THE SYNTHESIS AND CHARACTERIZATION OF METHYLMERCAPTYLDIFLUORO-PHOSPHINE AND BIS-METHYL-MERCAPTYLFLUOROPHOSPHINE

PART II INVESTIGATIONS OF THE USE OF LOW RESOLUTION MICROWAVE SPECTROSCOPY

> Thesis for the Degree of M. S. MICHIGAN STATE UNIVERSITY JACQUELINE GRACE HUERNER 1972





ABSTRACT

PART I

THE SYNTHESIS AND CHARACTERIZATION OF METHYLMERCAPTYLDIFLUOROPHOSPHINE AND BIS-METHYLMERCAPTYLFLUOROPHOSPHINE

By

Jacqueline Grace Huerner

Methylmercaptyldifluorophosphine, CH_3SPF_2 , was prepared by fluorination of methylmercaptyldichlorophosphine, CH_3SPCl_2 , with sodium fluoride in dry tetrahydrothiophene-1, 1-dioxide, $C_4H_8O_2S$. Methylmercaptyldichlorophosphine was prepared by the interaction of methyl mercaptan, CH_3SH , with phosphorus trichloride, PCl_3 . Bis-methylmercaptylfluorophosphine, $(CH_3S)_2PF$, was prepared by the interaction of methyl mercaptan, chlorodifluorophosphine, PF_2Cl , and trimethylamine, $(CH_3)_3N$. The compounds were characterized by ¹H and ¹⁹F nmr and mass spectral data and by elemental analysis.

Jacqueline Grace Huerner

PART II

INVESTIGATIONS OF THE USE OF LOW RESOLUTION MICROWAVE SPECTROSCOPY

Low resolution microwave spectra were recorded for the borane adduct of methoxydifluorophosphine, $CH_{3}OPF_{2} \cdot BH_{3}$. From these spectra a value was obtained for the sum of two of the rotational constants, (B + C). Theoretical values of (B + C) were determined for different conformers of the oxygen-boron and the phosphorus-boron adducts and the theoretical and experimental values compared in an attempt to determine which conformer existed. Several possible conformers were eliminated, but at least one conformer of both the oxygen-boron and the phosphorus-boron adducts remained as possibilities. An effort was made to record the microwave spectra of the boron trifluoride adducts of methoxydifluorophosphine, $CH_{3}OPF_{2} \cdot BF_{3}$, and dimethylaminodifluorophosphine, $(CH_{3})_{2}NPF_{2} \cdot BF_{3}$, but spectra were not observed for these adducts under the conditions of the experiment.

PART I

THE SYNTHESIS AND CHARACTERIZATION OF METHYLMERCAPTYLDIFLUOROPHOSPHINE AND BIS-METHYLMERCAPTYLFLUOROPHOSPHINE

PART II

INVESTIGATIONS OF THE USE OF LOW RESOLUTION MICROWAVE SPECTROSCOPY

By

Jacqueline Grace Huerner

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INTRODUCTION

A simplified bonding model involving a $(p--d)\pi$ bond has often been used to rationalize the chemistry and structures of compounds of sulfur, silicon, and phosphorus.¹ Structural determinations provide some of the best evidence for this type of bonding. It has long been known that the nitrogen in trisilylamine was in a planar environment.² More recently a planar arrangement of atoms about nitrogen has been found in dimethylaminodifluorophosphine and aminodifluorophosphine.^{3,4} In work recently completed at Michigan State University, methoxydifluorophosphine was determined to have a C-O-P bond angle of $123.5^{0.5}$ This suggests $(p--d)\pi$ bonding between oxygen and phosphorus.

Thus the stereochemical evidence strongly suggests that an interaction occurs between elements in the first row of the periodic table which have non-bonding electrons in p orbitals and elements in the second row which have vacant d orbitals which can be rationalized by the $(p--d)\pi$ bonding model. However, no strong evidence has yet been found for this type of bonding between elements in the second row. Trisilylphosphine is pyramidal.⁶ The H-P-P bond angle in phosphinodifluorophosphine is only 90.3⁰.⁷ The synthesis of methylmercaptyldifluorophosphine was

undertaken because it is the sulfur analog of methoxydifluorophosphine. The determination of its structure should help determine whether $(p--d)\pi$ bonding occurs in it. The larger size of the sulfur atom might prevent sufficient orbital overlap for π bonding to occur. However, sulfur is more basic than oxygen, and the strongly electronegative fluorine ligands on the phosphorus favor such a bonding scheme.⁸

