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STUDIES OF SOME PENTAVALENT PHOSPHORUS FLUORIDE COMPOUNDS

by

THOMAS LAURIE CHARLTON

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled:

"STUDIES OF SOME PENTAVALENT PHOSPHORUS
FLUORIDE COMPOUNDS"

submitted by THOMAS LAURIE CHARLTON in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

Anhydrous hydrogen iodide reacts with dimethylaminophosphoryl difluoride and dimethylaminothiophosphoryl difluoride to form hydrophosphoryl difluoride and hydrothiophosphoryl difluoride in good yield. Both compounds are volatile liquids, but the thiophosphoryl compound is much more stable than the oxygen analog. A number of reactions of hydrothiophosphoryl difluoride were used to prepare further compounds.

Iodothiophosphoryl difluoride, a volatile liquid, has been prepared from hydrothiophosphoryl difluoride by reaction with (a) N-iodosuccinimide, (b) sulphur and iodine, or (c) sulphur and hydrogen iodide. Several reactions of iodothiophosphoryl difluoride were studied, including its reduction by hydrogen iodide to hydrothiophosphoryl difluoride.

Difluorodithiophosphoric acid, a volatile, relatively strong acid, has been synthesized by either: (1) the reaction of iodothiophosphoryl difluoride with hydrogen sulfide, or (2) reaction of hydrothiophosphoryl difluoride with sulphur. A number of reactions of difluorodithiophosphoric acid are reported. The nmr spectrum of the acid indicates that rapid proton exchange occurs.

Difluorothiophosphoryl-μ-thio-difluorophosphine, a moderately stable volatile liquid, has been prepared by the reaction of iodothiophosphoryl difluoride with a stoichio-

metric amount of mercury and by reaction of difluorodithiophosphoric acid with dimethylaminodifluorophosphine. The reaction of difluorophosphoric acid with dimethylaminodifluorophosphine gives the considerably less stable oxygen analog, difluorophosphoryl-μ-oxo-difluorophosphine. Spectral and chemical studies indicate that the compounds have a bridged structure such that each molecule contains a pentavalent and a trivalent phosphorus atom.

The amino compounds, methylaminothiophosphoryl difluoride, aminothiophosphoryl difluoride, methylaminophosphoryl difluoride, and aminophosphoryl difluoride have been prepared by the reaction of methylamine or ammonia with the appropriate chlorodifluorophosphoryl compound. These compounds were then used to prepare the nitrogen-bridged bis(difluorophosphorus) compounds N-methyl bis(difluorothiophosphoryl)amine, N-methyl bis(difluorophosporyl) amine, and the trimethyl ammonium salts of bis(difluorothiophosphoryl) amide and bis(difluorophosphoryl)amide.

The compound μ-oxo-bis(thiophosphoryl difluoride) has been prepared by the reaction of (a) iodothiophosphoryl difluoride and oxygen (b) difluorodithiophosphoric acid and dimethylaminophosphoryl difluoride, or (c) difluorophosphoric acid and dimethylaminothiophosphoryl difluoride. The compound μ-thio-bis(thiophosphoryl difluoride) has been prepared by the reaction of difluorodithiophosphoric acid and dimethylaminothiophosphoryl difluoride. Difluorophos-

phoryl-μ-oxo-thiophosphoryl difluoride has been prepared by the reaction of either hydrothiophosphoryl difluoride or difluorodithiophosphoric acid with difluorophosphoric acid anhydride.

The above compounds were characterized by vapor phase molecular weights, chemical reactions, mass spectroscopy, including accurate mass measurement of the parent ions, and infrared and nuclear magnetic resonance spectroscopy. The nmr spectra of the symmetrical bridged compounds were of particular interest since they constitute AA'XX'X"X''' systems. These spectra have been analyzed and the various spectral parameters determined. The implications of these parameters are discussed.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Chapter I

Although the phosphorus fluoride compounds PF_3, PF_5, OPF_3, and SPF_3 were first prepared in the latter part of the nineteenth century, very little work was done in this field until the discovery of the fluorophosphoric acids in the late 1920's. The preparation of esters of these fluorophosphoric acids, and the discovery of their biological significance led to extensive studies prior to and during the Second World War. At the same time, more intensive interest in the purely inorganic phosphorus fluorides arose. In the past few years, a number of review articles concerning inorganic phosphorus fluorides have appeared including the very extensive review by Schmutzler.[1] The reader is referred to this review for a general background review of the chemistry of phosphorus fluorides.

The original purpose of the present work was to prepare the mixed halide phosphorus compounds, iodothiophosphoryl difluoride, SPF_2I, and iodophosphoryl difluoride, OPF_2I, which would have been the first preparation of pentavalent phosphorus compounds containing iodine and fluorine. It was proposed that these iodides could then be used in coupling reactions analagous to the preparation of diphosphorus tetrafluoride, P_2F_4 [2,3], to form pentavalent diphosphorus compounds containing a phosphorus-phosphorus bond. The interest in the phosphorus-phosphorus bond has been outlined by Cowley [4], and it was hoped that the preparation of pentavalent fluoro-diphosphorus compounds could extend the knowledge of the properties of such bonds.

However, as is frequently the case, the intentions of researchers are inconsistent with the actual realities of nature. Thus, the preparation of a pentavalent fluoro diphosphorus compound containing a phosphorus-phosphorus bond has not been accomplished.

This thesis describes the preparation and properties of a number of compounds which were obtained during the attempt to prepare the diphosphorus compounds. The compounds prepared, however, do add to our knowledge of the chemical behaviour of phosphorus compounds which is discussed in greater detail in succeeding chapters. Pertinent background information is also included in the discussion in the appropriate chapters.

Materials, Apparatus, and Techniques

Chapter II

This chapter describes the apparatus, materials and experimental techniques employed in the preparation and characterization of the compounds studied during the course of this work. Specific techniques, applicable only to individual experiments are described in the appropriate section.

1. Vacuum Apparatus and Techniques

All syntheses, purifications, and characterizations were carried out using high vacuum techniques[5b] where possible. The vacuum system was constructed with Pyrex glass tubing and vacuum cup stopcocks. The stopcocks were lubricated with Apeizon "N" grease. A LeRoy still[5] was built into the system to aid in difficult purifications.

Reactions were generally carried out in Pyrex glass tubes (either completely sealed, or fitted with a stopcock) of approximate volumes 10, 25 or 75 cc depending on the quantities and volatilities of the reactants and products, and the pressures to which the tubes were likely to be subjected during the course of the reactions. Reactions done at high temperatures were done in large volumes in order to prevent too high pressures from being established in the tubes. Gas phase reactions were carried out in a 1 ℓ. vessel fitted with stop-cocked sidearms into which the reactants could be condensed before reaction.[6] Large scale reactions which produced large quantities of highly volatile compounds were carried out in a 1 ℓ. vessel into which the reactants were condensed and allowed to react in either liquid or gaseous phase.

The vapor pressures of the various compounds were measured with an all-glass spiral gauge microtensimeter [7] with both ascending and descending temperatures. Maximum temperatures obtained were about 50°C, which was the maximum temperature at which the spiral could be conveniently thermostated. Temperatures were measured with either a copper-constantan thermocouple or an accurately calibrated mercury-filled thermometer. Pressures were read using a cathetometer readable to 0.001 mm.

2. Materials

The chemicals used in the reactions described in succeeding chapters were prepared according to the literature methods as noted, when not commercially available. Commercially available chemicals of "Reagent" quality were used without further purification. The main exception to this was hydrogen iodide (Matheson and Co.) which was fractionated before use to remove quantities of elemental iodine. Difluorophosphoric acid, OPF_2OH, was prepared from impure, commercially available material, by formation of the anhydride [8] followed by HCl cleavage and vacuum fractionation of the products. Gaseous chemicals were generally obtained from Matheson and Co., liquid and solid chemicals were obtained from the usual variety of sources.

3. Instrumental Techniques

All infrared measurements of the spectra reported in this study were done on either a Perkin-Elmer Model 421 dual grating spectrophotometer, or a Beckman IR-12 spectrophotometer operating at ambient temperatures. Both instruments were used to cover the range 4000-300 cm^{-1}. A 10 cm gas cell with caesium bromide windows was used to obtain the reported spectra. Normal "fingerprinting" infrared spectral measurements were made on a Perkin-Elmer 337 spectrophotometer using the 10 cm cell equipped with potassium bromide windows. Low temperature measurements were made using a specially built cell similar to that reported by Wagner and Hornig.[9]

All mass spectra were recorded on either AEI MS-2 or MS-9 instruments operating at ionizing voltages of 70 eV. High resolution scans and accurate mass measurements were made on the MS-9. General survey scans were made on the MS-2 as an aid to identification of unknown products. Samples were generally gaseous and a room temperature inlet was used. For low volatile compounds, a heated inlet was used and for non-volatile compounds, a direct probe was used.

All nmr spectra were recorded on either a Varian A-56/60 or a Varian HA-100 instrument. Proton and fluorine spectra were obtained on the A-56/60 while the HA-100, when operating at 100 MHz was used to obtain proton spectra, at 94.1 MHz to obtain fluorine spectra, and at 40.5 MHz to obtain phosphorus spectra. Both instruments were equipped with variable temperature probes. Each instrument was equipped with a Varian V6040 variable temperature controller which appeared to be accurate to within ± 5° of the temperature indicated on the controller. The temperature was dependent on the nitrogen flow rate and the depth of liquid nitrogen around the cooling coil. The spin-tickling experiment was done on the HA-100 instrument operating at 94.1 MHz using a Hewlitt-Packard model 200 AB audio oscillator to provide irradiation of the desired signal.

Samples for nmr measurement were prepared under vacuum by distilling appropriate samples and sufficient solvent into 5 mm o.d. medium wall sample tubes containing a capillary which held the reference compound. The samples were sealed under vacuum. Proton and fluorine spectra were generally obtained on about 10% solutions while phosphorus spectra were best obtained on neat samples. The reference compounds were tetramethylsilane for proton spectra, $CFCl_3$ for fluorine spectra, and P_4O_6 for phosphorus spectra. PBr_3 was used as a reference for the low temperature phosphorus spectra.

Hydrothiophosphoryl Difluoride and Hydrophosphoryl Difluoride[10,11]

Chapter III

Prior to this work, there had been very few reports of halogenated phosphines or phosphoranes in which both hydrogen and a halogen were bound to the same phosphorus atom. Indeed, it was only in 1960 that the first report of the preparation of secondary phosphine sulphides $R_1R_2P(S)H$, appeared.[22] The synthesis of difluorophosphine, PF_2H,[23] was the only substantiated example of a halophosphine while reports of the fluorophosphoranes PF_4H, and PF_3H_2,[24] and $C_6H_5PF_3H$ [25] had also appeared. A related compound containing the disubstituted hexa-fluorophosphate ion, $CF_3PF_4H^-$ had also been reported.[26]

Since the commencement of this work a number of additional reports of hydrido-fluoro phosphorus compounds have appeared. The fluorophosphoranes PF_4H and PF_3H_2 have been extensively studied.[27,28,29] The organo fluorophosphoranes CH_3PF_3H and $C_2H_5PF_3H$ [30] and $(CH_3)_2PF_2H$ [31] have also been reported. Two other reports of hydrophosphoryl difluoride have also appeared. The compound was first reported as a product of the reaction of PF_4H with glass.[28] Recently OPF_2H has been prepared by the HBr cleavage of μ-oxo-bis(difluorophosphine), $(PF_2)_2O$, by the partial hydrolysis of PF_3, and the reaction of $(CH_3)_3SnOH$ with PF_2Br.[18] OPF_2H has also been found as a hydrolysis product of other trivalent phosphorus halides.[32]

This chapter describes in detail, the preparation, and physical and chemical properties of the pentavalent phosphorylhydrofluorides, hydrothiophosphoryl difluoride, SPF_2H, and hydrophosphoryl difluoride, OPF_2H, and discusses the properties of these compounds.

1. Preparation and Characterization of Hydrothiophosphoryl Difluoride.

In a typical reaction, dimethylaminothiophosphoryl difluoride, $SPF_2N(CH_3)_2$,[13] (13.5 mmoles) was condensed with slightly more than a threefold molar ratio of anhydrous hydrogen iodide, HI, (41 mmoles) into a 1 ℓ. glass reaction vessel fitted with a stopcock. The reaction vessel was allowed to warm to room temperatures whereupon reaction began and proceeded at a moderate rate for 1 - 2 hr. During the reaction, the liquid dimethylaminothiophosphoryl difluoride slowly changed from a clear colorless liquid to yellow then to dark red and finally to a dark red crystalline mass. The reaction mixture was allowed to stand for at least 24 hr. to ensure complete conversion of the reactants.

The volatile products were removed from the reaction vessel and fractionated; the SPF_2H passed a trap cooled to

-81° and collected in a trap cooled to -131° giving yields of up to 95% of theoretical (equation 2). Excess hydrogen iodide and traces of other highly volatile products such as SPF_3 and SiF_4 passed -131° and were collected at -196°. The residual solids were identified as a mixture of molecular iodine and dimethylammonium iodide. Using less than the threefold molar ratio of hydrogen iodide led to the same products plus a quantity of unreacted $SPF_2N(CH_3)_2$ which stopped in the trap cooled to -81°. Most reactions were performed with excess HI since it was easier to remove from the desired product.

The rate of reaction depended on the pressure of gases in the reaction vessel. At hydrogen iodide pressures of 2 - 3 atm. (calculated from gas laws assuming no dissolution in the liquid reagent), the reaction was essentially complete in less than an hour, but at lower pressures (i.e. 1 atm. or less) 24 - 48 hr. were required for complete reaction.

The deuterium analog was synthesized as above using deuterium iodide, DI, in place of hydrogen iodide and was characterized by mass and nmr spectroscopy.

SPF_2H was characterized by vapor phase molecular weight (calcd. for SPF_2H: 102; found: 102), mass spectroscopy, including accurate mass measurement of the parent ion (calcd. for $^{32}SPF_2H$: m/e 101.9505; found: m/e 101.9503), and elemental analysis (calcd. for SPF_2H: S, 31.45; P, 30.38; F, 37.27%; found: S, 33.31; P, 29.19, 30.33; F, 37.52%).

2. Preparation and Characterization of Hydrophosphoryl Difluoride.

Hydrophosphoryl difluoride, OPF_2H, was prepared in the same manner as SPF_2H with some modifications in technique necessitated by the lower stability of the phosphoryl compound. Dimethylaminophosphoryl difluoride, $OPF_2N(CH_3)_2$,[13] was combined with slightly more than a threefold molar ratio of HI in a 1 ℓ. reaction vessel. The quantities of reactants were such that pressures of 2 - 3 atm. were initially obtained in order to ensure rapid conversion of the reactants to the desired products. The reaction was allowed to proceed at room temperature for no longer than 15 - 20 min. whereupon the products were fractionated to give OPF_2H in generally good yields (60 - 80%) (eq.2) at -81°. Unreacted $OPF_2N(CH_3)_2$ was stopped at -45° along with traces of molecular iodine. Very volatile products, including excess HI, OPF_3, and PF_3, which were subsequently identified as decomposition products of OPF_2H, were collected at -196°.

Hydrophosphoryl difluoride was characterized by vapor phase molecular weight (calcd. for OPF_2H: 86.0, found: 86.9) and by mass spectroscopy including accurate mass measurement of the parent ion (calcd. for OPF_2H: m/e 85.9733, found: m/e 85.9733).

The deuterium analog was prepared in an analogous manner using DI and was characterized by nmr and mass spectroscopy.

Pure OPF_2H could be stored for long periods of time at liquid nitrogen temperature without decomposition. The impure compound decomposed quickly at room temperature but highly purified samples were more stable. The decomposition appears to be catalyzed by the reagents or products involved in the synthesis since reactions which were allowed to proceed at room temperature for 6 - 8 hr. or longer gave only PF_3, OPF_3 and difluorophosphoric acid, OPF_2OH, and none of the desired OPF_2H. The products were identified by nmr and infrared spectroscopy.[14-17] The products obtained from several room temperature reactions of different duration are summarized in Table 1.

TABLE 1

Effect of Time on Products Obtained During Preparation of OPF_2H

Time	Volatile Products	Approx Ratio OPF_3:PF_3
4 days	OPF_3, PF_3, OPF_2OH	1:2
2 hr.	OPF_3, PF_3, OPF_2OH, OPF_2H	1:1
5 min.	OPF_3, OPF_2H	no PF_3

3. Reactions of Hydrophosphoryl Difluoride

(a) Thermal Decomposition of OPF_2H

A sample of pure OPF_2H (0.03 g, 0.27 mmole) was sealed in a 200 cc bulb and kept at room temperature for 14 days. The volatile products obtained after fractionation were PF_3 (0.01 g, 0.15 mmole) and unreacted OPF_2H (0.002 g, 0.025 mmole). Thus 92% of the OPF_2H had decomposed. The solid product remaining in the bulb was identified as phosphorous acid, $OPH(OH)_2$, by comparison of its infrared and proton nmr spectra with the spectra of an authentic sample of $OPH(OH)_2$.

In a separate reaction, a sample of OPF_2H was allowed to decompose in an nmr tube for about 3 weeks. The volatile products at that time were found to consist of PF_3 containing traces of SiF_4. The residue was dissolved in CH_3CN and its nmr spectrum obtained. The product was subsequently identified as OPF(OH)H by comparison of the observed nmr parameters with the values reported in the literature.[18] No lines were observed in the nmr spectrum which could be assigned to any species other than the OPF(OH)H and solvent.

(b) Hydrolysis of OPF_2H

Hydrophosphoryl difluoride (0.32 g, 3.65 mmoles) was sealed in a tube with 0.2 g water and allowed to react at room temperature for several days. The volatile products were an unseparated mixture of SiF_4 and traces of PF_3. No noncondensable gases were found. Removal of the excess water left a white crystalline material identified by infrared and nmr spectra as $OPH(OH)_2$.

(c) Reaction with OPF_3

Hydrophosphoryl difluoride (0.05 g, 0.63 mmoles) and OPF_3 (0.07 g, 0.63 mmoles) were sealed in a 10 cc reaction tube and allowed to stand for several days. Fractionation of the volatiles then gave PF_3 (0.04 g, 0.47 mmoles), OPF_3 (0.03 g, 0.33 mmoles) and OPF_2OH (0.03 g, 0.29 mmoles). A residue identified as $OPH(OH)_2$ remained.

4. Reactions of Hydrothiophosphoryl Difluoride

(a) Attempted Thermal Decomposition of SPF_2H

A sample of SPF_2H stored for several months at room temperature in a sealed glass ampoule was almost quantitatively recovered. Very small amounts of PF_3 and SPF_3 were obtained, and a trace of a yellow involatile solid remained in the ampoule. In a quantitative experiment, 0.5137 g of SPF_2H were sealed in a glass ampoule and kept at 110° for 4 weeks. Unchanged SPF_2H (0.5100 g) was 99% recovered. A trace of PF_3 was again found along with the previously mentioned yellow solid.

(b) Hydrolysis of SPF_2H

A sample of SPF_2H (0.24 g, 2.40 mmoles) was sealed in a glass tube with about 0.2 ml. water and allowed to react at room temperature. The SPF_2H was immiscible with water but reacted vigorously with the evolution of heat when mixed. After 24 hrs. the volatile products were found to consist of an unseparated mixture of SiF_4 and H_2S. The pale yellow involatile residue was identified as phosphorous acid by its proton nmr spectrum. The ^{19}F spectrum showed the presence of two broad singlets at +140 and +145 ppm vs. $CFCl_3$ which can be assigned to fluoride and bifluoride ions.[12] Estimation of the relative proportions of SiF_4 and H_2S in the total mass (0.155 g) of the volatile fraction from the average molecular weight (43.2) indicated that most of the sulphur in the original compound was evolved as H_2S but only a small fraction ($\sim$ 10%) of the fluorine as SiF_4. As with OPF_2H, no noncondensable gases were obtained. No volatile products were obtained when the hydrolysis was carried out in aqueous NaOH solution.

(c) Reaction with Amines

Several reactions of SPF_2H with dimethylamine, $(CH_3)_2NH$, and trimethylamine, $(CH_3)_3N$, were attempted. Generally, equimolar quantities of the reactants were condensed in suitable reaction tubes, although some reactions were carried out with a 1:2 molar ratio of $SPF_2H:(CH_3)_2NH$. In all cases, a reaction occurred immediately on warming the reaction tubes from -196° and a white or light yellow solid was formed. In all cases, only very minor quantities of volatile products were recovered and were found to include mainly PF_3 with traces of H_2S, $SPF_2N(CH_3)_2$ and dimethylaminodifluorophosphine, $PF_2N(CH_3)_2$, in the reactions with dimethylamine. $(CH_3)_3N$ only reacted in a 1:1 molar ratio but $(CH_3)_2NH$ reacted in both 1:1 and 1:2 molar ratios.

Attempts to characterize the solid product were generally unsuccessful. Reaction of the solid with water or HCl led to further solid products and only small traces of volatile products. Heating the solid at various temperatures and for various times again only produced further solids. Attempts to dissolve the residue in acetonitrile or dimethylsulfoxide in order to obtain nmr spectra of the product resulted in further reaction. The solids would dissolve in CH_3CN but a yellow solid would begin to precipitate within 15 - 20 min. Nmr spectra obtained at -35°, before precipitation began, showed a strong doublet at 34.0 ppm vs $CFCl_3$ with a coupling constant of 1180 cps. This doublet disappeared after reaction occurred.

A quantitative reaction between the SPF_2H - $(CH_3)_3N$ reaction product and acetonitrile was attempted. A sample of the solid was dissolved in a four molar equivalent excess of CH_3CN and allowed to react. After 24 hr. essentially all

CH_3CN was recovered. The solid product from this reaction could not be identified. Because the solid products obtained in the above series of reactions could not be conveniently studied, this problem was not pursued further.

(d) Reaction with HCl

Hydrothiophosphoryl difluoride and HCl in equimolar proportions were sealed in a 10 cc tube and allowed to react at 110° for one month. Fractionation of the volatiles gave 40% of the original amount of SPF_2H and an unseparated mixture of PF_3, HCl, SiF_4 and H_2S. A small amount of a yellow solid remained.

(e) Reaction with DI

An approximately equimolar mixture of SPF_2H and DI was allowed to react at 25° for about 3 weeks. A ^{19}F nmr spectrum of the resulting mixture of SPF_2H and SPF_2D indicated that the two compounds were present in an approximately equimolar ratio.

5. Discussion

The reactions of dialkylamino derivatives of phosphorus halides with hydrogen halides have been established as a convenient preparative route to the mixed tri- and pentavalent phosphorus halides.[12,13,19-21] At the beginning of this study, difluoroiodo phosphine[19] was the only known fluoroiodo phosphorus compound. The study of the reaction of $SPF_2N(CH_3)_2$ with HI was originally undertaken in an effort to prepare iodothiophosphoryl difluroide.

Instead of following the stoichiometry expressed by eq.1, the reaction of HI with $SPF_2N(CH_3)_2$ and also with

$$EPF_2NR_2 + 2HX \rightarrow EPF_2X + R_2NH_2^+X^- \qquad (1)$$
$$[E = S,O \quad ; \quad X = Cl, Br, I]$$

$OPF_2N(CH_3)_2$ provided complete conversion of the amino compound to the hydrido derivatives according to eq. 2

$$EPF_2N(CH_3)_2 + 3HI \rightarrow EPF_2H + (CH_3)_2NH_2^+I^- + I_2 \quad (2)$$
$$[E = S,O]$$

The use of HI and mercury to reduce PF_2I to PF_2H [23] and the perfluoroalkyliodophosphines and arsines to the hydrides [33] suggested that the above synthesis of hydrofluorides proceeded through the formation of the iodide, EPF_2I, in a reaction analogous to eq.1 followed by rapid

$$EPF_2I + HI \rightarrow EPF_2H + I_2 \qquad (3)$$

reduction by HI. This suggestion was later verified after preparation of SPF_2I, and observing its reduction to SPF_2H by HI. (see Chapt. IV). The reduction of SPF_2I to SPF_2H probably reflects the greater strength of the P-H bond relative to that of the P-I bond (76 vs. 51 kcal.)[34]

Hydrothiophosphoryl difluoride, the most stable of the two compounds, was the easier to isolate and characterize. It is a volatile liquid and the vapor pressure obeys the equation

$$\log P_{mm} = 8.44 - \frac{1518}{T}$$

which gives an extrapolated boiling point of 0.2°, a heat of vaporization of 6951 cal/mole, and a Trouton constant of 25.5 cal/deg mole. The vapor pressure data for SPF_2H and OPF_2H are given in Appendix A.

Hydrophosphoryl difluoride is considerably more difficult to prepare because of its instability and the apparent catalysis of the decomposition by the products or reagents involved in the synthesis. Once isolated and purified, however, the rate of decomposition was slow enough to permit convenient characterization of the compound. The vapor pressure obeyed the equation

$$\log P_{mm} = 8.63 - \frac{1886}{T}$$

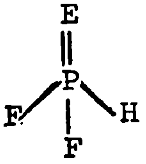
corresponding to an extrapolated boiling point of 55.0°, a heat of vaporization of 8632 cal/mole, and a Trouton constant of 26.3 cal/deg mole. The vapor pressures were not reproducible if the sample had been warmed above −25°, indicating that decomposition occurs at higher temperatures. The above equation was calculated from the reproducible vapor pressure data obtained on several samples in the range

-53 to -25° in order to minimize the effect of decomposition on the vapor pressure equation. The disagreement between this boiling point and the value reported by Treichel et. al.[28] can be attributed to decomposition of OPF_2H during measurement since the temperature in their study was allowed to reach a maximum of 0°.

Both compounds have abnormal Trouton constants and notably higher boiling points than those of the parent fluorides suggesting that they are associated, possibly through weak hydrogen bonding similar to that suggested for PF_2H.[23] Vapor phase molecular weights of SPF_2H obtained at a series of pressures indicated that at pressures approaching 1 atmosphere, the observed molecular weight was some 2% greater than the apparent molecular weight obse~ved with pressures of the order of 0.1 atm. More convincing support for association is provided by the concentration dependence of the proton chemical shift and by shifts in the infrared frequencies in the solid phase (Table 2). As was found for PF_2H [23] there is a pronounced shift of the P-H stretching frequency to a higher value which is contrary to what would be expected if hydrogen bonding occurred in the solid.

However, this apparent anomaly may be explained, as Rudolph and Parry have done,[23] by considering the effect of hydrogen bonding on the respective bond strengths and hence the stretching frequencies. In the solid phase, where greater hydrogen bonding to the fluorines occurs, the proton-fluorine interaction has the effect of decreasing the inductive effect of the fluorines with the result being an increase in the P-H bond strength. This increased bond strength is reflected in the increase in the P-H absorption frequency. All of the observed effects are greatest for the phosphoryl compound where greater hydrogen-bonded association is reasonably expected.

The nuclear magnetic resonance spectra of both compounds are very similar and are consistent with a structure in which two equivalent fluorine atoms interact with single phosphorus and hydrogen atoms. The proton spectra are doublets of triplets, the ^{19}F spectra are doublets of doublets, and the ^{31}P spectra show triplet of doublet structure. The parameters derived from these spectra are included in Appendix D. They strongly support the formulation of the compounds as derivatives of pentavalent phosphorus with the structure



[E = S,O]

rather than the trivalent isomers F_2PEH.

The large P-H and F-H coupling constants in particular support the pentavalent structure since the values are considerably larger than those typically observed for trivalent P-H compounds but close to those observed for pentavalent

P-H compounds.[23,28,29,30,21,35] The P-F coupling constants also suggest pentavalent rather than trivalent phosphorus.[1]

The infrared spectra, given in Appendix B, also support the pentavalent structure of the compounds. The OPF_2H shows a very strong band at 1377 cm^{-1} which is best assigned to the P=O stretch. The bands found at 2500 cm^{-1} and 993 cm^{-1} shift to 1820 cm^{-1} and 750 cm^{-1} on deuteration, suggesting that these bands are due to P-H stretch and bend, respectively. No band was observed in the 3500 cm^{-1} region which could be assigned to an O-H absorption. The infrared spectra observed in this work were confirmed by the results reported by Treichel et.al.[28] The spectrum of SPF_2H is similar to that of the oxygen compound. The shifts of the 2458 and 1019 cm^{-1} bands to 1782 and 768 cm^{-1} on deuteration show these bands involve proton motions. Since S-H stretching frequencies are usually observed above 2600 cm^{-1},[15,16] the above bands of the SPF_2H are best assigned to P-H stretching and bending vibrations, respectively. In the solid phase, the P-H stretching frequency is found at 2478 cm^{-1} for SPF_2H and 2571 cm^{-1} for OPF_2H. THe P-F stretching modes are observed at frequencies some 10 - 30 cm^{-1} lower than those observed in the gas phase (Table 2). No bands appear in the 1600 - 1200 cm^{-1} region in the spectrum of SPF_2H adding further support to the assignment of the 1377 cm^{-1} band in the phosphoryl

TABLE 2

Effect of Phase on PF and PH Stretching Frequencies

mode	SPF_2H frequency (cm^{-1}) gas	SPF_2H frequency (cm^{-1}) solid	OPF_2H frequency (cm^{-1}) gas	OPF_2H frequency (cm^{-1}) solid
ν(PH)	2458	2478	2500	2571
ν_a(PF)	923	895	932	919
ν_s(PF)	895	886	892	892

---

compound to the P=O stretching vibration. The P=S stretching frequency of SPF_2H can be assigned to the band at 709 cm^{-1} in agreement with the P=S stretching frequencies observed for other thiophosphoryl halides.[37]

The mass spectra of the phosphorylfluorohydrides, shown in Appendix C, are analogous and confirm the assigned molecular formulas. The most notable feature of the spectra is the appearance of the molecular ion as the strongest ion in the spectrum as in the mass spectrum of PF_2H,[23] but in contrast to the mass spectra of the phosphoranes HPF_4 and H_2PF_3 where the molecular ions were not observed.[28] Molecular ions were also not observed in the mass spectra of $(CH_3)_2PF_2H$,[31] CH_3PF_3H,[30] or $C_2H_5PF_3H$.[30] The mass spectrum of OPF_2H reported by Treichel et.al.[28] indicated the presence of impurities such as OPF_3 and SiF_4 which were not present in the spectrum of OPF_2H obtained in this work. A metastable peak in the mass spectrum of OPF_2H at m/e 50.7 amu indicates the elimination of HF from the molecular ion according to

$$OPF_2H^+ \rightarrow OPF^+ + HF$$

(calcd. m/e 50.6 amu.). No metastable ions were observed in the mass spectrum of SPF_2H.

Although pure samples of OPF_2H appear to be only moderately stable at room temperatures in the gas phase, impure samples or liquid phase samples rapidly decompose. This was especially noticeable during preparation of the compound where rapid reaction and quick separation of the products was required to produce significant yields. The mechanism and products of decomposition appear to be dependent on the impurities present and the phase or concentration of the OPF_2H . Centofanti and Parry [18] have shown that liquid OPF_2H disproportionates rapidly to PF_3 and monofluorophosphorous acid, OPFH(OH). This has been confirmed in this work when a sample of OPF_2H was allowed to decompose in an nmr tube. However, when gaseous samples of OPF_2H were allowed to decompose in large volumes, the products were PF_3 and $OPH(OH)_2$.

