It can then be seen that the larger dissociation constant of the mono relative to the bis complex can be explained by the presence of the two hydroxy groups in the former and not in the latter compound.

Inner-sphere hydroxide ion is known to exert a strongly labilizing effect on other ligands coordinated to the central metal ion.[19] In some cases, the effect appears to be due to the replacement of a neutral ligand—water, for example—by one with a negative charge, which repels the other groups still attached to the metal ion in the inner coordination shell.[20] There should be little difference in this regard between dinegative catechol and two hydroxide ions; a more specific influence of hydroxide ion should be sought. This effect is most likely the donation of electron density from coordinated hydroxide ion to central molybdenum ion through ligand to metal $\pi$ bonding.[21]

Catechol would not be expected to $\pi$ bond to the metal as well as hydroxide, since the catechol oxygen p orbitals probably interact with those on the benzene ring and are "drawn" away from the metal. Therefore, the single catechol molecule in the mono complex is more strongly labilized by the two hydroxide ions, than are either of the two bound catechols in the bis complex by one of the remaining ones. It is also interesting to point out that in the oxine system, the species corresponding to the 1:1 complex, namely $MoO_2(OH)_2Ox^-$, which also possesses two $OH^-$ groups, has a similar dissociation rate constant of 3.9 $sec^{-1}$.

The two forward rate constants, $k_1^{app}$ and $k_2$, suggest further lines of investigation into the mechanism of molybdate complex formation. The reaction leading to formation of the mono complex may be regarded as an addition reaction.[22] In this case, expansion of coordination would have to occur,[23] and the two forward rate constants should be different, as formation of the bis complex presumably involves no further changes in coordination number. The two rate constants are quite similar, however. We feel this result suggests that chelation of molybdate is fundamentally a condensation or substitution reaction, one or more waters being eliminated upon substitution. More rate data on the coordination of this, and other, oxyanions should be collected before any conclusions are drawn on the nature of the complex formation steps.

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(19) E. G. Moorehead and N. Sutin, *Inorg. Chem.*, **5**, 1866 (1966), *cf.* rate constants $k_{2f}$ and $k_{3f}$, therein.

(20) K. Kustin and J. Swinehart, *Progr. Inorg. Chem.*, **13**, 107 (1970).

(21) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 170–177, especially Figure 3.8.

(22) K. H. Tytko and O. Glemser, *Chimia*, **23**, 494 (1969).

(23) K. L. Kepert, *Progr. Inorg. Chem.*, **4**, 199 (1962); see also pp 261–263.

# Microwave Spectrum, Structure, Dipole Moment, and Barrier to Internal Rotation of Phosphine–Borane

**J. R. Durig,* Y. S. Li, L. A. Carreira, and J. D. Odom**

*Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208.* *Received September 29, 1972*

**Abstract:** The microwave spectra in the P, K, and R bands of 16 isotopic species of phosphine–borane ($H_3PBH_3$) have been measured and the following structural parameters have been determined: $d(BH) = 1.212 \pm 0.002$ Å, $d(PH) = 1.399 \pm 0.003$ Å, $d(PB) = 1.937 \pm 0.005$ Å, $\angle BPH = 116.9 \pm 0.2°$, $\angle PBH = 103.6 \pm 0.2°$, $\angle HBH = 114.6 \pm 0.2°$, $\angle HPH = 101.3 \pm 0.2°$. The molecule was found to be in the staggered conformation. The value of the dipole moment obtained from Stark splittings is 4.00 ± 0.03 D in the ground state and in the first excited state of the torsional mode. The barrier to internal rotation was determined from both the splitting and relative intensity methods to be 2.47 ± 0.05 kcal/mol. The structural parameters and barrier to internal rotation are compared to the corresponding values for similar molecules.

Phosphine–borane was first prepared in 1940 by Gamble and Gilmont by mixing diborane(6) and phosphine at low temperatures.[1] However, they postulated the structure $[PH_4]^+[H_3BPH_2BH_3^-]$ on the basis of chemical evidence, and it was not until 1961 that a crystallographic study showed unequivocally that the solid was the monomeric $H_3PBH_3$.[2] A later investigation by Parry and coworkers concluded that "diborane diphosphine" was the monomer $H_3PBH_3$ in the solid and liquid based on nmr, infrared, and Raman spectra.[3]

The nature and strength of the dative $\sigma$ bond formed between boron and phosphorus in trivalent electron-accepting boranes and electron-donating trivalent phosphines have been a source of considerable controversy. There are currently two hypotheses which have been advanced to explain the nature of the boron–phosphorus coordinate bond and which have attempted to shed some light on the "base strength reversal" which is observed with these molecules.[4,5] In addition, several microwave studies have been reported in which the structures of $F_3PBH_3$,[6] $HF_2BPH_3$,[7] $CH_3$-

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(1) E. L. Gamble and P. Gilmont, *J. Amer. Chem. Soc.*, **62**, 717 (1940).

