complex, the phospholes are not bulky, and a small degree of distortion of the complex toward tetrahedral geometry occurs. In the latter complex, the phosphole is significantly larger, and this gives rise to a larger amount of tetrahedral distortion and forces one of the thiocyanates to become N bound. The second thiocyanate, which remains S bound, is bent away from the phosphole toward the N-bound thiocyanate.

This leads us to the following conclusions. For linear complexes[22] such as LAu(CNS) where steric effects are unimportant, the thiocyanate bonding mode is determined by electronic effects. Burmeister[22] has recently studied a series of $(R_3P)Au(CNS)$ complexes and found them to be S bound in the solid state. In 1,2-dichloroethane, some of the N-bound isomer is present, varying from 13.4% for $[Au(P(OC_6H_{83})$-SCN] to 4.9% for $[Au(P(C_6H_8)_3SCN]$. Apparently the electronic influence on bonding mode, while operational, is small in magnitude, since a large change in the nature of the trans ligand brings only a small change in bonding mode. For square-planar complexes, electronic effects play a very important part in determining the coordination geometry as well as the thiocyanate bonding mode in $(R_3P)_2Pd(CNS)_2$ complexes. They favor the cis coordination geometry and the S-bonding mode. Steric effects are the discriminator for both of these structural features only when they are large in magnitude. When the steric effects are moderate, the coordination geometry will be cis, and as ligand bulk increases, first one and then the second thiocyanate will become N bound to accommodate this increasing steric demand. Then, as steric effects increase even further the coordination geometry will switch to trans and the thiocyanate will be S bound. With the largest steric effects the trans N-bound complexes will result. Bond distances and angles within any given complex will result from maximized electronic stability and minimized steric interactions. Further, it seems that the electronic effects are σ bonding in nature, and π bonding is not necessary to rationalize the observed structures. It also seems that the thiocyanate bonding mode is more responsive to small steric changes than is the coordination geometry. Additional structural data that will further test these ideas are currently being obtained.

For the title complex, it could be argued that because the two phospholes have different bond lengths to palladium, their electronic trans influences would determine the different thiocyanate bonding modes. In light of the results with the LAu(CNS)complexes, it is more likely that the different Pd–P bond lengths are a consequence of the different trans influences of thiocyanate and isothiocyanate.

There is one other structural feature of note for this complex. The ortho hydrogen H(212) of the phenyl ring on phosphole 2 essentially occupies the fifth coordination position, being situated 2.70 Å from palladium. This position is along the trajectory for orthometalation and perhaps for this complex orthometalation would be a low-energy process in the solid state.

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Registry No. *cis*-Pd(1-phenyl-3,4-dimethylphosphole)$_2$(SCN)(NCS), 73193-79-0.

Supplementary Material Available: Listings of temperature factors and observed and calculated structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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Molecular Structure Determination of Methyldiborane

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The microwave spectra of ten isotopic species of $B_2H_5CH_3$ were investigated in the region between 18.5 and 40.0 GHz. The complete structure (except the methyl group) was determined from these data by the Kraitchman method: B_1–B_2, 1.82 (2) Å; B_2–H_μ, 1.34 (6) Å; B_1–H_μ, 1.34 (4) Å; B_1–H_6, 1.195 (9) Å; B_1–H_7, 1.187 (5) Å; B_2–H_8, 1.20 (1) Å; H_μ–H_μ, 1.96 (3) Å; B_2–C, 1.49 (10) Å; $\angle B_2B_1H_\mu$, 47 (1)°; $\angle B_1B_2H_\mu$, 47 (1)°; $\angle B_1B_2C$, 120 (1)°. Thus, the B–H_μ–B group appears to be distorted such that the H_μ is displaced toward the methyl group.

