(9) Mass spectra were obtained with the use of an AEI MS 9 spectrometer and infrared spectra were measured on a Perkin-Elmer 621 or Beckman IR5A spectrometer. Thin-layer chromatography was performed on chloroform-impregnated Kieselgel or on Mallinckrodt Chrom AR chromatography sheet with elution by 10% tetrahydrofuran in benzene and detection by ultraviolet light or by development with iodine vapor. Sources and purification methods for chemicals were as described previously.[4]

Spectra and Structure of Phosphorus–Boron Compounds. XI.[1]
Microwave Spectrum, Structure, Dipole Moment, and Barrier to Internal Rotation in Phosphine–Trifluoroborane

J. D. ODOM, V. F. KALASINSKY,[2] and J. R. DURIG*

The microwave spectra in the R band of four isotopic symmetric-top species of phosphine–trifluoroborane ($H_3P \cdot BF_3$) have been observed. A staggered conformation and $r(P-H) = 1.40$ Å and $\angle HPB = 117°$ from $H_3P \cdot BH_3$ were assumed, and the remaining structural parameters were calculated, by a least-squares fitting of the four observed moments of inertia, to be the following: $r(P-B) = 1.921 \pm 0.007$ Å, $r(B-F) = 1.372 \pm 0.002$ Å, $\angle FBP = 106.69 \pm 0.38°$. The dipole moment was found from Stark splittings to be 3.73 ± 0.30 D in the ground state. The barrier to internal rotation was determined to be 3.39 ± 0.40 kcal/mol by using the relative intensity method. These quantities are compared to corresponding values for related molecules.

Introduction

The addition complexes formed between phosphorus and boron compounds have been investigated for a number of years. The development of a universal theory to explain the bonding in this class of compounds has been hampered by apparent contradictions to classical ideas of bond strengths, bond lengths, and dissociative stabilities. Reliable structures have been determined for a number of molecules from microwave absorption[1,3–6] and vibrational studies have prompted normal-coordinate calculations from which P–B stretching force constants are available.[7–13] Additionally, there are three such studies that deal with phosphine–trihaloboranes.[9,10,13] The calculations incorporate structural parameters[14] and the accuracy of these calculations can depend heavily on the assumed structures that were used. There have been no structures reported for the phosphine–trihaloboranes in the solid or gas phases. It was found that $H_3P \cdot BCl_3$ gave no microwave spectrum[13] even though it was reported to be substantially associated in the gas phase with a large dipole moment.[15] Further studies on phosphine–trihaloboranes[9] indicated that $H_3P \cdot BF_3$ might be more associated in the gas phase than was $H_3P \cdot BCl_3$.

Barriers to internal rotation around P–B bonds have been measured for only a few molecules.[3,5–7,9] In $H_3P \cdot BH_3$ and $F_3P \cdot BH_3$ the barriers are 2.47[3] and 3.24[5] kcal/mol, respectively. The BH_3 torsional barrier in $CH_3PH_2 \cdot BH_3$ has been found to be 1.57 kcal/mol.[7] These barriers were calculated from microwave data. From vibrational data in the solid state, barriers were found in $H_3P \cdot BBr_3$ (2.96–3.28 kcal/mole[9]) and $B_2Cl_4 \cdot 2PH_3$ (2.92 kcal/mol[16]). A comparison of substituent effects could be made if the barrier in $H_3P \cdot BF_3$ were known. These considerations and the possibility of determining the structure of $H_3P \cdot BF_3$ have prompted our investigation of the microwave spectra of four isotopic species of this molecule.

Experimental Section

Microwave spectra were recorded in the R band of a Hewlett-Packard Model 8460A MRR spectrometer with a Stark cell modulation frequency of 33.3 kHz. All frequencies were measured with the sample held slightly above Dry Ice temperature ($\sim$ –70°). To measure the frequencies of very weak lines, time averaging of the spectrum was accomplished with a Varian C-1024 time-averaging computer.

With the exception of those for phosphine, all preparations and purifications were carried out in a standard high-vacuum system employing greaseless stopcocks.[17] Boron trifluoride was obtained commercially (Matheson) and purified by vacuum fractionation until it exhibited a vapor pressure[17] of 301 mm at –112° (CS_2–liquid N_2 slush). Phosphine was prepared under a stream of gaseous nitrogen in a fume hood as described in the literature.[18] Phosphine-d_3 was prepared in a similar manner using D_2O and D_2SO_4. All phosphine species were purified by means of a low-temperature vacuum fractionation column.[19] Purity was monitored by vapor pressure measurements[17] and infrared spectra.[15]

Phosphine–trifluoroborane and phosphine–trifluoroborane-d_3 were prepared[20,21] by condensing equimolar amounts of PH_3 (or PD_3) and BF_3 into an evacuated tube at liquid nitrogen temperatures. The tube was isolated from the vacuum system and allowed to warm slowly to approximately –30°. The tube was then opened to the vacuum system and any unreacted PH_3 or BF_3 was removed under dynamic vacuum at –160° (i-C_5H_{12}–liquid N_2 slush).