(2) E. L. McGandy, *Diss. Abstr.*, **22**, 754 (1961).

(3) R. W. Rudolph, R. W. Parry, and C. F. Farran, *Inorg. Chem.*, **5**, 723 (1966).

(4) A. B. Burg, *Rec. Chem. Progr.*, **15**, 159 (1954).

(5) R. W. Rudolph and R. W. Parry, *J. Amer. Chem. Soc.*, **89**, 1621 (1967).

(6) R. L. Kuczkowski and D. R. Lide, *J. Chem. Phys.*, **46**, 357 (1967).

(7) J. P. Pasinski and R. L. Kuczkowski, *ibid.*, **54**, 1903 (1971).

$PH_2BH_3$,[8] and $(CH_3)_3PBH_3$[8] have been determined. Also, nmr studies have investigated the possible correlation of B–P bond strength with the boron–phosphorus coupling constant.[9,10]

Although it had been reported that at ambient temperature $H_3PBH_3$ is completely dissociated[5] into $PH_3$ and $B_2H_6$, it was felt that the disproportionation might be sufficiently slow at Dry Ice temperature to make it possible to observe its microwave spectrum. This molecule is of fundamental importance in elucidating the boron–phosphorus interaction and in critically evaluating the two bonding hypotheses; therefore, we were interested in the molecular structural parameters of this molecule.

In addition to the interest in the structural parameters of phosphine–borane, there is considerable interest in the value of the barrier to internal rotation. The molecule is isoelectronic with methylsilane for which a torsional barrier of $1.67 \pm 0.10$ kcal/mol has been determined.[11] However, Kuczkowski and Lide[6] found a barrier of $3.24 \pm 0.15$ kcal/mol for the internal rotation in $F_3PBH_3$ whereas the corresponding barrier[12] for the isoelectronic molecule $CH_3SiF_3$ is only $0.93 \pm 0.1$ kcal/mol although the central bond distances for these two compounds are nearly the same. In order to provide additional barrier data for testing theories on the origin of internal rotational barriers, we have determined the barrier in phosphine–borane, and, in addition, the dipole moment in the first excited state of the torsion was determined. These data are used for some critical comparisons of some recent calculations on barrier heights.

## Experimental Section

With the exception of phosphine, all preparative work was carried out in a conventional high-vacuum system employing greaseless stopcocks.[13] Sodium tetradeuterioborate, $NaBD_4$, and sulfuric acid-$d_2$ were obtained from Columbia Organic Chemical Co., Inc., and were stated to be 97 and 98 atom % deuterated, respectively. Aluminum phosphide was obtained from Alfa Inorganics. Phosphine was prepared under a stream of nitrogen in a fume hood as described in the literature.[14] Phosphine-$d_3$ was prepared in a similar manner using $D_2O$ and $D_2SO_4$. The mixed isotopic species $PD_2H$ was prepared by using 19.0 ml of $D_2O$, 24.3 ml of $H_2O$, and 16.7 ml of $D_2SO_4$. All phosphine species were purified by passing them through a −131° bath ($n$-$C_5H_{12}$ slush) into a −196° bath. Purity was monitored by vapor pressure measurements[15] and infrared spectra.[16]

Isotopically normal diborane(6) was prepared by the addition of $KBH_4$ to hot polyphosphoric acid[17] and deuteriodiborane(6) was prepared in a similar reaction using $NaBD_4$. Diborane(6) enriched in $^{11}B$ was prepared by the $LiAlH_4$ reduction of $^{11}BF_3 \cdot O(CH_3)_2$ (enriched to 96% by the Oak Ridge National Laboratories). All diborane(6) species were purified by passage through a −160° bath ($i$-$C_5H_{12}$ slush) into a −196° bath.

All phosphine–borane species were prepared in a similar manner. In a typical reaction phosphine and diborane were condensed in a 2:1 mole ratio at −196° into a 50-ml Pyrex reaction tube fitted with a greaseless stopcock. The tube was isolated from the vacuum line by closing the stopcock and allowed to warm slowly to −20°. The tube remained at that temperature for approximately 1 hr at which time it was reopened to the vacuum system and the volatile products pumped into −80 and −196° baths. Phosphine–borane stopped in the −80° bath and any unreacted $PH_3$ and $B_2H_6$ were collected at −196°. Purity in some cases was monitored by $^1H$ and $^{11}B$ nmr spectra after it was determined that the spectra of $H_3PBH_3$ in $CDCl_3$ were identical with that reported for the molten molecule.[3]

Microwave spectra were recorded in the P, K, and R bands using a Hewlett-Packard Model 8460A MRR spectrometer with a Stark cell modulation frequency of 33.3 kHz. All frequencies were measured slightly above Dry Ice temperature (∼−60°), and the accuracy was estimated to be better than ±0.1 MHz. Some of the ground-state lines were measured more exactly, but the fairly rapid loss of sample (decomposition or establishment of equilibrium) leads to an inaccuracy in determining peak maxima.