Introduction

Bridge hydrogens in boron hydrides and carboranes present interesting structural problems. Strong evidence has been obtained for the existence of a face-centered bridge hydrogen in CB_5H_7.[1] More recently, a microwave study of hexaborane(10), B_6H_{10},[2] has indicated an anomalous behavior of bridge hydrogens. Line splittings in the spectrum are dependent on hydrogen substitution. However, there are not sufficient data to determine uniquely the origin of these line splittings. The separations are too large to be due to electron nuclear quadrupole effects from the boron nuclei. Similar line splittings have been found in tetraborane(10),[3] B_4H_{10}, and pentaborane(9), B_5H_9.[4] In an attempt to add more data to these problems, we have undertaken a complete structural investigation of some simpler boron hydrides by microwave spectroscopy. The present purpose was to study the effect of terminal hydrogen substitution on the symmetry of the bridge hydrogen bonds by determining the structure of methyldiborane.

The structures of diborane and a few substituted derivatives have been studied by various techniques. Although the proton bridge structure was first confirmed by IR spectroscopy,[5-7]

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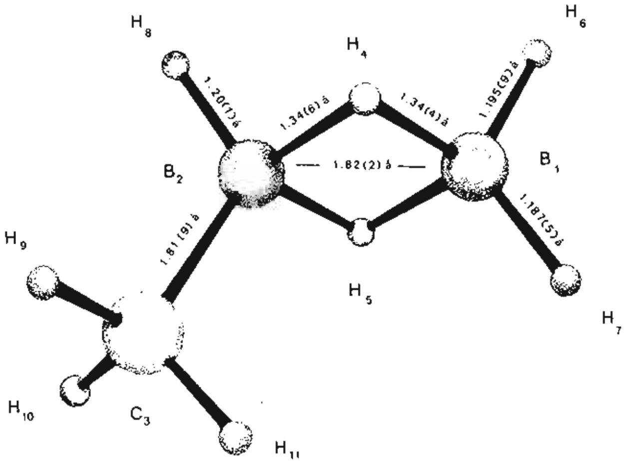

Figure 1. Molecular structure of methyldiborane.

the correct accurate molecular structure was obtained by electron diffraction.[8] The proton bridge structure was also confirmed by the microwave study of bromodiborane, B_2H_5Br.[9] In a more accurate structural study of B_2H_5Br carried out by Ferguson and Cornwell,[10] the spectra of the ^{10}B and the perdeuterated species were obtained. However, although insufficient data were available to determine all the proton positions, it was indicated that bromine substitution had no effect on the $B-H_\mu-B$ group, for the B–B bond length was identical with that in diborane.

An earlier study of the boron isotopic and the perdeuterated species of methyldiborane ($B_2H_5CH_3$) was carried out by Penn.[11]

For a more thorough study, we now have obtained the spectra of five mono- and two dideuterated species of $B_2H_5CH_3$. Also, we have measured the $J = 3 \leftarrow 2$ transitions of the species previously studied. From these data and Penn's results, we have determined the molecular structure of the boron and hydrogen framework. Since no ^{13}C isotopically enriched species have been prepared, the exact structure of the methyl group could not be calculated, but an approximate structure has been obtained by fitting the position of the methyl group to the moments of inertia and center-of-mass condition. The structure of $B_2H_5CH_3$ and the atom designation of the normal species are shown in Figure 1. Unfortunately, the central boron atom is situated very close to the b principal axis. Pierce's[12] second-difference method was used to obtain this b coordinate. However, a careful error analysis indicates that Penn's reasonable value was fortuitous. Since the central boron atom cannot be accurately located, the structure of the $B-H_\mu-B$ moiety cannot be determined as accurately as desired; however, the methyl group substitution seems to have no effect on the $B-H_\mu-B$ group.

Experimental Section

Methyldiborane, $B_2H_5CH_3$, was prepared by the reaction of excess diborane with trimethylboron (5:1) for 12 h[13] at room temperature. It was purified by high-vacuum fractional condensation. The deuterated species of $B_2H_5CH_3$ were prepared by using normal diborane, deuterated diborane, and trimethylboron in 2:4:1 ratio. All the samples were stored at liquid nitrogen temperature to prevent any decomposition.