Bis-methylmercaptylfluorophosphine was prepared during an attempted synthesis of methylmercaptyldifluorophosphine. It has been used for studies of Lewis base strengths of fluorophosphines towards borane.⁹ Studies of borane adducts of phosphines containing nitrogen, oxygen, and carbon had indicated that (J_{RP}) of the adduct was a measure of the basicity of the phosphine towards borane.¹⁰ The two mercaptylphosphines for which syntheses are reported here were found to have approximately the same base strength toward borane, but the borane adduct of methylmercaptyldifluorophosphine has a considerably higher value of (J_{RP}) .⁹ Reviews of base strengths of existing compounds had also indicated that the base strength should decrease as substituents of increasing electronegativity were attached to phosphorus.¹⁰,¹¹ The preparation of the mercaptylphosphines provided an excellent test of this theory since the oxygen analogs of both compounds were known. In contrast to this prediction, CH₃OPF₂ formed a stronger borane adduct than either CH₃SPF₂ or (CH₃S)₂PF.⁹

EXPERIMENTAL

General Procedure

Bis-methylmercaptylfluorophosphine was prepared by the use of standard vacuum techniques.¹²

Methylmercaptyldifluorophosphine was prepared under a nitrogen atmosphere. The glass apparatus was dried in an oven at 130°C for twenty-four hours before use, assembled while still warm, and immediately filled with dry nitrogen.

Elemental analyses were done by Galbraith Laboratories, Inc. (Knoxville, Tennessee).

Nuclear magnetic resonance spectra were recorded with a Varian A56/60D analytical spectrometer equipped with a variable temperature controller.

Mass spectra were obtained by the use of a Hitachi-Perkin Elmer RMU-6 mass spectrometer.

<u>Materials</u>

Methyl mercaptan was used as obtained from Amoco Chemicals Corporation (Chicago, Illinois). Aqueous trimethylmaine was obtained from the Matheson Company, Inc. (Cincinnati, Ohio) and dried over sodium.¹³ Chlorodifluorophosphine was prepared by the interaction of dimethylaminodifluorophosphine and hydrogen chloride.¹⁴ It was purified by codistillation.15

Sodium fluoride was used as obtained from Fisher Scientific Company (fair Lawn, New Jersey). Tetrahydrothiophene-1,1-dioxide (sulfolane) was obtained from Eastman Kodak Company (Rochester, New York) and was dried by distillation in vacuum from molecular sieve. It was stored over molecular sieve. Phosphorus trichloride was used as obtained from Mallinckrodt Chemical Works (St. Louis, Missouri).

Preparation of CH₃SPCl₂

The apparatus employed for the preparation of CH₃SPCl₂ was the same as that previously described for the preparation of $(CH_3)_2NPCl_2$.¹⁴ In a typical reaction a 30 ml (0.34 mol) sample of phosphorus trichloride was transferred to a round-bottom flask equipped with a magnetic stirrer. A 13 g (0.26 mol) sample of methyl mercaptan was added to the reaction mixture. The mixture was maintained at ambient temperature and stirred for three hours. One of the dry ice condensers was then replaced with a distillation column and water-cooled condenser. A heating mantle was placed around the reaction flask, and the mixture was distilled under nitrogen. Three fractions were collected. The first fraction, b.p. 75-85°C, consisted mainly of phosphorus trichloride, b.p. 75.5⁰C. The second fraction boiled at 161-162°C. The Third fraction boiled at a temperature greater than 172°C. The temperature was still rising when the distillation was stopped. Two overlapping doublets were observed in the ¹H nmr of the second fraction with the