During preparation of OPF_2H, OPF_3 and OPF_2OH appear to be formed as initial decomposition products while the final products of decomposition, PF_3 and $OPH(OH)_2$, were not observed at this stage. It is suggested that the initial decomposition product, OPF_3, possibly formed by some disproportionation reaction, reacts with OPF_2H to form OPF_2OH,

$$OPF_3 + OPF_2H \rightarrow PF_3 + OPF_2(OH)$$

and the $OPF_2(OH)$ in turn is consumed by reaction with the original OPF_2H

$$2OPF_2H + OPF_2OH \rightarrow PF_3 + OPF_3 + OPH(OH)_2$$

The sum of these two reactions

$$3OPF_2H \rightarrow 2PF_3 + OPH(OH)_2$$

gives an equation which is in fair agreement with the observed yield of PF_3. A reaction between equimolar quantities of OPF_3 and OPF_2H gave consumption of about half of the OPF_3 thus suggesting that OPF_3 was indeed involved in the decomposition of OPF_2H. The products of this reaction were identical to those obtained in the absence of additional OPF_3. The decomposition scheme of OPF_2H has not been definitely established however.

A very recent attempt to prepare iodophosphoryl difluoride, OPF_2I, by the reaction of OPF_2H with N-iodosuccinimide (NIS) in a manner analogous to the preparation of iodothiophosphoryl difluoride, SPF_2I, (Chapter IV), led to the recovery of significant quantities of OPF_2OH and µ-oxo-bis(difluorophosphine), $(PF_2)_2O$, in the volatile products, and molecular iodine in the residues. Although it has not been conclusively proven at this time, it is suggested that

OPF_2I undergoes self-condensation according to

$$2OPF_2I \rightarrow F_2POP(O)F_2 + I_2$$

The difluorophosphoryl-μ-oxo-difluorophosphine, $F_2POP(O)F_2$, (Chapter VI) could then be attacked by excess OPF_2H

$$F_2POP(O)F_2 + OPF_2H \rightarrow OPF_2OH + (PF_2)_2O$$

The reason for the cleavage of the bridge bond in the manner indicated is discussed in later chapters. If this reaction sequence occurs during the preparation of OPF_2H it could account for the presence of the OPF_2OH in the volatile products. The reaction of OPF_2H and NIS will be studied further.

Hydrophosphoryl difluoride gave $OPH(OH)_2$ and SiF_4 on hydrolysis; the latter is probably due to the reaction of HF with glass

$$OPF_2H + 2H_2O \rightarrow OPH(OH)_2 + 2HF$$
$$2HF + \tfrac{1}{2}SiO_2 \rightarrow \tfrac{1}{2}SiF_4 + H_2O$$

Extensive studies on this compound were not undertaken, however, because of its instability and the difficulties involved in working with it.

Hydrothiophosphoryl difluoride is an extremely stable compound even when subjected to prolonged heating. On hydrolysis, SPF_2H gave phosphorous acid, SiF_4 and H_2S. Monothiophosphorous acid $SPH(OH)_2$ is probably formed initially

$$SPF_2H + 2H_2O \rightarrow SPH(OH)_2 + 2HF$$

which is in turn hydrolyzed to $OPH(OH)_2$ and H_2S

$$SPH(OH)_2 + H_2O \rightarrow OPH(OH)_2 + H_2S$$

This reaction may also involve HF which may be present in solution, since the yield of SiF_4, resulting from the attack of the HF formed in the first step on glass, is not quantitative.

Hydrogen was not obtained in any of the hydrolysis reactions showing that the hydrogen atoms are not hydridic. The P-H bond probably maintains its integrity during hydrolysis as in the case of the hydrolysis of PF_2H.[38] The other reactions which SPF_2H undergoes suggest that the proton is acidic. While reaction with HCl produces only decomposition of the SPF_2H under severe conditions, equilibration with DI shows that the proton is labile and readily exchanged.

The reactions of SPF_2H with amines, although presently inconclusively studied, suggest the formation of the anion SPF_2^-

$$SPF_2H + (CH_3)_3N \rightarrow SPF_2^-(CH_3)_3NH^+$$

Unfortunately the adduct, when dissolved, either reacts with the solvent or undergoes some sort of self-condensation or disproportionation. Since quantitative reactions of the solid product formed in the above reaction with acetonitrile, CH_3CN, give essentially complete recovery of the CH_3CN, the possibility of self-condensation or disproportionation is strongly suggested. This type of reaction may be similar to the redox disproportionation found for alkylfluorophosphines,[39] and could possibly take the form

$$xSPF_2^- \rightarrow xSPF_4^= + (SP)_x$$

Hydrothiophosphoryldifluoride undergoes a number of additional reactions which are discussed in succeeding chapters since the products of these reactions are of much interest and have been extensively studied.

Iodothiophosphoryl Difluoride [40]

Chapter IV

Although the phosphorus iodides, PI_3 and P_2I_4,[41,42] have been known for many years, and the thiophosphoryl iodides SPI_3 [43] and $(SPI_2)_2$ [44] have more recently been reported, the only reports of a mixed fluorohalo phosphorus compound containing iodine, preceeding this work, have been reports of the preparation of difluoroiodophosphine, PF_2I.[19,21] In the preceeding chapter it was suggested that the preparation of SPF_2H and OPF_2H proceeded through the reduction of SPF_2I or OPF_2I by HI (eq.3). Very recently, the addition of elemental sulphur to PF_2I was reported as another route to SPF_2I.[45] The properties of SPF_2I reported[45] are in good agreement with those found in the present work.

This chapter describes in detail, the preparation, and chemical and physical properties of iodothiophosphoryl difluoride, SPF_2I, and discusses its properties.

1. Preparation and Characterization of Iodothiophosphoryl Difluoride.

(a) From SPF_2H and N-iodosuccinimide (NIS)

Hydrothiophosphoryl difluoride (0.64 g, 6.3 mmole) was condensed onto an excess of NIS contained in a 75 cc reaction tube. A moderately exothermic reaction occurred immediately on warming the tube to room temperature, forming a colorless liquid, and turning the NIS to a light reddish color. After 1 hr., the volatile products were fractionated to give SPF_2I (1.25 g, 5.5 mmole), in 95% yield, condensed at -81°. A trace of unreacted SPF_2H was stopped at -196° (0.04 g, 0.4 mmole). Also obtained, at -95°, were traces of a compound, later identified as μ-oxo-bis(thiophosphoryl difluoride), $(SPF_2)_2O$. Although the amount of $(SPF_2)_2O$ obtained could be reduced by prolonged pumping on the NIS before reaction with SPF_2H, it could never be eliminated by this method. Yields of SPF_2I decreased if the reaction time was allowed to exceed 3 - 4 hr., and the use of a large excess of NIS did not produce complete conversion of SPF_2H to SPF_2I. Lower yields also resulted if the temperature of the reaction vessel was allowed to increase much above room temperature.

(b) From SPF_2H, sulphur, and iodine

Hydrothiophosphoryl difluoride (0.09 g, 0.90 mmole) was condensed into a tube containing excess sulphur and iodine. The reaction was allowed to proceed for 8 hr. at 65°. Fractionation of the volatile products gave SPF_2I (0.15 g, 0.7 mmole), a trace of unreacted SPF_2H (0.02 g, 0.2 mmole), and H_2S (0.01 g, 0.33 mmole).

(c) From SPF_2H, sulphur, and HI

Equimolar quantities of SPF_2H (0.18 g, 1.85 mmole) and HI (0.27 g, 2.10 mmole) were condensed into a tube with an excess of sulphur. Immediately on warming the tube to room temperature, a reaction occurred with the formation of a dark brown solid. After 72 hr., fractionation of the volatile products gave SPF_2I (0.11 g, 0.48 mmole), SPF_2H (0.10 g, 0.98 mmole), and H_2S (0.05 g, 1.49 mmole). No HI was found in the products. Molecular iodine was observed in the residues. In a separate experiment, sulphur was found to react with HI under the above conditions to yield H_2S and iodine.

(d) Characterization of SPF_2I

Iodothiophosphoryl difluoride is a colorless, volatile liquid with an extrapolated boiling point of 81.6°. The vapor pressure data for SPF_2I are given in Appendix A and may be summarized by the equation

$$\log P_{mm} = 7.580 - \frac{1667}{T}$$

from which a heat of vaporization of 7.63 kcal/mole and a Trouton constant of 21.5 cal/mole deg. are derived. SPF_2I was characterized by vapor density molecular weight (calcd for SPF_2I: 227.8; found: 228.5), mass spectroscopy, including accurate mass measurement of the parent ion, (calcd for $^{32}SPF_2I$: m/e 227.8473; found: m/e 227.8473), and elemental analysis (calcd for SPF_2I: S, 14.0; P, 13.6; I, 55.7%; found: S, 14.4; P, 13.35; I, 55.5%).

Iodothiophosphoryl difluoride is a relatively stable compound and was found to suffer less than 5% decomposition after 4 days at 150°. At room temperature, under normal illumination, SPF_2I very slowly decomposes to give molecular iodine and some unidentified involatile material.

2. Reactions of Iodothiophosphoryl Difluoride

(a) With water

Iodothiophosphoryl difluoride and water in a 2:1 molar ratio were sealed in a 10 cc reaction tube. The two were initially immiscible but reacted on shaking to give a solution which gradually turned from light yellow to dark red. A viscous liquid separated from the solution. The volatile products were separated after 72 hr. with recovery of half of the original SPF_2I and an unseparated mixture of SiF_4, SPF_2H, PF_3, SPF_3 and H_2S, all identified spectroscopically. Molecular iodine and an unidentified colorless hygroscopic liquid remained as residues in the reaction tube. No excess H_2O was recovered.

In another reaction, SPF_2I (0.16 g, 0.68 mmole) and H_2O (0.01 g,0.60 mmole) were sealed together in a tube and allowed to react for 4 hr. The volatile products were then fractionated to give SPF_2I (0.01 g, 0.06 mmole) and an unseparated mixture of SiF_4, SPF_3, PF_3, and H_2S (0.02 g). Residues of the reaction were similar to those found previously.

(b) With Anhydrous Hydrogen Iodide

Iodothiophosphoryl difluoride (0.11 g, 0.48 mmole) and HI (0.08 g, 0.65 mmole) were sealed together in a 75 cc reaction tube. Immediately on warming to room temperature, the colorless liquid turned light yellow and then rapidly changed to dark red. After 1 hr. a crystalline solid started to form. The volatile products were fractionated to give SPF_2H (0.05 g, 0.45 mmole) and excess HI. Molecular iodine remained as a residue.

(c) With Anydrous Hydrogen Bromide

Iodothiophosphoryl difluoride (0.22 g, 0.96 mmole) and HBr (0.08 g, 1.02 mmole) were allowed to react in a 75 cc reaction tube. On warming to room temperature, the liquid turned pink and then rapidly darkened. The volatile products were fractionated after 48 hrs. to give SPF_2H (0.03 g, 0.29 mmole), SPF_2Br (0.07 g, 0.41 mmole), unreacted SPF_2I (0.04 g, 0.19 mmole), and an unseparated mixture containing HBr, H_2S, and PF_2Br identified spectroscopically. Molecular iodine remained as a residue.

(d) With Anhydrous Hydrogen Chloride

Iodothiophosphoryl difluoride (0.36 g, 1.57 mmole) and HCl (0.06 g, 1.64 mmole) were sealed in a 75 cc reaction tube. When no reaction was observed after several hours, the tube was placed in the oven at 65°. After 18 days, the volatiles were fractionated to give SPF_2H (0.16 g, 0.16 mmole), SPF_2Cl (0.55 g, 0.40 mmole), unreacted SPF_2I (0.19 g, 0.82 mmole), and an unseparated mixture of HCl, H_2S, and PF_2Cl (0.06 g) identified spectroscopically. Molecular iodine remained as a residue. A separate reaction carried out at 150° for a shorter period of time gave similar results.

(e) With Dimethylamine

Iodothiophosphoryl difluoride (0.10 g, 0.44 mmole) and $(CH_3)_2NH$ (0.04 g, 0.90 mmole) were sealed in a 25 cc reaction tube. Immediately on warming to room temperature a reaction occurred producing a white solid. After 1 hr., the volatiles were fractionated to give only $SPF_2N(CH_3)_2$ (0.06 g, 0.40 mmole).

(f) With Dimethylphosphine

Iodothiophosphoryl difluoride (0.18 g, 0.81 mmole) and $(CH_3)_2PH$ [66] (0.05 g, 0.87 mmole) were sealed in a 25 cc reaction tube. Immediately on warming to room temperature, a reaction occurred forming a light yellow solid and a slightly volatile liquid. After a few minutes the solid turned orange. The volatile products were fractionated after 7 days at room temperatures to give dimethylthiophosphorylfluoride, $SPF(CH_3)_2$, (0.06 g, 0.52 mmole), a small amount of CH_3PSF_2, and an unseparated mixture of SiF_4 and PF_3.

In another reaction, SPF_2I (0.49 g, 2.16 mmole) $(CH_3)_2PH$ (0.12 g, 1.89 mmole) and $(CH_3)_3N$ (0.12 g, 1.97

mmole) were sealed together in a 75 cc reaction tube. Immediately on warming to room temperature, a reaction occurred producing a white solid product which turned dark orange after 1 hr. No condensable material remained at this point. The reaction tube was heated to 150° for 2 days. The resulting volatile products were fractionated to give $SPF(CH_3)_2$ (0.16 g, 1.43 mmole), PF_3 containing a trace of SPF_3 (0.07 g). The unidentified dark orange residue remained.

(g) With Dimethylarsine

Iodothiophosphoryl difluoride (0.16 g, 0.71 mmole) and $(CH_3)_2AsH$ [40] (0.08 g, 0.72 mmole) reacted at room temperature in a 25 cc reaction tube to give a yellow solution and a small amount of yellow solid. Separation of the volatile products after 3 weeks gave a small amount of dimethyliodoarsine, $(CH_3)_2AsI$, (0.06 g, 0.02 mmole) and a mixture of SPF_2H, PF_3 and H_2S (0.06 g). An unidentified light orange residue remained.

(h) With Methanol

Iodothiophosphoryl difluoride (0.20 g, 0.86 mmole) and CH_3OH (0.03 g, 0.86 mmole) reacted in a 25 cc tube immediately on warming to room temperature to form a red solution. Separation of the volatiles after 30 min. gave SPF_2H (0.04 g, 0.37 mmole), SPF_2OCH_3 (0.05 g, 0.34 mmole) (identified by mass spectra including accurate mass measurement of the parent peak: calcd for $^{32}SPF_2OCH_3$; m/e 131.9610; found: m/e 131.9602; infrared and nmr spectra), unreacted SPF_2I (0.02 g, 0.08 mmole) and unreacted CH_3OH. Molecular iodine remained as a residue.

(i) With Methyl Mercaptan

Iodothiophosphoryl difluoride (0.35 g, 1.55 mmole) and CH_3SH (0.05 g, 1.05 mmole) were sealed in a 75 cc reaction tube. Separation of the volatiles after 7 days at 65° gave SPF_2H (0.05 g, 0.51 mmole), SPF_2SCH_3 (0.07 g, 0.48 mmole) (identified by mass spectroscopy, including accurate mass measurement of the parent peak: calcd for $^{32}S_2PF_2CH_3$; m/e 147.9382; found: m/e 147.9382; infrared and nmr spectra), unreacted SPF_2I (0.09 g, 0.40 mmole) and unreacted CH_3SH (0.02 g, 0.35 mmole). Molecular iodine remained as a residue.

(j) With Metal Chlorides

Iodothiophosphoryl difluoride (0.20 g, 0.87 mmole) and an excess of mercuric chloride, $HgCl_2$, were sealed in a 25 cc tube. Fractionation of the volatiles after 1 month at 65° quantitatively gave chlorothiophosphoryl difluoride (0.12 g, 0.87 mmole).

SPF_2I sealed in a tube with excess silver chloride were reacted for 12 days at 65°. Fractionation of the volatiles gave only a trace of SPF_2Cl. Most of the SPF_2I was recovered unchanged. The surface of the AgCl turned bright yellow during the reaction.

(k) With Mercury and Other Reactive Metals

Iodothiophosphoryl difluoride (0.36 g, 1.56 mmole) was sealed in a 75 cc tube with excess mercury. Immediately on warming to room temperature, a reaction occurred producing a greenish solid. After 4 days no volatile products could be recovered. HCl (0.06 g, 1.56 mmole) was condensed on to the mixture, and the tube was resealed. After 10 days, the volatile products were fractionated to give SPF_2SH (0.02 g, 0.18 mmole) and HCl (0.04 g, 1.09 mmole). The residue was again resealed with HCl and heated at 150° for 2 weeks. Fractionation of the volatiles after this treatment gave only HCl.

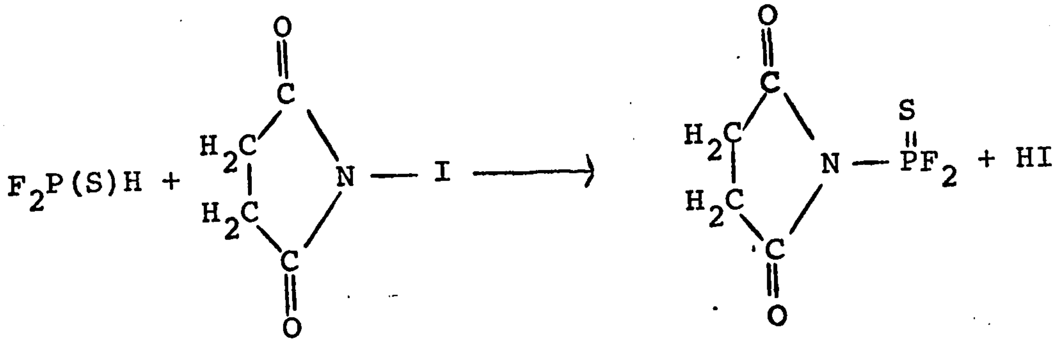
In another experiment, SPF_2I (1.16 g, 5.12 mmole) and a stoichiometric amount of mercury (0.51 g, 2.56 mmole) were sealed in a 75 cc reaction tube which was vigorously shaken for 1 week at room temperatures. Fractionation of the volatiles gave difluorothiophosphoryl-μ-thio-difluorophosphine, $F_2PSP(S)F_2$, (0.49 g, 2.42 mmole, 95% yield) collected at -81°, SPF_2H (0.02 g, 0.17 mmole) at -116° and a trace of μ-thio-bis(thiophosphoryl difluoride) at -65°. Recovery of the residual mercuric iodide (1.08 g, 2.38 mmole) remaining in the reaction tube was not quantitative because of handling losses, but the amount recovered was in good agreement with the expected amount.

Copper, antimony, and magnesium also consumed the

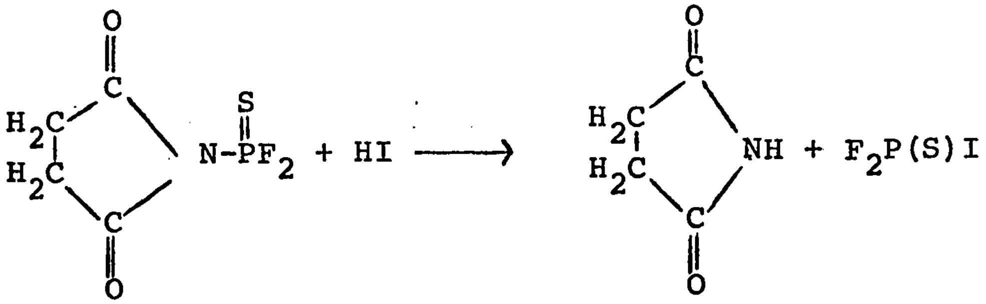
SPF_2I, giving only variable amounts of PF_3, OPF_3 and SPF_3 as volatile products and intractable residues.

3. Discussion

Iodothiophosphoryl difluoride was obtained in good yield from the reaction of hydrothiophosphoryl difluoride with N-iodosuccinimide (NIS). The reaction is analogous to the conversion of dialkyl phosphonates, $(RO)_2P(O)H$, to the appropriate dialkyl phosphorohaloidates by the action of N-chloro- or N-bromosuccinimide,[46] which appear to act as sources of "positive halogen." Recent studies suggest [47] that the reactions involve the formation of the N-phosphorylated intermediate so it seems reasonable to suggest that the present reaction proceeds through initial reaction of N-iodosuccinimide with the P-H link to form a neutral N-phosphorylated derivative (or perhaps an analogous phosphonium salt containing a P-N link), e.g.



followed by cleavage of the P-N link with hydrogen iodide to form the iodophosphorus compound and probably (although it was not specifically identified) succinimide



The acidic nature of succinimide [48] precludes the formation of a salt with hydrogen iodide or the attack on the P-F bonds analogous to the typical behavior of secondary amines. Both of these secondary reactions would prevent the isolation of good yields of $F_2P(S)I$.

Iodothiophosphoryl difluoride was also obtained from the reaction of hydrothiophosphoryl difluoride with sulphur and iodine or with sulphur and hydrogen iodide. Neither of these alternative methods was as effective as the NIS method. It seems reasonable to propose that these latter reactions involve attack of iodine on SPF_2H to form hydrogen iodide and the iodo compound

$$SPF_2H + I_2 \rightleftarrows SPF_2I + HI \qquad (4)$$

The equation is probably best written as an equilibrium, which, under ordinary circumstances, favors the formation of SPF_2H, since the hydride is normally prepared in the presence of molecular iodine. It was also shown in a separate experiment that hydrogen iodide rapidly converts iodothiophosphoryl difluoride to hydrothiophosphoryl difluoride and iodine. If, however, hydrogen iodide is removed from the system by reaction with sulfur

$$S + 2HI \rightarrow H_2S + I_2 \qquad (5)$$

(a reaction which was found to proceed readily under the experimental conditions used), the equilibrium expressed by equation 4 is displaced in favor of SPF_2I formation. The synthesis of SPF_2I involving hydrogen iodide and sulphur probably proceeds through the initial production of iodine by reaction (5) and thence through the equilibrium (equation 4). By appropriate choice of reagents and conditions, either iodo- or hydrothiophosphoryl compounds can be obtained.

It is interesting to note that mercury or other active metals were not required in the synthesis of hydrothiophosphoryl difluoride from hydrogen iodide and the iodo compound, whereas in previously reported reductions of phosphorus, arsenic, and carbon iodides with HI, mercury was found to be essential or at least desirable for a good yield of the hydride.[23,33,49] The function of the mercury in these cases appears to be the removal of iodine in the form of mercury iodide, with consequent displacement of an equilibrium similar to that of equation 4 toward the formation of the hydride.

The results of this study indicate that the synthesis of SPF_2H follows the mechanism suggested in Chapter III (equations 1 and 3). However, since SPF_2I was not isolated during the preparation of SPF_2H, it would appear that the rate of reduction of SPF_2I by HI to SPF_2H is more rapid than the rate of cleavage of the P-N bond in $SPF_2N(CH_3)_2$ by HI.

Of the three phosphorus-halogen bonds in iodothiophosphoryl difluoride, the phosphorus-iodine link is the most reactive. Replacement of iodine by chlorine can be effected with mercuric chloride [50,51] but silver chloride, which has often been used for this purpose, [52] did not react appreciably with SPF_2I, possibly because of the deactivation of the silver chloride surface by silver iodide as indicated by the bright yellow color of the silver chloride. With limited quantities of reagent the P-I bond can be preferentially reacted to provide substituted thiophosphoryl difluoride derivatives. For example, a stoichiometric quantity of dimethylamine gave a nearly quantitative yield of the dimethylamido compound

$$SPF_2I + 2(CH_3)_2NH \rightarrow (CH_3)_2NP(S)F_2 + (CH_3)_2NH_2^+I^-$$

Methanol and methyl mercaptan reacted with iodothiophosphoryl difluoride to form the oxygen or sulphur methyl esters $F_2P(S)ECH_3$ (where E = O or S). Also obtained in the latter two reactions was a quantity of hydrothiophosphoryl difluoride approximately equal to the amount of ester formed. These reactions probably proceed through initial formation of the ester and hydrogen iodide

$$SPF_2I + CH_3EH \rightarrow SPF_2{\cdot}ECH_3 + HI \quad [E = O,S]$$

followed by immediate reduction of unreacted iodofluoride by the liberated hydrogen iodide according to equation 4. The over-all reaction

$$2SPF_2I + CH_3EH \rightarrow SPF_2{\cdot}ECH_3 + SPF_2H$$

predicts the formation of equal proportions of ester and SPF_2H as observed. The reactions were not wholly quantitative however since unreacted iodofluoride was recovered.

The preparation of the methoxy ester from SPF_2Cl and CH_3OH has very recently been reported.[53] A detailed description of the infrared and Raman spectra of the compound is given and the results are in good agreement with the values obtained in this work.

In contrast to the straightforward behavior of dimethylamine, dimethylphosphine did not yield a compound containing a phosphorus-phosphorus bond as might have been anticipated. Instead dimethylphosphine consumed all of the available iodothiophosphoryl difluoride to give a 66% yield of dimethylthiophosphoryl fluoride, $(CH_3)_2P(S)F$, based on the initial quantity of SPF_2I and minor amounts of PF_3. Addition of an equimolar quantity of trimethylamine to the reaction mixture did not alter the proportion of $(CH_3)_2P(S)F$ obtained, although a solid intermediate was formed which gave dimethylthiophosphoryl fluoride only after heating the solid.

Dimethylarsine likewise did not yield a phosphorus-arsenic compound upon reaction with iodothiophosphoryl difluoride; instead a solid was formed and the volatile products of the reaction were SPF_2H, H_2S, PF_3, and a 5% yield of dimethyliodoarsine. The mechanism and intermediates of these reactions are not clear. It is interesting however to note that these reactions did not yield diphosphorus or phosphorus-arsenic compounds in contrast to the facile synthesis of the phosphorus-nitrogen derivative by the straightforward reaction of dimethylamine with iodothiophosphoryl difluoride.

Iodothiophosphoryl difluoride reacted with hydrogen chloride and bromide to yield the hydride and the halogenothiophosphoryl difluoride. The reaction probably proceeds through attack of hydrogen halide on SPF_2I yielding hydrogen iodide and halogenothiophosphoryl difluoride

$$SPF_2I + HX \rightarrow SPF_2X + HI$$

followed by fast reduction of SPF_2I by the hydrogen iodide according to equation 4, a sequence which also accounts for the formation of molecular iodine in the reaction products. Less hydrothiophosphoryl difluoride than expected from the above reaction sequence (which predicts an equimolar ratio of SPF_2H and SPF_2X) is obtained, however; the other products obtained were PF_2X and H_2S. The most reasonable explanation for these observations is that the hydrothiophosphoryl difluoride formed is decomposed in the presence of hydrogen halide under the reaction conditions employed. As shown in Chapter III a mixture of SPF_2H and HCl, when heated in a sealed tube, resulted in the consumption of 60% of the SPF_2H and the formation of PF_2Cl, PF_3, and H_2S.

Attempts to prepare diphosphorus compounds from SPF_2I using excess mercury or other reactive metals according to

$$2SPF_2I \xrightarrow{Hg} F_2(S)P\text{-}P(S)F_2$$

in a reaction analogous to the preparation of P_2F_4 [2,3] were unsuccessful. However, the reaction of SPF_2I with a stoichiometric amount of mercury led to the formation of the thio bridged compound $F_2PSP(S)F_2$. A more detailed discussion of this reaction will be presented in Chapter VI. The lack of success in the synthesis of directly bonded diphosphorus compounds by either the coupling reactions or the reaction with dimethylphosphine is probably an indication of the relative instability of pentavalent diphosphorus compounds with respect to the trivalent analogs. This problem is discussed more fully in Chapter VI. Other, specific reactions of SPF_2I, are discussed in appropriate succeeding chapters.

Hydrolysis of SPF_2I appears to involve all of the halogens as well as the sulphur. The reaction appears to involve equimolar proportions of SPF_2I and water to give SiF_4 (presumably from attack of the liberated HF on the glass vessel), H_2S, decomposition products SPF_3 and PF_3, and, when there is a deficiency of water, SPF_2H (presumably arising from the formation of HI followed by reduction of excess SPF_2I according to equation 4. The involatile residue is probably $OPH(OH)_2$ or the thio analog $SPH(OH)_2$, if hydrolysis is incomplete.

The spectral behavior of SPF_2I is not unexpected. The nmr spectra are first order and the parameters are given in Appendix D. The mass spectrum, given in Appendix C shows the molecular ion as the most intense ion in the spectrum. A metastable peak at 44.8 amu (calcd 44.7 amu) in the mass spectrum of SPF_2I demonstrates the expected loss of iodine from the molecular ion

$$SPF_2I^+ \rightarrow SPF_2^+ + I$$

The infrared spectrum is very similar to the spectra of other difluorothiophosphoryl compounds.[1] The spectrum is given in Appendix B.

Difluorodithiophosphoric Acid [54]

Chapter V

Although reports of the salts of the difluorodithiophosphate anion, $S_2PF_2^-$, including the hydronium salt,[56] had appeared in 1967,[56,57] it was not until late 1968 that reports of the anhydrous SPF_2SH appeared.[55,58] The anhydrous acid was prepared in those cases by distillation from a highly acidic solution of CsS_2PF_2. An analogous acid, $(CF_3)_2PS_2H$, has also been reported.[59,60] In contrast, the oxygen analog, difluorophosphoric acid, OPF_2OH,[1] and organic dithiophosphinic acids [61] are well known and have been extensively studied.

This chapter describes in detail, the preparation, and chemical and physical properties of difluorodithiophosphoric acid, SPF_2SH, and discusses its properties.

1. Preparation and Characterization of Difluorodithiophosphoric Acid.

(a) From SPF_2H and sulphur

In a typical reaction, hydrothiophosphoryl difluoride (0.90 g, 8.83 mmole) was heated to 150° for 48 hr. with an excess of sulphur in a 75 cm^3 sealed tube. Fractionation of the volatile products gave difluorodithiophosphoric acid (0.89 g, 6.67 mmole), collected at -81°, unreacted hydrothiophosphoryl difluoride (0.11 g, 1.11 mmole), collected at

-131°, and a mixture of SPF_3, PF_3, and H_2S (total weight 0.08 g), collected at -196°. The over-all yield of SPF_2SH was 76%, or 88% based on hydrothiophosphoryl difluoride consumed.

Higher reaction temperatures and/or longer reaction times led to reduced yields of the acid and increased quantities of SPF_3 and other decomposition products although all of the hydrofluoride was consumed. Lower temperatures and/or short reaction times gave reduced conversion of the hydride to the acid. Traces of $(SPF_2)_2O$ were found in some reactions but this product could be readily eliminated by prolonged evacuation of the reaction vessel and the sulphur before introduction of hydrothiophosphoryl difluoride.

(b) From SPF_2I and Hydrogen Sulfide.

In a typical reaction, iodothiophosphoryl difluoride (0.23 g, 0.99 mmole) and hydrogen sulfide (0.04 g, 1.08 mmole) were sealed in a 75 cm^3 reaction tube. Immediately on warming to room temperature, the liquid turned pink and then slowly darkened. After heating at 65° for 7 days, fractionation of the volatile products yielded difluorodithiophosphoric acid, SPF_2SH (0.07 g, 0.50 mmole), collected at -81° and contaminated with a small amount of unreacted iodothiophosphoryl difluoride. The more volatile fractions contained hydrothiophosphoryl difluoride (0.03 g, 0.26 mmole) and H_2S (found mol wt, 35.7)(0.02 g). Molecular iodine remained in the reaction vessel.