Results

The observed transitions for the various isotopic species of the symmetric tops of phosphine–trifluoroborane are listed in Table I. These were assigned by comparing their spacings to those predicted from an initial structure. The spectra were fitted to the equation

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

Individual values for B_0 and D_J are also listed in Table I. No contribution from a D_{JK} term could be resolved. The only observed vibrational satellite was assigned to the torsional mode. A partial structure was obtained from the rotational constants listed in Table I. The structure of the phosphine end of the molecule was assumed and constrained in all structural calculations. The three remaining structural parameters, for the assumed staggered conformation, were obtained by an iterative least-squares fitting to the four observed moments of inertia. The program allows one to choose weighting factors for the input moments. The structural parameters in Table II correspond to weighting factors of 1.0 for $H_3P \cdot {}^{11}BF_3$ and 0.5 for the other three species. This was

Table I. Observed Ground-State Rotational Transitions (MHz), Rotational Constants (MHz), and Centrifugal Distortion Constants (MHz) of $H_3P \cdot BF_3$

Species	$J = 7 \leftarrow 6$	$J = 6 \leftarrow 5$	$J = 5 \leftarrow 4$	B_0	D_J
$H_3P^{11} \cdot BF_3$		$34,610.96 \pm 0.02$	$28,857.96 \pm 0.20$	2889.32 ± 0.09	0.070 ± 0.011
$H_3P^{10} \cdot BF_3$		$34,664.00 \pm 0.05$	$28,897.92 \pm 0.50$	2892.35 ± 0.28	0.051 ± 0.033
$D_3P^{11} \cdot BF_3$	$37,114.99 \pm 0.05$	$31,829.89 \pm 0.05$	$26,525.75 \pm 0.50$	2654.14 ± 0.22	0.031 ± 0.021
$D_3P^{10} \cdot BF_3$	$37,168.08 \pm 0.10$		$26,562.55 \pm 0.50$	2657.71 ± 0.22	0.029 ± 0.021

Table II. Structural Parameters for $H_3P \cdot BF_3$

r(P-B) = 1.921 ± 0.007 Å	∠FBP = 106.69 ± 0.38°
r(B-F) = 1.372 ± 0.002 Å	∠FBF = 112.10 ± 0.35°
r(P-H)^a = 1.40 Å	∠HPB^a = 117°
	∠HPH^a = 101.1°

^{a} Assumed quantities.[11]

done because of the differences in the uncertainties of the calculated rotational constants of these species. Errors in the structural parameters are determined from the variance–covariance matrix, but those reported in Table II have been extended to account again for the uncertainties of the measured frequencies. In Table II it is shown that (a) the P-B bond is of moderate length and (b) the structure of the $-BF_3$ end is considerably different from that of the free acid.

Dipole Moment. The second-order Stark effect was observed and measured for the $6 \leftarrow 5$ transition of $H_3P \cdot {}^{11}BF_3$. Field strengths were calibrated by using the $3 \leftarrow 2$ transition of OCS (0.7152 D)[22] at 36488.82 MHz. The dipole moment of 3.73 ± 0.30 D in phosphine–trifluoroborane was calculated using equations given by Townes and Schawlow.[23] The most intense Stark lobe that moved to higher frequency with increasing field was assigned to the $K = 0$, $|M| = 1 \rightarrow 1$ component. This assignment gave a preliminary estimate of the dipole moment and this was used to calculate shifts for the $|M| = 0$, 2 that were consistent with observed data. The Stark lobes were very weak and the errors in measuring the frequencies of these give rise to the larger error limits on the dipole moment. Nonetheless, this value can be compared to similar quantities previously determined for phosphine–borane derivatives. In Table II these are listed for the methyl- and fluoro-substituted phosphine–boranes. It seems clear that substitution on phosphorus of an electron-donating group leads to dipole moments higher than in $H_3P \cdot BH_3$ while substitution of an electron-withdrawing group lowers the dipole moment. Substitution at the boron atom has not been studied. One might expect, however, that the addition of fluorine atoms might increase the dipole as compared to that of $H_3P \cdot BH_3$. This is not seen to be the case, for $H_3P \cdot BF_3$, since the two dipole moments are within the error limits of one another.