doublet at lower field five times more intense than the one at higher field. The lower field doublet was attributed to CH_3SPCl_2 and the higher field one to $(CH_3S)_2PCl$ because in the ¹H nmr spectra of the analogous compounds CH_3OPF_2 and $(CH_3O)_2$ PF, CH_3OPF_2 absorbs at lower field. The mass spectrum of this fraction consisted of the following peaks (listed as the m/e ratio, relative intensity, and tentative assignments): 154, 4.0, OP³⁵Cl₂³⁷Cl; 152, 4.1, OP³⁵Cl₃ and CH₃SP³⁷Cl₂; 150, 6.2, CH₃SP³⁵Cl³⁷Cl; 149, 8.5, CH₃SP³⁵Cl₂; 140, 7.5, P³⁵Cl³⁷Cl₂; 138, 22, P³⁵Cl₂³⁷Cl; 136, 23, P³⁵Cl₃; 121, 4.2, OP³⁷Cl₂; 119, 8.5, OP³⁵Cl³⁷Cl; 117, 12.8, OP³⁵Cl₂; 115, 5.0, CH₃S³⁷Cl; 113, 13.8, CH₃SP³⁵Cl; 105, 10, P³⁷Cl₂; 103, 64, P³⁵Cl³⁷Cl; 101, 100, P³⁵Cl₂; 77, 9.8, CH₂SP; 68, 8.3, P³⁷Cl; 66, 28, P³⁵Cl; 63, 8.5, SP; 47, 8.8, CH₃S; 46, 3.0, CH₂S; 45, 8.3, CHS; 38, 3.8, H³⁷Cl; 37, 6.0, ³⁷Cl; 36, 12.0 H³⁵Cl; 35, 18.8, ³⁵Cl; 31, 12.0, P. Elemental analysis was obtained on the third fraction because it was presumed to contain less phosphorus trichloride.

<u>Anal</u>. Calc CH₃SPCl₂: C, 8.0; H, 2.0; Cl, 47.6. Calc (CH₃S)₂PCl: C, 15.0, H, 3.4; Cl, 22.1. Found: C, 11.39; H, 2.96; Cl, 33.10.

Preparation of CH₃SPF₂

Equipment similar to that used for the preparation of $(CH_3)_2NPCl_2$ was employed.¹⁴ In a typical reaction a 15 g sample of sodium fluoride was transferred to a 3-necked

round-bottom flask equipped with a magnetic stirrer. An amount of previously dried tetrahydrothiophene-1,1-dioxide sufficient to dissolve the sodium fluoride, approximately 30 ml, was also transferred to the flask. A pressure equalized dropping funnel was attached to one neck. An adapter was attached to another neck and a U-trap equipped with high vacuum stopcocks was connected to the adapter with tygon tubing. The third neck was stoppered. Nitrogen was allowed to pass through the apparatus and then through a mineral oil bubbler. A 6 ml sample of the mixture of CH_3SPCl_2 and $(CH_3S)_2PCl$ prepared as previously described was transferred to the dropping funnel. It was added dropwise over a period of about two hours. After the addition of CH_3SPCl_2 and $(CH_3S)_2PCl$ the reaction mixture was stirred for an additional one-half hour. The volatile products were collected in the U-trap which was cooled to -196° . This volatile mixture was allowed to pass through traps held at -136 and -196[°]. The product collected at -136[°] was transferred to an evacuated nmr tube and the tube sealed. Spectra were obtained at -70°C. The ¹H spectrum, Figure 1, showed a doublet $({}^{3}J_{HP} = 7.3 \text{ Hz})$ centered at 20 ppm from TMS; each member of the doublet was split into a 1:2:1 triplet $({}^{4}J_{HF} = 2.2 \text{ Hz})$. The ${}^{19}F$ spectrum, Figure 2, consisted of a doublet $({}^{1}J_{PF} = 1248 \text{ Hz})$ centered at +72.2 ppm from CCl₃F; each member of the doublet was further split into a 1:3:3:1 quartet $({}^{4}J_{HF} = 2.1 \text{ Hz})$. These spectra are consistent with the predicted spectra for CH₃SPF₂ and are similar to

Figure 1. ¹H nmr spectrum of CH_3SPF_2 at $-70^{\circ}C$.

Figure 2. ^{19}F nmr spectrum of CH_3SPF_2 at $-70^{\circ}C$.

those reported for other fluorophosphines.¹⁶ This compound subsequently has been prepared by R. Foester and characterized by nmr, infrared, and mass spectra.⁹ The nmr data reported here are identical to those reported by Foester.