(c) From SPF_2H and H_2S

SPF_2H (0.10 g, 0.97 mmole) and H_2S (0.04 g, 1.03 mmole) were heated at 160° for 4 days. Separation of the volatile components gave SPF_2SH (0.01 g, 0.1 mmole), unreacted SPF_2H (0.04 g, 0.35 mmole), and an unseparated mixture of SiF_4, OPF_3, SPF_3, and PF_3 (0.08 g). A bright yellow residue remained in the reaction tube.

(d) Characterization of SPF_2SH

SPF_2SH is a clear, colorless, volatile liquid which freezes to a glass at low temperatures. The vapor pressure data, given in Appendix A, are best expressed by the non-linear equation

$$\log P_{mm} = \frac{-2243.7}{T} - 0.001\,T + 1.75 \log T + 8.946$$

over the range -40 to +50°, yielding an extrapolated boiling point of 74°, a heat of vaporization of 6876 cal/mole., and a Trouton constant of 19.8 cal/mole deg. Non-linearity of the vapor pressure equation is most pronounced at the lower temperatures. From 10 to 50° the vapor pressure is adequately expressed by the equation

$$\log P_{mm} = 7.900 - \frac{1732}{T}$$

which yields an extrapolated boiling point of 72°, a heat of vaporization of 7926 cal/mole., and a Trouton constant of 23 cal/deg mole. These results are in fair agreement with the results recently reported by Lustig et.al.[55]

Difluorodithiophosphoric acid was characterized by vapor phase molecular weight (calcd: 133.9; found: 134.6), and mass spectroscopy, including accurate mass measurement of the parent ion (calcd for $^{32}S_2PF_2H$, m/e 133.9225; found: m/e 133.9226). The acid is very stable at room temperatures and has been stored in sealed vessels for many months without apparent change. Indeed, the method of preparation gives an indication of the thermal stability of SPF_2SH.

2. Reactions of Difluorodithiophosphoric Acid.

(a) With Water

Difluorodithiophosphoric acid (0.12 g, 0.87 mmole) and a large excess of water were sealed in a 10 cm^3 reaction tube and kept at room temperature for 4 weeks. Fractionation of the volatile products gave only H_2S (0.06 g, 1.67 mmole) and unchanged water. A clear colorless liquid residue remained in the reaction tube. Fluorine nmr of the residues showed only one peak at $\phi = 149.5$ ppm (relative to $CFCl_3$). No ^1H signal was found.

In another experiment, SPF_2SH (0.13 g, 0.95 mmole), and an equimolar quantity of water (0.02 g, 0.97 mmole) were sealed in a 10 cm^3 reaction tube. After several hours at room temperature, a small amount of a light yellow solid had formed. After 4 days the volatiles were separated yielding unreacted SPF_2SH (0.06 g, 0.44 mmole) and a mixture of SiF_4 and H_2S (0.03 g). A white solid and a colorless liquid remained in the reaction vessel. The residues reacted with acetonitrile and the resultant sample gave neither ^1H nor ^{19}F nmr signals.

(b) With Dimethylamine

Difluorodithiophosphoric acid (0.16 g, 1.17 mmole) and dimethylamine (0.05 g, 1.21 mmole) were sealed in a 10 cm^3 reaction tube. Immediately on warming to room temperature, a reaction occurred forming a light yellow solid which melted at a relatively low temperature and resolidified as a crystalline solid. No volatile products were recovered. Nmr spectra of a CH_3CN solution of the solid showed a triplet (τ=7.32, J_{HH} = 5.75 cps) for the ^1H spectrum and a doublet (ϕ=4.63 ppm, J_{PF} = 1151.2 cps) for the ^{19}F spectrum.

(c) With Iodine

Difluorodithiophosphoric acid was heated to 70° for 10 days with an excess of iodine. Separation of the volatiles yielded unreacted acid plus traces of SPF_3 and HI.

(d) With Oxygen

Difluorodithiophosphoric acid was kept with a large excess of dry air in a sealed vessel for 4 days and recovered unchanged.

(e) With SPF_2I

Difluorodithiophosphoric acid (0.11 g, 0.82 mmole) and SPF_2I (0.35 g, 1.54 mmole) were sealed in a 75 cm^3 reaction tube and heated to 75° for 1 month. Fractionation of the volatiles gave a mixture of PF_3 and SPF_3 (0.04 g) and a mixture of SPF_2SH and SPF_2I (0.39 g). The SPF_2SH - SPF_2I mixture was resealed in a 75 cm^3 reaction tube and allowed to react at 150° for 10 days. Fractionation of the volatiles gave a further quantity of SPF_3 (0.09 g) and SPF_2SH (0.07 g). Molecular iodine and an orange-brown residue remained.

(f) With Anhydrous Hydrogen Iodide.

Equimolar quantities of SPF_2SH and HI did not react when sealed together and left at room temperature overnight. In a second experiment difluorodithiophosphoric acid (0.12 g, 0.91 mmole) was heated with excess hydrogen iodide (0.23 g, 1.76 mmole) for 3 weeks at 160°. Fractionation of the volatile products gave dithiodifluorophosphoric acid (0.04 g, 0.33 mmole) and an unseparated mixture of SPF_2H, SPF_3, PF_3, SiF_4, POF_3, and HI (all identified spectroscopically). Hydrogen sulfide was not present. Molecular iodine and an unidentified yellow-brown solid remained in the reaction tube.

(g) Reactions of the Amine Salt of Difluorodithiophosphoric Acid

(i) The dimethylamine salt of difluorodithiophosphoric acid prepared as described in part b above was sealed with an excess of anhydrous HCl. After 24 hr. at room temperatures all of the HCl was recovered unchanged.

(ii) In a similar fashion a sample of the salt was sealed with dry chlorine gas. After 3 days the volatiles contained SPF_2Cl, $SPFCl_2$, $SPCl_3$, SiF_4, and HCl. A yellow residue remained which was not identified.

3. Discussion

Difluorodithiophosphoric acid has been synthesized by two methods: (a) the reaction of sulphur with hydrothiophosphoryl difluoride and (b) the reaction of hydrogen sulfide with iodothiophosphoryl difluoride. Minor yields of the acid are obtained in the reaction of hydrothiophosphoryl difluoride with hydrogen sulfide. The reaction of SPF_2H and sulphur is the more effective and useful of the two principal methods giving the highest over-all yield of the acid and the purest product. The reaction of SPF_2I and H_2S is troubled by the difficulty of separating the acid from the iodofluoride and by secondary reactions which reduce the yield of the desired acid. In this case hydrogen iodide produced in the initial step

$$F_2P(S)I + H_2S \rightarrow F_2P(S)SH + HI \qquad (6)$$

reduces the unreacted iodo compound to the hydride by the fast reaction

$$F_2P(S)I + HI \rightarrow F_2P(S)H + I_2 \qquad (7)$$

In addition, however, a separate experiment showed that the difluoro acid slowly reacts with hydrogen iodide to form hydrothiophosphoryl difluoride, molecular iodine, and a complex mixture of volatile products. Since this reaction is slow at the synthesis temperature of 65° and has an appreciable rate only above 100°, it probably has only secondary importance in the synthesis of difluorodithiophosphoric acid. The combination of reaction 6 with the fast reduction (equation 7) leads to a maximum possible conversion of 50% of the iodothiophosphoryl difluoride to the desired difluorodithiophosphoric acid, and hence this synthetic route is not the most favorable one. A similar situation prevailed in the synthesis of bis(trifluoromethyl)-dithiophosphinic acid from the iodide and hydrogen sulfide.[60] In this case fast reduction of the iodo compound by hydrogen iodide [59] occurs with concomitant "anti-Arbuzov" rearrangements [59,62] to the more stable phosphinous state.

Difluorodithiophosphoric acid behaves as a strong acid, readily forming amine salts from which the acid cannot be recovered by treatment with anhydrous HCl. Examination of solutions of the amine salts by nmr shows the presence of the $S_2PF_2^-$ anion.[56] Chlorine attacks the salts leading to a variety of phosphorus chlorofluoride products. SPF_2SH readily attacks many metals to form the appropriate salt and accompanied by the liberation of hydrogen.[58,63]

The acid does not react with oxygen in air or with iodine. SPF_2I, which reacted with many "active hydrogen" compounds to give SPF_2 derivatives as described in Chapter IV, did not react with SPF_2SH; the majority of the starting material was recovered unchanged along with small amounts of PF_3 and SPF_3. SPF_2I has previously shown a reluctance to react with some "active hydrogen" compounds, such as hydrogen chloride or bromide (Chapter IV), and the behaviour of SPF_2SH is in keeping with this observation.

Difluorodithiophosphoric acid is hydrolyzed by an excess of water to hydrogen sulfide and, presumably, phosphoric acid. With an equimolar quantity of water, the acid was incompletely hydrolyzed; approximately half of the initial quantity of acid was recovered along with SiF_4 and H_2S. The consumed acid therefore reacted with 2 molar equivalents of water. The involatile residues were not identified.

In contrast to the ease with which the free acid is hydrolyzed is the extreme stability of ammonium salts of the acid to hydrolysis. The nmr spectrum of an aqueous solution of the trimethylammonium salt over several days showed no sign of hydrolysis products. The apparent stability of the $S_2PF_2^-$ ion is not presently explained.

The complex reaction of difluorodithiophosphoric acid with hydrogen iodide mentioned above is probably best understood by comparison with the analogous reaction of bis(trifluoromethyl)dithiophosphinic acid. The trifluoromethyl acid reacts quickly at room temperatures to form the trivalent phosphorus compound, $(CF_3)_2PSH$, iodine, and hydrogen sulfide.[64] The basic process in the reaction probably involves formation of the iodo compound and hydrogen sulfide

$$F_2P(S)SH + HI \rightarrow F_2P(S)I + H_2S$$

followed by fast reduction of the iodo compound to hydrothiophosphoryl difluoride (equation 7) giving an over-all conversion of the difluoro acid to hydrothiophosphoryl difluoride and hydrogen sulfide. The reaction products are analogous to those obtained from the reaction of bis(trifluoromethyl)dithiophosphinic acid with hydrogen iodide except for the "anti-Arbuzov" rearrangement which occurs in the trifluoromethyl system. The absence of hydrogen sulfide and the presence of OPF_3, SPF_3, SiF_4, and PF_3 in the products is probably best attributed to reaction of hydrogen sulfide with hydrothiophosphoryl difluoride since a separate experiment indicated that this reaction occurs readily at the temperatures employed and gives the above products. Thermal decomposition of all of the materials and reaction with the glass vessel at the relatively high reaction temperatures may also be responsible for the formation of the observed products.

It is interesting to note that consumption of the trifluoromethyl acid by hydrogen iodide is essentially complete after a few hours at room temperatures[64] whereas the fluoro acid reacts only after prolonged heating. Such a difference in reactivity is surprising in view of the general similarity of the properties of the two acids.

In view of the normal gas-phase molecular weight values obtained at low pressures, the gas-phase infrared spectra (given in Appendix B) are best interpreted in terms of a monomeric species. The band at 2608 cm^{-1} is obviously best assigned to the S-H stretch and the strong band at 732 cm^{-1} is probably due to the P=S stretch. The weak band at 524 cm^{-1} is probably the P-S stretch. Of the four bands between 950 and 800 cm^{-1}, two - those at 936 and 891 - 886 cm^{-1} - are probably due to antisymmetric and symmetric P-F stretching vibrations and the medium intensity band at 838 cm^{-1} is probably due to S-H bending since only this band of the four shifts upon deuteration . The deuterio acid was prepared by exchanging the hydro acid with DI at room temperatures. The 838 cm^{-1} band shifts to 740 cm^{-1} and the S-H stretch at 2608 cm^{-1} shifts to 1895 cm^{-1}, confirming these assignments. The rotational structure of the bands, when observed, was either of PQR or PQQ'R type, the latter generally with poorly resolved P and R branches.

Lustig et.al.[55] have also noted that a number of absorption bands are apparently doublets. In their case, they have discounted the possibility of rotational structure as a source of the doublet structure of the bands. Instead, it is suggested that the cause of this splitting is the co-existence of hydrogen- and non-hydrogen-bonded entities in the vapor phase. Although vapor phase molecular weights indicate a monomeric structure at low pressures, the nmr spectra, discussed below, indicate that some sort of sulphur-hydrogen association occurs in solution. Solid phase infrared spectra give similar indications. However, the bands at 891 and 886 cm^{-1} which show the most obvious doublet structure are best assigned to the symmetric PF_2 stretching frequency. In view of the type B bands which occur in the spectrum of OPF_2H, it is not possible to conclude that bands with a PQQ'R type structure do not occur in the spectrum of SPF_2SH. A microwave spectrum of SPF_2SH is currently being obtained elsewhere which will provide structural information which hopefully will provide a better understanding of the origin of the doublet structure observed here.

Mass spectra (Appendix C) show expected simple fragmentations and also a substantial proportion of S_2^+ which presumably arises from a rearrangement process, perhaps the process indicated by the metastable peak at m/e 30.6 which corresponds to the transition

$$PF_2S_2H^+ \rightarrow S_2^+ + PF_2H$$

(calcd m/e 30.6). A metastable peak at m/e 97.0 was also observed corresponding to the transition

$$PF_2S_2H^+ \rightarrow PFS_2^+ + HF$$

(calcd m/e 97.0).

The nuclear magnetic resonance spectra of difluorodithiophosphoric acid dissolved in trichlorofluoromethane show a doublet for the ^{19}F resonance spectrum and a singlet for the ^{1}H spectrum which is consistent with a rapidly exchanging proton. The ^{31}P nmr spectrum of a neat sample of the acid at room temperature was a triplet. Cooling an approximately 10% in $CFCl_3$ sample results in a gradual broadening of the ^{1}H singlet with resolution into two broad doublets and eventually at -110° (the lowest operating temperature of the spectrometer) the proton spectrum, illustrated in Figure 1, is resolved into a pair of triplets. At this temperature, as illustrated in Figure 1,

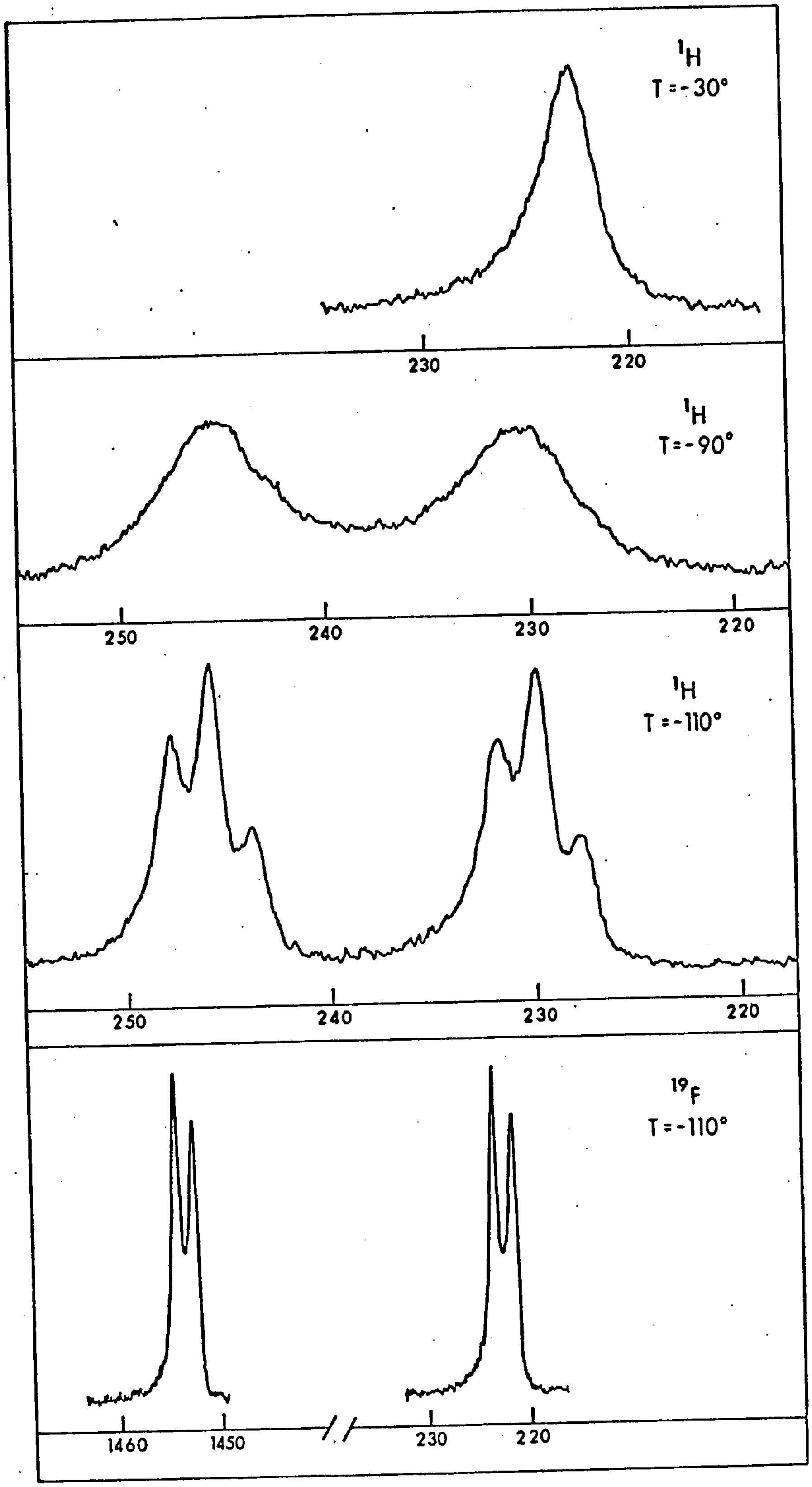


Figure 1. Temperature Dependence of the NMR Spectrum of Difluorodithiophosphoric Acid

the fluorine nmr spectrum shows a doublet of doublets. The spectra are best rationalized in terms of rapid proton exchange at normal temperatures which can be slowed sufficiently by cooling the sample so that normal first-order spin-spin interaction can be resolved. Preliminary nmr studies of this proton exchange as a function of concentration indicate that the exchange is an intermolecular process.[67] The multiplet pattern is consistent with the localization of the proton on one molecule rather than in a dimer or polymer unit. The nmr parameters are summarized in Appendix D.

Mixed Valence Fluorophosphorus Compounds [68,69]

Chapter VI

This chapter describes in detail, the preparation, and chemical and physical properties of difluorothiophosphoryl-μ-thio-difluorophosphine, $F_2PSP(S)F_2$, and difluorophosphoryl-μ-oxo-difluorophosphine, $F_2POP(O)F_2$, and provides a discussion of their properties.

1. Preparation and Characterization of difluorothiophosphoryl-μ-thio-difluorophosphine

(a) From SPF_2I and Mercury

The preparation of $F_2PSP(S)F_2$ from SPF_2I and a stoichiometric amount of mercury is described in Chapter IV.

(b) From SPF_2SH and Dimethylaminodifluorophosphine, $PF_2N(CH_3)_2$

Difluorodithiophosphoric acid (1.00 g, 7.50 mmole) and $PF_2N(CH_3)_2$[21] (0.46 g, 4.11 mmole) were condensed into a 75 cc reaction tube. Immediately on warming to room temperature, a reaction occurred forming a white solid and a volatile liquid. Fractionation of the volatile products after 15 min. gave $F_2PSP(S)F_2$ (0.72 g, 3.57 mmoles, 95% yield) collected at -81°, and a mixture of PF_3 and $PF_2N(CH_3)_2$ (0.05 g) at -196°. The white solid residue was found to be

$(CH_3)_2NH_2^+S_2PF_2^-$ by nmr spectroscopy.

(c) Characterization of $F_2PSP(S)F_2$

The compound, $F_2PSP(S)F_2$ is a colorless, volatile liquid which can be kept at room temperatures in a sealed glass tube without decomposition for one or two days. After several months at room temperature, however, the compound had decomposed completely to PF_3, SPF_2SH, $(SPF_2)_2O$, a light yellow involatile solid and a non-volatile colorless liquid. A sample heated to 70° was 90% decomposed after 2 hrs. Only PF_3 and an unidentified colorless non-volatile liquid were obtained.

The vapor pressure data, given in Appendix A, are best described by the equation

$$\log_{10} P_{mm} = 7.639 - \frac{1708}{T}$$

which gives an extrapolated boiling point of 85.7°, a heat of vaporization of 7814 cal/mole, and a Trouton constant of 21.8 cal/mole deg.

The pure compound was further characterized by vapor density molecular weight (calcd for $F_2PSP(S)F_2$: 202.0; found: (on two different samples) 199.7 and 200.4), by its spectroscopic properties and by chemical reactions described below. The compound did not show a parent ion in the mass spectrometer, but seemed to react in the inlet system to give $(SPF_2)_2O$ and other products.

2. Preparation and characterization of difluorophosphoryl-μ-oxo-difluorophosphine

Reaction of OPF_2OH (1.25 g, 12.21 mmole) with $PF_2N(CH_3)_2$ (0.95 g, 8.40 mmole) for 3 min. in a 40 cc glass tube followed immediately by fractionation of the volatile products gave PF_3 (0.15 g, 1.76 mmole) at -196°, $PF_2N(CH_3)_2$ (0.17 g, 1.49 mmole) collected at -116°, the desired $F_2POP(O)F_2$ (0.70 g, 4.10 mmole) collected at -81° and a small amount of unidentified material trapped at -65°. The residue remaining in the reaction tube was initially a clear colorless liquid which crystallized after standing for about 30 mins. Nmr spectroscopy showed only $(CH_3)_2NH_2^+O_2PF_2^-$ in the crystalline residues.[13]

The compound $F_2POP(O)F_2$ is a colorless, volatile liquid of limited stability at ordinary temperatures. A sample of the compound (0.17 g, 1.00 mmole) was sealed in a glass tube and warmed to room temperature. Noticeable formation of a white solid was observed within an hour and after 18 hrs. the original liquid was no longer visible. The only volatile product at this point was PF_3 (0.05 g, 0.58 mmole). The white solid material remaining in the reaction vessel was insoluble in $CHCl_3$ and CH_3CN but soluble in dimethylsulfoxide (DMSO) with apparent reaction. The ^{19}F nmr spectrum of the resultant DMSO solution showed only $O_2PF_2^-$ ions.

The vapor pressure data, given in Appendix A, are somewhat unreliable because of fairly rapid decomposition at temperatures above 0°. The data obeyed the equation

$$\log_{10} P_{mm} = 8.83 - \frac{1925}{T}$$

giving an extrapolated boiling point of 50°, a heat of vaporization of 8800 cal/mole and Trouton constant of 27 cal/mole deg.

The compound $F_2POP(O)F_2$ was further characterized by mass spectroscopy, including accurate mass measurement of the parent peak (calcd for $F_4P_2O_2$: m/e 169.9310; found: m/e 169.9308). The mass spectral cracking pattern is given in Appendix C, the nmr parameters in Appendix D, and the infrared spectrum in Appendix B.

3. Difluorothiophosphoryl-μ-thio-difluorophosphine

(a) With Anhydrous HCl

A quantity of $F_2PSP(S)F_2$, (0.08 g, 0.40 mmole) was sealed with HCl (0.01 g, 0.38 mmole) in a 10 cc reaction tube and allowed to react at room temperature for 24 hrs. Fractionation of the volatile products gave SPF_2SH (0.05 g, 0.39 mmole) and PF_2Cl (0.04 g, 0.39 mmole). The latter, identified spectroscopically,[70] was contaminated with small traces of HCl and SPF_2H. A trace of unreacted $F_2PSP(S)F_2$ was recovered.

(b) With Water

A quantity of $F_2PSP(S)F_2$ (0.10 g, 0.49 mmole) was condensed with water (0.02 g, 0.85 mmole) in a 10 cc reaction tube. At room temperature, a rapid exothermic reaction occurred leading to evolution of a gas and the formation of a yellow liquid. Fractionation of the volatile products after 24 hrs. gave SPF_2SH (0.05 g, 0.37 mmole) at -95°, and a mixture of SiF_4 and PF_3 (0.02 g) at -196°, but no H_2S. A non-volatile clear liquid remained.

(c) With Mercury

A quantity of $F_2PSP(S)F_2$ (0.05 g, 0.25 mmole) was sealed in a 10 cc tube with excess mercury and vigorously shaken for 3 days. The products obtained were a mixture of PF_3 and SPF_3 (0.02 g), and an involatile yellow-green solid.

(d) With Methyl Mercaptan

Reaction of $F_2PSP(S)F_2$ (0.07 g, 0.36 mmole) with CH_3SH (0.02 g, 0.48 mmole) in a 10 cc tube for 48 hrs. at room temperature gave SPF_2SH (0.03 g, 0.26 mmole) and PF_3 (0.03 g, 0.34 mmole), the latter contaminated with traces of SPF_2H. A bright orange solid residue and a pale yellow liquid of low volatility remained in the reaction tube.

(e) With Methanol

A quantity of $F_2PSP(S)F_2$ (0.10 g, 0.51 mmole) was combined with CH_3OH (0.02 g, 0.54 mmole) in a 10 cc reaction tube at room temperature for 3 hrs. Fractionation of the volatile products gave SPF_2SH (0.07 g, 0.50 mmole) containing a trace of SPF_2OCH_3 at -116° and PF_3 (0.05 g, 0.54 mmole) also containing traces of SPF_2H and SPF_3 at -196°. A small amount of a light yellow solid residue remained in the reaction vessel.

(f) With Dimethylamine

Immediate reaction occurred at room temperature when $F_2PSP(S)F_2$ (0.10 g, 0.48 mmole) and $(CH_3)_2NH$ (0.050 g, 1.01 mmole) were combined in a 10 cc reaction tube. Fractionation of the volatile products after 48 hrs. at room temperature gave $SPF_2N(CH_3)_2$ (0.01 g, 0.06 mmole) at -81°, $PF_2N(CH_3)_2$ (0.03 g, 0.24 mmole) at -116°, and PF_3 (0.01 g, 0.17 mmole) at -196°. The solid residue was shown by infrared and nmr spectroscopy to be a mixture of $(CH_3)_2NH_2{}^+S_2PF_2{}^-$ and $(CH_3)_2NH_2{}^+SPF_2{}^-$.

(g) With Chlorine

Reaction of $F_2PSP(S)F_2$ (0.06 g, 0.31 mmole) and Cl_2 (0.02 g, 0.31 mmole) in a 10 cc reaction tube at room temperature for 48 hrs. gave SPF_2Cl (0.02 g, 0.15 mmole) containing traces of OPF_3 and PF_3 at -196°, unreacted $F_2PSP(S)F_2$ (0.02 g, 0.09 mmole) at -81° and 0.02 g of an unidentified unstable product at -45°. A white solid residue remained in the reaction tube.

(h) With SPF_2H

Hydrothiophosphoryl difluoride (0.07 g, 0.71 mmole) and $F_2PSP(S)F_2$ (0.15 g, 0.76 mmole) were combined in a 10 cc reaction tube. Fractionation of the volatiles after 48 hrs. at room temperature gave PF_3 (0.04 g, 0.48 mmole), SPF_2H (0.06 g, 0.59 mmole), and $F_2PSP(S)F_2$ (0.03 g, 0.17 mmole). A light yellow solid and non-volatile liquid remained as residues. The liquid appeared to be of a similar constitution to that obtained from the decomposition of $F_2PSP(S)F_2$.

(i) With Sulphur

A quantity of $F_2PSP(S)F_2$ (0.08 g, 0.39 mmole) and an excess of sulphur were sealed in a 10 cc tube. Fractionation of the volatiles after 60 hrs. at room temperature gave only $F_2PSP(S)F_2$ (0.06 g, 0.29 mmole) and PF_3 (0.01 g, 0.07 mmole).

4. Discussion

Coupling of halogeno-phosphorus compounds with active metals has long been employed as a synthetic route to compounds containing a phosphorus-phosphorus bond.[4] Recently, the elusive [4] tetrafluorodiphosphine, P_2F_4, was successfully prepared from PF_2I and mercury [2,3] using this general type of reaction. As was mentioned in Chapter IV, however, SPF_2I, when reacted with a large excess of mercury or other active metals, gave only small amounts of PF_3 and SPF_3 and a large amount of an intractible solid residue.

All known organophosphorus analogs, $R_4P_2E_2$ (E=O,S), of the diphosphorus tetrafluoride compounds prepared in this study have the phosphorus-phosphorus bonded structure.[4,71,72] Organodiphosphorus monosulfides, R_4P_2S, also exist in the isomeric form with a phosphorus-phosphorus bond,[61] which, of necessity, must be a mixed valence compound. An exception to this general monosulfide structure is the sulphur bridged structure found for the trifluoromethyl analog, $(CF_3)_4P_2S$,[59, 60, 73, 74] with equivalent trivalent phosphorus atoms. Similarly, $(CF_3)_4P_2O$, and F_4P_2O appear to exist only in the form with an oxygen bridged structure.[2,3,65]

The reaction of SPF_2I with a stoichiometric amount of mercury gave a good yield of the coupled thiophosphoryl-difluoride "dimer"

$$2SPF_2I + Hg \rightarrow F_4P_2S_2 + HgI_2 \qquad (8)$$

When, as a result of structural studies described below, the structure of the "dimer" became apparent, an alternate synthetic route was devised. The reaction of SPF_2SH with $PF_2N(CH_3)_2$ according to (with E=S)

$$2EPF_2EH + F_2PN(CH_3)_2 \rightarrow F_4P_2E_2 + (CH_3)_2NH_2^{+}E_2PF_2^{-} \qquad (9)$$

gave a good yield of difluorothiophosphoryl-μ-thio-difluorophosphine. Although the stoichiometry of reaction (9) requires the consumption of two moles of acid for each mole of product, the reaction is much preferred to reaction (8) where much longer reaction times are required and where the desired products are only purified with difficulty.

The oxygen analog, difluorophosphoryl-μ-oxo-difluorophosphine, $F_2POP(O)F_2$, was successfully synthesized from OPF_2OH and $PF_2N(CH_3)_2$ according to equation (9) (with E=O). A good yield can be obtained if the reaction and subsequent fractionation are executed quickly. This is the only method applicable to the synthesis of the oxo compound since OPF_2I is presently unknown.

The chemical behaviour of $F_2PSP(S)F_2$ agrees with a formulation involving both trivalent and pentavalent phosphorus atoms (structure II below). With molar quantities of HCl, nearly quantitative yields of SPF_2SH and PF_2Cl are obtained according to (with X = Cl)

$$F_2PSP(S)F_2 + HX \rightarrow SPF_2SH + F_2PX \qquad (10)$$

Water also reacts with the sulphur "dimer" to form SPF_2SH. By analogy, the unknown compound F_2POH would be expected (with X = OH in equation 10). Neither the trivalent compound, F_2POH, nor the pentavalent isomer, $F_2P(O)H$, was isolated, probably because the former isomer readily rearranges to the latter in keeping with a proposal to explain the observed products of the hydrolysis of PF_3.[75] The instability of OPF_2H (Chapter III) precludes its isolation under the conditions used for reaction.

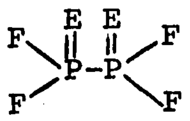
Methanol and methyl mercaptan appear to react with $F_2PSP(S)F_2$ in the same manner, however, the major products are SPF_2SH and PF_3. Although SPF_2SH is formed, the trivalent fluorophosphines, CH_3EPF_2 (E = O,S), expected from initial cleavage of the P(III)-S bridge bond, are not obtained. Instead, PF_3 was obtained suggesting that decomposition of the CH_3EPF_2 compounds occurs, possibly as the result of acid catalysis. The stability of CH_3EPF_2 compounds, especially in the presence of acids, is presently unknown and further study of the system is clearly warranted.