Table I. Relative Abundance of Isotopic Species of $B_2H_5CH_3$ Whose Spectra Have Been Determined[a]

species	substituted atoms	rel isotopic abundance
normal	normal isotope	1.00
^{10}B	$^{10}B_1$	0.25
	$^{10}B_2$	0.25
	$^{10}B_1$, $^{10}B_2$	0.06
deuterated	$^{10}B_2$, D_μ	0.25
	D_μ	1.00
	D_6	0.50
	D_7	0.50
	D_8	0.50
	D_μ, D_μ	0.25
	D_μ, D_8	0.25

[a] The relative abundance in each sample is statistically estimated.

The microwave spectra were recorded between 18.0 and 26.5 GHz on a Hewlett-Packard 8460A MMR spectrometer and between 26.5 and 40 GHz on a Hewlett-Packard KII-8400B spectrometer, both Stark modulated at 33 kHz. All the spectra were observed at dry ice temperature between 0.02 and 0.08 mm of pressure. The millimeter wave spectra were recorded by using a millimeter wave Oki 90V10 klystron phase locked to the 11th harmonic of an X-band backward wave oscillator.

Spectra and Assignment

As has been shown by previous investigations,[11] methyldiborane is a slightly asymmetric prolate rotor with a total dipole moment of 0.56 D. Because the b dipole moment is very small, only μ_a-type transitions were observed. The boron framework has been determined from two low-J transitions, $J = 1 \leftarrow 0$ and $J = 2 \leftarrow 1$, by Penn. However, the investigation of the rotational spectra of the deuterated isotopes is required to determine a complete structure of methyldiborane. In this work, the spectra of the normal species and ten isotopic substituted molecules have been analyzed and used to calculate the structure. Table I gives a list and the abundance of the isotopic species estimated from the known D:H ratio in the starting materials. Complete randomization was assumed.

The calculated spectra of the isotopic species were obtained by assuming a rigid rotor model with no centrifugal distortion. The predicted a-type spectra were composed mainly of strong R-branch and very weak Q-branch transitions.

The line frequencies of the transitions of the isotopic species previously studied by Penn were measured. In the initial microwave search for the deuterated isotopic species, observation of several strong $J = 3 \leftarrow 2$ transitions with simple Stark lobe structures led to the assignment of the deuterated bridge isotope $(\mu\text{-D})B_2H_4CH_3$. The spectra of the singly and doubly substituted isotopes were assigned with little difficulty, although the intensities were about one-fourth as great as for the normal species and the deuterated bridge species. The $J = 2 \leftarrow 1$ transitions were broadened due to unresolvable nuclear quadrupole splittings, which made the measurement of some of these weak lines difficult. The measured frequencies and assignments are given in Table II. All of the observed lines of both series $J = 2 \leftarrow 1$ and $J = 3 \leftarrow 2$ were fitted to a rigid rotor model by the least-squares method to determine the A, B, and C rotational constants. The rotational constants and the moments of inertia are given in Table III.

Since the μ_a-type spectra were insensitive to the A rotational constant, an attempt was made to measure some of the μ_a-type transitions in the millimeter wave region, since they were more dependent on A. However, we were limited to selected regions by the available klystrons.

Several of the $J = 7 \leftarrow 6$ transitions of the normal species were observed. The $7_{07} \leftarrow 6_{06}$ and $7_{25} \leftarrow 6_{24}$ transitions observed were doublets separated by 1 MHz. At first, the