Preparation of (CH₃S)₂PF

Equimolar samples of approximately 3.7 mmol of methyl mercaptan and chlorodifluorophosphine were transferred in vacuum to a 1-liter reaction bulb maintained at -196°C. A 4-mmol sample of trimethylamine was also transferred to the bulb. The bulb was allowed to warm to room temperature and then cooled to -196°. This process was repeated several times. The products were allowed to pass through traps held at -96.7° and -196°. The less volatile product was transferred to an nmr tube and the tube sealed. Spectra were obtained at -50° . The ¹H spectrum, Figure 3, showed a doublet $({}^{3}J_{HP} = 12.3 \text{ Hz})$ centered at 2.4 ppm from TMS; each member of the doublet was split into a doublet $({}^{4}J_{\mu\nu} = 2.6)$ Hz). The ¹⁹F spectrum, Figure 4, showed a doublet $({}^{1}J_{PF} =$ 1114 Hz) centered at +116.4 ppm from CCl₃F; each member of the doublet is further split into a 1:6:15:20:15:6:1 septet $({}^{4}J_{HF} = 2.4 \text{ Hz})$. Both the coupling constants and chemical shifts are consistent with the proposed formulation and are similar to values previously reported for fluorophosphines.¹⁶ The mass spectrum also was consistent with the proposed formulation. The spectrum consisted of the following peaks

Figure 3. ¹H nmr spectrum of $(CH_3S)_2PF$ at $-50^{\circ}C$.

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Figure 4. ¹⁹F nmr spectrum of $(CH_3S)_2PF$ at $-50^{\circ}C$.



Figure 4.

(listed as the m/e ratio; relative intensity, and tentative assignments): 144, 72, $(CH_3S)_2PF$; 129, 23, CH_3SPSF ; 97, 68, CH_3SPF ; 88, 14, PF_3 ; 69, 23, PF_2 ; 63, 18, SP; 59, 55, $(CH_3)_3N$; 58, 23, $(CH_3)_2NCH_2$; 47, 100, CH_3S ; 46, 23, CH_2S ; 45, 68, CHS; 42, 23, CH_3NCH . PART II

INVESTIGATIONS OF THE USE OF LOW RESOLUTION MICROWAVE SPECTROSCOPY

INTRODUCTION

The structural changes which would be expected in molecules in which $(p--d)\pi$ bonding occurs were discussed in the introduction to Part I. If a π bond does occur in which non-bonding p electrons on one atom are donated into empty d orbitals of an adjacent atom, a decrease in Lewis basicity should occur for the first atom accompanied by a corresponding increase in the Lewis basicity of the second atom. This argument has been used to explain the relative Lewis basicities of phosphorus and nitrogen in several aminophosphines 17-21 Low resolution microwave studies of the borane and boron trifluoride adducts of methoxydifluorophosphine and the boron trifluoride adduct of dimethylaminodifluorophosphine were undertaken in the hope that, although we did not know the limitations of the microwave technique, we could determine in each case whether the boron were bonded through phosphorus or through the other donor atom, oxygen or nitrogen.

Nmr data for the borane adduct of methoxydifluorophosphine, particularly the $J_{BP} = 69.3$ Hz, strongly suggested coordination through phosphorus.⁹ A boron-phosphorus adduct would be favored because of the effects of $(p--d)\pi$ bonding. Furthermore, the borane group, which is a soft acid, would be predicted to bond preferentially to the phosphorus atom since phosphorus is a soft base and oxygen a hard base. Thus the examination of the BH₃ adduct of

 CH_3OPF_2 by low resolution microwave was conducted to determine the limits and accuracy of the technique.

The boron trifluoride adduct of methoxydifluorophosphine was more interesting. The effect of $(p--d)\pi$ bonding should still favor a boron-phosphorus adduct. But BF₃, a hard acid, would normally be expected to coordinate through oxygen. The unpublished nmr data which are available are conflicting and cannot be used to distinguish between the two possible adducts.²²

The structure of the boron trifluoride adduct of dimethylaminodifluorophosphine provided an interesting test of the (p--d) π interaction. The x-ray diffraction study of the crystal structure of dimethylaminodifluorophosphine had found a planar arrangement of atoms around nitrogen.⁴ This indicated sp² hybridization of nitrogen so that nitrogen would have no non-bonding electrons and would not function as a Lewis base. Infrared and nmr spectral data obtained on the BF₃ adduct had been interpreted in terms of a boronnitrogen adduct.²³⁻²⁵ However, some features of the infrared spectrum were also characteristic of a boron-phosphorus adduct.^{25,26} We hoped to establish the coordination site unequivocally by the use of low resolution microwave spectroscopy.

THEORY

The rotational spectrum of a polar molecule arises from the interaction of the molecular dipole moment with an electromagnetic field. The frequencies of the electromagnetic radiation are in the microwave range (ca. 1-600 GHz), and the determination of molecular structures and other types of molecular information from the rotational spectrum is called microwave spectroscopy or molecular rotational resonance.