Barrier to Internal Rotation. The preferred method of determining barriers to internal rotation by microwave spectroscopy is by observing splittings in torsional excited states. This method is applicable to asymmetric tops, and unfortunately no transitions attributable to the partially deuterated phosphine–trifluoroborane were observed in this study. The transitions for the symmetric tops were only strong enough to observe the first excited state of the torsion. Relative intensity measurements at approximately $-70°$ were used to determine the frequency of the torsional mode, ν_6. In $H_3P \cdot BF_3$

measurements on the $6 \leftarrow 5$ transition with the $\nu = 1$ line at 34,606.4 MHz at a number of Stark voltages gave 190 ± 20 cm^{-1} for the torsional frequency. In $D_3P \cdot BF_3$ the $7 \leftarrow 6$ transition was used ($\nu = 1$ at 37,112.5 MHz) and gave 141 ± 15 cm^{-1}.

The measurements were made with Dry Ice packed around the wave guide because it was not possible to find the transitions at ambient temperatures. The uncertainty in the temperature introduces a rather small fraction to the error limits on the frequency of the torsion. Most of the error is due to problems in correcting for an uneven base line. Also weakness of the lines contributes to the error.

Using the above torsional frequencies and F numbers of 3.756 cm^{-1} for $H_3P \cdot BF_3$ and 1.965 cm^{-1} for $D_3P \cdot BF_3$, periodic barriers of 3.34 ± 0.35 and 3.44 ± 0.30 kcal/mol, respectively, can be calculated. The barrier in this molecule is then higher than that in $H_3P \cdot BH_3$[3] but nearly the same as the barrier in $F_3P \cdot BH_3$.[5]

Discussion

The structural parameters for phosphine–trifluoroborane are compared to some other related molecules in Table III. The P-B bond length is seen to be shorter than in $H_3P \cdot BH_3$,[3] longer than in $F_3P \cdot BH_3$,[5] and equal, within experimental error, to that in the methylphosphine–boranes.[1,4] The dissociative stabilities of these compounds are in the order $(CH_3)_{3-n}PH_n \cdot BH_3 \gg F_3P \cdot BH_3 > H_3P \cdot BH_3 \gg H_3P \cdot BF_3$. The lack of direct correspondence between these properties has been the subject of many studies.[4,24,25] The theory,[25] as expressed by Bryan and Kuczkowski[4] in discussing $(CH_3)_3$-$P \cdot BH_3$ and $CH_3PH_2 \cdot BH_3$, which makes a distinction between the stability of a complex and the strength of the dative bond seems applicable to $H_3P \cdot BF_3$. The enthalpy of dissociation (ΔH_g) is composed of two terms: ΔH_r, the enthalpy of reorganization, and ΔH_k, the enthalpy of dative-bond formation.[25] In $H_3P \cdot BF_3$ one would expect ΔH_r to be the more important term. Upon coordination the BF_3 moiety must be altered from its planar D_{3h} structure in which considerable π back-bonding has been postulated to a nearly pyramidal symmetry with ∠FBF = 112.10°. This treatment is qualitative and tentative since it does not consider that reasonably stable complexes of amines with BF_3 show similar changes in the structure of the BF_3 group.[26,27]

The microwave spectra were very weak and this fact impeded initial progress. Absorption lines were between 20 and 30 times weaker than those observed in $H_3P \cdot BH_3$, although the dipole moments are of similar magnitude. Additionally, the intensity of lines depended directly upon the pressure in the wave guide. This kinetic stability became important when lines arising from species with ^{10}B were to be found. Deu-

Table III. Comparison of Structural Parameters of Some Phosphorus–Boron Compounds

Molecule	r(P-B), Å	r(B-X),^{a} Å	∠XBX,^{a} deg	r(P-X),^{a} Å	∠XPX,^{a} deg	r(P-C), Å	∠CPB, deg	∠CPC, deg
$H_3P \cdot BF_3$,^{b}	1.921 ± 0.007	1.372 ± 0.002	112.10 ± 0.35	1.40^c	101^c			
$H_3P \cdot BH_3$,^{c}	1.937 ± 0.005	1.212 ± 0.002	114.6 ± 0.2	1.399 ± 0.003	101.2 ± 0.2			
$F_3P \cdot BH_3$,^{d}	1.836 ± 0.006	1.206 ± 0.003	115.1 ± 0.5	1.538 ± 0.008	99.8 ± 1.0			
$(CH_3)_3P \cdot BH_3$,^{e}	1.901 ± 0.007	1.212 ± 0.010	113.5 ± 0.5			1.819 ± 0.010	113.6 ± 0.4	105.0 ± 0.4
$(CH_3)_2PH \cdot BH_3$,^{f}	1.898 ± 0.010	1.216 ± 0.005	113.7 ± 0.4	1.414 ± 0.009	118.1 ± 4.0^g	1.813 ± 0.010	114.6 ± 1.0	105.4 ± 1.0
		1.212 ± 0.005						
$CH_3PH_2 \cdot BH_3$,^{e}	1.906 ± 0.006	1.234 ± 0.023	116.1 ± 0.8	1.404 ± 0.006	99.9 ± 0.4	1.809 ± 0.006	115.7 ± 0.4	
		1.229 ± 0.022	112.3 ± 1.2		116.3 ± 0.6^g			

