34}$	35 046.81	−0.07	36 594.70	−0.09			33 078.10	−0.06
$8_{44} \leftarrow 8_{36}$	35 737.76	0.03	37 132.92	0.05	35 050.03	0.04	34 226.57	−0.08
$8_{45} \leftarrow 8_{35}$	34 416.87	0.05	36 065.97	0.03	33 377.97	−0.05	32 168.39	0.09
$5_{32} \leftarrow 5_{24}$			27 065.85	0.05				
$6_{33} \leftarrow 6_{25}$	26 737.42	−0.01	27 601.04	0.02				
$7_{34} \leftarrow 7_{26}$	27 779.57	0.05	28 499.25	0.02	27 660.89	0.00		
$8_{35} \leftarrow 8_{27}$	29 408.68	0.00	29 904.61	−0.01				
$9_{36} \leftarrow 9_{28}$	31 798.61	0.00	31 975.60	−0.05	32 405.00	0.06		
$10_{37} \leftarrow 10_{29}$	35 099.60	−0.01	34 861.49	0.02	36 247.40	−0.05		

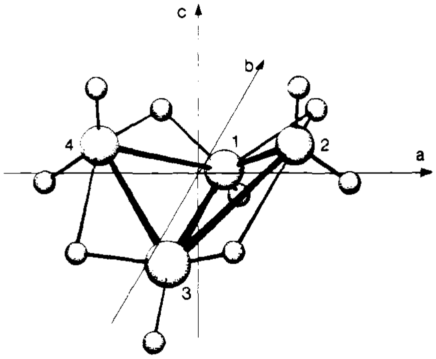

Figure 1. Molecular structure of tetraborane.

Microwave spectra were recorded on a Hewlett-Packard K11-8400B spectrometer and on a home-built 100-kHz Stark modulated spectrometer, both operating in the range 8–40 GHz. All measurements were made with the Stark cells cooled to dry-ice temperatures to reduce sample decomposition and with vapor pressures in the range 0.020–0.070 torr.

Stark effect measurements were made by using a zero-based square wave modulation voltage, and effective electric field strengths were determined by calibration with the $J = 3 \leftarrow 2$ transition of OCS, by assuming a dipole moment of $\mu_{ocs} = 0.71521$ D.[10]

Spectra and Assignment

From the early X-ray structural studies,[2] tetraborane was known to have C_{2v} symmetry, and initial calculations based on this structure showed it to be a prolate asymmetric rotor ($\kappa \simeq -0.74$). The orientation of the principal axes is such that μ_c is the only nonzero dipole moment component, which allows only μ_c-type transitions to be observed in the microwave spectrum. The magnitude of the dipole moment in part determines line intensities, and published work on the dielectric properties of tetraborane solutions[11] indicated that it was small, about 0.5 D; thus the spectrum was not expected to be very intense.

Initial predictions of the form of the microwave spectrum showed it to be sparse in the R-band region (26.5–40 GHz) and composed mainly of Q-type transitions with a few low J R-type transitions interspersed. The preliminary search of the microwave spectrum centered on three $J = 2 \leftarrow 1$ transitions, $2_{11} \leftarrow 1_{01}$, $2_{21} \leftarrow 1_{11}$, and $2_{20} \leftarrow 1_{10}$, which were predicted to have moderate strength and simple Stark lobe structure.

Table II. Rotational Constants (MHz) and Quartic Centrifugal Distortion Constants (kHz) of B_4H_{10} Boron Isotopic Species

const	normal	$^{10}B_1$	$^{10}B_2$
A	11013.388 (19)	11248.386 (15)	11055.969 (17)
B	6198.643 (23)	6215.416 (20)	6368.152 (20)
C	5592.817 (21)	5638.440 (20)	5718.786 (18)
Δ_{JK}	−4.77 (59)	−5.36 (54)	−5.24 (48)
Δ_K	+14.89 (91)	+14.77 (72)	+14.9 (1.0)
δ_K	+4.3 (2.7)	+5.8 (2.7)	+3.9 (2.0)
κ	−0.77647	−0.79430	−0.75666

These three transitions were located and assigned on the basis of their nearness to the predicted positions (within 150 MHz) and their Stark behavior. As expected the lines were broad, about 1.5 MHz full width at half-maximum intensity, due to the presence of unresolved hyperfine components from boron nuclear quadrupole interactions. Such broadening is typical for very low J transitions of boranes and carboranes.