The $^1H$ nmr spectra were obtained at ambient temperature on a Varian Associates A-60 spectrometer operating at 60 MHz. Boron-11 nmr spectra were obtained at ambient temperature on a Varian Associates XL-100-15 spectrometer operating at 32.1 MHz. Field/frequency lock was provided by locking to the $^2H$ resonance in the $CDCl_3$ solvent.

## Results

The transitions observed for the symmetric isotopic species are listed in Table I. The ground-state lines were assigned by their typical first- and second-order Stark effects and by the frequency fit. The spectra were fitted to the equation

**Table I.** Symmetric Top Rotational Transition Frequencies (MHz) of Phosphine–Borane in the Ground and Excited States of the Torsional Mode

| Species | $v = 0$ | $v = 1$ | $v = 2$ | $v = 3$ |
|---|---|---|---|---|
| | | Transition $J = 1 \leftarrow 0$ | | |
| $^{11}BH_3PH_3$ | 21,182.63 | 21,043.74 | 20,925.94 | 20,830.73 |
| $^{10}BH_3PH_3$ | 22,091.56 | 21,944.98 | | |
| $^{11}BD_3PH_3$ | 17,494.9 | 17,392.9 | 17,307.7 | |
| $^{10}BD_3PH_3$ | 18,022.3 | 17,916.9 | 17,822.4 | |
| $^{11}BD_3PD_3$ | 15,602.8 | 15,520.2 | 15,450.4 | 15,390.4 |
| $^{10}BD_3PD_3$ | 16,069.1 | 15,982.9 | 15,908.7 | |
| $^{11}BH_3PD_3$ | 18,714.0 | 18,598.4 | 18,505.8 | |
| $^{10}BH_3PD_3$ | 19,493.5 | 19,371.5 | 19,274.4 | |
| | | Transition $J = 2 \leftarrow 1$ | | |
| $^{11}BD_3PH_3$ | 34,988.5 | 34,785.1 | 34,614.6 | |
| $^{10}BD_3PH_3$ | 36,044.2 | 35,832.6 | 35,643.4 | |
| $^{11}BD_3PD_3$ | 31,205.2 | 31,039.2 | 30,900.3 | |
| $^{10}BD_3PD_3$ | 32,137.8 | 31,964.8 | 31,813.5 | |
| $^{11}BH_3PD_3$ | 37,427.6 | 37,196.1 | 37,010.6 | |
| $^{10}BH_3PD_3$ | 38,987.0 | 38,742.3 | 38,547.4 | |

$$\nu_{J,J+1} = 2B_v(J + 1) - 4D_J(J + 1)^3$$

with an average $D_J$ of $2.1 \times 10^{-2}$ MHz. No contribution from a $D_{JK}$ term could be detected because of the line breadth, nor could quadrupole splitting due to the boron nucleus be resolved. Each ground-state transition was accompanied by several satellite lines to lower frequency (see Figure 1). The most intense satellite is assigned to the transition resulting from the first excited state of the low-frequency torsional motion. With this assignment the higher excited states were readily identified (see Figure 1). In addition, the satellite arising from the $PH_3$ rocking mode (447 cm$^{-1}$) was also identified.

The transitions observed for the asymmetric top species are listed in Table II. These were assigned on the basis of their Stark effect, frequency fit, and ex-

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[8] P. S. Bryan and R. L. Kuczkowski, *Inorg. Chem.*, **11**, 553 (1972).

[9] A. H. Cowley and M. C. Damasco, *J. Amer. Chem. Soc.*, **93**, 6815 (1971).

[10] R. W. Rudolph and C. W. Schultz, *ibid.*, **93**, 6821 (1971).

[11] R. W. Kilb and L. Pierce, *J. Chem. Phys.*, **27**, 108 (1957).

[12] J. R. Durig, Y. S. Li, and C. C. Tong, *J. Mol. Struct.*, **4**, 255 (1972).

[13] D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

[14] R. C. Marriott, J. D. Odom, and C. T. Sears, *Inorg. Syn.*, in press.

[15] S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 779 (1961).

[16] D. A. Tierney, D. W. Lewis, and D. Berg, *J. Inorg. Nucl. Chem.*, **24**, 1165 (1962).

[17] A. D. Norman and W. L. Jolly, *Inorg. Syn.*, **11**, 15 (1968).