A common approximation in microwave spectroscopy is to treat the molecule as an effective rigid rotor. Then, the moment of inertia, I, about any axis through the center of mass of the molecule is defined by

$$\mathbf{I} = \sum \mathbf{m}_{i} \mathbf{r}_{i}^{2} \tag{1}$$

where m_i is the mass of the i th atom and r_i is its effective perpendicular distance from the axis. The sum runs over all the atoms in the molecule. Information about rotational energies is also commonly reported in terms of the rotational constants which are defined by

$$A = \frac{h}{8\pi^2 I_a}, \quad B = \frac{h}{8\pi^2 I_b}, \quad C = \frac{h}{8\pi^2 I_c}, \quad A \succeq B \succeq C \quad (2)$$

In these equations I_a , I_b , and I_c are the principal moments of inertia. A computer program has been written by Schwendeman which calculates the rotational constants from bond distances and bond angles.²⁷

The calculation of rotational energy levels is greatly simplified for molecules which have a proper axis of rotation of order three or higher. Such molecules are known as symmetric tops and are further classified as oblate symmetric tops ($\kappa = +1$ and A = B > C) and prolate symmetric tops ($\kappa = -1$ and A > B = C) where κ is the asymmetry parameter defined by²⁸

$$\kappa = \frac{2B - A - C}{A - C} . \qquad (3)$$

If centrifugal distortion and hyperfine structure are neglected, the rotational frequencies are given by²⁹

$$v_{J->J+1} = 2B(J + 1).$$
 (4)

The molecules studied in these investigations are near prolate symmetric tops ($A > B \approx C$, $\kappa \leq -0.80$). The asymmetry of these molecules causes the rotational energy levels to be split and shifted, and many more lines are observed than would be predicted from equation (4) for symmetric top molecules. The number of extra transitions depends in part on the orientation of the dipole moment in the molecule. If the dipole moment has a significant component in the direction of the a principal axis (for a near prolate top), transitions will occur in groups centered about³⁰

$$v_{J->J+1} = 2(\frac{B+C}{2})(J+1) = (B+C)(J+1).$$
 (5)

In a fast scan such as that used here these groups of transitions will predominate. Other weaker transitions associated with components of the dipole moment in the b or c principal axis directions will occur, but they will not follow any simple patterns.

A value of (B + C) was calculated from the frequency at the center of each group of peaks. This value of (B + C)was then treated empirically as one piece of structural information. Theoretical values of (B + C) were calculated by computer for each possible structure and compared with the experimental value. If the experimental value of (B + C) did not fall within the range of values calculated for a proposed structure, that structure was eliminated. Some proposed structures were also eliminated because they were not near prolate symmetric top molecules (κ not \approx -0.1). This empirical treatment of the rotational constants (B + C) is called low resolution microwave spectroscopy.

This manner of calculation of (B + C) from experimental data involves several approximations. A more precise determination is possible but has proven not to be of value in this work. The error introduced by the approximations is negligible compared with the variations in (B + C) which result from uncertainties in the structural parameters.

In this manner one piece of structural information, a value of (B + C), was easily obtained and treated with a

relatively small amount of computer time. The available instrumentation and computer programs would have allowed the observation and assignment of all rotational transitions. The complete structures of the molecules could then have been determined using isotopically substituted species. However, the process is generally not routine. Complexities of interest only to spectroscopists are often encountered, and large amounts of computer time may be needed. The investigation of low resolution microwave spectroscopy described here was undertaken to determine if that part of the molecular structure of greatest interest to inorganic chemists, the coordination site of borane or boron trifluoride groups, could be established without determining the complete structure.

EXPERIMENTAL

General Procedure

Diborane, B_2H_6 , and all adducts were prepared by the use of standard vacuum line techniques.¹² All ground glass joints were greased with halocarbon grease for reactions involving BF_3 . Ligands were prepared by fluorination reactions under a nitrogen atmosphere.

Microwave spectra were recorded by means of a Hewlett-Packard model 8460A spectrometer. Spectra were recorded in K-band (18,000 to 26,500 MHz) and R-band (26,500 to 40,000 MHz) frequency ranges. The Stark voltage was set at 500 volts. The crystal current was approximately 80 amps. A scanning rate of 10 MHz/sec with a chart speed of 2 in/min was used. Frequencies were determined from markers recorded every 10 MHz. The sample pressure was approximately 100 μ except where otherwise noted. In order to eliminate traces of moisture adhering to the spectrometer, diborane was introduced into the spectrometer and then removed prior to the introduction of the sample.