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Table II. Measured Rotational Transition Frequencies of $B_2H_5CH_3$ (MHz)[a]

	substituted atoms							
	normal		$^{10}B_2$		$^{10}B_1$		$^{10}B_1$ and $^{10}B_2$	
transition	ν_{obsd}	Δ	ν_{obsd}	Δ	ν_{obsd}	Δ	ν_{obsd}	Δ
$2_{12} \leftarrow 1_{11}$	25 525.500	−0.217	25 596.945	−0.246	26 342.57	0.07	26 416.32	0.23
$2_{02} \leftarrow 1_{01}$	26 254.534	0.228	26 302.767	0.625	27 112.70	0.04	27 162.05	0.12
$2_{11} \leftarrow 1_{10}$	27 017.07	−0.01	27 039.41	0.22	27 919.88	−0.02	27 941.62	0.06
$3_{13} \leftarrow 2_{12}$	38 227.64	0.14	38 385.60	0.31	39 502.58	−0.06	39 613.47	0.19
$3_{03} \leftarrow 2_{02}$	39 340.97	0.02	39 418.62	−0.42	*b*		*b*	
$3_{22} \leftarrow 2_{21}$	39 407.38	−0.62	39 477.32	−0.08	*b*		*b*	
$3_{21} \leftarrow 2_{20}$	39 472.06	0.28	39 536.50	−0.21	*b*		*b*	
$3_{12} \leftarrow 2_{11}$	*b*		*b*		*b*		*b*	

	substituted atoms							
	$^{10}B_2$ and D_μ		D_μ		D_6		D_7	
transition	ν_{obsd}	Δ	ν_{obsd}	Δ	ν_{obsd}	Δ	ν_{obsd}	Δ
$2_{12} \leftarrow 1_{11}$	25 332.270	0.063	25 262.412	−0.080	24 359.532	−0.021	23 606.381	−0.087
$2_{02} \leftarrow 1_{01}$	25 946.810	0.073	25 899.508	0.076	25 178.098	0.163	24 238.560	0.119
$2_{11} \leftarrow 1_{10}$	26 585.94	0.196	26 563.469	0.200	26 045.053	0.094	24 895.427	−0.039
$3_{13} \leftarrow 2_{12}$	37 990.40	0.45	37 884.92	0.28	36 524.17	0.26	35 401.68	0.23
$3_{03} \leftarrow 2_{02}$	38 889.90	−0.42	38 815.90	−0.03	37 707.41	−0.06	36 327.66	−0.02
$3_{22} \leftarrow 2_{21}$	38 939.2	−0.3	38 870.02	−0.52	37 804.10	−0.61	36 376.75	−0.49
$3_{21} \leftarrow 2_{20}$	38 988.5	0.3	38 923.08	0.05	37 899.58	0.06	36 424.80	0.08
$3_{12} \leftarrow 2_{11}$	39 871.04	0.37	39 836.94	0.09	39 052.27	0.19	37 335.21	0.20

	substituted atoms					
	D_8		D_μ and D_μ		D_μ and D_8	
transition	ν_{obsd}	Δ	ν_{obsd}	Δ	ν_{obsd}	Δ
$2_{12} \leftarrow 1_{11}$	24 855.437	−0.214	25 015.015	−0.02	24 603.50	0.02
$2_{02} \leftarrow 1_{01}$	25 787.399	0.160	25 558.694	0.07	25 441.38	0.15
$2_{11} \leftarrow 1_{10}$	26 788.83	−0.445	26 123.248	0.24	26 337.78	0.17
$3_{13} \leftarrow 2_{12}$	37 262.03	−0.23	37 515.70	0.31	36 887.15	0.18
$3_{03} \leftarrow 2_{02}$	38 596.23	−0.22	38 312.04	−0.04	38 089.50	0.006
$3_{22} \leftarrow 2_{21}$	38 732.96	−0.25	38 354.50	−0.64	38 206.65	0.55
$3_{21} \leftarrow 2_{20}$	38 868.53	0.87	38 395.69	0.04	38 322.64	0.07
$3_{12} \leftarrow 2_{11}$	*b*		39 178.50	0.13	39 488.27	0.08

[a] $\Delta = \nu_{obsd} - \nu_{calcd}$. [b] These transitions are over 40 GHz.