Cleavage of the P(V)-S bridge bond, which would result in the formation of SPF_2H and SPF_2ECH_3 (E = O,S), does not appear to be an important pathway since only minor amounts of these compounds were obtained.

The reaction of $(CH_3)_2NH$ with $F_2PSP(S)F_2$ appears to involve cleavage of both the P(III)-S and P(V)-S bridges since the tentatively identified (Chapter III) SPF_2^- and $S_2PF_2^-$ ions were both observed in the non-volatile residues. The required quantity of $PF_2N(CH_3)_2$ for reaction (10) (with $X = N(CH_3)_2$) was obtained, along with significant quantities of $SPF_2N(CH_3)_2$ and PF_3.

Elemental sulphur did not oxidize the $F_2PSP(S)F_2$ to μ-thio-bis(thiophosphoryldifluoride), $(SPF_2)_2S$, because, under the reaction conditions, decomposition of the $F_2PSP(S)F_2$ probably occurs before the S_8 ring opens. SPF_2H did not react with the $F_2PSP(S)F_2$ even though the proton on SPF_2H appears to be acidic. It is possible that equation (10) exists as an equilibrium (with $E = SPF_2$) in the case of SPF_2H, but because SPF_2SH is a stronger acid, the equilibrium lies very much to the left and the only products actually observed are decomposition products of $F_2PSP(S)F_2$.

There are three possible isomeric structures which can be reasonably suggested for these compounds: (a) a structure with a phosphorus-phosphorus bond (I) in which both phosphorus atoms are pentavalent; (b) one with a single sulphur or oxygen bridge between the phosphorus atoms (II) in which the phosphorus atoms are necessarily dissimilar, one being trivalent and one pentavalent; (c) a structure with a dithio or dioxo bridge (III) in which both phosphorus atoms are trivalent.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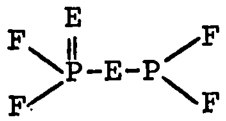
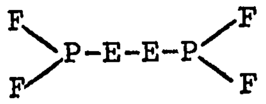

II


III

Although a phosphorus-phosphorus bonded structure (I) might be expected from the coupling reactions and by structural analogy with many known organodiphosphorus compounds,[4] the spectroscopic evidence discussed below favors the mixed valence structure (II). Although oxygen and sulphur analogs need not necessarily have the same structure, this appears to be the case. However, the observed structure of the oxygen compound may be a consequence of the synthetic method used to prepare it.

Comparison of the gas phase infrared spectra of the oxo and thio compounds to that of similar compounds such as $(SPF_2)_2S$, $(SPF_2)_2O$, $(OPF_2)_2O$ [8] and $(PF_2)_2O$ [3] indicate several features in support of structure (II). The spectrum of $F_2PSP(S)F_2$ shows four bands in the P-F stretching region instead of two observed in the pentavalent compounds $(EPF_2)_2E$. The pair of strong bands at 925 and 898 cm^{-1} can be assigned to pentavalent P-F stretching frequencies in agreement with the 974, 949 cm^{-1} pair observed for $(SPF_2)_2O$ and the 952, 923 cm^{-1} pair for $(SPF_2)_2S$. The additional pair of bands of approximately equal intensity at 847 and 834 cm^{-1} do not have a counterpart in the pentavalent molecules but since trivalent fluorophosphorus compounds,[1] including $(PF_2)_2O$,[3] have strong P-F bands in the 825 - 860 cm^{-1} region, it seems reasonable to assign this latter pair of bands to trivalent P-F stretching vibrations.

The strong band at 731 cm^{-1} in the spectrum of $F_2PSP(S)F_2$ can be associated with a P=S absorption in keeping with bands at 708 cm^{-1} in $(SPF_2)_2O$ and 703 cm^{-1} in $(SPF_2)_2S$. The band at 480 cm^{-1} for $F_2PSP(S)F_2$ has a counterpart in the spectrum of $(SPF_2)_2S$ at 501 cm^{-1} but no counterpart in the spectrum of $(SPF_2)_2O$. This band may thus be assigned to the P-S-P stretch.

Although the extreme reactivity of the oxygen compound, $F_2POP(O)F_2$, with cell windows and its instability hampered the infrared spectral measurements, some evidence in support of the mixed valence structural isomer (II) was obtained. The strong bands at 1384 and 1025 cm^{-1} may be readily associated with P=O and P-O-P stretching vibrations by analogy to the spectrum of $(OPF_2)_2O$.[8] Other features of the spectrum are consistent with a $F_2POP(O)F_2$ structure (II).

The nmr spectra support stucture (II) for both compounds, and indeed provides the most compelling evidence for this structure, especially when taken with the rational synthesis (equation 9) developed with this knowledge. At room temperature, the ^{19}F spectrum of both compounds shows a pair of doublets with chemical shifts and coupling constants (Appendix D) which can reasonably be associated with P-F coupling in pentavalent, four-coordinate phosphoryl or thiophosphoryl structural units, and a trivalent $-PF_2$ group [1,76,77] in each molecule.

The low temperature ^{19}F spectra of $F_2PSP(S)F_2$ provide additional evidence in favor of structure (II). As the temperature of the sample is lowered, all four peaks begin to broaden, with those assigned to the trivalent phosphorus fluorines broadening at higher temperatures than the peaks corresponding to the pentavalent phosphorus fluorines. At about -40°, the lines at $\phi = 60.2$ ppm begin to show a discernible doublet structure while the lines at $\phi = 13.7$ ppm show the doublet structure at about -60°. At -80° each line begins to resolve further into a triplet so that at -90°, the lowest attainable temperature, the spectrum shows a doublet of doublet of triplets for each of the two chemical shift regions which would be expected if, in addition to the adjacent P-F coupling observed at room temperatures, long range P-F and F-F couplings are also observed. Heating the sample above room temperature causes the lines at $\phi = 13.7$ ppm to broaden until, at 100°, (the highest temperature attainable without severe decomposition of the compound) they are extremely broad. The lines at $\phi = 60.2$ ppm remain relatively sharp throughout this temperature range. The spectral changes are illustrated in fig. 2.

The fluorine spectra indicate that the compounds $F_2PSP(S)F_2$ and $F_2POP(O)F_2$, exist in the isomeric form (II) with trivalent and pentavalent phosphorus atoms in the same molecule. The thermal behavior of the spectra are likely due to rapid averaging processes. At room temperatures, rapid interconversion between the possible conformations of the molecule results in the observation of only short range P-F couplings since the two ends of the molecule are effectively decoupled from each other by the rotation. As the temperature is lowered, the rate of rotation is slowed and long-range coupling is re-established giving rise to the observed multiplet structure.

In a molecule of structure (II), it is obvious that the averaging process is due to rotation around P-S or P-O bridge bonds. The different rates of collapse in trivalent and pentavalent regions of the spectrum may be due to a difference in the rate of rotation around P(III)-S and P(V)-S bonds since there is no reason to assume that these

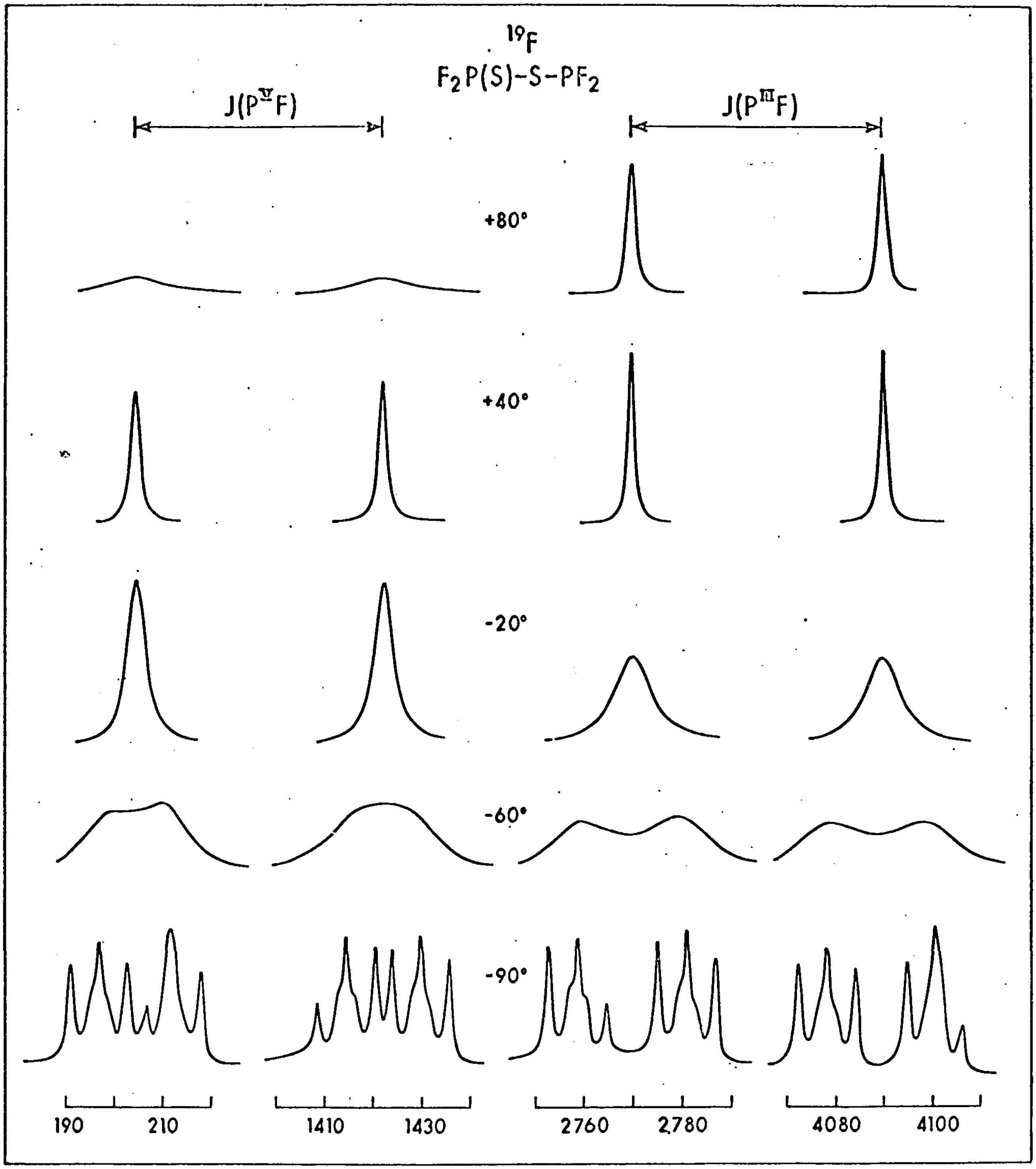


Figure 2. Temperature Dependence of the ^{19}F NMR Spectrum of Difluorothiophosphoryl-μ-Thio-Difluorophosphine

rotations will have identical rates. The non-observance of multiplet structure in the low temperature spectrum of $F_2POP(O)F_2$ implies lower energy barriers to rotation around the P-O bonds. The higher barriers in $F_2PSP(S)F_2$ may arise as a consequence of greater S-F steric interactions caused by the larger size of the sulphur atom and the longer P=S bond length relative to the oxygen analog.

The reason for the observed structural preference of these compounds and $(CF_3)_4P_2S$, $(CF_3)_4P_2O$, and F_4P_2O, may be a stabilization of the trivalent phosphorus by the very electronegative groups, CF_3 and F. If this stabilization has a significant structural influence, however, it is not readily apparent why the $F_2PSP(S)F_2$ does not adopt the disulfide structure (III). If trans fluorine geometry is considered for structure (I) of $F_4P_2S_2$ by analogy with the structure of P_2F_4, for which a trans configuration is indicated,[78] and which minimizes interaction between fluorine atoms, models quickly demonstrate that the two additional sulphur atoms produce four S-F interactions at about the Van der Waals distance.

In contrast, minimal S-F interactions and a single P-S interaction are the apparent steric features of isomer (II). Even less steric interaction might be expected in structure (III). However, the disulfide or peroxo bridge probably provides a weaker bonding situation than that provided by a single bridging atom. The preference for the adoption of the structural isomer (II) is probably a consequence of both electronic and steric contributions to the system.

Oxygen, Sulphur, and Nitrogen Bridged Phosphoryl and Thiophosphoryl Difluorides

Chapter VII

Many diphosphorus compounds are known in which the phosphorus atoms are linked by a difunctional bridging unit such as oxygen, sulphur, or mono-substituted nitrogen.[65,73,74,80-86] The only known fluorophosphorus derivatives of this type however, are the well known difluorophosphoric acid anhydride, $(OPF_2)_2O$,[1,8] the analogous chlorofluoro compound, $(OPFCl)_2O$,[87] and μ-oxo-bisdifluorophosphine, $(PF_2)_2O$.[2,3] Very recently, a report has described the nmr spectrum of μ-oxo-bis(thiophosphoryl difluoride), $(SPF_2)_2O$, which was prepared in the same manner as this work.[88]

This chapter describes in detail, the preparation, and chemical and physical properties of μ-oxo-bis(thiophosphoryl difluoride), $(SPF_2)_2O$, μ-thio-bis(thiophosphoryl difluoride), $(SPF_2)_2S$, difluorophosphoryl-μ-oxo-thiophosphoryl difluoride, $(SPF_2)O(OPF_2)$, N-methyl-bis(difluorophosphoryl) amine, $(OPF_2)_2NCH_3$, N-methyl-bis(difluorothiophosphoryl) amine, $(SPF_2)_2NCH_3$, trimethyl ammonium bis(difluorophosphoryl) amide, $(SPF_2)_2N^-(CH_3)_3NH^+$. The preparation and some of the properties of methyl amino-thiophosphoryl difluoride, SPF_2NHCH_3, methyl amino-phosphoryl difluoride, OPF_2NHCH_3, and amino-thiophosphoryl difluoride, SPF_2NH_2 are also described. The properties of these compounds are discussed.

1. Preparation of μ-oxo-bis(thiophosphoryl difluoride)

(a) From SPF_2I and Oxygen.

Iodothiophosphoryl difluoride (0.22 g, 0.98 mmole) was condensed into a 75 cc reaction tube which was then filled with excess oxygen (as air, from which all material condensable at -196° had been removed). Fractionation of the volatile products after 2 weeks at 70° gave $(SPF_2)_2O$ (0.07 g, 0.33 mmole) condensing at -95°, traces of OPF_3 condensing at -196° and unreacted SPF_2I (0.05 g, 0.23 mmole) condensing at -81°. Molecular iodine was collected in the least volatile fraction. Separation of $(SPF_2)_2O$ from traces of SPF_2I under vacuum was very difficult, and very pure samples of $(SPF_2)_2O$ were obtained only after repeated distillation from a LeRoy still. The yield of $(SPF_2)_2O$ was 88% based on consumed SPF_2I. Higher reaction tempercatures and longer reaction times gave more complete consumption of SPF_2I at the expense of more pronounced decomposition of the desired product.

(b) From SPF_2SH and $OPF_2N(CH_3)_2$.

Difluorodithiophosphoric acid (0.13 g, 0.97 mmole) and $OPF_2N(CH_3)_2$ (0.07 g, 0.57 mmole) were sealed in a 25 cc reaction tube. After 4 days at room temperature, fractionation of the volatile products gave only $(SPF_2)_2O$ (0.10 g, 0.48 mmole) in 99% yield. A yellow, unidentified crystalline solid remained in the reaction vessel.

(c) From OPF_2OH and $SPF_2N(CH_3)_2$

$SPF_2N(CH_3)_2$ (0.33 g, 2.28 mmole) and OPF_2OH (0.41 g, 4.05 mmole) were sealed in a 25 cc reaction tube and allowed to react at 70° for 1 hr. Fractionation of the volatiles gave OPF_3 (0.08 g, 0.74 mmole), $(SPF_2)_2O$ (0.19 g, 0.85 mmole) and a mixture of $SPF_2N(CH_3)_2$ and $OPF_2N(CH_3)_2$ (0.09 g). A clear, colorless, non-volatile liquid residue remained.

(d) Characterization of $(SPF_2)_2O$

The compound μ-oxo-bis(thiophosphoryl difluoride), $(SPF_2)_2O$, (also called difluorothiophosphoric acid anhydride), is a colorless volatile liquid which has been kept in sealed glass tubes for several months at room temperature without decomposition. It was characterized by vapor phase molecular weight (calc for $(SPF_2)_2O$: 217.9; found: 216.8) and mass spectroscopy, including accurate mass measurement of the parent ion (calcd for $(^{32}SPF_2)_2O$: 217:8803 found: 217.8803). The vapor pressure data, given in Appendix A, are best described by the equation

$$\log_{10} P_{mm} = 7.734 - \frac{1566}{T}$$

from which an extrapolated boiling point of 49.5° is obtained. A heat of vaporization of 7166 cal/mole and a Trouton constant of 22.2 cal/deg mole are also obtained.

2. Preparation and Characterization of μ-thio-bis(thiophosphoryl difluoride).

The reaction of $SPF_2N(CH_3)_2$ with an excess of SPF_2SH at 70° in a sealed tube as described above proved to be the most effective synthetic route to $(SPF_2)_2S$. The excess acid, SPF_2SH, is effectively removed from the crude product by trapping the crude product at -63°. A light yellow solid, presumably $(CH_3)_2NH_2^+S_2PF_2^-$, remained in the reaction tube. Even large excess concentrations of acid and several days of reaction did not result in complete consumption of the $SPF_2N(CH_3)_2$ which traps along with the desired product in crude vacuum fractionation. Repeated distillation from the LeRoy still gave pure samples of $(SPF_2)_2S$.

Difluorothiophosphoric acid thioanhydride $(SPF_2)_2S$ (more properly called μ-thio-bis(thiophosphoryl difluoride), is a colorless, volatile liquid, stable at room temperatures and has been stored in sealed glass tubes for several months without decomposition. It was characterized by vapor phase molecular weight (calcd for $(SPF_2)_2S$: 233.9; found: 235.6) and mass spectroscopy, including accurate mass measurement of the parent ion (calcd for $(^{32}SPF_2)_2{}^{32}S$: 233.8575 found: 233.8572). The vapor pressure data, given in Appendix A, are best described by the equation

$$\log_{10} P_{mm} = 7.808 - \frac{1930}{T}$$

which gives rise to an extrapolated boiling point of 118.4°, a heat of vaporization of 8830 cal/mole, and a Trouton constant of 22.5 cal/deg mole.

3. Difluorophosphoryl-μ-oxo-thiophosphoryl difluoride

Hydrothiophosphoryl difluoride (0.62 g, 6.08 mmole) and $(OPF_2)_2O$ (1.30 g, 6.97 mmole) were sealed in a 25 cc reaction tube and placed in the oven at 70°. After 7 days the volatiles were fractionated to give OPF_3 and PF_3 (0.20 g) at -196°, SPF_2H (0.25 g, 2.45 mmole) at -116°, $(OPF_2)_2O$ (0.62 g, 3.34 moles) at -65°, OPF_2OH (0.28 g, 2.74 mmole) at -81°, and $(SPF_2)O(OPF_2)$ (0.39 g, 1.93 mmole) at -95°. A quantity of light yellow, solid residue remained which appeared to be sulphur.

In another reaction, traces of $(SPF_2)_2O$ were obtained so a sample of relatively pure $(SPF_2)O(OPF_2)$ was sealed in an nmr tube and heated at 100° for several days. As time progressed, the peaks corresponding to $(SPF_2)O(OPF_2)$ decreased in intensity while those due to $(SPF_2)_2O$ and $(OPF_2)_2O$ increased in intensity.

A similar reaction between SPF_2SH and $(OPF_2)_2O$ also gave $(SPF_2)O(OPF_2)$, but the resulting mixture of compounds was too difficult to separate.

$(SPF_2)O(OPF_2)$ was characterized by its infrared and nmr spectra. Although a sample pure enough to establish its mass spectral cracking pattern was not obtained, accurate mass measurement of the parent ion confirmed the presence of $(SPF_2)O(OPF_2)$ (calcd for $(^{32}SPF_2)O(OPF_2)$: 201.9031; found:

201.9031).

4. Amino and Methylamino Phosphoryl and Thio-phosphoryl Difluorides.

(a) Preparation of SPF_2NHCH_3, SPF_2NH_2, OPF_2NHCH_3 and OPF_2NH_2

All four compounds were prepared by the same method. Two molar equivalents of ammonia or methylamine were condensed into the sidearm of a 1 ℓ vessel connected via a stopcock to the main reaction vessel. One molar equivalent of chlorophosphoryl difluoride (or the thio analog) was then condensed into the main part of the reaction vessel and allowed to warm to room temperature. The amine was then warmed and slowly admitted to the gaseous chlorophosphorus compound through the stopcock. Reaction occurred immediately on contact of the reagents with the visible formation of a white solid. After allowing 15 mins for the complete mixing of the reactants to ensure completion of the reaction, the volatile products were fractionated with the desired product stopping at -45°. Reactant and product quantities are given in Table 3. The low volatility of amino phosphoryl difluoride, OPF_2NH_2, rendered a slightly modified recovery procedure more convenient. After reaction of OPF_2Cl and NH_3, the high volatile products were removed into the vacuum system and then the OPF_2NH_2 was condensed into an nmr tube which had

TABLE 3

Data for preparation of amino- and methylamino-phosphoryl- and thiophosphoryl difluorides

Compound	EPF_2Cl		RNH_2		Yield of EPF_2NHR			Other Products	
	g	mmol.	g	mmol.	g	mmol.	%	compound	g
SPF_2NHCH_3	0.74	5.39	0.32	10.3	0.61	4.67	94.3	SPF_2Cl	0.06
SPF_2NH_2	1.14	8.36	0.28	16.51	0.51	4.36	58.4	SPF_2Cl	0.12
OPF_2NHCH_3	0.74	6.11	0.37	11.82	0.56	4.85	84.0	OPF_2Cl	0.04
OPF_2NH_2	see text.								

Data for preparation of $(SPF_2)_2NCH_3$, $(OPF_2)_2NCH_3$, $(SPF_2)_2N^-(CH_3)_3NH^+$, and $(OPF_2)_2N^-(CH_3)_3NH^+$

Compound	EPF_2NHR		EPF_2Cl		$(CH_3)_3N$		yield of $(EPF_2)_2NR$		
	g	mmol.	g	mmol.	g	mmol.	g	mmol.	%
$(SPF_2)_2NCH_3$	0.29	2.24	0.34	2.46	0.15	2.58	0.46	2.01	89.6
$(OPF_2)_2NCH_3$	0.57	4.97	0.63	5.19	0.30	5.11	0.71	3.59	72.2
$(SPF_2)_2NH$	see text								
$(OPF_2)_2NH$	see text								

previously been attached to the 1 ℓ reaction vessel. The yield of OPF_2NH_2 was not determined. Its nmr parameters are in agreement with previously reported results.[79]

Reactions of the chlorophosphorus compound with amine carried out in the condensed phase gave poor yields of the desired monosubstituted product and significant proportions of the disubstituted products. With reaction temperatures as low as -95°, improved yields of the desired product were obtained, but the reactions were never as successful as those carried out in the gas phase.

An alternative preparation of methylaminophosphoryl difluoride involved reaction of $(OPF_2)_2O$ (0.99 g, 5.31 mmole) and CH_3NH_2 (0.34 g, 10.97 mmole) in the gas phase in the 1 ℓ reactor. Reaction occurred immediately on mixing. Fractionation of the volatile products gave only OPF_2NHCH_3 (0.44 g, 3.79 mmole; 72% yield). A white solid and a small amount of an involatile colorless liquid remained in the reaction vessel.

(b) Characterization of SPF_2NHCH_3, OPF_2NHCH_3, SPF_2NH_2 and OPF_2NH_2

All the above compounds are clear, colorless, relatively low volatile liquids. Because of their low volatility, only the vapor pressure of SPF_2NHCH_3 was conveniently obtained. The vapor pressure data for SPF_2NHCH_3, given in Appendix A, is best described by the equation

$$\log_{10} P_{mm} = 8.065 - \frac{2105}{T}$$

from which may be obtained an extrapolated boiling point of 132.9°, a heat of vaporization of 9632 cal/mole and a Trouton constant of 23.7 cal/mole deg. The boiling points of the other amino compounds are somewhat higher. The increased volatility of the thiophosphoryl compounds relative to their phosphoryl analogs is generally observed[1] and can be attributed to increased hydrogen bonding in the latter compounds.

The compounds were further characterized by their infrared, nmr and, particularly, mass spectra including accurate mass measurement (for $^{32}SPF_2NHCH_3$, calcd: 130.9761; found: 130.9759; for OPF_2NCH_3, calcd: 113.9921; found: 113.9913; for $^{32}SPF_2NH_2$, calcd: 116.9614; found: 116.9613). Of the above compounds, only the mass spectrum of SPF_2NH_2 shows a metastable peak (obs. m/e: 80.4; calcd. m/e: 80.4) which may be assigned to the transition

$$SPF_2NH_2^+ \rightarrow SPFNH^+ + HF$$

Infrared data are given in Appendix B, mass spectra data in Appendix C, and nmr data in Appendix D.

5. Nitrogen-Bridged Phosphoryl- and Thiophosphoryl Difluorides.

(a) N-methyl bis-difluorophosphoryl- and thiophosphoryl amines

Equal molar ratios of methylaminodifluorophosphorus compound, the appropriate phosphorus chloro-fluoride and trimethylamine were condensed into a 50 cc reaction tube equipped with a stopcock. Reaction occurred immediately on warming the contents of the tube to room temperature. (No reaction occurred in the absence of trimethylamine). The desired products were trapped at -45°. Quantities and yields are given in Table 3.

Only the $(SPF_2)_2NCH_3$ was sufficiently volatile to permit convenient measurement of the vapor pressure. The vapor pressure data, given in Appendix A, are best described by the equation

$$\log_{10} P_{mm} = 8.009 - \frac{2065}{T}$$

from which is obtained an extrapolated boiling point of 129.5°, a heat of vaporization of 9449 cal/mole, and a Trouton constant of 23.5 cal/mole deg.

The compounds were further characterized by their infrared (Appendix B), nmr (Appendix D), and mass (Appendix C) spectral properties, including accurate mass measurement (for $(^{32}SPF_2)_2NCH_3$, calcd: 230.9120; found: 230.9118; for $(OPF_2)_2NCH_3$, calcd: 197.9492; found: 197.9495).

The compound $(SPF_2)_2NCH_3$ was characterized chemically by its reaction with HCl. $(SPF_2)_2NCH_3$ (0.10 g, 0.42 mmole) and HCl (0.02 g, 0.48 mmole) were sealed in a 10 cc reaction tube. When no reaction was observed after several hours at room temperature or at 70°, the reaction tube was heated to

150° for 16 hr. The volatile products were then fractionated to give $(SPF_2)_2NCH_3$ (0.07 g, 0.27 mmole) condensed at -65°, and a mixture of HCl and SPF_2Cl condensed at -196° (0.02 g). A solid white residue and traces of an involatile, colorless liquid remained in the tube.

5. Trimethyl ammonium salts of bis-difluorophosphoryl and -difluorothiophosphoryl amides.

Equal molar proportions of amino difluorophosphorus compound and the appropriate phosphorus chlorofluoride and a two fold molar quantity of trimethylamine were condensed into a 50 cc reaction tube. Reaction occurred immediately on warming to room temperature to form solid and liquid products. The desired compounds were obtained as a non-volatile oil by subliming trimethyl ammonium chloride out of the reaction products. No reaction was observed in the absence of trimethylamine, and the use of a unimolar ratio led to incomplete consumption of the aminophosphorus and chlorophosphorus compounds which were later recovered by fractionation. Because of the non-volatile nature of the products, yields were not calculated, although they appeared to be substantial.

Again, because of their non-volatile nature, the compounds were most conveniently characterized by their nmr spectra (Appendix D) and their mass spectra (Appendix C) including accurate mass measurement of the parent ion corresponding to $(EPF_2)_2NH$ (E = S,O). (For $(^{32}SPF_2)_2NH$, calcd. 216.8973; found: 216.8971); for $(OPF_2)_2NH$; calcd: 184.9419, found: 184.9421).

An attempt was made to characterize $(SPF_2)_2N^-(CH_3)_3NH^+$ chemically by allowing $(SPF_2)_2N^-(CH_3)_3NH^+$ (0.28 g, 1.01 mmole) and HCl (0.03 g, 0.90 mmole) to react at 150° for 16 hrs in a sealed tube. Fractionation of the volatiles gave only SPF_3 with a trace of SPF_2Cl. A colorless liquid residue remained which was mainly unchanged $(SPF_2)_2N^-(CH_3)_3NH^+$.

7. Discussion

The reaction of SPF_2SH with either $OPF_2N(CH_3)_2$ or $SPF_2N(CH_3)_2$ was the most convenient general synthetic route to the bridged thiophosphoryl difluorides. The reaction follows the equation (where E = S,O)

$$2SPF_2SH + EPF_2N(CH_3)_2 \rightarrow F_2P(S)EP(S)F_2 + (CH_3)_2NH_2{}^+S_2PF_2{}^- \tag{11}$$

The reaction of OPF_2OH with $SPF_2N(CH_3)_2$ gave about a 40% yield of $(SPF_2)_2O$, so that reaction (11) cannot be completely generalized. Although the asymetrical compound, $(SPF_2)O(OPF_2)$, may be obtained by reaction of either SPF_2H or SPF_2SH with $(OPF_2)_2O$, it has not yet been possible to prepare the symmetrical form of the compound, $(OPF_2)_2S$.

Since $(OPF_2)O(SPF_2)$ does not result from the reaction of OPF_2OH and $SPF_2N(CH_3)_2$, it is possible that the reaction proceeds initially through attack of the acid on the P-N bond followed by rearrangement of the initial asymmetric form. Since $OPF_2N(CH_3)_2$ was obtained in the reaction products, this rearrangement may involve a reaction such as

$$(SPF_2)O(OPF_2) + SPF_2N(CH_3)_2 \rightarrow (SPF_2)_2O + OPF_2N(CH_3)_2$$

A disproportionation of the type

$$2(SPF_2)O(OPF_2) \rightarrow (SPF_2)_2O + (OPF_2)_2O$$

may also be involved, although no indication of the presence of $(OPF_2)_2O$ was obtained. However, a pure sample of $(SPF_2)O(OPF_2)$ was found to disproportionate to a mixture of the symmetric compounds. The non-observance of the $(OPF_2)_2O$ in the above mixture might be attributed to its further reaction with other compounds in the mixture.

It has also not been possible to isolate the unsymmetric compound $(SPF_2)S(OPF_2)$, although such a product might be expected from reaction (11) with E = 0. This reaction has also been carried out in an nmr tube and followed from the early stages. Only starting materials, the $S_2PF_2^-$ ion and the symmetric compound $(SPF_2)_2O$ were observed in the spectrum indicating that, if the unsymmetric compound is formed at all, it rapidly rearranges into the oxygen-bridged form. The reaction of OPF_2OH with $SPF_2N(CH_3)_2$ has also been studied in this manner with similar results.

An alternative route to $(SPF_2)_2O$ is the reaction of SPF_2I with elemental oxygen

$$2PF_2I + \frac{1}{2}O_2 \rightarrow (SPF_2)_2O + I_2$$

This method is not particularly useful because the reaction is slow and incomplete (at temperatures which do not lead to excessive decomposition of the iodofluoride), and the separation of SPF_2I from $(SPF_2)_2O$ is difficult. It was not possible to oxidize SPF_2I to $(SPF_2)_2S$ with elemental sulphur.