Table II. Asymmetric Top Ground-State Rotational Transition Frequencies (MHz) of Phosphine–Borane

| Species | $1_{01} \leftarrow 0_{00}$ | $2_{02} \leftarrow 1_{01}$ | $2_{11} \leftarrow 1_{10}$ | $2_{12} \leftarrow 1_{11}$ |
|---|---|---|---|---|
| $^{11}BD_2HPH_3$ | 18,530.7 | 37,059.6 | 37,317.9 | 36,804.0 |
| $^{10}BD_2HPH_3$ | | 38,305.4 | 38,582.8 | 38,031.4 |
| $^{11}BDH_2PH_3$ | | 39,479.5 | 39,727.2 | 39,234.2 |
| $^{11}BD_2HPD_3$ | 16,482.6 | 32,965.1 | 33,168.4 | 32,764.7 |
| $^{10}BD_2HPD_3$ | 17,029.3 | 34,057.0 | 34,274.5 | 33,842.1 |
| $^{11}BH_3PD_2H$ | 19,452.9 | 38,903.2 | 39,201.5 | 38,598.0 |
| $^{11}BD_2HPD_2H$ gauche | 17,108.9 | | | |
| $^{11}BD_2HPD_2H$ trans | 17,077.8 | | | |

pected isotopic shift. The rotational constants derived from frequencies in Table I and II are listed in Table III.

Table III. Ground-State Rotational Constants (MHz) of Phosphine–Borane

| Species | *B* | *C* |
|---|---|---|
| $^{11}BH_3PH_3$ | 10,591.31 | 10,591.31 |
| $^{10}BH_3PH_3$ | 11,045.78 | 11,045.78 |
| $^{11}BD_3PH_3$ | 8,747.45 | 8,745.45 |
| $^{10}BD_3PH_3$ | 9,011.18 | 9,011.18 |
| $^{11}BD_3PD_3$ | 7,801.40 | 7,801.40 |
| $^{10}BD_3PD_3$ | 8,034.55 | 8,034.55 |
| $^{11}BH_3PD_3$ | 9,357.00 | 9,357.00 |
| $^{10}BH_3PD_3$ | 9,746.75 | 9,746.75 |
| $^{11}BD_2HPH_3$ | 9,393.73 | 9,136.78 |
| $^{10}BD_2HPH_3$ | 9,714.63 | 9,438.93 |
| $^{11}BDH_2PH_3$ | 9,993.43 | 9,746.93 |
| $^{11}BD_2HPD_3$ | 8,342.58 | 8,140.73 |
| $^{10}BD_2HPD_3$ | 8,622.68 | 8,406.48 |
| $^{11}BH_3PD_2H$ | 9,879.93 | 9,572.68 |

**Structure.** The present experimental information allows a complete structural determination of phosphine–borane. The measurements of the moments of inertia of six asymmetric top species, $^{11}BD_2HPH_3$, $^{10}BD_2HPH_3$, $^{11}BDH_2PH_3$, $^{11}BD_2HPD_3$, $^{11}BD_2HPD_3$, and $^{11}BH_3PD_2H$, make it possible to calculate the coordinates of the hydrogen atoms in the principal axis system of the symmetric molecule by using the multiple substitution method.[18] The boron coordinate was determined by means of Kraitchman's equation[19] utilizing the case in which the substitution occurs on an atom located on the symmetry axis. Thus, an $r_s$ structure for the $BH_3$ group was obtained.

In order to determine the coordinate of the phosphorus atom and, thereby, the complete molecular structure, both the first- and the second-moment equations were used. Both methods were found to give consistent results; their discrepancies fall within the quoted experimental errors.

Table IV. Structural Parameters for Phosphine–Borane

| | |
|---|---|
| $r(BP) = 1.937 \pm 0.005$ A | $\angle PBH = 103.6 \pm 0.2°$ |
| $r(BH) = 1.212 \pm 0.002$ Å | $\angle BPH = 116.9 \pm 0.2°$ |
| $r(PH) = 1.399 \pm 0.003$ A | $\angle HBH = 114.6 \pm 0.2°$ |
| | $\angle HPH = 101.3 \pm 0.2°$ |

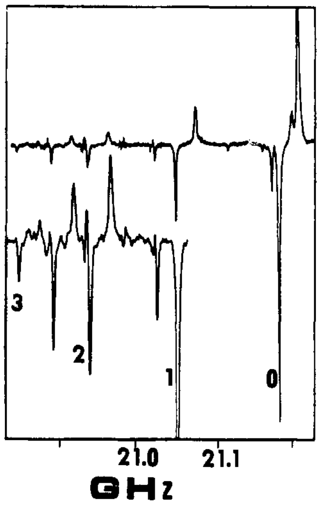

Figure 1. Microwave spectrum of $H_3P^{11}BH_3$ for the transition $J = 1 \leftarrow 0$. The numbers 0, 1, 2, 3 refer to the quantum numbers for the internal rotational vibration.