Table III. Rotational Constants and Moments of Inertia of $B_2H_5CH_3$ Isotopic Species (MHz)[c]

isotopic species	A[a]	B[a]	C[a]	I_a	I_b	I_c
$B_2H_5CH_3$[b]	31 992 (109)	6940.74 (12)	6194.85 (10)	15.80 (5)	72.8134 (13)	81.5805 (13)
$^{10}B_2$	33 015 (157)	6940.35 (19)	6218.76 (14)	15.31 (7)	72.8175 (20)	81.2669 (18)
$^{10}B_1$	31 970 (166)	7177.12 (4)	6388.51 (3)	15.81 (8)	70.4153 (4)	79.1075 (4)
$^{10}B_2$ and D_μ	30 351 (132)	6803.26 (8)	6176.36 (8)	16.65 (7)	74.2848 (9)	81.8248 (11)
$^{10}B_1$ and $^{10}B_2$	32 533 (600)	7176.12 (12)	6413.33 (9)	15.53 (29)	70.4251 (12)	78.8014 (11)
D_μ	30 142 (88)	6803.58 (6)	6152.92 (6)	16.77 (5)	74.2813 (7)	82.1365 (8)
D_6	28 430 (52)	6721.99 (7)	5879.17 (7)	17.78 (3)	75.1829 (8)	85.9609 (10)
D_7	31 679 (98)	6384.98 (6)	5740.44 (6)	15.95 (5)	79.1512 (7)	88.03841 (9)
D_8	26 909 (38)	6938.74 (12)	5972.16 (10)	18.78 (3)	72.8344 (13)	84.6225 (14)
D_μ and D_μ	28 388 (125)	6669.44 (7)	6115.19 (7)	17.80 (8)	75.7754 (8)	82.6433 (9)
D_μ and D_8	25 672 (33)	6801.29 (6)	5934.08 (6)	19.69 (3)	74.3064 (6)	85.1656 (8)

[a] Quoted errors are standard deviations from the least-squares fitting process. [b] Rotational constants for the normal species are obtained from least-squares fitting of seven lines (Table II). [c] Conversion factor used: 505 379.05 amu Å^2 MHz.[14]

Table IV. High-Frequency Rotational Transition Frequencies (MHz) of Normal $B_2H_5CH_3$

transition	ν_{obsd}	Δ[a]
$7_{17} \leftarrow 6_{16}$	89 132.10	4.02
$7_{07} \leftarrow 6_{06}$	91 054.32 91 054.85	−1.66
$7_{20} \leftarrow 6_{25}$	91 816.77	4.56
$7_{35} \leftarrow 6_{34}$	92 067.88	4.15
$7_{34} \leftarrow 6_{33}$	92 095.83	4.67
$7_{25} \leftarrow 6_{24}$	92 700.83 92 701.28	16.17

[a] $\Delta = \nu_{obsd} - \nu_{calcd}$.

splittings were thought to be due to internal rotation. However, by use of the torsional barrier, 4.28 (9) kcal/mol, from Penn's

Table V. Atomic Coordinates in the Principal Axis System of Normal $B_2H_5CH_3$[a]

atom	*a*	*b*	*c*
B_2	−0.09 (2)	0.558 (2)	0.0
B_1	1.534 (4)	−0.265 (4)	0.0
H_μ	0.73 (3)	0.16 (10)	0.98 (2)
H_μ	0.73 (3)	0.16 (10)	−0.98 (2)
H_6	1.525 (4)	−1.460 (8)	0.0
H_7	2.537 (3)	0.369 (4)	0.0
H_8	−0.140 (4)	1.754 (7)	0.0
C[b]	−1.34 (10)	−0.26 (10)	0.0

[a] These coordinates of the atoms in the plane of asymmetry were determined by Kraitchman's monosubstituted method for a planar molecule. [b] Errors shown are calculated by assuming the rotational constant given in Table III.