Reaction of SPF_2I with Cu_2O gave an approximately 50% yield of $(OPF_2)_2O$ and then only after heating the initially formed adduct quite strongly.

It is possible that although the desired reaction, which is analogous to that employed in the synthesis of $(PF_2)_2O$, occurs, the products are so strongly complexed to the metal that only decomposition results when the complex is heated in an attempt to liberate the phosphorus compound. Other non-metallic oxides, such as antimony (V) oxide were also used in attempts to prepare $(SPF_2)_2O$, but were found to be unsuitable. Although Ag_2CO_3 converts $(CF_3)_2PI$ into $[(CF_3)_2P]_2O$,[65,83] its reaction with SPF_2I gave only OPF_3 (in about 15% yield) and no other volatile products, even after heating the reaction mixture quite strongly.

Cuprous sulfide did not react with SPF_2I, and SPF_2SH, even after 10 days at 150° gave only SPF_3 when reacted with SPF_2I although both of these reactions might have been expected to yield $(SPF_2)_2S$. Reaction of elemental sulphur with $(PF_2)_2O$ did not produce a pentavalent thiophosphoryl compound although organo-phosphines readily add sulphur to form the pentavalent thiophosphoryl compounds.[61]

The amino- and methylamino- phosphoryl and thiophosphoryl difluorides are conveniently prepared by the gas phase reaction of the appropriate phosphorus chlorofluoride with ammonia or methylamine. The reaction follows the usual stoichiometry and involves preferential aminolysis of the P-Cl bond (with E = S,O; R = H,CH_3)

$$EPF_2Cl + 2RNH_2 \rightarrow EPF_2NHR + RNH_3Cl$$

Low yields of the desired product and appreciable proportions of di-aminated product were obtained when the reactions were carried out in the condensed phase. It appears that aminolysis of the P-F bonds also occurs, probably as a result of high local concentrations of amine in the condensed phase. This situation can be avoided by the use of gas phase reaction conditions in which the chlorofluoride is maintained in excess concentration in the reaction vessel.[21]

An alternate route to the synthesis of OPF_2NHCH_3 is the gas phase reaction of CH_3NH_2 with $(OPF_2)_2O$

$$(OPF_2)_2O + 2CH_3NH_2 \rightarrow OPF_2NHCH_3 + (CH_3)NH_3{}^+O_2PF_2{}^-$$

which is analogous to the preparation of OPF_2NH_2 from $(OPF_2)_2O$ and NH_3[79] which was done in solution rather than in the gas phase.

Both the phosphoryl and thiophosphoryl N-methyl bridged compounds are easily prepared from the above methylamino compounds by the trimethylamine assisted condensation reaction (with E = S,O)

$$EPF_2NHCH_3 + EPF_2Cl + (CH_3)_3N \rightarrow (EPF_2)_2NCH_3 + (CH_3)_3NH^+Cl^-$$

Only the symmetrically substituted compounds were attempted. No reaction occurs in the absence of $(CH_3)_3N$ probably because of the reduced basicity of the $NHCH_3$ group resulting from the strong electron withdrawing properties of the EPF_2 group.

The reaction of $(SPF_2)_2NCH_3$ with HCl gives only very difficult cleavage of the P-N bonds as was noted for the hydrogen halide cleavage of $[(CF_3)_2P]_2NCH_3$ and $[(CF_3)_2P]_2NH$.[86] In contrast, the cleavage of the P-N bonds of $(PF_2)_2NC_2H_5$ by HCl occurs readily,[84,85] even below room temperatures.

Reaction of the aminophosphorus compounds with chlorophosphorus difluorides did not yield the NH bridged species, but rather its trimethylamine adduct (with E=S,O)

$$EPF_2NH_2 + EPF_2Cl + 2(CH_3)_3N \rightarrow (EPF_2)_2N^-(CH_3)_3NH^+ + (CH_3)_3NH^+Cl^-$$

Nmr and infrared spectroscopy of the adduct suggested that the hydrogen had been transferred to the amine cation. HCl did not displace the $(EPF_2)_2NH$ compound from the adduct but cleaved the P-N bonds instead. The parent N-H bridged compound was observed in the mass spectrometer upon volatilizing the adduct directly into the ionization chamber by means of the direct probe. The formation of an adduct rather than the N-hydro compound is analogous to the behaviour of $[(CF_3)_2P]_2NH$, which also forms a $(CH_3)_3N$ adduct,[86] and suggests that the hydrogen is fairly acidic due to the electronegativity of the EPF_2 groups. The $[(CF_3)_2P]_2NH\cdot(CH_3)_3N$, however, was readily dissocated at 25° whereas much higher temperatures are required for dissociation of the pentavalent phosphorus compounds.

The mass spectral cracking patterns for the above compounds are summarized in Appendix C, and the metastable transitions associated with these spectra are outlined in Table 4. Most of the compounds exhibit straight forward cracking patterns with the molecular ion as the most intense feature in the spectrum. Contrasting behaviour is shown by the compounds $(SPF_2)_2S$ and $(SPF_2)_2NH\cdot(CH_3)_3N$ which show PF_2^+ as the strongest ion and by $(OPF_2)_2NCH_3$ in which the strongest ion is $OPF_2NCH_3^+$. Surprisingly, the molecular ion is not observed in the latter compound. The mass spectra of the trimethylamine adducts of $(EPF_2)_2NH$ show the parent N-H compound as well as ions corresponding to fragmentation of $(CH_3)_3N$.

The infrared spectra of the compounds discussed in this chapter exhibit a general similarity to each other and to that reported for $(OPF_2)_2O$[8] as might be expected in view of the structural similarity of the compounds. The spectra are summarized in Appendix B. Qualitative assignments,

TABLE 4

Metastable Peaks Observed in the Mass Spectra of Some Nitrogen-Bridged Diphosphorus Compounds

Compound	Metastable Peak	Transition
$(SPF_2)_2NCH_3$	73.0	$(SPF_2)_2NCH_3^+ \rightarrow SPF_2NCH_3^+ + SPF_2$
$(OPF_2)_2NCH_3$	142.5	$(OPF_2)_2NCH_2^+ \rightarrow PF_2NP(O)F_2^+ + CH_2O$
$(SPF_2)_2NH\cdot(CH_3)_3N$	178.7	$(SPF_2)_2NH^+ \rightarrow SPFNP(S)F_2^+ + HF$
	57.4	$PF_2N^+ \rightarrow PF_2^+ + N$
	18.8	$(SPF_2)_2NH^+ \rightarrow S_2^+ + (PF_2)_2NH$
$(OPF_2)_2NH\cdot(CH_3)_3N$	152.6	$(OPF_2)_2NH^+ \rightarrow PF_2NP(O)F_2^+ + OH$
	147.2	$(OPF_2)_2NH^+ \rightarrow OPFNP(O)F_2^+ + HF$
	128.4	$OPFNHP(O)F_2 \rightarrow (OPF)_2N^+ + HF$
	57.3	$PF_2N^+ \rightarrow PF_2^+ + N$

included in Appendix B were made by analogy to related systems.[1,8,36,90]

Phosphorus-fluorine stretching frequencies are observed in the range 970 - 920 cm^{-1}. In molecules of this type, characteristic frequencies are also to be expected from the bridge unit. Thus the relatively strong band at 501 cm^{-1} in $(SPF_2)_2S$ is probably best assigned to the P-S-P stretching vibration. The band at 1037 cm^{-1} in the spectrum of $(SPF_2)_2O$ is probably due to asymmetric P-O-P stretching in keeping with the value of 1075 cm^{-1} observed in the infrared spectrum of $(OPF_2)_2O$. Robinson has assigned the band at 987 cm^{-1} in the Raman spectrum of $(OPF_2)_2O$ to the P-O-P asymmetric stretch. Because of the ambiguity in this assignment and the assignment of the P-O-P symmetric stretch noted below, the Raman and infrared spectra of $(OPF_2)_2O$ are currently being reinvestigated. The P-O-P stretching frequency in (SPF_2) $O(OPF_2)$ may be assigned to the band at 1055 cm^{-1} by analogy to the analogous frequencies in the spectra of $(SPF_2)_2O$ and $(OPF_2)_2O$.

The symmetric P-O-P stretching vibration is not as readily assigned since it appears in the same region as the P-F stretch. In $[(CF_3)_2P]_2O$,[65,83] the band at 678 cm^{-1}, and in $(PF_2)_2O$,[2] the band at 715 cm^{-1} are assigned to the symmetric P-O-P vibrations. Therefore, it seems more reasonable to assign the fairly weak band at 855 cm^{-1} in $(OPF_2)_2O$ to the symmetric P-O-P stretch, in keeping with other assignments[91,92] but in disagreement with the original assignment of 480 cm^{-1} to the symmetric P-O-P stretch in $(OPF_2)_2O$.[8] Similarily, the medium intensity band at 847 cm^{-1} in the spectrum of $(SPF_2)_2O$ is assigned to symmetric P-O-P stretching. By analogy, the P-O-P symmetric stretch in $F_2POP(O)F_2$ may be assigned to the band at 724 cm^{-1} which is the approximate average of the P-O-P symmetric stretching frequencies in the pentavalent and trivalent analogs.

If these tentative assignments are correct, it indicates that the symmetric bridge stretching frequency is increased on going from trivalent to pentavalent phosphorus. This suggests that the bridge bond is stronger in the latter, possibly because of a greater π-contribution to the bridge bond in the pentavalent phosphorus compounds.

This suggestion appears to be confirmed by the bridge frequencies in nitrogen bridged compounds. Nixon has assigned the P-N-P asymmetric stretching frequency to bands in the 880-950 cm^{-1} region for a number of compounds of the type $RN(PX_2)_2$ (where X = Cl,F).[84,85] Similarly, Burg and Heners,[86] have assigned P-N-P asymmetric stretches in the CF_3 analogs to the 850-930 cm^{-1} region. However, the P-N-P asymmetric stretching frequencies in the pentavalent N-bridged compounds $(EPF_2)_2NCH_3$ are best assigned to bands in the 1080-1100 cm^{-1} region. (These bands appear to be shifted to the 980-1000 cm^{-1} region in the spectra of the amide salts of the type $(EPF_2)_2N^-(CH_3)_3NH^+$). This implies a large increase in P-N bond strength which appears to be substantiated by the relative ease of HCl cleavage of the P-N bonds.

If the ease of cleavage is indeed a function of the P-N bond strength rather than a kinetic effect of some sort, it might imply that cleavage of the P-N bond by HX proceeds through protonation of the nitrogen followed by X^- attack on the phosphorus.

This same sort of relative ease of cleavage of P-N bonds has also been observed for hydrogen halide cleavage of $PF_2N(CH_3)_2$,[21] $OPF_2N(CH_3)_2$,[13] and $SPF_2N(CH_3)_2$.[12] The explanation for this behaviour may lie in the fact that in the trivalent compounds, the phosphorus lone pair is utilized in satisfying the electronegativity of the fluorine or CF_3 groups, leaving the nitrogen lone pair available for proton attack. However, when the phosphorus lone pair is not available, being used in bonding oxygen or sulphur as in the pentavalent compounds, the nitrogen lone pair tends to be utilized to a greater extent in satisfying the electronegativity of the phosphorus substituents, with a subsequent reduction in the possibility of protonation of the nitrogen.

The N-H bridged compounds have complicated infrared spectra which show a series of bonds consistent with the $(CH_3)_3NH^+$ ion.[93] There appears to be no band which could be reasonably assigned to a P_2NH stretching frequency. This, in conjunction with the fact that the nmr spectra of these compounds show no hydrogen-phosphorus or hydrogen-fluorine coupling, is consistent with the formulation of these compounds as adducts with the structure $(EPF_2)_2N^-(CH_3)_3NH^+$.

The NMR Spectra of Some Bridged Diphosphorus Tetrafluoride Compounds

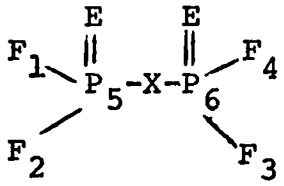
Chapter VIII

Although the diphosphorus tetrafluoride compounds $(OPF_2)_2O$,[8] $(PF_2)_2O$,[3] and P_2F_4 [2,3] have been known for some time, only the nmr spectrum of P_2F_4 [78] has been reported in detail. Very recently, the nmr spectra of the compounds $(SPF_2)_2O$ and $(OPF_2)_2O$ were reported.[88] The resolution of these spectra, however, were somewhat limited by the instrumentation used. The ^{19}F spectrum of $(OPF_2)_2O$ was originally reported as a simple doublet,[8] while the spectrum of $(PF_2)_2O$ was found to be complex,[3] but was interpreted on the basis of an $AA'X_2X_2'$ system using the expressions derived by Harris [94,95] for such systems assuming that $J_{XX'} = 0$. The spectrum of P_2F_4 was correctly analyzed on the basis of an AA'XX'X"X'" system, using the explicit solution for such systems provided by Lynden-Bell.[96] The recent solutions of the nmr spectra of $(SPF_2)_2O$ and $(OPF_2)_2O$ [88] were also based on an AA'XX'X"X'" system.

The present chapter discusses the nmr spectra of the oxygen, sulphur, and nitrogen-bridged diphosphorus tetrafluoride compounds prepared in this study, as well as the spectra of the previously studied compounds $(OPF_2)_2O$ [8] and $(PF_2)_2O$.[3]

1. Analysis of the Spectra

All the compounds in this study may be represented by the formula:



E = S,O, or nothing

X = S,O,N^-,NCH_3

The spectra of such symmetrical compounds are of a second-order nature as a consequence of the magnetic non-equivalence of the nuclei in the system. This magnetic non-equivalence arises in the following manner. Although the fluorine atoms F_1 and F_4 are in chemically equivalent positions, their interaction with the other atoms in the molecule are not the same (eg. $J_{F_1P_5} \neq J_{F_4P_5}$). However the electronic environment of each of the fluorines or phosphorus atoms is the same, even though interactions with individual atoms may be different. Thus, the fluorines all have the same chemical shift as do both phosphorus atoms. Observed ^{19}F half-spectra, the central component of the ^{31}P spectra, and stick diagrams of the calculated spectra are shown in Figures 3 - 10.

A feature common to all the spectra is the presence of a strong doublet in the ^{19}F spectra and a strong triplet in the ^{31}P spectra except in the case of the NCH_3-bridged compounds where these strong lines are further split into 1:3:3:1 quartets. Lynden-Bell [96] has shown that the ^{19}F

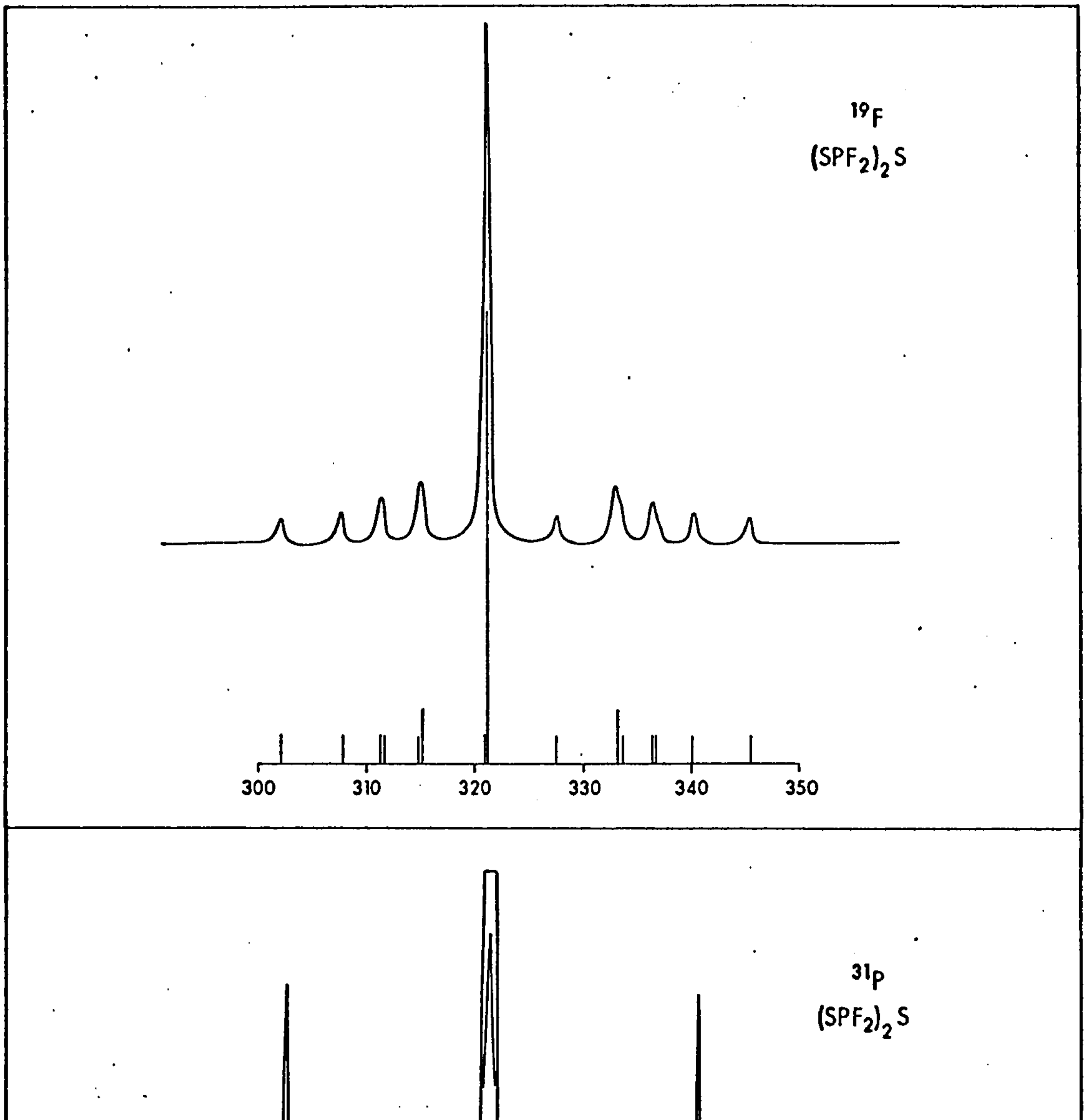


Figure 3. Representative ^{19}F and ^{31}P NMR Spectra of μ-Thio-Bis(Thiophosphoryl Difluoride)

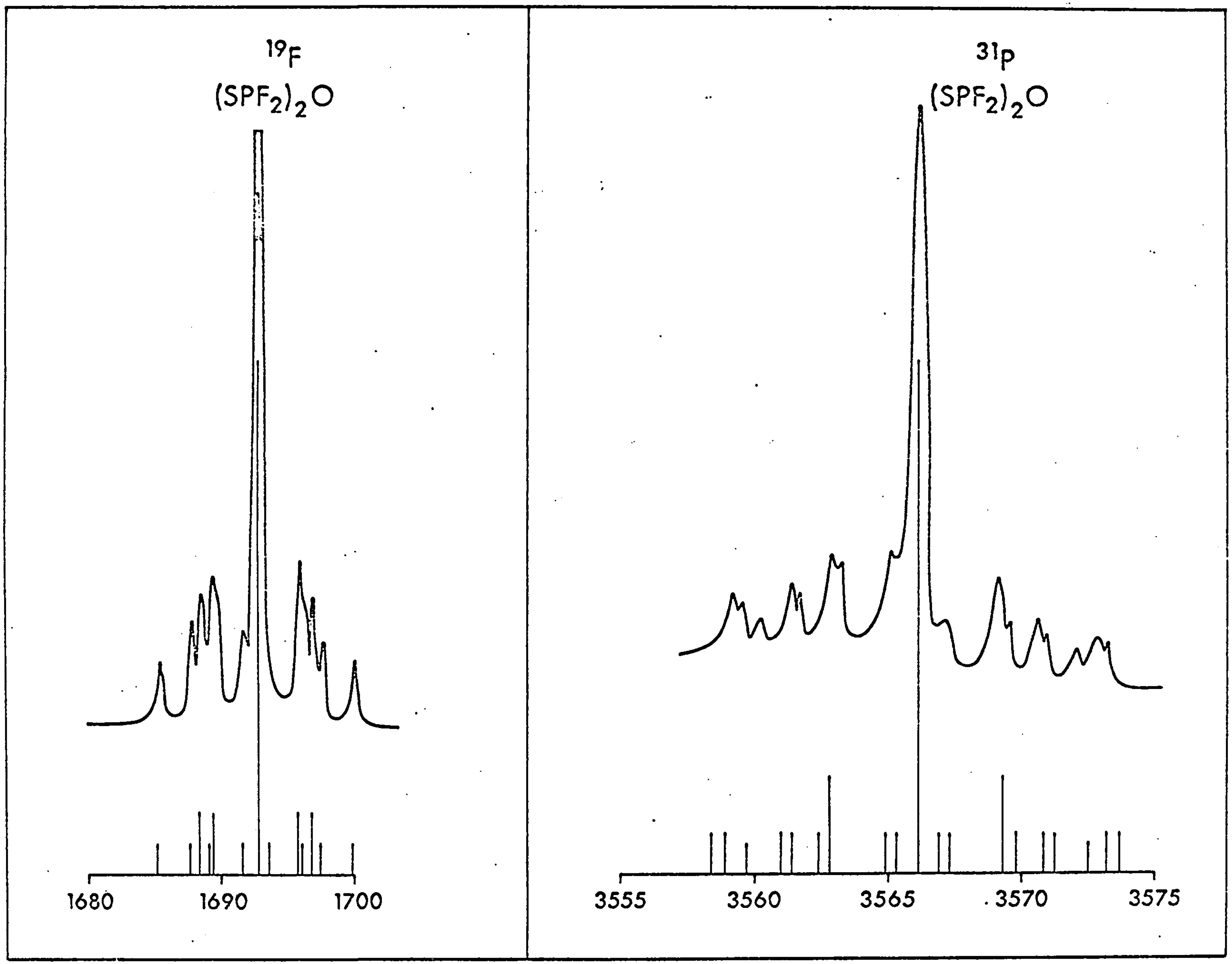


Figure 4. Representative ^{19}F and ^{31}P NMR Spectra of μ-Oxo-Bis(Thiophosphoryl Difluoride)

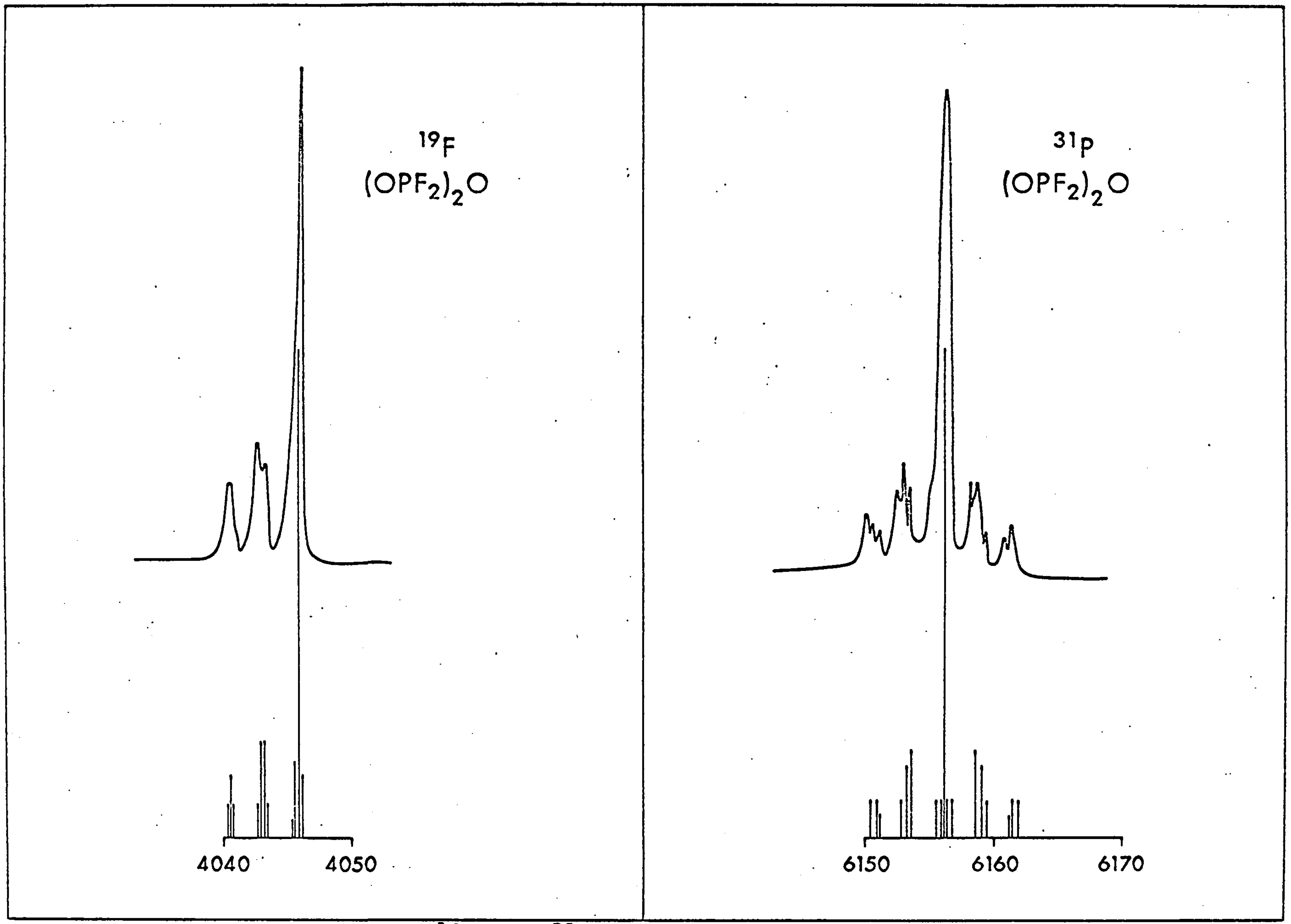


Figure 5. Representative ^{19}F and ^{31}P NMR Spectra of Difluorophosphoric Acid Anhydride

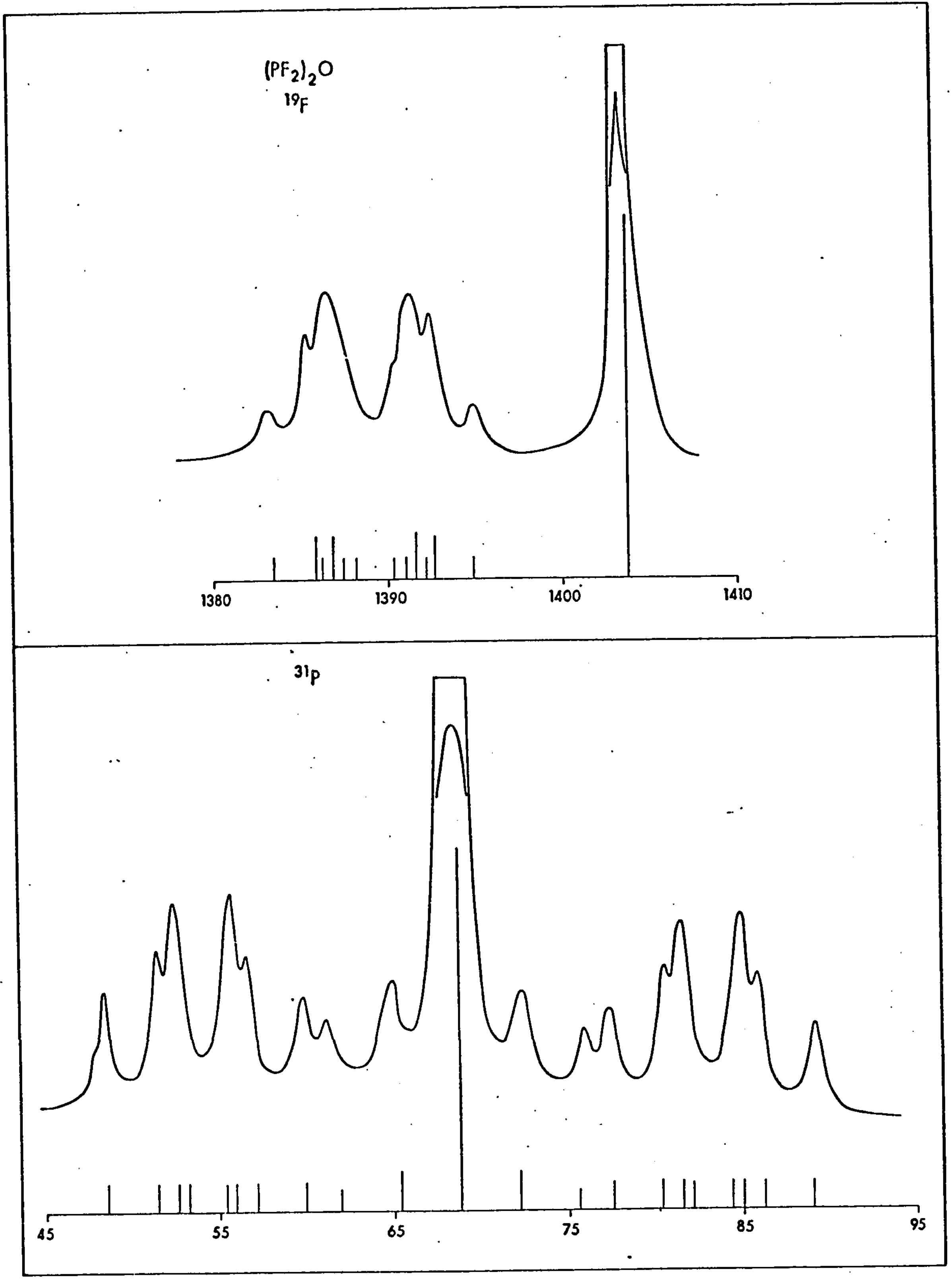


Figure 6. Representative ^{19}F and ^{31}P NMR Spectra of μ-Oxo(Bis(Difluorophosphine)