^{a} X = H, F. ^{b} This work. ^{c} Reference 11. ^{d} Reference 14. ^{e} Reference 12. ^{f} Reference 15. ^{g} ∠HPB.

Table IV. Dipole Moments (D) of Phosphine–Borane Derivatives

$(CH_3)_3P \cdot BH_3$	4.99 ± 0.02^a	$F_3P \cdot BH_3$	1.64 ± 0.02^c
$(CH_3)_2PH \cdot BH_3$	4.85 ± 0.06^b	$F_2HP \cdot BH_3$	2.50 ± 0.03^d
$CH_3PH_2 \cdot BH_3$	4.66 ± 0.05^a	$H_3P \cdot BH_3$	4.00 ± 0.03^e
		$H_3P \cdot BF_3$	3.73 ± 0.3^f

a Reference 12. b Reference 15. c Reference 14. d Reference 13. e Reference 11. f This work.

terium exchange was a problem as well. Typical spectra showed strong lines attributable to the mixed H–D species of phosphine. These were 10–20 times stronger than $H_3P \cdot BF_3$ lines (depending upon pressures from 90 to 33 mTorr).

Inductive effects of substituents in relation to dipole moments in phosphine–boranes might predict the dipole moment in $H_3P \cdot BF_3$ to be higher than in $H_3P \cdot BH_3$. In Table IV it is shown that an inductive effect is qualitatively consistent when substitution is on the phosphorus atom. Simplified σ inductive effects then are not sufficient to rationalize the value of the dipole moment in $H_3P \cdot BF_3$. Additionally, since the dipole moment of $H_3P \cdot BCl_3$ in benzene solution has been found[15] to be 5.2 ± 0.1 D, we expected the moment in $H_3P \cdot BF_3$ in the gas phase to be of comparable magnitude. At this time we are unable to explain this apparent discrepancy. It would be interesting to compare the dipole moments in some R_3N-BF_3 compounds with those in corresponding $-BCl_3$ and $-BH_3$ analogs.

The barrier in $H_3P \cdot BF_3$ is larger than in $H_3P \cdot BH_3$. Fink and Allen[28] have proposed a model for explaining barrier trends which offers a balance of the sum of a nuclear–electronic potential (V_{ne}), a nuclear–nuclear potential (V_{nn}), and a kinetic term (T) with the electron–electron repulsive potential (V_{ee}) as the factor determining the barriers. This model has been used qualitatively for other coordination compounds of phosphorus and boron.[1,7] Ab initio calculations[29] on $H_3P \cdot BH_3$ have shown that the inclusion of phosphorus d-orbital overlap raises the calculated barrier and it approaches the experimental value.

This d-orbital overlap must involve hyperconjugation in the BH_3 moiety. Since the likelihood of this effect is absent in $H_3P \cdot BF_3$, we must consider the sum of the contributions of the individual terms of Allen's theory. Fluorine substitution, because of the greater atomic charge and large number of electrons, might be expected to increase the barrier through the V_{nn} and V_{ee} terms, while the V_{ne} term might lower the barrier. Qualitatively, these effects can explain both a higher

barrier in $H_3P \cdot BF_3$ than in $H_3P \cdot BH_3$ and the fact that the barriers in $H_3P \cdot BF_3$ and $F_3P \cdot BH_3$ are similar.