The structural parameters for phosphine–borane are listed in Table IV. The quoted errors are believed to arise from the experimental uncertainties in the moments of inertia and the uncertainty in locating the atomic positions from different combinations of isotopic species. From this table, it can be seen that (a) the PB distance is the longest yet measured for a boron–phosphorus molecule in the gas phase, (b) the HBH angle is quite different from the tetrahedral angle, and (c) the HPH angle is considerably smaller than the tetrahedral angle. The determined structure gives rotational constants consistent with the experimental values better than 5 MHz for all cases. For this reason, one expects to calculate reasonably well the rotational constants for the species $^{11}BD_2HPD_2H$ which exists as an isotopic "impurity" in the sample of $BD_3PD_3$. For $^{11}BD_2HPD_2H$, there are two possible rotamers for either the staggered or eclipsed conformations. The calculated $1_{01} \rightarrow 0_{00}$ frequencies for the four possible forms are listed in Table V and compared with the observed values. Any deviation from the observed values should not exceed 10 MHz. We have observed two microwave lines at 17,108.9 and 17,077.8 MHz with an intensity ratio of 2:1. The comparison given in Table V shows that the stable form is the staggered conformation. Also, we could not find any line close to the frequency predicted for the eclipsed conformation. Thus, it can be concluded that the staggered form is the stable form of phosphine–borane.

Table V. Observed and Calculated $1_{01} \leftarrow 0_{00}$ Transitions for the Staggered and Eclipsed Forms of $^{11}BD_2HPD_2H$

| Calcd, MHz | | |
|---|---|---|
| Staggered | Eclipsed | Obsd, MHz |
| 17,105.4<br>(gauche) | 17,079.2<br>(gauche) | 17,108.9 |
| 17,075.6<br>(trans) | 17,128.2<br>(cis) | 17,077.8 |

**Dipole Moment.** The dipole moment of phosphine–borane was calculated from the measured second-order Stark effect of the 1 ← 0 transition in the ground vibrational state of the two symmetric tops, $^{11}BH_3PH_3$ and $^{10}BH_3PH_3$. In addition, the dipole moment was deter-

(18) Y. S. Li, K. L. Kizer, and J. R. Durig, *J. Mol. Spectrosc.*, **42**, 430 (1972).

(19) J. Kraitchman, *Amer. J. Phys.*, **21**, 17 (1953).

mined for the first excited state of the torsional mode from the same transition of the $^{11}BH_3PH_3$ molecule. Field strengths were calibrated by using the 2 ← 1 transition of OCS[20] at 24,325.92 MHz. The Stark coefficient for the three species was calculated from the equations given in Townes and Schawlow.[21] The dipole moment was found to be 4.00 ± 0.03 D for both the $^{10}B$ and $^{11}B$ as well as for the first excited state of the torsional mode for the $^{11}B$ compound. This value agrees well with those obtained by Bryan and Kuczkowski[8] for the $CH_3PH_2BH_3$ ($\mu$ = 4.66 ± 0.05 D) and $(CH_3)_3PBH_3$ ($\mu$ = 4.99 + 0.2 D) molecules,[7] but it is considerably lower than the theoretical value of 5.5 D calculated by Demuynck and Veillard.[22] The discrepancy between the experimentally determined value and the calculated one can be attributed to the poor choice of the structural parameters used in the *ab initio* calculation.

Weaver and Parry[23] have considered the dipole moment trends of a series of methyl-substituted phosphines and amines. They have shown that as the number of methyl groups increases, the dipole moment of the phosphines increases, whereas the exact opposite trend is observed for the amines. The amine–boranes follow the same trend as the methyl-substituted amines except for $H_3NBH_3$ which has a slightly lower dipole moment than $CH_3NH_2BH_3$. These trends were rationalized in terms of a model which was based on lone-pair moments and the polarizability of the central atom. The dipole moments of the methyl-substituted phosphines and phosphine–boranes are compared in Table VI. The observed trends for the dipole moments for the phosphine–boranes are the same as the methylphosphines. Thus, these data for the adducts seem to be consistent with Weaver and Parry's model.

**Table VI.** Dipole Moments (D) of Methyl-Substituted Phosphines and Their Borane Adducts

| | $\mu$ of donor | $\mu$ of adduct |
|---|---|---|
| $(CH_3)_3P$ | 1.19 ± 0.05[a] | 4.99 ± 0.2[b] |
| $(CH_3)_2PH$ | 1.23 ± 0.01[c] | |
| $CH_3PH_2$ | 1.10 ± 0.01[d] | 4.66 ± 0.05[e] |
| $PH_3$ | 0.58[f] | 4.00 ± 0.03[g] |

[a] D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **29**, 914 (1958). [b] Reference 8. [c] R. Nelson, *J. Chem. Phys.*, **39**, 2382 (1963). [d] T. Kojima, E. L. Breig, and C. C. Lin, *ibid.*, **35**, 2139 (1961). [e] Reference 8. [f] C. A. Burrus, *J. Chem. Phys.*, **28**, 427 (1958). [g] This work.