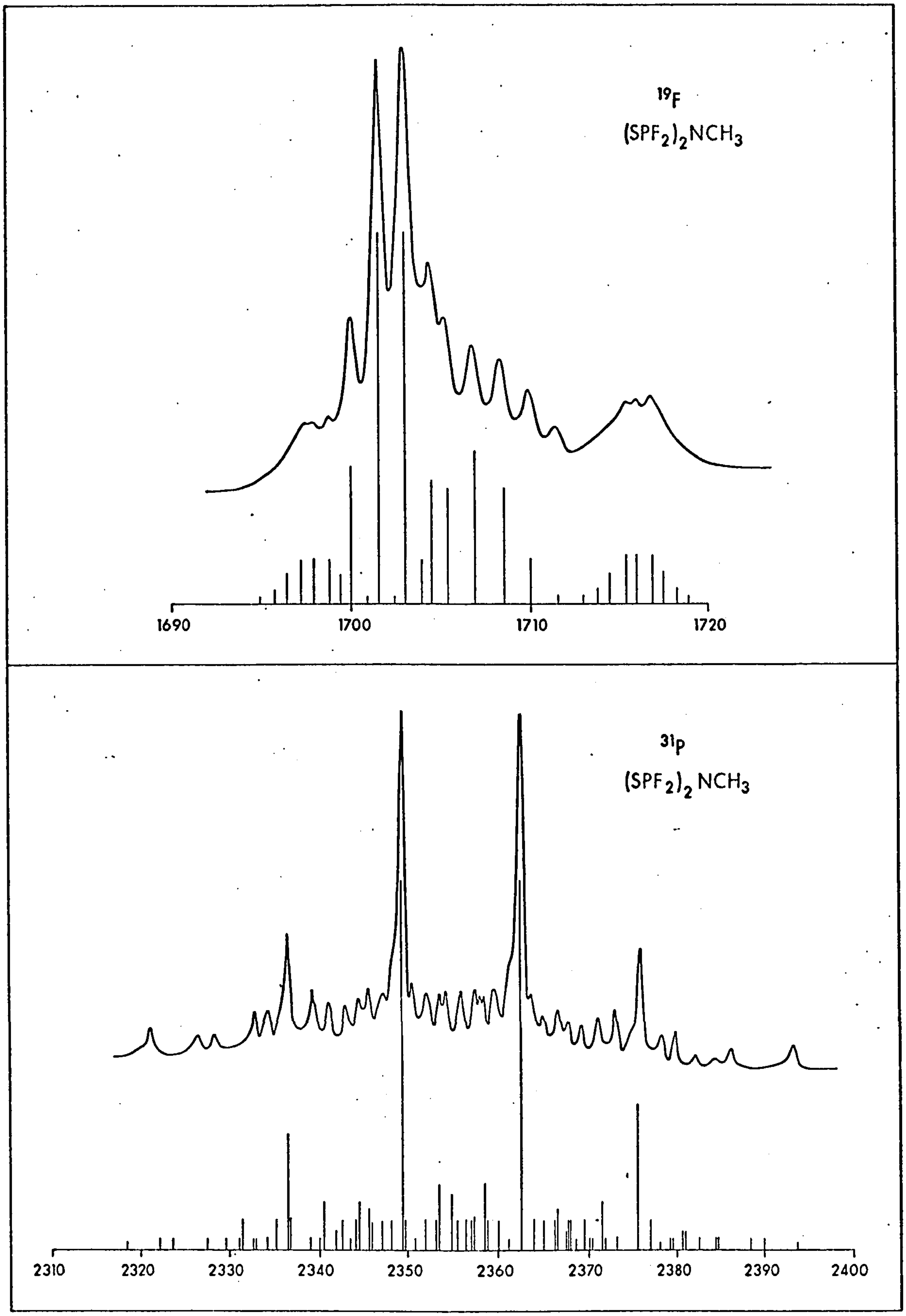


Figure 7. Representative ^{19}F and ^{31}P NMR Spectra of N-Methyl-Bis(Difluorothiophosphoryl) Amine

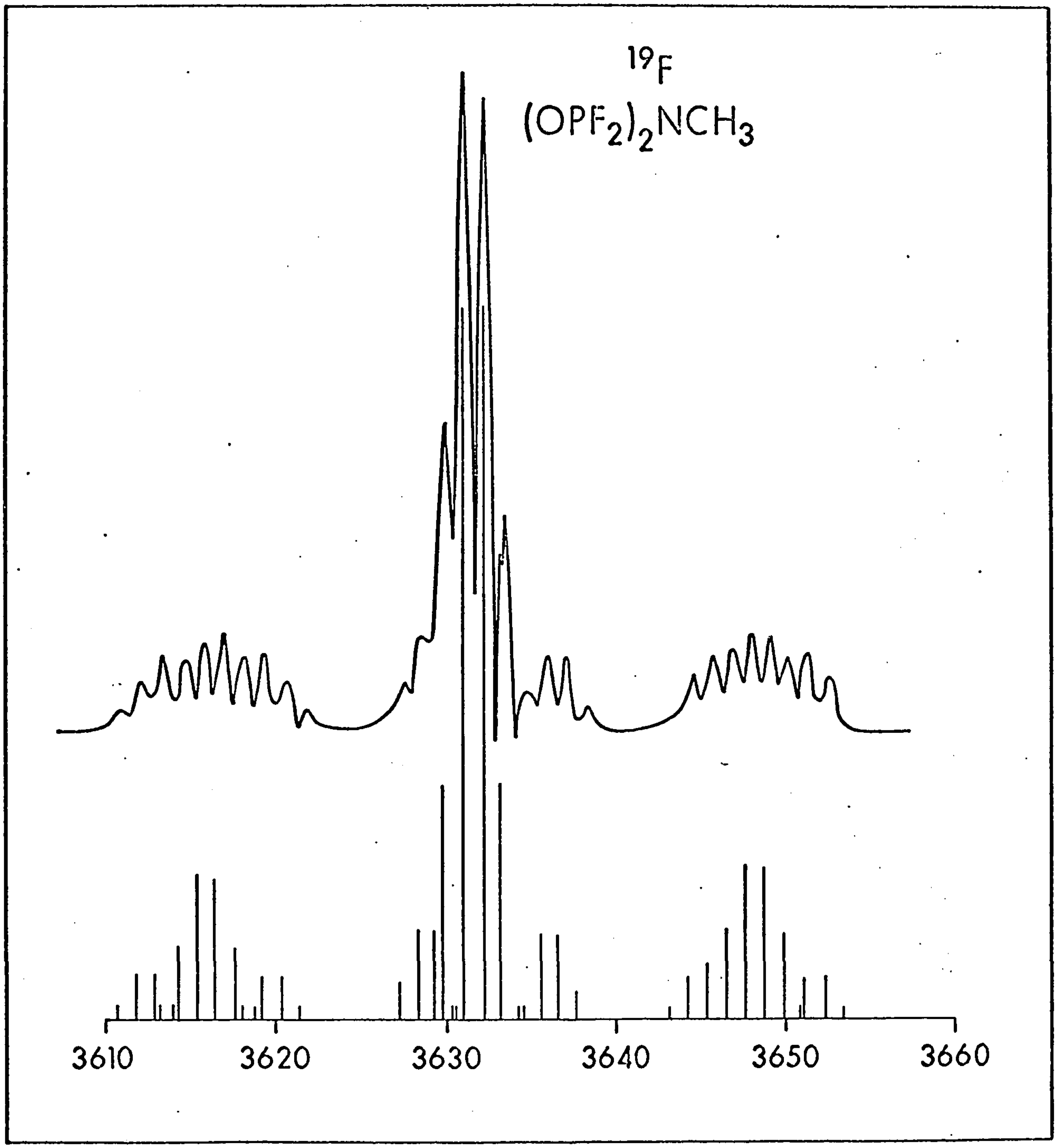


Figure 8. Representative ^{19}F Spectrum of N-Methyl-Bis(Difluror-phosphoryl) Amine.

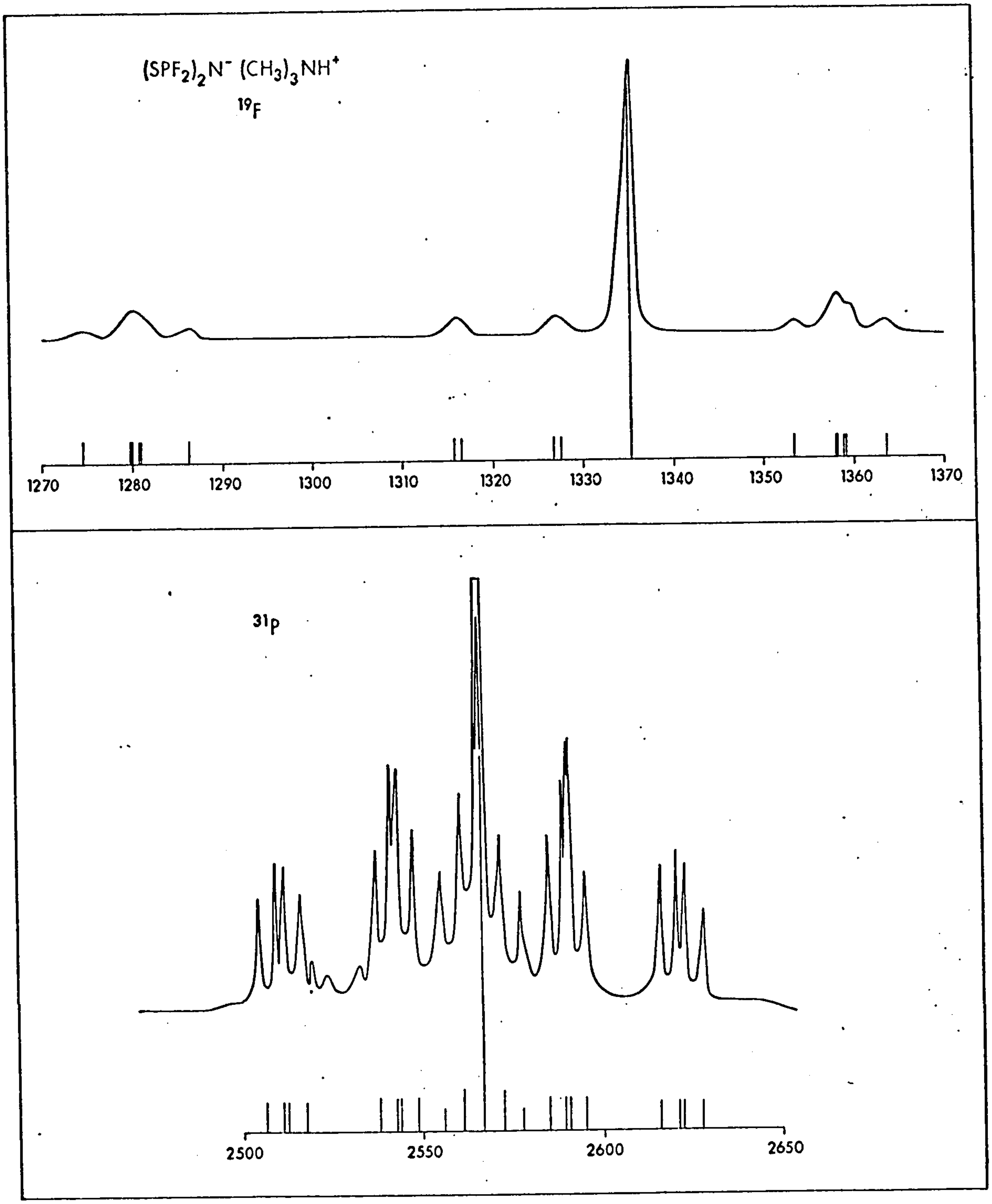


Figure 9. Representative ^{19}F and ^{31}P NMR Spectra of Trimethyl Ammonium Bis(Difluorothiophosphoryl) Amide.

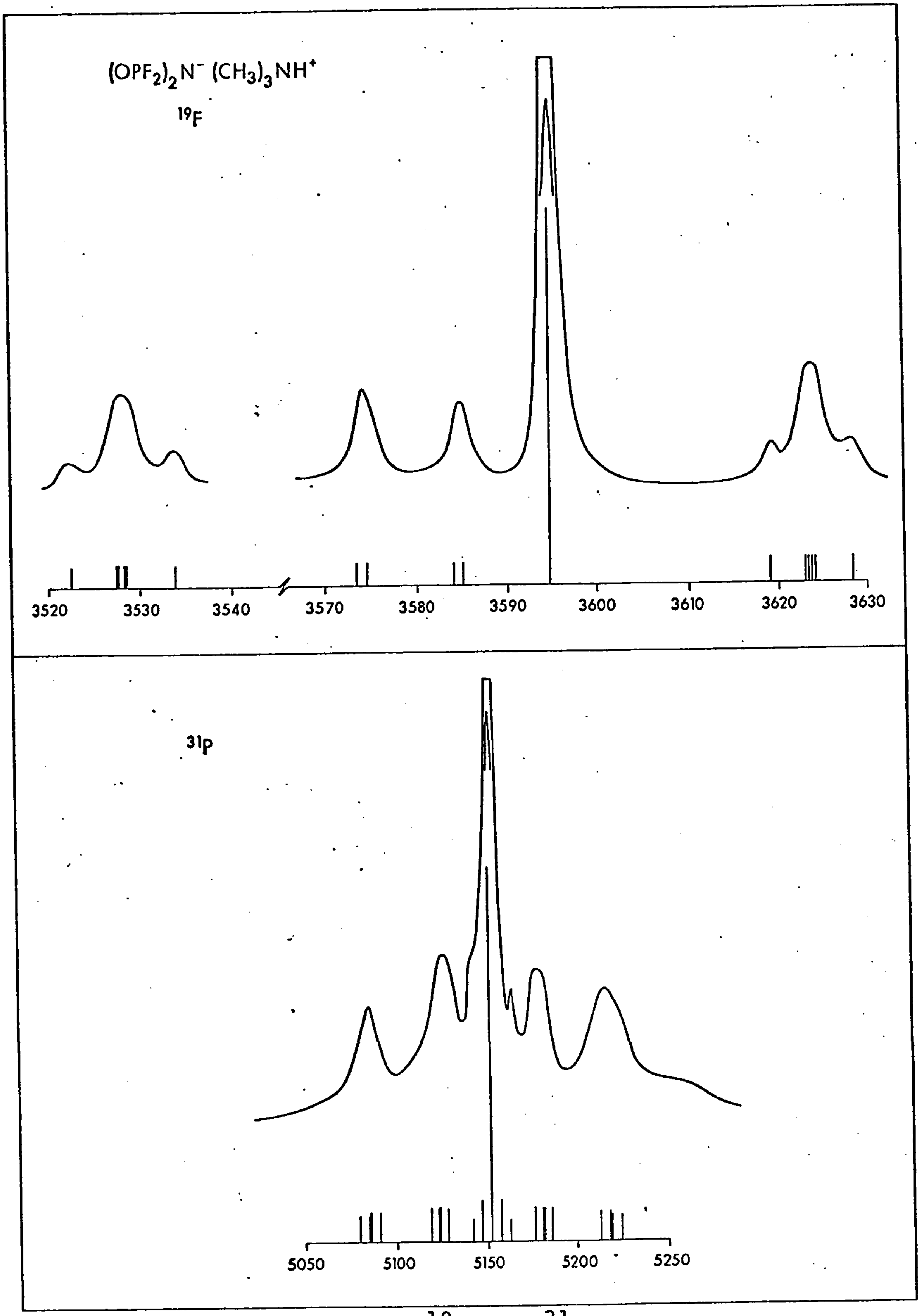


Figure 10. Representative ^{19}F and ^{31}P NMR Spectra of Trimethyl Ammonium Bis(Difluorophosphoryl) Amide.

doublet has a separation given by $K = \frac{1}{2}({}^{1}J_{PF} + {}^{3}J_{PF})$ and is symmetrically located around the ${}^{19}F$ chemical shift position ν_F. The strong ${}^{31}P$ triplet shows the same separation and is symmetrically located about the ${}^{31}P$ chemical shift position ν_P.

Although the remaining weak lines in both the ${}^{19}F$ and ${}^{31}P$ spectra are symmetrically arranged around ν_F and ν_P, no other prominent feature is immediately obvious which can be used as a means of analyzing the spectra. Lynden-Bell [96] has shown that there should be a set of eight lines which occur twice in the ${}^{19}F$ spectrum and four times in the ${}^{31}P$ spectrum which can be identified and from which the other spectral parameters can be determined. The theoretical positions of the lines in one of the sets for the ${}^{19}F$ spectrum [96] are shown in Table 5. However, the spectra of the present compounds vary widely in complexity and in many cases show an apparent deficiency of lines. Thus, another procedure had to be used to deduce the remaining coupling constants.

Generally, each of the ${}^{19}F$ half-spectra extend over a very limited frequency range, in the order of 10 - 40 Hz. This implies that the coupling constants involved are very small, relative to the large, short-range P-F coupling constant. Additionally, the weak lines in each of ${}^{19}F$ half-spectrum appear to be symmetrical about a point somewhat separated from the position of the strong line in each half-spectrum. Reconsideration of the expressions for the transition frequencies given in Table 5 indicate that if ${}^1J_{PF}$ or, more specifically, $L = \frac{1}{2}({}^1J_{PF} - {}^3J_{PF})$ is very much larger than ${}^4J_{FF}$, ${}^4J_{FF'}$, and ${}^2J_{PP}$, then in the expressions $[L^2 + (N + X)^2]^{\frac{1}{2}}$ etc., the second squared term can be neglected, and the expressions for the transition frequencies may be reduced to the values shown in Table 5.

Consideration of these reduced expressions shows that a set of four pairs of lines may be observed in each half-spectrum with the separations given in Table 6 and which are symmetrically arranged around a point in each half-spectrum with a position relative to ν_F of $\pm\ ({}^1J_{PF} - {}^3J_{PF})$. In addition to these four pairs of lines, inspection of the spectra showed that two further pairs of lines could be found in some spectra with separations of ${}^2J_{PP}$ and $({}^4J_{FF} + {}^4J_{FF'})$ giving a possible total of twelve weak lines in each half spectrum.

Since the intensities of any of the weak lines are very roughly equivalent, as is found when a maximum number of weak lines is observed, the presence of a relatively strong line among the weak lines indicates the accidental coincidence of two or more of the weak lines.

On the basis of the foregoing assumptions, and using a series of simultaneous equations involving the coupling constants, a set of coupling constants may be derived which, when used to calculate spectra, give very good agreement

TABLE 5

Theoretical and Approximate Expressions for Some Frequencies in the X Spectrum of an AA'XX'X"X'" System

Exact Frequency	Approximate Frequency
$\nu_X + (N + X) \pm [L^2 + (N + X)^2]^{\frac{1}{2}}$	$\nu_X + (N + X) \pm L$
$\nu_X + (N - X) \pm [L^2 + (N - X)^2]^{\frac{1}{2}}$	$\nu_X + (N - X) \pm L$
$\nu_X + (M - X) \pm [L^2 + (M - X)^2]^{\frac{1}{2}}$	$\nu_X + (M - X) \pm L$
$\nu_X + (M + X) \pm [L^2 + (M + X)^2]^{\frac{1}{2}}$	$\nu_X + (M + X) \pm L$

$X = J_{AA}$, $N = \frac{1}{2}(J_{XX}(\text{cis}) + J_{XX}(\text{trans}))$, $M = \frac{1}{2}(J_{XX}(\text{cis}) - J_{XX}(\text{trans}))$, $L = \frac{1}{2}(J_{AX} - J_{A'X})$

TABLE 6

Approximate Separations of Lines in the X Half Spectrum

J_{AA}

$(J_{XX}(\text{cis}) + J_{XX}(\text{trans}))$

$J_{AA} \pm (J_{XX}(\text{cis}) + J_{XX}(\text{trans}))$

$J_{AA} \pm (J_{XX}(\text{cis}) - J_{XX}(\text{trans}))$

with the observed spectra. Slight modification to the initially derived coupling constants, usually less than 0.5 Hz, then gave excellent agreement with the observed spectra. In the case of NCH_3-bridged compounds, each of the lines is split into a quartet by the methyl protons and appropriate approximations had to be made to locate the center of each quartet, since mutual overlap of each component was observed.

The chemical shifts and coupling constants derived from the spectra are given in Appendix D and a comparison of the observed and calculated frequencies is given in Appendix E. The theoretical spectra were calculated using the program NSPECT III.[97] As can be seen from the tables, the observed and calculated ^{19}F spectra are generally in excellent agreement. The agreement for the ^{31}P spectra, however, is not as good and the reasons for this are discussed below.

The method of analysis described above works very well when one coupling constant is very much greater than any others in the compound, such as in the case of the bridged diphosphorus compounds. However, in the case of compounds with directly bonded phosphorus atoms having a P-P coupling constant in the same order of magnitude as $^1J_{PF}$, as in the case in the spectrum of P_2F_4, the assumptions on which the above analysis is based are no longer valid. Similarly, in the case of the bridged diphosphorus anionic species, $(OPF_2)_2N^-$ and $(SPF_2)_2N^-$, where $^2J_{PP}$ is considerably larger than in the other compounds, the first attempt to determine the coupling constants by the above method was not as successful as with the other compounds because of the deficiencies of the initial approximation.

It appears that this simple method can however be applied successfully to AA'XX'X"X''' systems in which $^1J_{AX}$ is a factor of about 10^2 larger than any other couplings in the systems. This method provides a good deal of simplification over Lynden-Bell's method since it is not always possible to identify the necessary sets of lines when several of the coupling constants are of roughly the same magnitude. It is also possible, by use of the above method, to derive all the coupling constants from only the X spectrum.

The spectra in all cases were found to be extremely insensitive to the magnitude and sign of the geminal F-F coupling constant. Therefore, a value of 200 Hz was arbitrarily assigned to $^2J_{FF}$ (gem.) for all compounds. The magnitude of this coupling constant could be varied over a range of several hundred Hz with no observable change in the spectrum. Generally, calculated spectral differences were detectable only when $^2J_{FF}$ (gem) was taken to be less than 50 Hz, and in these cases calculated spectra did not agree too well with the observed.

Although the magnitudes of the couplings were determined readily from the spectra, the relative signs of most of the constants are not as easily obtained. The relative signs of $^{1}J_{PF}$ and $^{3}J_{PF}$ may be determined by the position of the weak lines relative to the strong lines in each half spectrum. If the centers of the weak lines lie outside the strong lines then $|^{1}J_{PF} - ^{3}J_{PF}| > |^{1}J_{PF} + ^{3}J_{PF}|$ and thus $^{1}J_{PF}$ and $^{3}J_{PF}$ must be of different sign.

Heteronuclear double resonance experiments [98-101] have shown the absolute sign of $^{1}J_{PF}$, in several phosphorus fluorides, to be negative. Assuming that the sign of $^{1}J_{PF}$ in the present compounds is also negative, then $^{3}J_{PF}$ must be positive in the above case. If the centers of the weak lines lie inside the strong doublets, then the signs of $^{1}J_{PF}$ and $^{3}J_{PF}$ must both be negative.

A "spin-tickling" experiment was performed on the ^{19}F spectrum of $(SPF_2)_2O$ to determine the relative signs of $^{4}J_{FF}$ and $^{4}J_{FF'}$. Because a heteronuclear decoupling apparatus is presently unavailable, absolute signs could not be determined. The tickling experiment involved the following procedure.

A series of spectra were calculated using different combinations of signs of the coupling constants. It was found that while the overall spectrum did not change the spin states associated with some of the transitions for some of the sign combinations were interchanged. It was further found that the signs of $^{1}J_{PF}$ and $^{3}J_{PF}$ relative to the remaining coupling constants, had no effect on the calculated spectra. Similarily, the sign of $^2J_{PP}$ did not cause interchange of spin states in the ^{19}F calculated spectra. Only the signs of $^4J_{FF}$ and $^4J_{FF'}$ relative to one another affected the calculated spectrum.

The calculated ^{19}F spectra consisted of up to 80 transitions, many of which occurred at coincident frequencies. Only a small number of these transitions were affected by the change of signs of $^4J_{FF}$ and $^4J_{FF'}$. The interchanged lines are related by a series of common spin states, but these common states were dependent on the relative signs of $^4J_{FF}$ and $^4J_{FF'}$. Thus, by irradiating a line in the observed spectrum which was associated with a single transition in all calculated spectra and was dependent on the relative signs of $^4J_{FF}$ and $^4J_{FF'}$, and scanning the remainder of the spectrum, the lines associated with the irradiated line could be determined. The results of this experiment showed that $^4J_{FF}$ and $^4J_{FF'}$ must be of the same sign. It was then assumed that $^4J_{FF}$ and $^4J_{FF'}$ had the same sign in all the other compounds.

It is also possible to determine the sign of $^2J_{PP}$ relative to $^4J_{FF}$ and $^4J_{FF'}$ by obtaining the best fit to the ^{31}P spectrum.[96] As with the ^{19}F spectrum, only a small number of lines in the ^{31}P spectrum are affected by the relative sign of $^2J_{PP}$. Also, since the apparent agreement between the observed and calculated ^{31}P spectra is not as good as with the ^{19}F spectra a change in sign of some of the $^{2}J_{PP}$, such as in $(OPF_2)_2O$, shows no significant change in the agreement. Thus the signs of $^{2}J_{PP}$, when $^{2}J_{PP}$ is very small, are doubtful. In the case of the oxygen-containing, nitrogen bridged compounds, the ^{31}P spectra were very poorly resolved and a change in sign of $^{2}J_{PP}$ gave no better fit. The sign of $^{2}J_{PP}$ in the oxygen-containing species was assigned by analogy to the sulphur-containing species.

McFarlane [102] has performed a double resonance experiment on the pyrophosphite anion and found $^{2}J_{PP}$ to be negative. If $^{2}J_{PP}$ is negative in the present compounds, then $^{4}J_{FF}$ and $^{4}J_{FF'}$ must be positive. The only exceptions to this, are the nitrogen-bridged anionic species where the signs of $^{2}J_{PP}$, $^{4}J_{FF}$ and $^{4}J_{FF'}$ appear to be the same. Although temperature dependent studies have shown that $^{2}J_{PP}$ may be of either sign in the same compound, the signs of $^{4}J_{FF}$ and $^{4}J_{FF'}$ do not appear to change within the series of compounds investigated here. On the basis of the present work then, it would appear that $^{4}J_{FF}$ and $^{4}J_{FF'}$ are always positive.

The compounds $(SPF_2)_2N^-(CH_3)_3NH^+$ and $(OPF_2)_2N^-(CH_3)_3NH^+$ are normally very viscous liquids at room temperatures. Because of their viscosity, spin-lattice relaxation times are much shorter than in the other compounds and, as a consequence, their room temperature ^{19}F spectra are generally much broader and not as well resolved. However, the spectra become much sharper if the temperature of the sample is raised, with a corresponding decrease in viscosity. Better resolution of the spectra of these compounds could also be achieved by dissolution of the compounds in an appropriate solvent, such as CH_3CN.

An additional source of broadening in the spectra of the nitrogen-bridged compounds is quadrupole broadening due to the ^{14}N quadrupole. A theory of the broadening of multiplet components in the spectra of coupled nuclei due to electric quadrupole spin-lattice relaxation [103] indicates that the line shapes obtained when the observed nuclei are coupled to quadrupolar nuclei such as ^{14}N, depend on the rate of this spin-lattice relaxation. This relaxation rate is dependent on the interaction of the electric quadrupole moments with the fluctuating electric field gradients produced at the quadrupolar nucleus by other molecular degrees of freedom. Thus the line shapes will depend on the symmetry of the electric field around the ^{14}N nucleus. Since this effect has a relatively short range, the only spectra which are likely to be affected are the ^{31}P spectra of the nitrogen-bridged compounds.

This quadrupole broadening is very evident in the ^{31}P spectra of the oxygen-containing, nitrogen-bridged compounds. The ^{31}P spectra of the sulphur analogs are relatively sharp, however. This implies that the electric field around the nitrogen atom in the sulphur-containing compounds is more symmetric than in the oxygen analog but the reason for such symmetry is not immediately apparent.

In the case of the NCH_3-bridged compounds, the proton spectra were first order, showing the triplet of quintets expected from two equivalent phosphorus and four equivalent fluorine atoms. The H-P and H-F interaction is of a first order nature since there appears to be unrestricted rotation about the C-N bond and thus each proton sees an average value for all couplings to each phosphorus or fluorine. The relative signs of $^{3}J_{PH}$ and $^{4}J_{FH}$ were not determined.

The existence of two long range F-F coupling constants in the room temperature spectra was considered as a possible indicator of the occurrence of conformational isomerism in the bridged compounds. Two approaches were utilized in an attempt to clarify the situation. The first involved a study of the temperature dependence of the spectra, and the second involved calculations based on variations in the derived coupling constants for the various compounds.

Models of the present compounds indicated that interactions between the substituents on the two phosphorus atoms might be sufficient to cause the compounds to be locked into a single conformation. Temperature studies of several of the compounds were thus undertaken to investigate this possibility. The results are tabulated in Table 7 and illustrated in Figure 3. Only the spectrum of $(PF_2)_2O$ showed no significant temperature dependence.

These results are most easily understood if the observed long-range F-F coupling constants are the result of a rotational averaging of the coupling constants for a number of rotational conformers. A plot of observed coupling constants versus temperature shows that at the highest temperatures obtained in the present study, the rate of change of the F-F coupling constants with temperature is less than at lower temperatures. This indicates that at high temperatures the compounds are approaching a point where all rotational conformers are equally probable and the F-F coupling constants are concurrently approaching equality because of the averaging process that is occurring. In the case of some of the compounds, such as $(SPF_2)_2O$ or $(OPF_2)_2O$, the spectra, above normal ambient spectrometer temperatures, begin to collapse and form a simple doublet. A similar effect was noted in the mixed valence compounds, $F_2PSP(S)F_2$ and $F_2POP(O)F_2$, and suggests that the rate of rotation is becoming sufficiently rapid to provide effective decoupling of the ends of the molecule so that the only coupling observed is the short-range P-F coupling.

At intermediate temperatures, the rate of change in

TABLE 7

Temperature Dependence of the NMR Parameters of Some Bridged Diphosphorus Tetrafluoride Compounds

(a) $(SPF_2)_2O$

		Coupling Constants (cps)				
Temp(°C)	ϕ_{ppm}	$^1J_{PF}$	$^3J_{PF}$	$^2J_{PP}$	$^4J_{FF}$	$^4J_{FF'}$
+100[(a)]	40.5	-	-	-	-	-
+ 80[(a)]	40.5	-1169.0	0.1	-10.75	3.7	2.45
+ 60[(a)]	40.5	-1169.15	0.15	- 9.5	3.7	2.4
+ 40[(a)]	40.3	-1168.8	0.2	- 8.05	3.95	2.4
+ 40[(b)]	40.5	-1171.0	0.2	- 8.4	3.9	2.5
+ 20[(b)]	40.5	-1170.7	0.3	- 6.2	3.75	2.25
0[(b)]	40.4	-1169.6	0.3	- 4.5	3.75	2.15
- 20[(b)]	40.3	-1170.2	0.3	- 2.9	4.0	1.6
- 40[(b)]	40.3	-1169.7	0.3	- 0.5	3.7	1.7
- 60[(b)]	40.3	-1169.8	0.3	+ 0.5	3.7	1.7
- 80[(b)]	40.2	-1169.2	0.3	+ 2.6	4.2	1.3
- 80[(b,c)]	40.1	-1171.4	0.4	+ 3.2	4.2	1.6
-100[(b)]	40.2	-1170.3	0.3	+ 5.0	3.95	1.55
-100[(b,c)]	40.1	-1172.2	0.4	+ 5.4	4.1	1.5
-114[(b,c)]	40.1	-1169.5	0.5	+ 7.0	4.2	1.5

(a) neat sample (b) 5% sample in $CFCl_3$ (c) values obtained at 100 MHz.