Materials

Antimony trifluoride was used as obtained from Alfa Inorganics, Inc. (Beverly, Massachusetts). Antimony pentachloride was used as obtained from Allied Chemical (Morristown, New Jersey). Diborane was prepared by reduction of boron trifluoride with sodium tetrahydroborate (sodium borohydride).³¹ Boron trifluoride was obtained from the Matheson Company, Inc. (Joliet, Illinois). It was allowed to pass through traps held at -145° and -196°. Only the material which passed through the -145° trap was used in the syntheses.

Preparation of Compounds

 CH_3OPF_2 was prepared by fluorination of CH_3OPCl_2 with antimony trifluoride. Antimony pentachloride was used as a catalyst in this reaction.³² The borane adduct was prepared by condensing 0.76 mol samples of B_2H_6 and of CH_3OPF_2 into a 60-ml bulb equipped with a teflon stopcock and a magnetic stirrer. The -196° bath was then replaced with a -78.5° bath, and the mixture was allowed to warm to approximately -5° over a period of one-half hour. The -78.5° bath was then replaced with a 0° bath. The reaction flask was maintained at 0° for three hours while the mixture was stirred continuously. After three hours the mixture was allowed to pass through traps held at -111° and -196°. The fraction retained at -111° was further purified and its microwave spectrum recorded.¹⁵

Several attempts were made to prepare the BF3 adduct of CH₃OPF₂. This adduct is not reported in the literature. Its preparation had been attempted before in this laboratory, but no definite compound which could be characterized by infrared or nmr spectra had been obtained. A 1.5 mmol sample of BF₃ was transferred to a 60-ml flask equipped with a teflon stopcock. A 1.0 mmol sample of CH_3OPF_2 was also transferred to the flask. The flask was maintained at -126° for thirty minutes. The flask was then opened to a trap held at -196° for one and a half minutes. A 1.25 mmol sample of BF₃ was collected in the trap. The material remaining in the reaction flask was transferred to a storage bulb maintained at -196°. During the transfer some volatile material was observed subliming before the bulk of the sample. If the sample were transferred to the microwave spectrometer, only this very volatile material would enter the waveguide (sample cell). This material, which was more volatile than CH₃OPF₂, could not be the adduct and was discarded. In another attempted preparation a 2 mmol sample of BF₃ and a 1 mmol sample of CH₃OPF₂ were transferred to a bulb equipped with a magnetic stirrer. The bulb was maintained at -78.5° for one half hour, and the mixture was stirred continuously. A -126° bath was then placed around the bulb, and the bulb was opened to a trap held at -196°. A 1.1 mmol sample of BF_3 was collected in the trap. The material remaining in the reaction bulb was transferred to a storage container held at -196°. A -126°

bath was then placed around the storage container and the storage container opened to the trap held at -196° which contained the sample of BF₃ collected previously. The total sample of BF₃ in the trap then constituted 1.4 mmol. It appeared that the BF₃ adduct disproportionated whenever it was allowed to warm to a temperature at which it had a sufficient vapor pressure for transfer to occur and that there would be no way to transfer it to the microwave spectrometer.

Equimolar samples of 2 mmol of BF_3 and CH_3OPF_2 were transferred to a 250-ml bulb held at -196°. The bulb was allowed to equilibrate at room temperature for one half hour. It was then attached to the microwave spectrometer and sample was introduced at pressures as high as 100μ . The waveguide was then covered with dry ice. Microwave spectra were recorded during the next three and a half hours as the dry ice sublimed and the temperature of the sample gradually rose to room temperature. These spectra were identical to those of CH_3OPF_2 . No further effort was made to record the microwave spectrum of this adduct.

The BF₃ adduct of $(CH_3)_2NPF_2$ is a well characterized compound. Its synthesis was reported independently by two workers, and it was characterized by its infrared spectrum and by elemental analysis.^{23,33} It has also been characterized by its ¹H, ¹⁹F, ³¹P, and ¹¹B nmr spectra. However, estimates have been made that it is only 0-5% associated in the gas phase at room temperature.²⁵

The synthesis was conducted as described in the preceding references.^{23,25} The products were allowed to warm through traps held at -63.5 and -196°. The material which remained in the trap at -63.5° was transferred to a storage container held at -196°. When this sample was introduced into the microwave spectrometer and its spectrum recorded, the only peaks observed were those for $(CH_3)_2NPF_2$. The sample remaining in the storage container was allowed to pass through traps held at -45° and -196°. The portion which remained in the trap at -45° was transferred back to the storage container.