**Barrier to Internal Rotation.** In order to obtain the necessary data to determine the barrier height to internal rotation from the splitting method, the microwave spectra of the asymmetrically deuterated species, $^{11}BH_3PD_2H$ and $^{11}BD_2HPH_3$, were investigated in the first torsionally excited states. Even under the highest resolution of our equipment, none of the 2 ← 1 transitions appeared to have any observable splitting in the ground state. In Table VII are listed the first torsionally excited-state transitions of $^{11}BD_2HPH_3$. Assignments were made on the basis of the Stark effect, relative intensity, and the internal rotational splitting. Transitional frequencies due to the first torsionally excited state of $^{11}BH_3PD_3H$ are not listed since one of the two transitions ($2_{12} \leftarrow 1_{11}$), which appears to be split due to the internal rotation, is interferred with by an intense ground-state line ($2_{02} \leftarrow 1_{01}$).

**Table VII.** First Torsionally Excited-State Transitions of $^{11}BD_2HPH_3$

| Transition | State | Frequency, MHz |
|---|---|---|
| $1_{01} \leftarrow 0_{00}$ | A, E | 18,419.3 |
| $2_{02} \leftarrow 1_{01}$ | A, E | 36,836.9 |
| $2_{12} \leftarrow 1_{11}$ | A | 36,601.4 |
| | E | 36,643[a] |
| $2_{11} \leftarrow 1_{10}$ | E | 37,031.8 |
| | A | 37,074.5 |

[a] Interferred by the second torsionally excited line due to $2_{02} \leftarrow 1_{01}$.

Calculations for the internal rotational splitting were carried out by the principal axis method, assuming the potential function of the form $V = (V_3/2)(1 - \cos 3\theta)$. The products of the Mathieu's eigenfunctions and the symmetric top wave functions were used as the matrix representation.[24] The calculated and observed internal rotational splittings are compared in Table VIII. The uncertainty in the measured splitting is not expected to introduce any error in the calculated barrier, since the splitting is so sensitive to the barrier heights that a small change in the barrier will cause an appreciable change in the internal rotational splitting. For example, a change in the barrier height by 8 cal/mol will change the splitting by 1.24 MHz. Also listed in Table VIII are the internal rotational parameters obtained from the molecular structure as given in Table IV. These internal rotational parameters give a splitting of 0.03 MHz for the ground vibrational state line which explains why we did not observe any splitting of these lines. From the resulting barrier ($V_3$ = 2.47 kcal/mol) it is believed that the potential function governing the internal rotation converges rapidly and thereby the absence of a $V_6$ term in the calculation would cause a negligible change in the barrier height. The uncertainties in the barrier heights are believed to arise solely from the uncertainties in the structural parameters. From the structural parameters and the barrier height calculated by the splitting method, the frequency for the internal rotational mode $\nu_6(A_2)$ was calculated to be 225 cm⁻¹. This value compared favorably with the value of 235 ±

**Table VIII.** Internal Rotational Splittings (MHz) for the $V(T) = 1$ State and Internal Rotational Parameters for $^{11}BD_2HPH_3$

| Transition | $V_A - V_E$ (obsd) | $V_A - V_E$ (calcd) |
|---|---|---|
| $2_{12} \leftarrow 1_{11}$ | −42.0 ± 1.0 | −43.0 |
| $2_{11} \leftarrow 1_{10}$ | 42.7 ± 0.2 | 43.0 |
| | $I_\alpha = 4.71$ amu Å² | $\lambda_c = 0.0483$ |
| | $F = 6.03$ cm⁻¹ | $S = 63.4$ |
| | $\lambda_a = 0.9988$ | $V_3 = 2.467 \pm 0.050$ kcal/mol |
| | $\lambda_b = 0.0000$ | |

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(20) J. S. Muenter, *J. Chem. Phys.*, **48**, 4544 (1968).

(21) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill, New York, N. Y., 1955.

(22) J. Demuynck and A. Veillard, *Chem. Commun.*, 873 (1970).

(23) J. R. Weaver and R. W. Parry, *Inorg. Chem.*, **5**, 718 (1966).

(24) K. K. Lau, Ph.D. Thesis, Princeton University, 1972.

10 cm$^{-1}$ obtained from relative intensity measurements but the 225 cm$^{-1}$ value should be more accurate.