In the rigid rotor approximation the frequencies of these transitions are given by simple algebraic expressions in A, B, and C and may be solved exactly to give experimental values of the rotational constants. Q-branch transitions predicted by using these values were readily located allowing refinement of A, B, and C and determination of three quartic distortion terms[12] (Δ_{JK}, Δ_K, and δ_K) by least-square methods. Insufficient information was available for Δ_J and δ_J to be determined. The measured transition frequencies are given in Table I.

The microwave spectra of the singly substituted boron species $^{10}B_1$ and $^{10}B_2$ were observed in natural abundance (~20%) while the bridge substituted μ-B_4H_9D was specifically synthesized from B_5H_{11} with approximately 90% deuteration. The spectra of all but the deuterated species were well reproduced by the six terms A, B, C, Δ_{JK}, Δ_K, and δ_K, which are given in Table II.

The bridge-deuterated species produced a poorer fit and seemed to indicate incompatibility of the $J = 2 \leftarrow 1$ transitions with the Q-branch lines. From the Q-branch lines alone one obtains values of $A - C$ and the asymmetry parameter κ, and hence the value of $B - C$ is also defined. The separation of the $2_{21} \leftarrow 1_{11}$ and $2_{20} \leftarrow 1_{10}$ lines depends mainly on $B - C$ plus a small A contribution. The value of $B - C$ as determined by the Q-branch lines is larger than that from the $J = 2 \leftarrow 1$ transitions by approximately 1.5 MHz. This disagreement usually showed up as a large error on the $2 \leftarrow 1$ transitions

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Table III. Boron Atom Coordinates (Å)[a]

coordinate	general eq	C_{2v} eq	diff
B_1 r_A	[0.0615][b]	0.0	
r_B	0.8616 (14)	0.8592 (14)	0.0024
r_C	0.4496 (27)	0.4459 (27)	0.0037
B_2 r_A	1.4036 (8)	1.4031 (8)	0.0005
r_B	[0.0380][b]	0.0	
r_C	0.4096 (29)	0.4078 (29)	0.0018

[a] Errors based on $\delta r \approx 0.0012/r$ given by Costain.[14] Conversion factor used was 505 379 amu Å^2 MHz.[16] [b] Imaginary value.

in least-squares refinements using all available lines. Assignments have been carefully checked and all transition frequencies remeasured. It is unlikely that any of the Q-branch lines have been incorrectly assigned since as a group they show good internal consistency and are well reproduced by calculations. On the other hand, the Stark effects and intensity relationships of the three $J = 2 \leftarrow 1$ transitions also appear to be correct.

Hyperfine splittings have been observed on several Q-type lines belonging to the $K_{-1} = 4 \leftarrow 3$ series and get larger with increasing J value. The origin of these splittings is thought to be from quadrupole interactions since the pattern changes between the boron isotopes. In the normal species the gross pattern is an equally spaced 1:2:1 triplet; however there appear to be shoulders on these lines indicating the presence of more than just three components. For the $^{10}B_2$ species this structure is completely lost, and the lines merely get broader with increasing J, while $^{10}B_1$ lines are intermediate with a definite triplet structure but not in a 1:2:1 ratio. The magnitude of the splittings appears to correlate well with the changes in the square of the b and c components of the angular momentum, $\Delta\langle P_b^2\rangle$ and $\Delta\langle P_c^2\rangle$, for the transitions involved, both of which increase rapidly with increasing J value. Hence it is possible that even the small electric quadrupole coupling constants typical of boron nuclei could give rise to significant splittings when combined with large angular-momentum-type terms.

No attempt has been made to account quantitatively for these splittings, since only a few lines are involved and use of the center component for the transition frequency produces good least-squares fits. Quadrupole calculations would involve the interaction of the rotational angular momentum with two pairs of boron nuclei of spin $^3/_2$, both with similar coupling—the resulting detailed hyperfine structure is expected to be very complex.

Q-branch transitions of the above type were not identified for the μ-B_4H_9D species and so are not the source of the anomalies found in the analysis of the microwave spectrum of this species.

Molecular Structure

The molecular structure of the boron atom framework and the bridging hydrogen atoms around the edge of this framework can be determined from the experimental results obtained by using Kraitchman's equations.[13]

Initially, the boron atom coordinates were calculated by using Kraitchman's equations for the general asymmetric rotor without assuming C_{2v} symmetry. The resulting coordinates were so close to C_{2v} symmetry (see Table III) that they were recalculated from a simplified set of equations which incorporated this symmetry. The changes in the nonzero coordinates were no greater than 0.004 Å.