Table 7 (continued)

(b) $(SPF_2)_2S$		Coupling Constants (cps)				
Temp(°C)	ϕ_{ppm}	$^1J_{PF}$	$^3J_{PF}$	$^2J_{PP}$	$^4J_{FF}$	$^4J_{FF'}$
+160$^{(a)}$	16.3	-1251.45	-2.05	-23.4	11.5	6.9
+140$^{(a)}$	16.4	-1251.05	-2.15	-23.3	11.6	6.7
+120$^{(a)}$	16.5	-1252.95	-2.25	-23.7	11.8	6.45
+100$^{(a)}$	16.7	-1253.15	-2.35	-24.0	12.0	6.25
+ 80$^{(a)}$	16.7	-1255.05	-2.45	-24.2	12.1	5.9
+ 80$^{(b)}$	16.9	-1253.2	-2.2	-23.8	11.95	5.85
+ 60$^{(a)}$	16.8	-1255.5	-2.6	-24.45	12.3	5.65
+ 60$^{(b)}$	16.9	-1252.7	-2.6	-24.35	12.2	5.6
+ 40$^{(a)}$	16.8	-1256.3	-2.7	-24.85	12.5	5.2
+ 40$^{(b)}$	17.0	-1255.4	-3.0	-25.0	12.9	5.6
+ 10$^{(b)}$	17.0	-1257.85	-2.85	-25.6	13.5	4.65
- 10$^{(b)}$	17.1	-1257.55	-2.95	-25.95	13.95	4.15
- 30$^{(b)}$	17.1	-1260.35	-3.05	-26.7	14.6	3.85
- 50$^{(b)}$	17.1	-1260.2	-3.2	-27.35	15.2	3.45
- 70$^{(b)}$	17.1	-1263.15	-3.15	-27.8	15.65	2.95
- 80$^{(b,c)}$	17.0	-1261.5	-3.6	-28.9	16.6	2.8
- 90$^{(b)}$	17.0	-1263.0	-3.3	-28.3	16.4	2.4
-100$^{(b,c)}$	16.9	-1263.3	-3.6	-29.3	16.6	2.6
-114$^{(b,c)}$	16.9	-1264.0	-3.6	-29.7	16.3	3.0

(a) neat sample (b) 5% sample in $CFCl_3$ (c) values obtained at 100 MHz

TABLE 7 (continued)

(c) $(SPF_2)_2N^-(CH_3)_3NH^+$ (a)			Coupling Constants (cps)			
Temp(°C)	φppm	$^1J_{PF}$	$^3J_{PF}$	$^2J_{PP}$	$^4J_{FF}$	$^4J_{FF'}$
+ 40	33.6	-1047.8	13.75	83.0	6.2	5.15
+ 20	33.6	-1045.9	14.5	86.15	6.3	5.2
0	33.7	-1046.6	14.8	88.1	6.75	4.6
- 20	33.8	-1045.3	15.15	90.4	7.0	4.45
- 40	33.8	-1043.6	15.4	93.35	7.45	3.95
- 50	33.8	-1042.05	15.75	95.1	7.55	3.85
(d) $(PF_2)_2O$ (b)						
+ 40	36.8	-1356.25	14.65	- 4.8	4.1	3.0
+ 20	36.9	-1356.9	14.6	- 5.2	3.9	2.9
0	37.0	-1354.85	14.65	- 5.2	4.3	2.35
- 20	37.0	-1356.05	14.95	- 4.7	4.2	3.1
- 40	37.0	-1354.65	15.15	- 4.85	4.25	2.5
- 60	37.1	-1256.15	15.35	- 4.8	3.75	2.85
- 80	37.2	-1354.2	15.6	- 4.55	3.9	2.8

(a) 5% sample in CH_3CN (b) 5% sample in $CFCl_3$

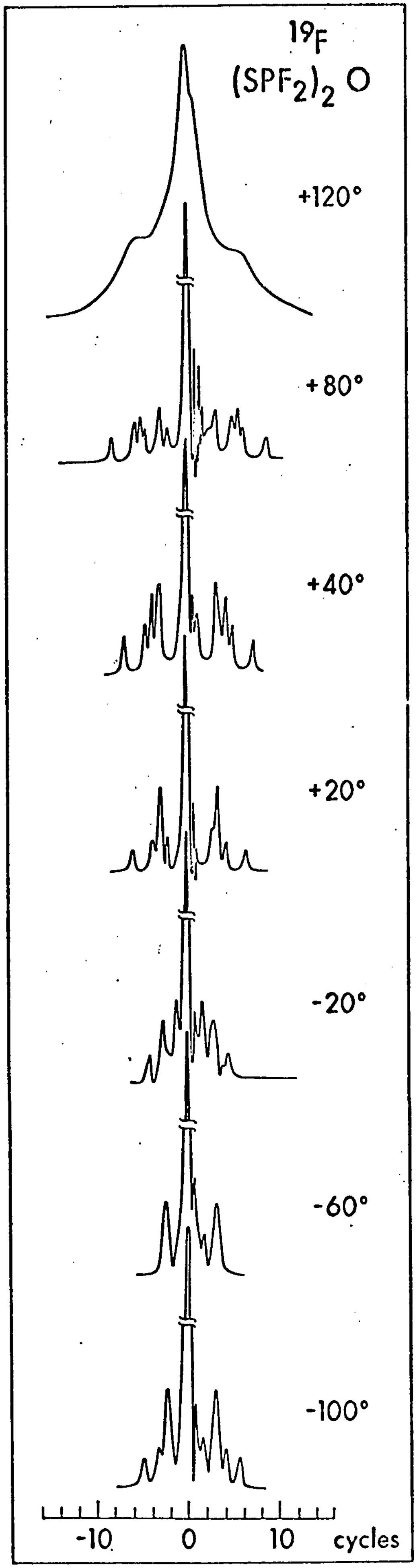


Figure 11

Temperature Dependence of the ^{19}F NMR Spectrum of μ-Oxo-Bis(Thiophosphoryl Difluoride)

$^4J_{FF}$ and $^4J_{FF'}$ increases, indicating that the conformational populations are becoming more unequal, with the most preferred conformer having the largest population. However, at the lowest temperatures attained, there does not appear to be any indication that the spectra have reached limiting values where the molecules may be assumed to be locked into one conformation.

The temperature dependence of the spectra readily account for the poor agreement between the observed and calculated ^{31}P spectra. The ^{19}F spectra were obtained on the A56/60 instrument operating at 40° while the ^{31}P spectra were obtained on the HA-100 instrument which normally operates at a temperature of 33°. Since the ^{31}P spectra were calculated on the basis of the coupling constants obtained from the 40° ^{19}F spectra, there is no reason to expect exact agreement with the observed ^{31}P spectra. This same difficulty arose with the temperature dependency studies. Because the two temperature controllers involved did not maintain identical temperatures at specific settings, differences of several degrees between the temperatures at which spectra were obtained on different instruments were commonly encountered. This is apparent, for example, in the parameters for $(SPF_2)_2O$ at -80 and -100° (Table 7) when obtained on the A56/60 and HA-100 instruments. The parameters obtained in the temperature studies are estimated to be accurate to about ± 0.2 Hz.

If the bridged diphosphorus tetrafluoride compounds are locked into one conformation, it is possible that there could be as many as four different long range F-F coupling constants. These different F-F coupling constants might, in turn, imply the existence of different fluorine chemical shifts and possibly different P-F coupling constants. That is, the spectral patterns may be due to the presence of chemical non-equivalence. With these thoughts in mind, a series of theoretical spectra were calculated in which the various parameters were altered in such a way that the originally determined values were maintained as an average value. (For example, if the chemical shift of one fluorine on a specific phosphorus atom was increased by 10 Hz, the chemical shift of the other fluorine was decreased by 10 Hz.)

In this manner, it was found that the spectral parameters could be changed significantly without affecting the calculated spectrum. The first obvious change in the calculated spectra resulting from fairly large alterations of the parameters was a broadening of the calculated lines. Since the lines in the observed spectra always have a finite width, changes in the spectral parameters as outlined above are not necessarily excluded by the observed line shapes. However, since there are other effects [105,114] which contribute to natural line widths, broad lines do not necessarily indicate a variation in the spectral parameters. It was found that the parameters could be altered by as much as 5 Hz without significantly changing the agreement of the calculated spectra with the observed. Since this is of the magnitude of some of the coupling constants, these changes, in terms of the spectral parameters, can be very significant.

However, the assumption that the molecules exist in a single conformation at room temperature, as postulated above, does not allow an explanation of the observed changes in the spectra as the temperature was lowered. Interpretation of the spectra in terms of chemically equivalent but magnetically non-equivalent nuclei is therefore more satisfying and flexible. On the basis of the temperature dependence of the spectra of the bridged compounds then, it would appear that there is relatively free rotation about the bridge bonds even at temperatures well below 0°.

An anomaly, which is as yet unexplained, occurs in the ^{31}P spectrum of $(SPF_2)_2S$. At room temperature, the low field third of the ^{31}P spectrum shows four fewer lines than are predicted by the theoretical spectrum. The high field third of the spectrum which should be a mirror image of the low field third, shows the expected number of lines. However, as the temperature is lowered, the four missing lines in the low field third of the spectrum appear as fairly broad, relatively weak lines. Even at the lowest temperatures attained, the low field and high field thirds of the spectrum were not mirror images. Further studies are in progress, which hopefully will explain this phenomenon.

2. Discussion

Nmr spectral parameters arise from electron-coupled nuclear spin-spin interactions and a knowledge of these parameters should lead to an understanding of the electronic environment associated with the interactions. Although many theoretical studies have been done in which attempts have been made to predict spin-spin interactions, they all fail to produce quantitative results because of the lack of accurate molecular wave functions.[104] However, a knowledge of the various ways in which interactions between nuclear spins and the surrounding electrons occur can lead to a qualitative assessment of the molecular electronic configuration.

It has been shown [105] that the spin-spin coupling in nmr spectra can be described in terms of the Hamiltonian operator

$$H = H_1 + H_2 + H_3$$

where H_1 represents the magnetic shielding of the direct interaction of the nuclear spins by electron orbital motion, H_2 represents the dipole-dipole interaction between the nuclear magnetic moments and the magnetic moments of the electrons. The third term, H_3, is usually referred to as the "Fermi Contact" term, and expresses the property that H_3 operates on the wave function only at the nucleus.

It has further been shown that for directly bonded nuclei, the Fermi contact term is by far the most important term in contribution to the total coupling. For non-bonded nuclei, however, the relative influence of the contact term diminishes, and contributions from the spin-orbit and dipole-dipole terms have increased relative importance.

The Fermi contact term has been shown to be very sensitive to the s-character in the bonds joining coupled nuclei. This arises because only the s-orbitals have non-zero electron densities at the nucleus.[104] The phosphorus atoms in the compounds under study are tetracoordinate with four bonded atoms (excluding $(PF_2)_2O$). In addition to the σ- bonding framework, some degree of participation of phosphorus d-orbitals might be expected. Such involvement could lead to a decrease in the s-character of the σ-bonding orbitals. Although the phosphorus d-orbitals might be expected to contribute mainly to π-bonding, it is conceivable that changes in bond angles, as the electronegativities or sizes of the substituents change, will result in greater (or smaller) contributions of the d-orbitals to σ-bonding. These changes will ultimately affect the contact term and thus the coupling constant between directly bonded nuclei.

Wagner [106] has shown that calculated bond characters in phosphoryl compounds may be correlated with the electronegativities of the substituents on phosphorus. It is shown that as the sum of the substituent electronegativities increases, the P-O π-bond character increases (to an essentially triple P-O bond in OPF_3). The increase in π-bond character suggests an increase in the utilization of phosphorus d-orbitals with a subsequent decrease in s-character in the hybrid bonds that are formed.

On this basis then, the directly bonded P-F coupling constant should decrease with an increase in electronegativities of the substituents on phosphorus. The $^1J_{PF}$ values obtained in this study do indeed show this trend. The P-F coupling constants in trivalent compounds are larger than those in similar pentavalent compounds. If d-orbital participation in the σ-bonding does occur, the above trend might well be interpreted in terms of greater dilution of the s contribution to σ-bonding in pentavalent compounds as compared to trivalent compounds. This conclusion is not unreasonable in view of other evidence which suggests that greater d-orbital participation is to be expected in the pentavalent systems.

In the series of pentavalent compounds, the magnitude of $^1J_{PF}$ in nitrogen-bridged compounds appears somewhat contradictory since it suggests that the nitrogen is more electronegative than oxygen in the bridging position. However, as was mentioned previously, some π-bonding might be expected in the P-N-P bridge system. The existence of additional π-bonding to phosphorus will probably involve more d-character in the bonding with the consequent reduction in the P-F bond s-character and therefore the P-F coupling constant. Even more π-bonding might be expected in the anionic species $(EPF_2)_2N^-$ as is suggested by the PF coupling constant. If this is the case, then the apparent reduction in the P-N-P asymmetric stretching frequency of these compounds as discussed in Chapter VII may be somewhat misleading or the two effects may have different origins. Obviously, further investigation of these systems is indicated.

The magnitudes of the directly-bonded P-F couplings found in this study are in the same range as those found for other similar compounds.[1] Although the magnitudes of many P-F coupling constants have been reported, very few relative signs have been established until recently. Pople and Santry [107] have shown, in approximate calculations based on a LCAO-MO theory determination of wave functions, that single bond, directly-bonded coupling constants between fluorine and first-row elements should be negative. Harris et.al.[108] have suggested that this treatment may be extended to later elements, specifically to phosphorus.

Heteronuclear double resonance experiments [98-101] have confirmed the theoretical prediction that $^1J_{PF}$ is negative. The signs of all directly bonded P-F coupling constants are thus taken to be negative since the range of magnitude of these couplings excludes a possible change in sign.

The complexity of effects which can contribute to non-directly bonded coupling constants is somewhat overwhelming. A number of studies [109-112] have been done, mainly with fluoroalkyl compounds, in which attempts have been made to relate long-range F-F couplings to specific effects such as substituent electronegativities, bond characters, or spatial configurations. Although there are always anomalous results which cast doubt on the validity of any attempted correlation, there appears to be some merit in the non-specific concept of through-bond and through-space interactions.[109]

The relationship of vicinal H-H couplings in organic compounds to the dihedral angle is well known.[104,105] It has also been indicated that the vicinal H-H couplings are also dependent on bond lengths and the C-C-H angles.[113] It is reasonable to extend these arguments to other systems. In the present compounds, because of the variety of bridging atoms, significant variations in bond lengths and angles are expected and are probably reflected in the long-range P-F couplings ($^3J_{PF}$).

If the molecular-orbital approximation is used in calculating the contact term for vicinal atoms, only positive values for the vicinal H-H couplings are predicted. Both negative and positive long range P-F coupling constants are observed in the above compounds, and both signs for this coupling can be predicted by the valence bond approximation depending on structural parameters, particularly the dihedral angle.[105,114]. The lack of accurate structural data on any of the bridged compounds prohibits the formation of definite conclusions, but it is not unreasonable to assign some structural significance to the observed long range P-F coupling.

Very few determinations of P-F couplings through three bonds have been reported. Values for $^3J_{PF}$ of +2 Hz for $(OPFCl)_2O$ [115] and +32 Hz for $(F_2PNCH_3)_2$ [95] have previously been reported. Values for $^3J_{PF}$ obtained from the spectra of phosphonitrilic fluorides include $^3J_{PF} = +11$ Hz for $P_3N_3Cl_5F$ [116] and $^3J_{PF} = +14$ Hz for $P_3N_3Cl_4F_2$.[117] Mahler[118] reported values for $^3J_{PF}$ of about 20 Hz for some polyphosphine heterocycles, but no signs were indicated. These values for $^3J_{PF}$ are all of the same order of magnitude as the values found in this investigation.

Although the sign of the P-O-P coupling constant in the pyrophosphite cation was shown to be negative [102] (with $^2J_{PP} = -17$ Hz), studies of the nmr spectra of some phosphonitrilic compounds indicates that the P-N-P coupling constant for these compounds are positive [116,117] ($^2J_{PP} = +100$ Hz for $P_3N_3Cl_4F_2$ and $^2J_{PP} = +78.3$ Hz for $P_3N_3Cl_5F$). A value of $^2J_{PP} = 17.7$ Hz was found for the isohypophosphate cation, but no sign was reported.[119]

The results of the present work confirm the previous observations that $^2J_{PP}$ may have a wide range of values with either sign. Indeed, as the temperature studies of

$(SPF_2)_2O$ have shown, $^2J_{PP}$ in a given compound may have a similar wide range of values with either sign. It has been observed for some fluoroalkyl compounds, that F-F coupling constants increase (that is, become more positive), if one of the intermediate atoms is nitrogen.[109] This finding would appear to be followed in the present study and would tend to support the assignment of signs for $^2J_{PP}$. The observed increase of $^2J_{PP}$ when nitrogen is the intermediate atom could be due to increased π-bonding in the system, as suggested earlier. The values of $^2J_{PP}$ would thus appear to be a function of the electronegativities of the phosphorus substituents and the degree of π-bonding in the system. It should be noted, however, that the substituent electronegativities could provide the means for establishment of the π-bonding by increased electron withdrawal from phosphorus [106] and the two effects need not be mutually exclusive.

The two different long-range F-F couplings may be thought of as an average <u>cis</u> coupling and an average <u>trans</u> coupling, the averaging arising through rotation around the bridge bonds. The pronounced variations in $^4J_{FF}$ and $^4J_{FF'}$, especially with $(SPF_2)_2S$, indicate that as the molecule adopts a preferred conformation at lower temperatures, one F-F interaction (presumably the <u>cis</u> interaction, although there is no method by which the two interactions may be differentiated) increases while the other decreases.

Petrakis and Sederholm [109] have indicated that F-F couplings through four bonds are at a minimum and couplings through five bonds are negligible. They further suggest that fluorines separated by more than 2.73 Å through space will have negligible interaction by this means. Boden, Feeney, and Sutcliffe [120] have agreed with the concept proposed by Petrakis and Sederholm but suggest that there is no smooth relationship between conformationally corrected values of J_{FF} and the spatial separation of the fluorine atoms concerned.

Calculations of F-F internuclear separations based on assumed bond lengths and bond angles for the bridged compounds indicate that only cis fluorines in a gauche structure may be close enough to permit such through-space interaction. Because the fluorines are separated by four bonds, the difference between cis and trans coupling constants are not expected to be significant, despite the differences in dihedral angles. This is supported by the fact that the magnitude of $^4J_{FF}$ or $^4J_{FF'}$ in most of the bridged compounds is relatively small. It would thus appear that the increase in the cis F-F coupling constant ($^4J_{FF}$) can be attributed to a larger through-space interaction as a preferred gauche structure is adopted at lower temperatures. Similarly, the decrease in the trans F-F coupling ($^4J_{FF'}$) can be attributed to a decrease in the through-space contribution to the rotational average of the coupling constant.

CONCLUSIONS

Chapter IX

The reaction of anhydrous hydrogen iodide with dimethylaminothiophosphoryl difluoride and dimethylaminophosphoryl difluoride gave the new hydrido phosphorus compounds, hydrothiophosphoryl difluoride, SPF_2H, and hydrophosphoryl difluoride, OPF_2H. Hydrothiophosphoryl difluoride is more stable than the oxygen analog and several previously unknown compounds have been prepared from it. Many of its reactions appear to involve an acidic hydrogen substituent. Some of its reactions should, however, be further investigated. These include the reaction of SPF_2H with amines, which appear to give the apparently reactive, unique anion, SPF_2^-. It would also be appropriate to study the reaction of OPF_2H with N-iodosuccinimide, which might be expected to yield iodophosphoryl difluoride. Since SPF_2I has been shown to undergo many useful and specific reactions, the preparation of the oxygen analog could provide the means for a parallel study.

One of the original aims of this work has been achieved in the preparation of SPF_2I by the reaction of SPF_2H with N-iodosuccinimide. However, the preparation of a pentavalent diphosphorus compound with a direct phosphorus-phosphorus bond by the coupling of SPF_2I by mercury, has not been successful. Instead, the coupling of SPF_2I with mercury gave difluorothiophosphoryl-μ-thio-difluorophosphine, $F_2PSP(S)F_2$, an example of a new class of compound, the mixed valence halo diphosphorus compounds. A knowledge of the structure of $F_2PSP(S)F_2$ obtained from spectral investigations suggested the more direct synthesis of $F_2PSP(S)F_2$ and its oxygen analog, $F_2POP(O)F_2$ from the reaction of dithiodifluoro- or difluorophosphoric acid with dimethylaminodifluorophosphine.

The reaction of SPF_2H with elemental sulphur gave the previously unknown anhydrous acid, difluorodithiophosphoric acid, SPF_2SH. This relatively strong acid, which appears to be a particularly good bidentate ligand, has been used successfully in the preparation of a number of bridged diphosphorus tetrafluoride compounds. Although the present method of preparation of SPF_2SH is relatively efficient, it is not readily applicable to the large scale preparation of the acid. The development of a more direct synthesis of the acid suitable for large scale use could be the key to a very interesting and extensive study of the chemistry of this new acid and its derivatives.

A number of bridged diphosphorus tetrafluoride compounds have been prepared by various methods. A study of their nmr spectral properties has yielded the successful assignment of all of the coupling constants in the molecules. The variations in these parameters have been interpreted in terms of the bonding in the compounds. Although the results are still somewhat fragmentary, preliminary assessment of the results indicate that the observed variations may be a result of π-bonding in the molecules. The degree of π-bonding, and the amount of phosphorus d-orbital contribution to the total bonding implied by the presence of such π-bonding, may be correlated to the electronegativities of the substituents on the phosphorus atoms. Further studies of an extended series of such compounds could provide more useful information. The preparation of both asymmetrical bridged compounds such as difluorothiophosphoryl-μ-oxo-phosphoryl difluoride, $(SPF_2)O(OPF_2)$, and bridged compounds in which one or more of the fluorines are replaced by other substituents, and the study of their nmr spectra should provide a better understanding of the type of bonding that occurs in all phosphorus compounds.

A point has now been reached where further studies of the compounds and reactions developed in this work would involve rather extensive investigation. A number of suggestions have been made in the preceeding paragraphs concerning some of the systems studied here which may be of further interest. That there is wide spread interest in the compounds prepared in this study has been demonstrated by the concurrent publication of reports of a number of these compounds by other, independent workers. It is hoped that the work described by this thesis contributes in some way to the total understanding and knowledge of the chemistry of phosphorus.

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Chapter X

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APPENDIX A.

Summary of Observed and Calculated Vapor Pressures for Compounds Prepared in this Study.

(a) SPF_2H

Temp. °C	Pressure, (mm) obs.	Pressure, (mm) calc.
-85.2	2.0	2.4
-76.3	5.9	5.4
-71.0[a]	9.1	8.6
-65.5[a]	15.5	13.5
-60.0	20.9	20.9
-54.8	32.2	30.9
-49.0	46.2	46.8
-41.8	75.7	76.0
-39.5	91.4	88.1
-29.0	162.7	167.5
-25.2[a]	204.9	208.9
-15.5	343.2	354.8

(b) OPF_2H

Temp. °C	Pressure, (mm) obs.	Pressure, (mm) calcd.
-53.3	1.2	1.1
-47.6[b]	2.0	1.9
-45.5	2.3	2.4
-45.3[c]	5.9	2.4
-38.0	3.8	4.1
-34.8[b]	4.4	5.2
-37.5	6.6	6.2
-29.5[b]	7.7	7.8
-29.6[c]	11.2	7.8
-25.5	10.8	10.5
-19.1	16.4	16.6
-17.1	22.4	18.6
-10.8	28.2	27.5
- 2.6	47.2	45.7

(a) measured with descending temperatures.

(b) measured with descending temperatures, maximum temperature of sample -25°.

(c) measured with descending temperatures, maximum temperature of sample 0°.

APPENDIX A (contined)

(c) SPF_2I

Temp °C	Pressure, (mm) obs.	calc.
-37.2	3.3	3.3
-36.9[a]	3.4	3.4
-27.0	6.6	6.5
-22.2[a]	8.3	8.7
-14.0[a]	14.3	14.1
- 7.1	20.5	20.5
2.6	34.2	34.4
8.0[a]	45.6	44.9
12.6	56.8	55.9
14.2[a]	60.0	60.3
21.6	86.2	84.3
25.6	100.5	100.8

(d) SPF_2SH

Temp °C	Pressure, (mm) obs.	calc.
-36.8	2.6	2.5
-36.6[a]	2.4	2.6
-32.3[a]	3.3	3.6
-24.8	6.4	6.5
-20.2[a]	9.2	9.2
-10.9[a]	17.7	17.4
- 6.6	24.1	22.8
- 3.2[a]	28.2	28.1
4.4	45.3	44.0
7.2[a]	52.3	51.4
13.7	73.3	72.3
16.4	78.9	83.1
17.0[a]	86.6	85.6
22.8	111.4	113.6
26.0[a]	131.3	131.6
30.7	159.4	162.0
35.3[a]	195.1	197.2
40.9	242.4	247.8
43.3[a]	267.6	272.0
49.3	339.2	341.1
52.3	377.8	380.6

(a) measured with descending temperatures.

APPENDIX A (continued)

(e) $F_2PSP(S)F_2$

Temp	Pressure, (mm)	
°C	obs.	calc.
0.0	24.1	24.5
5.8[a]	35.5	33.0
10.7	39.0	42.1
16.4[a]	57.7	55.3
20.7	64.7	67.4
25.9[a]	87.1	85.1
29.7	97.6	100.3
35.7[a]	130.6	129.1
40.0	154.8	153.8
45.9[a]	194.7	193.1
50.5	231.3	231.0

(f) $F_2POP(O)F_2$

Temp	Pressure, (mm)	
°C	obs.	calc.
-36.6	4.4	4.9
-31.4[a]	7.4	7.3
-29.4	8.6	8.5
-21.6[a]	16.3	15.0
-19.4	18.2	17.5
-11.8[a]	30.3	29.1
- 9.6	33.4	33.5
- 2.4[a]	53.0	52.4
+ 0.4	60.0	61.9
+10.2	101.8	108.5

(g) SPF_2NHCH_3

0.0	2.3	2.3
6.7[a]	3.5	3.5
9.9	4.0	4.2
15.5[a]	6.0	5.9
20.8	8.2	8.0
25.3[a]	10.6	10.3
30.9	14.2	13.9
35.6[a]	17.0	17.7
39.8	21.5	21.8
45.7[a]	28.7	29.1
52.0	39.8	39.0

(h) $(SPF_2)_2NCH_3$

0.0	2.6	2.8
7.1[a]	4.7	4.4
12.1	5.7	5.9
17.3[a]	8.3	8.0
20.7	9.3	9.6
25.9[a]	14.3	12.7
30.1	15.6	15.9
35.7[a]	20.5	21.1
40.2	26.1	26.3
44.7[a]	31.4	32.6
51.6	44.8	44.8

(a) measured with descending temperatures.

APPENDIX A (continued)

(i) $(SPF_2)_2O$

Temp.	Pressure, (mm)	
°C	obs.	calc.
-38.3	11.2	11.7
-37.8[a]	12.1	12.1
-33.6[a]	15.4	15.8
-28.2	22.3	22.0
-22.4[a]	31.2	30.9
-17.7	41.4	40.3
-13.6[a]	51.0	50.4
- 7.8	70.1	68.2
- 3.6[a]	86.7	84.3
+ 2.5	115.2	113.3
+ 7.4[a]	142.8	142.4
+12.6	179.7	179.9
+18.0[a]	220.5	227.3
+23.9	280.9	290.7

(j) $(SPF_2)_2S$

Temp	Pressure, (mm)	
°C	obs.	calc.
0.0	5.7	5.6
7.9[a]	8.9	8.8
11.1	10.5	10.5
16.2[a]	13.8	13.8
20.1	16.9	16.9
25.4[a]	20.7	22.2
30.2	27.3	28.0
35.5[a]	37.0	36.1
40.8	46.2	46.0
45.4[a]	57.8	56.4
51.8	75.2	74.3

(a) measured with descending temperatures.

APPENDIX B

Summary of the Infrared Spectra of the Compounds Prepared in this Study.

(a) SPF_2H

2458	m	ν(PH)
1054	w	
1019	vs[a]	δ(PH)
973	m	
958	w	
923	vs[a]	ν_a(PF)
895	sh	ν_s(PF)
844	vw	
709	m	ν(PS)
420	w	
336	w	

(b) OPF_2H

2500	w[a]	ν(PH)
1377	s[b]	ν(PO)
1020	w[b]	
994	s	δ(PH)
932	s[b]	ν_a(PF)
892	s[a]	ν_s(PF)
511	m[a]	
491	w,sh	
388	m[a]	

(c) SPF_2I

1821	vw	
1787	vw	
1635	vw	
1427	vw	
1422	vw	
1081	vw	
1021	w[a]	
929	w,sh	
923	vs	ν_a(PF)
899	s[b]	ν_s(PF)
828	vw	
796	vw	
713	vs[c]	ν(PS)
606	vw	
476	w,sh	
453	s[a]	ν(PI)
413	w[a]	
376	m[a]	δ(PF)
287	vw	

s = strong, m = medium, w = weak, v = very, sh = shoulder

ν = stretch, δ = deformation, a = antisymmetric, s = symmetric.

(a) PQR band structure, (b) PQQ'R band structure, (c) PR band structure.

APPENDIX B (continued)

(d) SPF_2SH

3660	vw	
2608	w[a]	$\nu(SH)$
2568	vw	
1820	vw	
1765	vw	
1655	vw	
1450	vw	
1115	vw	
1032	vw[a]	
936	vs	$\nu_a(PF)$
888	s[b]	$\nu_s(PF)$
838	m[a]	$\delta(SH)$
809	w[b]	
739	w,sh[a]	
732	s	$\nu(PS)$
722	sh	
524	m[a]	$\delta(PF_2)$
389	w	
348	w[a]	
305	vw	

(e) $F_2PSP(S)F_2$

1380	vw	
925	s	$\nu_a(P^V\text{-}F)$
898	s	$\nu_s(P^V\text{-}F)$
847	s	$\nu_a(P^{III}\text{-}F)$
834	s	$\nu_s(P^{III}\text{-}F)$
731	s	$\nu\ (P{=}S)$
705	w	
580	vw	
534	w	
500	vw	
480	s	$\nu\ (P\text{-}S\text{-}P)$
402	vw	
391	vw	
358	w	
350	sh	

(f) $F_2POP(O)F_2$

1384	s	$\nu(P{=}O)$
1025	vs	$\nu_a(P\text{-}O\text{-}P)$
975	s	$\nu_a(P^V\text{-}F)$
914	w	$\nu_s(P^V\text{-}F)$
872	s	$\nu(P^{III}\text{-}F)$
724	m	$\nu_s(POP)$
505	m	
447	w	
405	w	

s = strong, m = medium, w = weak, v = very, sh = shoulder,

ν = stretch, δ = deformation, a = antisymmetric, s = symmetric

(a) PQR band structure (b) PQQ'R band structure.

APPENDIX B (continued)

(g) OPF_2NHCH_3

3256	m	ν(NH)
2955	w	ν(CH)
1416	m[a]	δ(NH)
1327	s	ν(PO)
1125	m	ν(CN)
937	w,sh	
916	s	ν(PF)
460	m	

(h) SPF_2NHCH_3

3476	w	ν(NH)
2960	w	ν(CH)
2850	vw	ν(CH)
1390	m	δ(NH)
1110	s	ν(CN)
920	vs	ν_a(PF)
876	vs	ν_s(PF)
696	w	ν(PS)
458	w	
410	w	
383	w	

(i) SPF_2NH_2

3543	w	ν_a(NH)
3438	w	ν_s(NH)
1542	m	δ(NH)
1000	vs[a]	ν(PN)
959	s	ν_a(PF)
885	vs	ν_s(PF)
674	w	ν(PS)
410	w	

(j) $(SPF_2)_2NCH_3$

2975	vw	ν(CH)
1636	vw	
1212	m	ν(CN)
1072	s	ν(PNP)
953	vs	ν_a(PF)
933	w,sh	
917	s	ν_s(PF)
788	w	
698	m	ν_a(PS)
688	m	ν_s(PS)
455	w	
429	m	
385	w	
365	m	

(k) $(OPF_2)_2NCH_3$

2975	vw	ν(CH)
1389	s	ν_a(PO)
1370	s	ν_s(PO)
1231	w	ν(CN)
1086	m	ν(PNP)
974	vs	ν(PF)
937	m	ν(PF)
878	m	
663	w	
500	m[a]	
423	w	
388	w	

(l) $(SPF_2)_2N^-(CH_3)_3NH^+$

3420	w,br	ν(NH)
2980	m,br	ν(CH)
2730	m,br	
2518	w	
2470	w	
1477	s	
1453	w,sh	
1415	w,sh	
1300	vs,br	δ(CH)
1045	w	
980	m	ν(PNP)
850	vs,br	ν(PF)
727	w	
659	s	ν(PS)

s = strong, m = medium, w = weak, v = very, sh = shoulder,
ν = stretch, δ = deformation, a = antisymmetric, s = symmetric
(a) - PQR band structure, (br) = broad.