## Discussion

An intriguing feature of phosphine–boranes is that there appears to be no real correlation between the B–P bond length and stability among these adducts as pointed out by Bryan and Kuczkowski.[8] Structural data for these compounds and trends that have been found have also been discussed in relation to various semiempirical models by these authors.[8] One of the more logical models which has attempted to explain the nature of the coordinate bond in these adducts was that advanced by Rudolph and Parry.[5] However, as was noted by these authors, their hypothesis made some very definite predictions about the then unknown structures of $HPF_2$ and $HPF_2BH_3$. Certain of these predictions proved to be incorrect;[7,25] thus, although their postulate cannot be the entire explanation concerning the stability of these compounds, it does explain how a bond can be short yet weak.

It is interesting to note that $F_3PBH_3$ and $H_3PBH_3$ represent extremes in terms of the B–P bond lengths in the phosphine–boranes and that both are highly dissociated in the gas phase at room temperature. The P–B bond length of $HPF_2BH_3$ is essentially the same as that of $F_3PBH_3$ and the bond lengths of $(CH_3)_3PBH_3$ and $CH_3PH_2BH_3$ are essentially the same and slightly shorter than that found in $H_3PBH_3$. However, these three compounds, $HPF_2BH_3$, $(CH_3)_3PBH_3$, and $CH_3PH_2BH_3$, are much more stable than either $F_3PBH_3$ and $H_3PBH_3$ which have the extremes in the P–B bond lengths (see Table IX).

Bryan and Kuczkowski[8] have pointed out that a definite distinction exists between the stability of a complex and the strength of the dative bond. The enthalpy of dissociation ($\Delta H_g$) has two contributing terms: $\Delta H_r$, the enthalpy of reorganization; $\Delta H_k$, the enthalpy of dative bond formation.[26] Thus, one must consider the relative contributions of these two terms, in order to determine the stability of the complex.

It is apparent from this and other work that the true nature of this P–B coordinate bond is not understood and further work is needed to elucidate the nature of the interaction in these compounds. However, it should be pointed out that the P–B bond distance of 1.937 Å in the gas phase is essentially the same as the value reported from the crystallographic study.[2] This would seem to indicate that the dative bond does not change markedly with change in phase.

From a comparison of the structural parameters of $H_3PBH_3$ with those of $PH_3$ as given in Table IX, it can be seen that the ∠HPH increases from 93.3 to 101.2° upon borane coordination, which indicates a significant increase in the s character of the P–H bonds. Consistent with this is the significant decrease of the P–H bond length in the adduct. The same trends have been noted for $(CH_3)_3P$ and $CH_3PH_2$ and their borane adducts.[8] These results are in marked contrast to the trend[27] in the corresponding structural parameters of $(CH_3)_3N$ and $(CH_3)_3NBH_3$.

The internal rotational barrier of 2.47 kcal/mol

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(25) R. L. Kuczkowski, *J. Amer. Chem. Soc.*, **90**, 1705 (1968).

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**Table IX.** Comparison of the Structural Parameters of Some Boron–Phosphorus Compounds

| Molecule | r(PB) | r(BH) | ∠HBH | r(PH) | ∠HPH | r(PC) | ∠CPC | r(PF) | ∠FPF |
|---|---|---|---|---|---|---|---|---|---|
| $H_3PBH_3$[a] | 1.937 ± 0.005 | 1.212 ± 0.002 | 114.6 ± 0.2 | 1.399 ± 0.003 | 101.2 ± 0.2 | | | | |
| $H_3P$[b] | | | | 1.420 ± 0.005 | 93.3 ± 0.2 | | | | |
| $(CH_3)_3PBH_3$[c] | 1.901 ± 0.007 | 1.212 ± 0.010 | 113.5 ± 0.5 | | | 1.819 ± 0.010 | 105.0 ± 0.4 | | |
| $(CH_3)_3P$[d] | | | | | | 1.843 ± 0.003 | 98.9 ± 0.2 | | |
| $CH_3PH_2BH_3$[e] | 1.906 ± 0.006 | 1.234 ± 0.023<br>1.229 ± 0.022 | 116.1 ± 0.8<br>112.3 ± 1.2 | 1.404 ± 0.006 | 99.9 ± 0.4 | 1.809 ± 0.006 | | | |
| $F_3PBH_3$[f] | 1.836 ± 0.006 | 1.206 ± 0.003 | 115.1 ± 0.5 | | | | | 1.538 ± 0.008 | 99.8 ± 1.0 |
| $F_3P$[g] | | | | | | | | 1.535 ± 0.02 | 100 ± 2 |
| $F_2PHBH_3$[h] | 1.832 ± 0.009 | 1.226 ± 0.005<br>1.200 ± 0.007 | 115.9 ± 0.4<br>112.7 ± 0.5 | 1.409 ± 0.004 | | | | 1.552 ± 0.006 | 100.0 ± 0.5 |