Table VI. Molecular Structure of $B_2H_5CH_3$

	$B_2H_5CH_3$				
	this work[a]	ref 10	BrB_2H_5[d]	$NH_2B_2H_5$[e]	B_2H_6[f]
B_1–B_2, Å	1.82 (2)	1.773 (5)	1.773 (3)	1.916 (2)	1.7628 (26)
B_2–H_μ, Å	1.34 (6)			1.335 (5)	1.3204 (10)
B_1–H_μ, Å	1.34 (4)				
B_1–H_6, Å	1.195 (9)	1.19		1.193 (1)	1.2005 (36)
B_1–H_7, Å	1.187 (5)				
B_2–H_8, Å	1.20 (1)				
B_2–Br, Å			1.930 (5)		
B_2–C, Å	1.49 (10)	1.59			
B_2–N, Å				1.558 (1)	
H_μ–H_μ, Å	1.96 (3)		1.99 (3)		
C–H[c], Å	1.095[b]				
∠$B_2B_1H_\mu$, deg	47 (1)				
∠$B_1B_2H_\mu$, deg	47 (1)				
∠B_1B_2C, deg	120 (1)				

[a] The quoted errors are from errors in Table V. [b] Assumed position of C. [c] Assumed methyl group is tetrahedral. [d] Reference 10. [e] Reference 17. [f] Reference 18.

work and the experimental values of the rotational constants to calculate the difference in energy of the E and A torsional sublevels, no splittings should occur. The origin of the splitting is not clear. Since only a few lines with splitting were observed, it is not certain whether or not these splittings are accidental. The lines of the $J = 7 \leftarrow 6$ transition which were unsplit were included in the overall least-squares fit to obtain the centrifugal distortion constant, $D_{JK} = 5.728 \times 10^{-5}$. The values of the A rotational constant obtained differ greatly (360 MHz) from those obtained by fitting only the low-J lines, but the B and C constants agreed fairly well. The frequencies of the $J = 7 \leftarrow 6$ lines are given in Table IV.

Molecular Structure

The coordinates of all the hydrogen atoms and the B_1 atom were determined by using the Kraitchman method.[15] The a coordinate of the B_2 atom cannot be calculated by Kraitchman's equation because it is situated very close to the b principal axis. Pierce's second-difference method was used to obtain the a coordinate of the B_2 atom. The position of the bridge hydrogen was calculated by Kraitchman's equation for both singly deuterated species ((μ-D)$CH_3B_2H_4$) and doubly deuterated species ((μ-D_2)$CH_3B_2H_3$). The center of mass of the methyl group was located by fitting to the center of mass condition $\sum_i m_i q_i = 0$ ($i = a, b, c$). The coordinates of the methyl atoms were then estimated by assuming the methyl group to have C_{3v} symmetry with $r(\text{C–H}) = 1.095$ Å and ∠HCH = 107.7°.

Planar symmetry of the molecule was assumed in the calculation of all coordinates, except those of the bridge hydrogens. In the Kraitchman method, the coordinates of the nucleus in the principal axis frame were calculated from the differences in the moment of inertia that arise when an isotopic substitution is made at that nucleus. This method required ΔI_a, ΔI_b, and ΔI_c for asymmetric molecules. Since I_a is not accurately determined for this molecule, ΔI_a was calculated from the expression $\Delta I_a = \Delta I_c - \Delta I_b$ for species substituted in the plane of symmetry. For substitution at the bridge hydrogen position, this was not possible, so I_a had to be used. Hence, the errors in the H_μ coordinates are larger than normally expected. The signs of all the coordinates were chosen to be consistent with the mass condition $\sum_i m_i q_i = 0$ ($i = a, b, c$) and the products of inertia $\sum_i m_i p_i q_i = 0$.

The calculated coordinates of the molecule are given in Table V. The quoted errors are correlated errors which reflect the dependence of the coordinates on each rotational constant, including the large errors in A when it was used. The errors are calculated by using the standard deviations of the rotational constants in Table II. The errors calculated by this method are much larger than those calculated by using the empirical relationship suggested by Costain.[16] The bond lengths and bond angles derived from the coordinates are tabulated in Table VI. The structure of other derivatives of methyldiborane are given for comparison. The errors quoted in Table VI are obtained by calculating the propagation of errors, including the correlation term.