Because of the difficulties encountered with fitting the microwave spectrum of the bridge deuterated species, μ-B_4H_9D, two sets of rotational constants have been used to calculate the coordinates of the bridging hydrogen atom: the first calculated from the three $J = 2 \leftarrow 1$ transitions with use of the rigid rotor approximation and the second from a least-square refinement using all observed transitions. The resulting coordinates are given in Table IV.

Table IV. Rotational Constants (MHz) and Quartic Centrifugal Distortion Constants (kHz) of μ-B_4H_9D

const	rigid rotor[a]	LS refinement
A	10621.826	10621.95 (19)
B	6078.731	6078.70 (17)
C	5389.033	5390.91 (20)
Δ_{JK}		−2.6 (10)
Δ_K		+76 (14)
δ_K		[4.0][b]

[a] Using only $J = 2 \leftarrow 1$ transitions—exact solution. [b] Assumed value.

Table V. Bridge Hydrogen Atom Coordinates (Å)

coordinate	a	b	difference
r_A	1.2675 (79)	1.2615 (79)	0.0060
r_B	1.3663 (73)	1.3582 (73)	0.0081
r_C	[0.2714][c]	[0.2304][c]	[0.0410][c]

[a] Using rotational constants for μ-B_4H_9D derived from $J = 2 \leftarrow 1$ transitions only. [b] Using rotational constants for μ-B_4H_9D derived from the least-square refinement method using all transitions. The conversion factor used was 505 379 amu Å^2 MHz.[16] [c] Imaginary value.

Table VI. Molecular Structure of Tetraborane

parameter	this work[a]	X-ray[b]
B_1–B_2, Å	1.854 (2)	1.842 (6)
B_2–B_4, Å	2.806 (1)	2.800
B_1–B_3, Å	1.718 (2)	1.712
B_1–H_μ, Å	1.428 (20)	1.16 (3)
B_2–H_μ, Å	1.425 (20)	1.37 (6)
angle between boron planes, deg	117.4 (3)	118.3

[a] B–H_μ bond lengths calculated by using $r_c(H_\mu) = 0.0 \pm 0.1$ Å. [b] See ref 17.

The consistency of the bridge hydrogen coordinates is pleasing; however the c coordinate turns out to be imaginary with either approach. Ordinarily such a result indicates that the coordinate in question is near to zero, but the magnitude of the calculated value in this case is greater than one might have expected. The usual reason for imaginary coordinates being generated is that vibrational contributions to the moments of inertia of the normal and substituted species differ, and since near-zero coordinates depend upon measuring small differences in relatively large moments of inertia, the vibrational effects dominate. The size of the c coordinate would suggest that deuteration causes large changes in vibrational contributions, perhaps indicating that the bridge hydrogen atoms undergo large-amplitude vibrations.

Uncertainties in the boron atom coordinates given in Table III are based upon an empirical relationship suggested by Costain[14] where the reliability of a coordinate obtained by the substitution method is $\delta r \approx 0.0012/r$ Å. Because of the large uncertainty in the values of the rotational constants for μ-B_4H_9D, this estimate was considered inappropriate for the hydrogen coordinates. A propagation of errors calculation, based on the experimental uncertainties in the rotational constants, shows that the reliability of these coordinates is better estimated as $\delta r \approx 0.010/r$ Å. This expression was used to calculate the error limits given in Table V.

The bond lengths and bond angles derived from these coordinates are given in Table VI and are compared with the

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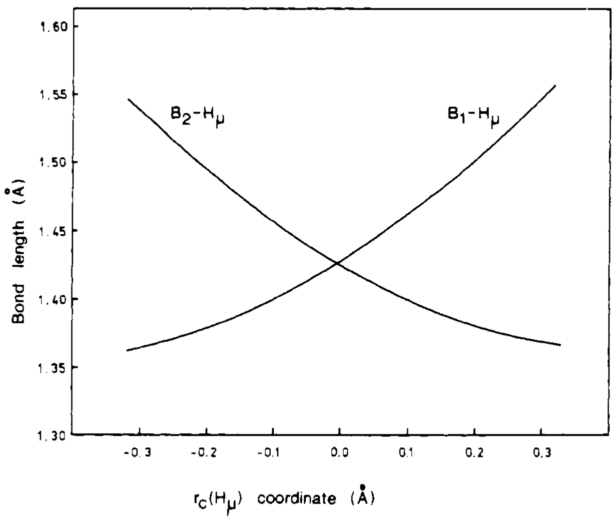

Figure 2. Calculated variation of B-H_μ bond lengths with $r_c(H_\mu)$ coordinate.