[a] This work. [b] C. A. Burrus, *J. Chem. Phys.*, **28**, 427 (1958). [c] Reference 8. [d] P. S. Bryan and R. L. Kuczkowski, *J. Chem. Phys.*, **55**, 3049 (1971). [e] Reference 8. [f] Reference 6. [g] Y. Morino, K. Kuchitsu, and T. Moritani, *Inorg. Chem.*, **8**, 867 (1969). [h] Reference 7.

for $H_3PBH_3$ is significantly larger than the 1.67 kcal/mol value for $CH_3SiH_3$ although the P–B bond distance is 1.937 Å compared to the 1.863 Å distance found for the C–Si bond for these isoelectronic molecules. However, this increase of 0.8 kcal/molc an be rationalized by an examination of the nonbonded distances between the boron and phosphorus hydrogens. Because of the significant differences in the ∠HBP and ∠HCSi angles, the H···H distances of closest approach decrease by 0.5 Å for the phosphine-borane. Thus a significant increase in the contribution from the "hydrogen repulsive potential"[28] can be attributed to the shorter H···H distance which results in the marked increase in barrier height. Further *ab initio* calculations with better structural parameters should be carried out in order to provide better insight into the origin of barriers for single bonds.

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# Application of Line Narrowing to $^{11}$B Nuclear Magnetic Resonance Spectra

**A. O. Clouse, D. C. Moody, R. R. Rietz, T. Roseberry, and R. Schaeffer***

*Contribution No. 2172 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. Received September 18, 1972*

**Abstract:** The exponential line-narrowing technique is applied to $^{11}$B nmr spectra, and previously unobservable splittings are resolved under the normally broad resonances. The line-narrowed 70.6-MHz $^{11}$B nmr spectra of $B_4H_{10}$, $B_5H_9$, $B_5D_9$, $B_5H_{11}$, $B_6H_{12}$, $B_{10}H_{14}$, and *n*-$B_9H_{15}$ are discussed in relation to their structures as liquids or in solution.

Recently the partially relaxed Fourier transform (PRFT) technique has been applied to $^{11}$B nmr, and structural data not normally available have been obtained.[1] The technique reveals the previously unobservable $^{11}$B 1:2:1 triplet, hidden by accidental overlap of other resonances, due to the –$BH_2$ group of *n*-$B_9H_{15}$. Certain problems are not resolved by this technique, however. For example, line widths of 60–100 Hz are common, and, as a result, one usually observes only splitting by the directly bonded terminal hydrogens.[2] Measurement of $^{11}$B and $^{10}$B relaxation times in $B_5H_9$ have shown that this broadening is probably caused by unresolved fine structure and not by quadrupolar relaxation.[3] Recently the $^{11}$B(apex)–$^{11}$B(base) coupling constant in $B_5H_9$ was reported for the first time and found to be 19.4 Hz.[4] Splittings of this magnitude could easily overlap with envelopes of bridge hydrogen–boron couplings ($J_{^{11}B-^{1}H_{bridge}}$) to give line widths of 60–100 Hz. The research described here applies a new Fourier transform (FT) nmr technique which is especially applicable to the unresolved fine structure causing the broad lines in $^{11}$B nmr spectra.

It has been known for some time that the free induction decay signal following a 90° pulse can be multiplied by an exponential function prior to the transform to increase the ratio of signal to noise at the expense of an artifically broadened line. Similarly, if the decay is retarded by multiplication of the raw signal by a function exponential in time, narrower lines are produced in the transform. This enhanced resolution is accompanied by a substantial reduction in signal/noise,[5] which is probably the reason why the technique has not been seriously applied before now. An example of the data manipulation is shown in Figure 1 for $B_5H_9$. The apodization function shown in the figure has been discussed elsewhere[6] and needs no further explanation. It should be noted that the data are collected in the usual manner, and the exponential multiplication is a mathematical operation performed by the computer on raw data.

We have applied this technique to a number of boron hydrides and have resolved $^{11}$B–$^{11}$B couplings and $^{11}$B–$^{1}H_{bridge}$ couplings under the broad $^{11}$B resonances. The line-narrowed 70.6-MHz $^{11}$B nmr spectra of $B_4H_{10}$, $B_5H_9$, $B_5D_9$, $B_5H_{11}$, $B_6H_{12}$, $B_{10}H_{14}$, and *n*-$B_9H_{15}$ are discussed.

## Experimental Section

The compounds studied in this experiment were readily available from laboratory samples. The spectra were obtained at 16° on a Varian Associates HR-220 spectrometer operating at 51.7 kG and using a "home-built" pulse apparatus operating at 70.6 MHz. A Nicolet 1080 computer was used to process the data, using Nicolet supplied software.

## Results and Discussion

**$B_5H_9$, Pentaborane(9).** The normal 70.6-MHz $^{11}$B nmr spectrum of $B_5H_9$ is shown in Figure 2. The

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(6) Reference 5b, p 76.