Internal Rotation

Penn observed vibrational satellites that he assigned to be "$v = 1$" and "$v = 2$" excited vibrational states. Splittings due to methyl group internal rotation were observed for "$v = 2$" transitions, but not for the "$v = 1$" transitions. For the 3-fold barrier height, V_3 there is a discrepancy between Penn's reported value of 4.28 (9) kcal/mol and the assumed value of *trans*-1,2-dimethyldiborane,[19] 2 (1) kcal/mol. Due to the similarity of the structure of these molecules, there should not be such a large difference for the barrier height. Also, one would estimate the barrier height in methyldiborane to be similar to that in propylenes, ~2 kcal/mol, because the diborane and the ethylene frameworks both have C_2 symmetry. Also, the discrepancy in the value of the rotation-vibration interaction constant, α, obtained from the expression $B_v = B_e - (v + {}^1/_2)\alpha$ calculated from the "$v = 1$" and "$v = 2$" states are unusually large: 9.6 and 6.3, respectively.

In this work, we observed splittings for both the "$v = 1$" and "$v = 2$" transitions. Since a similar splitting is not observed for the $v = 0$ ground-state level, the splitting is not due to the boron nuclear quadrupole interaction. On the other hand, if these two satellites are both $v = 1$ levels of two different normal modes, both sets cannot be the torsional mode. Attempts to measure the satellites of the $J = 2 \rightarrow 3$ transition were unsuccessful due to the accidental overlaps of other transitions in each case. So, unambiguous assignments were not possible. From the observed splittings for the "$v = 1$" transition, the barrier height was estimated to be 2.5 (5) kcal/mol. This value seems to be more reasonable for this case.

Discussion

The positions of the bridge hydrogens were calculated by using both singly ((μ-D)$CH_3B_2H_4$) and doubly ((μ-D_2)-$CH_3B_2H_3$) deuterated species. The results from both sets agree very well. Unfortunately, the structure determination is limited by the accuracy of the a coordinate of B_2. The Pierce sec-

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ond-difference method is not capable of locating this coordinate very well since the $\Delta\Delta I$ value is too dependent on small errors in the rotational constant measurements. The accuracy of these results then does not appear to show any distortion of the $B-H_\mu-B$ moiety by the substitution of the methyl group.

Comparison of $r(B_1-B_2)$ with similar molecules in Table VI does indicate that this bond length in methyldiborane is longer than it is in similar molecules. If the B-B bond length is set at 1.77 Å by displacing B_2 along the *a* axis, then its *a* coordinate becomes −0.04 Å. With use of this value for the *a* coordinate of B_2, the B_2-H_μ bond length is reduced to 1.31 Å. A determination of $r(C-B_2)$ by electron diffraction and a reanalysis of the combined microwave and electron diffraction data would elucidate this structure.

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Registry No. $CH_3B_2H_5$, 23777-55-1; $(^{10}B_1)CH_3B_2H_5$, 80082-37-7; $(^{10}B_2)CH_3B_2H_5$, 80082-38-8; $(^{10}B_1,^{10}B_2)CH_3B_2H_5$, 80082-39-9; $(^{10}B_2,D_\mu)CH_3B_2H_5$, 80082-40-2; $(D_\mu)CH_3B_2H_5$, 80106-01-0; $(D_6)CH_3B_2H_5$, 80082-41-3; $(D_7)CH_3B_2H_5$, 80082-42-4; $(C_8)CH_3B_2H_5$, 80082-43-5; $(D_\mu,D_\mu)CH_3B_2H_5$, 80082-44-6; $(D_\mu,D_8)CH_3B_2H_5$, 80082-45-7.