X-ray structure published by Nordman and Lipscomb.[2] Calculating reliable values for the boron-bridge hydrogen bond lengths presents some difficulties since the $r_c(H_\mu)$ coordinate appears anomalous. Instead, values of these bond lengths have been calculated as a function of $r_c(H_\mu)$, keeping the remaining coordinates fixed, and are shown graphically in Figure 2. The $r(B-H_\mu)$ bond lengths given in Table VI are calculated at $r_c(H_\mu) = 0$; assuming a nominal error of ±0.1 Å for this coordinate results in bond length uncertainties of ±0.02 Å.

Dipole Moment

The dipole moment was determined from the measured Stark shifts of the $2_{11} \leftarrow 1_{01}$ and $2_{21} \leftarrow 1_{11}$ transitions. The Strark coefficients of the $|M| = 1$ components were calculated as 3.317 ± 0.019 and $2.761 \pm 0.016 \times 10^{-6}$ MHz cm^2/V^2, respectively, yielding dipole moments of $\mu = 0.487 \pm 0.002$ and 0.486 ± 0.002 D. The average value of the dipole moment from these measurements is $\mu = 0.486 \pm 0.002$ D. Standard propagation of errors methods were used to estimate the quoted uncertainties.

Discussion

The agreement between the microwave and X-ray structure of the boron atom framework is remarkably good, with the X-ray structure approximately 0.5% smaller. This compares with other carboranes[6] and boranes[5] where differences are generally about 2%.

Boron-bridge hydrogen bond lengths differ between the two determinations, but this is understandable given the poor reliability of X-ray methods for locating hydrogen atoms. The greatest uncertainty in the microwave structure determination is in the bridge hydrogen *c* coordinate since this is most sensitive to slight changes in the moments of inertia.

The variation of the boron-bridge hydrogen distances with this coordinate, graphed in Figure 2, shows that a symmetrical bridge occurs when $r_c(H_\mu)$ is practically zero, resulting in a bond length of 1.426 Å. In this configuration the bridging hydrogen atoms are not coplanar with the $B_1B_2B_3$ or $B_1B_3B_4$ boron atom planes to which they are attached (see Figure 1) but are displaced to the convex side of the framework. It is very unlikely that the bridge hydrogen atoms are coplanar with the boron planes since this would require the $r_c(H_\mu)$ coordinate to be about 0.32 Å, at which point Kraitchman's equations should not break down to produce imaginary values. A coplanar arrangement would also require the B_1-H_μ bond length to be unusually long (~1.56 Å) for a bridging hydrogen atom.

Pentaborane(9), B_5H_9, is the only other boron hydride whose bridge hydrogen structure has been determined by microwave spectroscopy,[5] and this too presented problems when attempts were made to calculate the bridge hydrogen positions. Essentially it was found that upon deuteration a correction to the *C* constant of about 5.8 MHz per bridge deuterium was required to offset changes in vibration contributions to the moments of inertia and make all sets of data consistent.

In tetraborane it is not clear which rotational constant would be most sensitive to such vibrational effects nor how much correction would be needed; however, by analogy with the pentaborane(9) structure it may be the *C* constant. A change of 5 MHz in either *B* or *C* would be sufficient to change $r_c(H_\mu)$ from a relatively large imaginary value to a small real value.

One technique which goes some way toward eliminating such effects is the method of double substitution developed by Pierce[15] whereby second differences in the moments of inertia are used to calculate coordinates. Unfortunately, twice as much isotopic substitution data is required along with high accuracy of the determined rotational constants. Even in the most favorable substitution cases for tetraborane the accuracy requirements turn out to be greater than the experimental uncertainties so far found; hence the use of this method would seem to be ruled out.

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Registry No. B_4H_{10}, 18283-93-7; μ-B_4H_9D, 37474-12-7; $^{10}B_1$-B_4H_{10}, 75600-17-8; $^{10}B_2$-B_4H_{10}, 75600-18-9.

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