The adduct reportedly sublimes <u>in vacuo</u> at $-23^{0}.^{25}$ A -22.9⁰ bath was placed around the storage container while the container was attached to the microwave spectrometer. The waveguide was partially covered with dry ice. Sample was then introduced at pressures as high as 100μ . Again the spectrum indicated the presence of only $(CH_3)_2NPF_2$. The waveguide was evacuated. The -22.9^{0} bath was replaced with a -78.5^{0} bath, and the waveguide was completely covered with dry ice. The sample was introduced into the spectrometer. The sample pressure was approximately 10μ at -78.5^{0} . The spectrum was weaker than those recorded at a higher pressure, but it clearly indicated $(CH_3)_2NPF_2$ and nothing else.

In a procedure analogous to that used for BF_3 and CH_3OPF_2 , equimolar quantities of BF_3 and $(CH_3)_2NPF_2$ were introduced into the spectrometer at room temperature. The

waveguide was then covered with dry ice. Spectra recorded at intervals as the temperature gradually increased indicated only $(CH_3)_2NPF_2$.

No further attempt was made to record the spectrum of $(CH_3)_2NPF_2 \cdot BF_3$. The adduct appears to be almost completely dissociated in the vapor phase at all temperatures studied. However, the possibility remains that the adduct was present in the vapor, but its spectrum was not observed under the experimental conditions. The spectrum might not be observed if the lines were very weak because the dipole moment of the molecule was small. The spectrum also might not be observed at low resolution if the lines did not occur in groups because the molecule was not a near prolate symmetric top. Preliminary calculations indicated that kappa was only approximately -0.6 for either the boron-phosphorus or the boron-nitrogen adduct. If this is the case, the molecule is not a suitable subject for this study.

RESULTS AND DISCUSSION

In the low resolution microwave spectrum of $CH_3OPF_2 \circ BH_3$ two groups of peaks were observed in the K-band and three in the R-band. They were centered at 18,380 MHz; 23,000 MHz; 27,590 MHz; 32,170 MHz, and 36,790 MHz. These were associated with transitions between J levels 3-4, 4-5, 5-6, 6-7, and 7-8. From these data the value of (B + C) was calculated to be 4596 ± 5 MHz.

Values were assigned to each structural parameter which did not involve hydrogen atoms for both the phosphorusboron and the oxygen-boron adducts. Tetrahedral methyl groups and symmetrical borane groups were assumed. Limits within which the values would be expected to vary were also set. These data are summarized in Table I. The structure of CH_3OPF_2 determined by high resolution microwave spectroscopy was used as a starting point for the structural parameters employed.⁵ Values could be assigned with more confidence for the phosphorus-boron adduct because several structural studies have been done of phosphine molecules and the corresponding phosphine-borane adducts.^{4,26,34-37} The values for the P-F bond distance and the F-P-F bond angle could be assigned within fairly small limits from data obtained from studies of other boron adducts of

Table I. Structural parameters of CH₃OPF₂ •BH₃.

Param-		Р	Adduct	0 Adduct					
eter	CH ₃ OPF ₂	Best	Limits	Best	Limits				
P-F(Å)	1.587	1.557	1.556-1.561	1.587	1.587-1.597				
$P-O(\overset{O}{A})$	1.569	1.54	1.52 - 1.56	1.59	1.59 -1.61				
c-0(Å)	1.446	1.446	1.44 - 1.55	1.466	1.446-1.486				
$\mathbf{P}-\mathbf{B}(\overset{\mathbf{O}}{\mathbf{A}})$		1.88	1.83 - 1.93						
о-в(⁰ А)				1.50	1.45 -1.55				
∠ OPF	101.7 ⁰	103.3 ⁰	103° -107°	101.70	100.70-102.70				
∠ cod	123.5 ⁰	123.5 ⁰	121.5 ⁰ -123.5 ⁰	120 ⁰	118 ⁰ -122 ⁰				
/ FPF	95.2 ⁰	96.8 ⁰	96.2 ⁰ - 97.2 ⁰	95 .2 0	94.2 ⁰ - 96.2 ⁰				
∠ орв		116 ⁰	111 ⁰ –118 ⁰						
∠ сов				120 ⁰	118 ⁰ -122 ⁰				

fluorophosphines.³⁷ The crystal structures determined by Nordman and co-workers of both $(CH_3)_2NPF_2$ and $(CH_3)_2NPF_2 \cdot B_4H_8$ were used to predict what changes in bond lengths and angles occur when boron complexes with phosphorus.^{4,26}