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Molecular Stereochemistry of a Low-Spin Five-Coordinate Iron(II) Porphyrinate. (Thiocarbonyl)(octaethylporphinato)iron(II)

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The molecular stereochemistry of the low-spin five-coordinate (porphinato)iron(II) complex (thiocarbonyl)(octaethylporphinato)iron(II) has been determined by X-ray diffraction methods. The molecule crystallizes as the toluene solvate in the triclinic system, space group $P\bar{1}$. The unit cell has a = 12.396 (3) Å, b = 15.393 (3) Å, c = 10.726 (2) Å, α = 93.08 (1)°, β = 98.62 (2)°, γ = 75.53 (1)°, and Z = 2. Diffraction data were collected by the $\theta-2\theta$ scan technique, and a total of 6919 unique observed reflections were used in refinement of the structure. The final values of the discrepancy indices are R_1 = 0.070 and R_2 = 0.092. The Fe-C-S group is essentially linear. The FeC(CS) distance is 1.662 (3) Å, and the average Fe-N distance is 1.982 (5) Å. The low-spin iron(II) atom is displaced by 0.23 Å from the mean plane of the porphinato core.

We and others have been investigating the structures of iron porphyrinate derivatives with the view of completely establishing the spin-state/stereochemical relationships of these species.[1] In the iron(II) and iron(III) derivatives, variation in the nature and number of axial ligands allows the isolation of all possible spin states, (for iron(II) these are low spin (S = 0), intermediate spin (S = 1), and high spin (S = 2)). Most of the experimentally accessible possibilities have now been adequately characterized structurally. A possible exception is the low-spin five-coordinate porphinato complexes of iron(II). The only structurally characterized species, Fe(TPP)(NO),[2,3] suffers from possible ambiguity in the oxidation state of iron and in any event has an electronic structure that is unusual for an iron(II) species. (This molecule has an S = $^1/_2$ spin state owing to the odd electron originally on the NO ligand.)

Other ligands that can lead to low-spin five-coordinate (porphinato)iron(II) species include CO,[4] CS,[5,6] and in special circumstances, isocyanides, phosphines, and phosphites.[7] The preparation of the monocarbonyl complexes in solution has been described. Isolation of the complex is complicated by relatively unfavorable equilibria:[4,8]

$$Fe(P) + CO \rightleftarrows Fe(P)(CO) + CO \rightleftarrows Fe(P)(CO)_2$$

Table I. Summary of Crystal Data and Intensity Collection Parameters for $Fe(OEP)(CS)\cdot C_7H_8$

formula	$FeSN_4C_{44}H_{52}$	α, deg	93.08 (1)
fw, amu	724.8	β, deg	98.62 (2)
crystal dimensions, mm	0.7 × 0.3 × 0.1	γ, deg	75.53 (1)
space group	$P\bar{1}$	V, Å^3	1959.2
temp, K	293	Z	2
a, Å	12.396 (3)	d_{calcd}, g/cm^3	1.229
b, Å	15.393 (3)	d_{obsd}, g/cm^3	1.26
c, Å	10.726 (2)		

radiation	graphite-monochromated Mo Kα (λ = 0.710 73 Å)
scan technique	θ-2θ
scan range	0.55° below Kα_1 to 0.55° above Kα_2
scan rate, deg/min	2-12
bckgrd	equal scan time at extremes of scan
2θ limits, deg	3.5-54.9
criterion for observation	$F_o > 3\sigma(F_o)$
unique obsd data	6919
μ, mm^{-1}	0.468
R_1	0.070
R_2	0.092
goodness of fit	2.691

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(3) Abreviations used: TPP, the dianion of *meso*-tetraphenylporphyrin; OEP, the dianion of octaethylporphyrin; P, the dianion of any porphyrin; TTP, the dianion of *meso*-tetratolylporphyrin; deut, the dianion of deuteroporphyrin IX dimethyl ester; py, pyridine; THF, tetrahydrofuran; N_p, porphinato nitrogen atom.

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