References and Notes

(1) Part X: J. R. Durig, B. A. Hudgens, Y. S. Li, and J. D. Odom, *J. Chem. Phys.*, **61**, 4890 (1974).
(2) Taken in part from the thesis of V. F. Kalasinsky, submitted to the Department of Chemistry in partial fulfillment of the Ph.D. degree, May 1975.
(3) J. R. Durig, Y. S. Li, L. A. Carreira, and J. D. Odom, *J. Am. Chem. Soc.*, **95**, 2491 (1973).
(4) P. S. Bryan and R. L. Kuczkowski, *Inorg. Chem.*, **11**, 553 (1972).
(5) R. L. Kuczkowski and D. R. Lide, Jr., *J. Chem. Phys.*, **46**, 357 (1967).
(6) J. P. Pasinski and R. L. Kuczkowski, *J. Chem. Phys.*, **54**, 1903 (1971).
(7) J. R. Durig, V. F. Kalasinsky, Y. S. Li, and J. D. Odom, *J. Phys. Chem.*, **79**, 468 (1975).
(8) J. D. Odom, V. F. Kalasinsky, and J. R. Durig, *J. Mol. Struct.*, **24**, 139 (1975).
(9) J. R. Durig, S. Riethmiller, V. F. Kalasinsky, and J. D. Odom, *Inorg. Chem.*, **13**, 2729 (1974).
(10) J. E. Drake, J. L. Hencher, and B. Rapp, *J. Chem. Soc., Dalton Trans.*, 595 (1974).
(11) J. D. Odom, S. Riethmiller, S. J. Meischen, and J. R. Durig, *J. Mol. Struct.*, **20**, 471 (1974).
(12) J. D. Odom, B. A. Hudgens, and J. R. Durig, *J. Phys. Chem.*, **77**, 1972 (1973).
(13) J. D. Odom, S. Riethmiller, J. D. Witt, and J. R. Durig, *Inorg. Chem.*, **12**, 1123 (1973).
(14) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, N.Y., 1955.
(15) P. A. Tierney, D. W. Lewis, and D. Berg, *J. Inorg. Nucl. Chem.*, **24**, 1163 (1962).
(16) J. D. Odom, V. F. Kalasinsky, and J. R. Durig, *Inorg. Chem.*, **14**, 434 (1975).
(17) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
(18) R. C. Marriott, J. D. Odom, and C. T. Sears, *Inorg. Synth.*, **14**, 1 (1973).
(19) J. Dobson and R. Schaeffer, *Inorg. Chem.*, **9**, 2183 (1970).
(20) D. R. Martin and R. E. Dial, *J. Am. Chem. Soc.*, **72**, 852 (1950).
(21) E. Wiberg and U. Heubaum, *Z. Anorg. Allg. Chem.*, **225**, 270 (1935).
(22) J. S. Muenter, *J. Chem. Phys.*, **48**, 4544 (1968).
(23) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy", McGraw-Hill, New York, N.Y., 1955, p 250.
(24) R. W. Rudolph and R. W. Parry, *J. Am. Chem. Soc.*, **89**, 1621 (1967).
(25) T. D. Coyle and F. G. A. Stone, *Prog. Boron Chem.*, **1**, 137 (1964).
(26) S. Geller and J. L. Hoard, *Acta Crystallogr.*, **3**, 121 (1950); **4**, 399 (1951).
(27) J. L. Hoard, S. Geller, and W. M. Cashin, *Acta Crystallogr.*, **4**, 396 (1951).
(28) W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2261 (1967).
(29) J. R. Sabin, *Chem. Phys. Lett.*, **20**, 212 (1973).

Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

Spectra and Structure of Some Silicon-Containing Compounds. VIII.[1]
Vibrational Spectra of Hexafluorodisiloxane

J. R. DURIG,* V. F. KALASINSKY, and M. J. FLANAGAN[2]

The Raman spectra (50–2000 cm^{-1}) of gaseous, liquid, and solid $(F_3Si)_2O$ have been recorded. The infrared spectra of the gas and solid have been recorded from 55 to 2500 cm^{-1}. The spectra of all three physical states have been interpreted in detail on the basis of C_{2v} symmetry. The A_1 skeletal Si–O–Si bend was assigned at 85 cm^{-1} in the infrared spectra. Normal-coordinate calculations using a valence force field gave the Si–O and Si–F stretching force constants as 5.48 ± 0.13 and 5.07 ± 0.08 mdyn/Å, respectively. Extensive mixing was found in the A_1 block, the reasons for which are discussed. Comparisons are made between $(F_3Si)_2O$ and other substituted disiloxanes.

Introduction

Almenningen et al.[3] have found the Si–O–Si angle in disiloxane, $(H_3Si)_2O$, to be $144 \pm 1°$ from electron diffraction investigations of this molecule. Since the skeletal bending mode is found[4] at 68 cm^{-1}, the angle in disiloxane must be increased by an uncertain amount depending on the nature

of the potential function governing this bending motion to allow[5,6] for the "shrinkage". The large skeletal angle in disiloxane compared to the corresponding one (112°) in dimethyl ether[7] can be interpreted in terms of the delocalization of the electrons in the lone pairs on the oxygen atom into the vacant 3d silicon orbitals. The replacement of the hydrogen