Assignment of appropriate values for the structural parameters of the oxygen-boron adduct was more difficult. Only one structural determination of an oxygen-boron adduct has been published, an electron diffraction study of $(CH_3)_2 O \cdot BF_3$ which is of questionable reliability.³⁸ Comparison of bond lengths in that adduct with those determined for the free ligand indicated that adduct formation might result in a slight increase in the bond lengths of the atoms bonded to oxygen.³⁹ Changes in bond angles after adduct formation were based on considerations of steric hindrance. The value for the O-B bond length which was used (1.50 ± 0.5 Å) was established by considering that determined in the electron diffraction study (1.50 Å) and that predicted from Schomaker-Stevenson single bond radii (1.55 Å).³⁸,⁴⁰

Theoretical values of (B + C) and κ were calculated for four conformations of the phosphorus-boron adduct and two conformations of the oxygen-boron adduct, Figure 5. Conformations II-IV of the phosphorus-boron adduct were eliminated because they were not near prolate symmetric tops. Conformations such as III and IV in which the methyl or borane groups were not in the same plane as the phosphorus and oxygen atoms were not considered for the oxygen-

Figure 5. Theoretical values of (B + C) and kappa (κ) for possible conformations of $CH_3OPF_2 \cdot BH_3 \cdot$





Oxygen Adduct



I

B+C = 4428MHz κ = -0.933



II

B+C = 4335MHz $\kappa = -0.966$

Figure 5.

boron adduct because they were not likely to be near symmetric tops, and they were less probable because of steric hindrance. Qualitatively, the value of (B + C) for the phosphorus adduct, 4573 MHz, is much closer to the experimental value of 4596 MHz than are the values calculated for the oxygen adduct, 4428 MHz and 4335 MHz. For low resolution microwave studies of several organic molecules, values of (B + C) calculated for assumed structures, based upon structural parameters of similar molecules, generally agreed with the experimental value within 1%.

For the three remaining adducts, values of (B + C)were then calculated with each parameter varied to its limits and all other parameters held at the original value to determine if increasing that parameter would increase or decrease the value of (B + C). The experimental value of (B + C) was easily within the range of values possible for the phosphorus adduct. For example, if a value of 1.52 Å rather than 1.54 Å was used for the P-O bond length and all other parameters held constant, the resulting (B + C) was 4610 MHz. For the two conformations of the oxygen-boron adduct, a theoretical value of (B + C) was calculated with each structural parameter fixed at the limit which would yield the highest possible value of (B + C). For conformation I, the highest possible (B + C) was calculated to be 4614 MHz, and for conformation II, 4566 MHz. Conformation II was thus eliminated as a possibility.

The ¹⁰B isotope occurs in 18.83% natural abundance. Therefore a microwave spectrum associated with this isotope is generally observed when the spectrum of any molecule containing boron is recorded. The transitions occur at higher frequencies and are of course much weaker than those for the normal species. Transitions associated with the ¹⁰B isotope were observed at 37,540 MHz; 32,880 MHz; 28,160 MHz; and 23,460 MHz. These were assigned to transitions between J levels 7-8, 6-7, 5-6, and 4-5, respectively. The value of (B + C) was calculated to be 4694 ± 3 MHz. A theoretical value of 4670 MHz was calculated for the ^{10}B isotope of conformation I of the phosphorus-boron adduct and 4526 MHz for conformation I of the oxygen-boron adduct. As in the case of the normal species the experimental value of (B + C) was clearly within the range of possible values for the phosphorus adduct, and that appeared to be the actual species. However, the maximum possible value of (B + C) for the oxygen adduct was 4717 MHz.

Conformations I of both the boron-phosphorus and boronoxygen adducts remained as possibilities. In this case the technique of low resolution microwave could not distinguish between the two possible coordination sites. The value of (B + C) was as sensitive to a fairly minor change in structure, e.g. a change in a bond length of 0.1 Å or approximately 7%, as to a major change in structure: the change in coordination site of a borane group. The utility of this technique is thus quite limited, but it has been used to

determine conformations of molecules such as alkanes for which structural parameters are well established.^{30,41} It does not yield useful information about the structures of molecules for which only limited structural data are available. This latter group includes most inorganic molecules, and therefore few applications of this technique presently exist in inorganic chemistry.

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