APPENDIX C

Summary of the Mass Spectra of the Compounds Prepared in this Study.(a)

	(a) SPF_2H			(b) OPF_2H	
m/e	rel. int.(c)	ion	m/e	rel. int.(c)	m/e
102	52.9	SPF_2H	86	40.8	OPF_2H
101	6.9	SPF_2	85	10.6	OPF_2
83	1.6	SPFH	69	19.6	PF_2
82	3.2	SPF	67	8.6	OPFH
69	28.0	PF_2	66	10.2	OPF
63	4.2	SP	50	1.6	PF
50	3.2	PF	31	1.2	P

	(c) SPF_2I			(d) SPF_2SH	
230	2.4	$^{34}SPF_2I$	136	3.7	$^{34}SPF_2SH$
228	51.9	SPF_2I	135	0.8	$^{34}SPF_2S$
159	2.1	SI	134	39.6	SPF_2SH
127	3.8	I	133	0.8	SPF_2S
103	1.4	$^{34}SPF_2$	114	0.8	S_2PF
101	24.0	SPF_2	102	1.4	PF_2SH
82	1.4	SPF	101	9.8	PF_2S
69	8.9	PF_2	95	0.8	PS_2
63	1.4	SP	82	1.7	PFS
50	1.4	PF	69	19.4	PF_2
32	1.4	S	64	8.7	S_2
			63	2.0	PS
			50	1.4	PF
			34	2.0	H_2S, ^{34}S
			33	1.4	HS
			32	5.6	S

APPENDIX C (continued)

(e) $F_2POP(O)F_2$

m/e	rel. int.	ion
170	21.5	$F_4P_2O_2$
154	0.7	F_4P_2O
151	2.1	$F_3P_2O_2$
135	0.7	F_3P_2O
106	2.1	
104	9.0	OPF_3
101	0.4	F_2PO_2
88	0.7	PF_3
85	6.2	OPF_2
69	50.0	PF_2
66	1.4	OPF
50	2.4	PF
47	2.8	PO

(f) $(SPF_2)_2O$

m/e	rel. int.	ion
220	3.5	$^{34}SF_4P_2OS$
219	0.7	$^{33}SF_4P_2OS$
218	35.6	$F_4P_2S_2O$
148	1.3	F_2P_2OS
135	2.6	F_3P_2O
133	0.7	S_2PF_2
120	3.5	SPF_3
101	10.7	SPF_2
98	0.7	SPFO
85	0.8	OPF_2
82	0.8	SPF
69	16.3	PF_2
66	1.4	OPF
64	14.2	S_2
63	0.8	SP
50	1.1	PF
47	1.5	PO
32	1.9	S

(g) $(SPF_2)_2S$

236	3.2	$^{34}SF_4P_2S_2$	101	8.8	SPF_2
235	0.6	$^{33}SF_4P_2S_2$	82	3.3	SPF
234	25.7	$F_4P_2S_3$	69	31.4	PF_2
165	1.9	S_3PF_2	66	1.1	
148	0.8	$^{34}SPFS_2$	64	11.8	S_2
146	6.2	S_3PF	63	2.7	PS
133	4.3	S_2PF_2	50	2.7	PF
120	0.6	SPF_3	32	2.4	S
114	2.7	S_2PF			

APPENDIX C (continued)

(h) SPF_2NHCH_3

m/e	rel. int.	ion
133	1.4	$^{34}SPF_2NCH_4$
132	1.1	$^{33}SPF_2NCH_4$
131	28.8	SPF_2NCH_4
130	2.6	SPF_2NCH_3
112	2.0	$SPFNCH_4$
110	2.0	$SPFNCH_2$
103	1.7	SPF_2H_2
102	1.7	SPF_2H
101	8.9	SPF_2
98	25.6	PF_2NCH_3
80	1.1	$PFNCH_4$
78	1.7	$PFNCH_2$
69	12.9	PF_2
63	1.1	PS
60	0.9	$PNCH_3$
50	1.7	PF
47	0.9	PNH_2
46	1.4	PNH
45	0.9	PN
32	1.1	S

(i) OPF_2NHCH_3

m/e	rel. int.	ion
115	21.6	OPF_2NCH_4
114	23.2	OPF_2NCH_3
112	2.5	OPF_2NCH
104	2.0	OPF_3
98	1.3	PF_2NCH_3
96	2.8	$OPFNCH_4$
94	5.3	$OPFNCH_2$
87	10.6	$O_2PF_2H_2$
86	2.0	OPF_2H
85	8.1	OPF_2
69	7.6	PF_2
67	4.3	HPOF
66	1.3	OPF
50	1.0	PF
47	1.8	PO
43	1.3	NC_2H_5
42	1.3	NC_2H_4
32	2.3	S

(j) SPF_2NH_2

119	1.9	$^{34}SPF_2NH_2$	69	15.7	PF_2
117	46.0	SPF_2NH_2	66	3.7	$PFNH_2$
101	6.0	SPF_2	50	1.8	PF
98	2.8	$SPFNH_2$	48	8.9	
97	1.8	SPFNH	47	2.8	PNH_2
85	1.4	PF_2NH_2	46	3.9	PNH
84	2.0	PF_2NH	32	1.2	S

APPENDIX C (continued)

(k) $(SPF_2)_2NCH_3$

m/e	rel.int.	ion
233	2.1	$^{34}SSP_2F_4NCH_3$
232	0.8	$^{33}SSP_2F_4NCH_3$
231	17.1	$S_2P_2F_4NCH_3$
216	1.0	$S_2P_2F_4N$
198	1.9	$SP_2F_4NCH_2$
166	1.1	$P_2F_4NCH_2$
148	1.5	$P_2F_3NCH_3$
131	1.9	
130	12.4	SPF_2NCH_3
129	1.4	SPF_2NCH_2
128	1.6	SPF_2NCH
110	4.9	$SPFNCH_2$
107	0.9	
102	4.4	SPF_2H
101	9.0	SPF_2
98	3.2	PF_2NCH_3
97	1.8	PF_2NCH_2
96	1.8	PF_2NCH
82	1.1	PSF
79	0.9	$PFNCH_3$
78	3.3	$PFNCH_2$
69	13.9	PF_2
64	3.9	S_2
63	1.4	PS
61	0.8	
60	1.7	$PNCH_3$
50	1.7	PF
46	1.1	PNH
32	1.5	S

(l) $(OPF_2)_2NCH_3$

m/e	rel.int.	ion
198	4.9	$O_2P_2F_4NCH_2$
180	1.5	$O_2P_2F_3NCH_3$
171	6.2	
168	2.3	OP_2F_4N
115	2.0	OPF_2NCH_4
114	42.6	OPF_2NCH_3
112	6.7	OPF_2NCH
97	1.2	PF_2NCH_2
94	2.1	$OPFNCH_2$
87	1.7	OPF_2H_2
86	6.3	OPF_2H
85	7.0	OPF_2
69	12.3	PF_2
67	1.0	OPFH
66	0.9	OPF
47	1.4	PO

APPENDIX C (continued)

(m) $(OPF_2)_2NH\cdot N(CH_3)_3$(b)

m/e	rel.int.	ion
185	23.7	$O_2P_2F_4NH$
168	1.4	OP_2F_4N
166	5.2	$O_2P_2F_3NH$
165	5.2	$O_2P_2F_3N$
146	1.4	$O_2P_2F_2N$
102	16.9	$O_2P_2F_2H$
86	0.6	PF_2OH
85	14.2	OPF_2
84	5.0	PF_2NH
83	5.2	PF_2N
82	3.1	O_2PF
81	1.8	OPFNH
69	7.1	PF_2
67	0.6	OPFH
66	1.1	OPF
63	2.4	PO_2
61	1.0	PON
50	1.0	PF
47	2.7	PO

(n) $(SPF_2)_2NH\cdot N(CH_3)_3$(b)

m/e	rel.int.	ion
219	1.2	$^{34}SSP_2F_4NH$
217	12.9	$S_2P_2F_4NH$
134	2.0	P_2F_3NH
128	0.7	SP_2FNH
118	0.8	
115	0.8	SPF_2N
107	1.3	
101	3.4	SPF_2
97	2.4	SPFNH
96	1.2	SPFN
84	1.2	PF_2NH
82	1.0	SPF
77	1.6	SPN
69	24.4	PF_2
66	4.4	
65	2.9	PFNH
64	33.6	S_2,PFN
63	2.1	PS
50	2.2	PF

(a) All ions listed are positive ions.

(b) This table contains only those ions which may be assigned to the phosphorus containing species. Ions which may be assigned to $N(CH_3)_3$ have been deleted.

(c) Intensities are expressed as percent total ionization, defined as $\sum I_n$ where n refers to all ions with m/e > 30 whose intensity is > 2% of the base peak.

APPENDIX D

Summary of the NMR Parameters of the Compounds Prepared in this Study

Compound	Chemical Shifts (a)			Coupling Constants (b)					
	τ	ϕ	Δ	J_{PH}	J_{PF}	J_{HF}	$J_{HH'}$	$J_{PH'}$	$J_{FH'}$
SPF_2H	1.93	46.1	-	726.9	1153	99.0	-	-	-
SPF_2D	-	46.9	-	-	1148.2	15.1(c)	-	-	-
OPF_2H	2.5	61.9	-	844	1121.6	116.2	-	-	-
OPF_2D	-	63.8	-	-	1120	18(c)	-	-	-
SPF_2I	-	-11.2	183.5	-	1274	-	-	-	-
SPF_2SH(d)	6.04	14.85	30.9	16.0	1231.0	2.0	-	-	-
SPF_2NHCH_3(e)	7.07	52.4	46.2	14.3	1082.8	1.0	5.2	20.7	5.2
OPF_2NHCH_3(e)	7.23	80.5	-	13.7	991.4	1.2	5.6	20	1.5
SPF_2NH_2	5.60	43.1	-	-	1086.0	-	-	-	-

(a) τ vs TMS, ϕ vs $CFCl_3$, Δ vs P_4O_6

(b) H refers to methyl protons, H' to amino protons.

(c) $J_{HF} \equiv J_{DF}$

(d) values obtained at -110°

(e) average values obtained at several temperatures.

APPENDIX D (continued)

Compound	Chemical Shifts (a)			Coupling Constants						
	ϕ	Δ	τ	$^1J_{PF}$	$^3J_{PF}$	$^4J_{FF}$	$^4J_{FF'}$	$^2J_{PP}$	$^3J_{PH}$	$^4J_{FH}$
$F_2PSP\underline{(S)F_2}$	14.4	-35.3		-1209.9	22.5	5.9	-	(-)67.8	-	-
$(SPF_2)_2S$	16.9	53.3		-1255.4	- 3.0	12.9	5.6	-25.0	-	-
$(SPF_2)_2N^-(CH_3)_3NH^+$	32.9	66.1	6.70	-1055.3	14.3	6.1	4.9	78.1	-	-
$(PF_2)_2O$	36.8	1.7		-1355.8	14.5	4.0	2.8	- 4.7	-	-
$\underline{F_2}POP(O)F_2$	38.3	-66.4	-	-1396.4	-	-	-	-	-	-
$(SPF_2)_2NCH_3$	40.2	58.3	6.48	-1133.1	- 4.7	10.5	7.5	1.5	13.0	1.5
$(SPF_2)_2O$	40.3	88.3	-	-1171.0	0.2	3.9	2.5	- 8.4	-	-
$\underline{(SPF_2)}O(OPF_2)$	41.0	-	-	-1177.1	3.5	2.7	-	-	-	-
$\underline{F_2}PSP(S)F_2$	60.8	-151.5	-	-1323.6	14.3	5.9	-	(-)67.8	-	-
$(OPF_2)_2N^-(CH_3)_3NH^+$	71.9	127.4	6.90	- 937.0	16.6	5.5	5.0	95.7	-	-
$(OPF_2)_2NCH_3$	73.6	127.1	6.51	-1040.2	- 0.9	4.7	2.5	32.2	10.9	1.1
$(SPF_2)O(\underline{OPF_2})$	79.4	-	-	-1057.2	< 0.5	2.7	-	-	-	-
$F_2PO\underline{P(O)F}_2$	80.0	73.7	-	-1032.5	-	-	-	-	-	-
$(OPF_2)_2O$	81.1	152.3	-	-1055.1	3.0	2.7	2.4	- 0.5	-	-

APPENDIX E

Observed and Calculated Transition Frequencies - ^{19}F Spectra

$(SPF_2)_2S$

obs.	calc.
302.0	302.1
307.6	307.8
311.3	311.3
	311.7
315.0	314.8
	315.2
321.2	321.0
	321.2
327.4	327.4
	333.0
333.0	333.3
	333.7
336.3	336.3
	336.6
340.2	340.1
345.5	345.6
1555.2	1555.2
1560.3	1560.6
1564.1	1564.1
	1564.4
1567.2	1567.1
	1567.4
	1567.8
1573.2	1573.4
1579.5	1579.6
	1579.9
1585.5	1585.6
	1585.9
1589.4	1589.1
	1589.5
1593.2	1592.9
1598.7	1598.7

$(OPF_2)_2N^-(CH_3)_3NH^+$

obs.	calc.
3522.5	3522.2
	3527.3
	3527.6
3528.4	3528.2
	3528.4
3534.0	3533.8
3574.3	3573.5
	3574.6
3584.9	3584.0
	3585.1
3594.8	3594.8
3619.4	3619.0
	3623.0
	3623.4
3623.9	3623.8
	3624.1
3628.2	3628.4
4482.0	4481.6
	4485.8
	4486.0
	4486.4
4486.7	4486.5
	4486.8
4491.1	4491.1
4515.2	4515.2
4525.4	4524.8
	4525.8
4535.8	4535.2
	4536.3
4577.0	4576.3
	4581.4
	4581.6
4582.6	4582.2
	4582.5
4588.6	4587.9

$(SPF_2)_2N^-(CH_3)_3NH^+$

obs.	calc.
1274.5	1274.5
	1279.8
1280.0	1280.0
	1280.8
	1281.1
1286.4	1286.3
1316.1	1315.7
	1316.5
1327.0	1326.7
	1327.5
1335.2	1335.2
1353.6	1353.4
1358.0	1358.0
	1358.1
1359.4	1358.9
	1359.1
1363.4	1363.6
2347.5	2347.8
2352.0	2352.3
	2352.5
2353.5	2353.3
	2353.4
2357.6	2358.0
2376.2	2376.2
2383.8	2383.8
	2384.6
2395.0	2394.8
	2395.7
2425.3	2425.1
	2430.3
2430.6	2430.6
	2431.4
	2431.6
2436.9	2436.9

$(OPF_2)_2NCH_3$

obs.	calc.
3610.7	3610.7
3611.9	3611.8
3613.2	3612.9
	3613.2
3614.5	3614.0
	3614.3
3615.6	3615.4
3616.8	3616.5
3618.1	3617.7
	3618.1
3619.1	3618.8
	3619.2
3620.4	3620.3
3621.6	3621.4
3627.3	3627.2
3628.4	3628.3
3629.7	3629.3
	3629.8
	3630.3
3630.9	3630.6
	3630.9
3632.1	3632.0
3633.1	3633.1
3634.5	3634.2
	3634.5
3635.8	3635.5
3636.9	3636.5
3738.1	3637.6
	3643.1
3644.2	3644.2
3645.6	3645.3
3646.7	3646.5
3647.8	3647.6
3648.9	3648.7
3650.0	3649.9
3651.1	3650.9
	3651.1
3652.5	3652.3
	3653.4
	4650.7
4651.6	4651.8
4653.0	4652.8
	4653.0
4654.2	4654.1
4655.2	4655.2
4656.3	4656.3
4657.4	4657.4
	4657.7
4658.6	4658.5
	4658.7
4659.9	4659.8
	4660.9
4666.2	4666.2
4667.3	4667.3
4668.5	4668.4
4669.7	4669.6
4671.0	4670.8
4672.1	4671.9
4673.2	4673.0
	4673.4
4674.3	4674.1
	4674.5
4675.6	4675.6
4676.9	4676.7
	4682.7
4683.7	4683.7
4684.9	4684.9
	4685.2
4686.3	4686.1
4687.4	4687.3
4688.6	4688.4
4689.7	4689.6
	4690.1
4690.9	4690.7
	4691.2
4692.3	4692.3
	4693.4

$(SPF_2)_2NCH_3$

obs.	calc.
	1694.9
	1695.7
	1696.4
1697.4	1697.3
1697.9	1697.9
1698.7	1698.8
	1699.4
1700.0	1700.1
	1701.9
1701.5	1701.5
	1702.5
1703.0	1703.1
	1704.0
1704.4	1704.5
1705.4	1705.5
1706.9	1707.0
1708.4	1708.5
1709.9	1710.0
1711.4	1711.5
	1712.9
	1713.7
	1714.4
1715.4	1715.3
1715.9	1715.9
1716.7	1716.7
	1717.4
	1718.2
	1718.9
	2823.5
	2824.1
	2825.0
2825.7	2825.6
2826.5	2826.5
2827.1	2827.1
	2828.0
	2828.6
	2829.5
2830.9	2830.9
2832.4	2832.4
2834.0	2833.9
2835.5	2835.4
2837.1	2836.9
2837.9	2837.8
	2838.4
2839.4	2839.3
2839.9	2839.9
	2840.8
	2841.5
	2842.1
2842.4	2842.3
	2843.0
2843.8	2843.6
2844.7	2844.5
2845.3	2845.1
	2846.0
	2846.6
	2847.4

$(SPF_2)_2O$

obs.	calc.
1685.3	1685.2
1687.7	1687.7
1688.4	1688.4
1689.4	1689.1
	1689.4
1691.6	1691.6
1692.8	1692.8
1693.7	1693.6
1695.8	1695.8
	1696.1
1696.8	1696.8
1697.6	1697.5
1699.9	1700.0
2856.5	2856.4
2859.0	2858.9
2859.6	2859.6
2860.4	2860.3
	2860.6
	2862.8
2863.6	2863.6
2864.8	2864.8
2866.9	2867.0
	2867.3
2868.0	2868.0
2868.8	2868.7
2871.0	2871.3

$(PF_2)_2O$

obs.	calc.
1383.4	1383.5
1385.7	1385.8
	1386.3
1386.9	1386.9
	1387.5
	1388.2
1390.5	1390.3
	1391.0
1391.6	1391.6
	1392.2
1392.7	1392.7
1395.2	1394.9
1403.7	1403.7
2745.1	2745.0
2754.1	2753.9
2756.4	2756.1
	2756.6
	2757.2
2757.7	2757.8
	2758.5
	2760.6
	2761.3
2762.1	2761.9
	2762.5
2762.9	2762.9
2765.2	2765.3

$(OPF_2)_2O$

obs.	calc.
	4040.2
4040.5	4040.4
	4040.7
	4042.5
4042.7	4042.7
	4042.9
	4043.1
4043.3	4043.2
	4043.4
	4045.4
4046.0	4046.0
5098.1	5098.0
	5098.4
	5098.7
5100.8	5100.6
	5100.8
5101.4	5101.1
	5101.4
	5103.3
5103.4	5103.5
	5103.8

APPENDIX E (continued)

Observed and Calculated Transition Frequencies - ^{31}P Spectra

$(SPF_2)_2NCH_3$

obs.	calc.	obs.	calc.	obs.	calc.
	1190.8		2318.5		3447.7
1192.5	1193.6	2321.2	2322.2		3455.2
	1195.1		2323.7	3459.5	3460.0
1198.0	1198.3	2326.5	2327.6		3460.7
1198.9	1198.8	2328.3	2329.6	3463.1	3461.4
	1201.2		2331.1	3464.3	3464.2
1201.9	1202.7		2331.5		3465.7
1202.9	1203.8		2332.6	3467.5	3467.4
	1204.2	2332.8	2332.9		3468.3
1205.5	1205.7	2334.3	2334.1		3468.9
	1206.6		2335.2		3470.4
	1207.3	2336.5	2336.5	3472.2	3471.9
	1208.1	2339.3	2339.0		3473.0
1209.1	1208.8		2340.1		3473.7
1210.5	1211.3		2340.5	3474.4	3474.4
1211.8	1211.8	2341.2	2341.7	3475.8	3474.7
	1213.1		2342.0	3477.1	3477.2
1214.9	1214.2	2343.0	2342.6		3477.9
1215.8	1215.7		2343.5		3478.7
1216.9	1216.8		2344.1		3479.5
	1217.2	2344.4	2344.5	3480.7	3480.4
	1217.8	2345.6	2345.6		3481.3
1218.5	1218.7		2345.9		3481.9
	1219.6	2347.3	2347.1	3482.2	3482.2
	1220.3		2348.2	3483.2	3483.4
	1221.1	2349.5	2349.5	3484.2	3484.9
1221.9	1221.8		2349.7	3485.2	3486.0
1223.5	1224.3	2350.5	2350.9		3486.7
1224.9	1224.8		2352.0	3487.8	3487.4
	1225.3	2353.2	2353.2	3488.5	3487.7
	1226.1	2353.6	2353.5	3490.1	3490.2
1227.0	1227.2	2354.3	2354.7		3491.0
1227.9	1228.7		2355.0	3491.6	3491.7
1229.2	1229.8		2355.6		3492.5
1230.0	1230.2	2356.1	2356.5	3493.4	3493.4
	1230.8		2357.1		3494.3
1231.5	1231.7	2357.7	2357.4	3495.1	3494.9
	1232.6	2358.1	2358.6		3495.2
	1233.3	2358.6	2358.9	3496.4	3496.4
	1234.1	2359.7	2360.1	3497.3	3497.9
1235.1	1234.8		2361.2		3499.0
1236.6	1237.3	2362.6	2362.5	3500.5	3500.4
1238.0	1237.7	2363.6	2363.9	3501.5	3500.7
	1238.3	2365.1	2365.0	3502.9	3503.2
	1239.1		2366.2		3504.0
1240.2	1240.2	2366.6	2366.5		3504.7
	1241.7		2367.5		3505.5
	1243.2	2367.7	2367.7	3506.8	3506.4
	1243.8		2368.0		3507.9
1244.8	1244.7	2369.2	2368.6		3508.2
	1246.3		2369.5	3509.3	3509.4
1248.3	1247.8		2370.1	3510.4	3510.9
1249.7	1250.6		2370.4	3513.5	3513.3
	1251.3	2371.2	2371.5	3514.5	3513.7
1253.5	1252.1		2371.9		3516.9
	1256.8	2373.0	2373.1		3518.5
	1264.3	2375.8	2375.5	3520.1	3521.1
			2376.9		
		2378.2	2378.0		
			2379.1		
		2379.8	2379.5		
			2380.5		
			2380.7		
			2381.0		
		2382.4	2382.5		
		2384.3	2384.5		
		2386.3	2388.4		
			2389.9		
		2393.0	2393.5		

$(OPF_2)_2NCH_3$

obs.	calc.	obs.	calc.	obs.	calc.
	4061.5	5100.5	5101.6		6141.4
4061.0	4062.5		5102.5		6142.5
	4064.1		5104.0		6145.0
	4066.1		5105.1	6146.5	6147.1
4067.5	4066.4	5106.0	5106.0		6142.4
	4068.9		5107.3		6152.2
	4072.4		5108.5	6154.5	6153.4
4071.5	4073.4		5109.9		6155.9
	4075.0	5111.5	5112.4	6158.5	6157.9
4077.0	4077.0		5113.4		6160.4
	4077.3		5114.7		6162.7
	4079.8		5116.0	6163.5	6163.2
4081.5	4080.8	5117.5	5117.0		6164.3
	4083.3		5118.2		6166.7
	4084.3		5119.4	6169.0	6168.8
	4085.9		5120.8		6169.9
	4087.9	5121.5	5121.6		6171.2
	4088.2		5123.3	6174.0	6173.6
	4089.7		5124.3		6174.3
4092.0	4091.6		5125.3		6175.3
	4093.9		5125.8		6177.1
	4094.3		5126.9		6177.7
	4095.1		5127.9		6179.3
	4096.4		5129.0		6179.8
	4096.8		5130.3		6180.8
	4098.4		5131.7		6181.9
	4098.9	5132.5	5132.5		6182.1
	4099.1		5133.5	6185.0	6184.5
	4101.0		5134.2		6185.4
	4101.8		5135.1		6188.0
4103.0	4102.5		5136.2		6190.2
	4104.9		5136.7		6191.6
	4106.0		5137.6		6192.8
4107.5	4107.3		5138.3	6195.0	6195.3
	4109.3		5138.8		6196.3
	4111.9		5139.7	6199.0	6198.9
4113.5	4112.9		5140.1		6201.1
	4113.4		5141.0		6202.5
	4115.8		5142.6	6205.5	6203.7
4118.5	4118.2	5143.5	5143.4		6207.2
	4120.2		5144.4		6209.8
4123.0	4122.8		5145.9		6212.0
	4123.7		5147.0		6213.5
	4126.7		5148.3	6218.0	6214.6
4129.0	4129.1		5149.2		
	4131.0		5150.5		
	4131.2		5151.8		
	4133.6		5152.8		
	4134.6	5154.5	5154.3		
			5155.3		
			5156.8		
		5158.5	5157.9		
			5159.2		
			5160.1		
			5161.4		
			5162.6		
		5164.5	5163.7		
			5166.1		
			5167.7		
		5169.5	5168.8		
			5170.1		
			5171.1		
			5172.2		
			5173.6		
		5175.0	5174.6		

APPENDIX E (continued)

Observed and Calculated Transition Frequencies - ^{31}P Spectra

$(SPF_2)_2O$

obs.	calc.
2388.6	2387.6
2390.7	2390.2
2391.4	2390.7
2392.3	2391.6
	2392.7
2394.5	2394.1
2395.3	2395.3
2395.8	2396.1
2396.2	2397.1
2398.5	2398.6
2399.1	2399.1
2400.1	2400.0
2402.2	2402.3
	3558.4
3559.1	3558.9
3559.4	3559.7
3560.1	3561.0
3561.3	3561.4
3561.6	3562.4
3562.8	3562.8
3563.1	3562.9
3565.1	3564.9
	3565.3
3566.1	3566.1
3566.9	3566.9
	3567.3
3569.0	3569.3
3569.4	3569.8
3570.5	3570.8
3570.9	3571.2
3572.0	3572.5
3572.7	3573.2
3573.1	3573.7
4730.3	4729.8
4732.5	4732.2
4733.4	4733.1
4734.0	4733.6
4736.1	4735.1
	4736.1
4736.9	4736.9
4738.0	4738.1
	4739.5
4740.3	4740.6
4741.2	4741.5
4741.8	4742.0
4744.2	4744.6

$(OPF_2)_2O$

obs.	calc.
5093.4	5093.3
5095.2	5095.3
5097.7	5097.9
5098.4	5098.4
5098.8	5098.9
5100.5	5100.7
5100.9	5100.9
	5101.1
5101.4	5101.6
5103.1	5102.9
	5103.5
5103.9	5104.0
	5104.2
6149.9	6150.4
6150.3	6150.9
6150.9	6151.0
6152.2	6152.7
6152.8	6153.2
6153.2	6153.6
6154.9	6155.5
6156.1	6156.1
	6156.3
	6156.8
6157.9	6158.6
6158.5	6158.7
6159.2	6159.1
	6159.5
6160.5	6161.2
6161.2	6161.4
	6161.9
7207.9	7208.2
	7208.4
7208.8	7208.8
	7209.3
7210.6	7210.7
7210.9	7211.0
	7211.2
7211.4	7211.3
	7211.5
7213.3	7213.4
7213.8	7213.9
	7214.4
7216.6	7216.9
7218.7	7218.9

$(SPF_2)_2S$

obs.	calc.
879.6	879.3
	882.6
884.9	885.0
	891.8
892.8	892.5
898.5	898.4
904.9	904.6
910.2	910.2
	916.8
917.9	917.4
922.9	922.8
	925.9
2133.0	2132.4
2137.9	2137.8
2138.6	2138.4
2143.2	2143.4
2145.4	2145.0
2147.7	2147.6
2150.4	2150.5
2151.1	2150.9
	2156.5
2156.8	2156.8
	2157.0
2162.6	2162.7
2163.2	2163.0
2165.9	2166.0
2168.2	2168.6
2170.6	2170.2
2175.0	2175.2
2176.0	2175.8
2181.1	2181.2
3388.6	3387.7
3391.9	3390.8
3396.8	3396.2
3397.5	3396.8
3404.4	3403.4
3409.4	3408.9
3415.8	3415.3
3421.6	3421.1
3422.6	3421.8
3429.6	3428.5
3432.0	3430.9
3435.0	3434.3

$(PF_2)_2O$

obs.	calc.
-1307.5	-1307.2
	-1306.0
-1303.7	-1303.8
-1299.4	-1299.2
-1296.0	-1297.0
-1295.1	-1295.8
-1293.0	-1292.7
-1289.7	-1289.9
-1288.7	-1288.7
	-1288.1
	-1285.9
-1285.4	-1285.3
-1284.4	-1284.1
-1281.1	-1281.3
-1272.3	-1272.5
48.7	48.5
51.7	51.4
52.7	52.6
	53.2
	55.4
56.0	56.0
56.9	57.2
60.1	60.0
61.5	62.0
65.2	65.4
68.8	68.8
72.6	72.2
76.2	75.6
77.7	77.6
80.9	80.4
81.9	81.6
	82.2
85.2	84.4
	85.0
86.2	86.2
89.5	89.1
1410.3	1410.1
1418.9	1418.9
1422.2	1421.7
1423.1	1422.9
	1423.5
1426.4	1425.7
	1426.3
1427.4	1427.5
1430.7	1430.4
1433.6	1433.4
1434.2	1434.6
1437.1	1436.8
1441.6	1441.4
	1443.6
1445.3	1444.8

$(OPF_2)_2N^-(CH_3)_3NH^+$

obs.	calc.
4134	4138.7
4147	4149.2
	4154.5
4161	4159.1
	4164.5
4167	4165.1
	4170.6
4230	4231.6
	4239.7
4241	4244.9
4252	4255.4
	4255.6
	4260.2
	4260.6
	4265.1
	5079.4
	5084.8
5085	5085.4
	5090.9
	5118.4
	5122.9
	5123.3
5126	5127.9
	5141.4
	5146.6
5152	5151.9
	5157.1
	5162.4
5177	5176.1
	5180.7
	5181.1
	5185.6
	5212.9
5217	5218.5
	5219.0
	5224.5
	6038.7
6040	6043.2
	6043.6
	6048.3
6055	6058.8
	6064.1
6067	6072.4
	6133.4
6136	6139.0
	6139.5
	6145.0
6152	6149.3
	6154.5
6163	6165.0

$(SPF_2)_2N^-(CH_3)_3NH^+$

obs..	calc.
1445.7	1446.4
1456.2	1457.4
1461.8	1462.9
1463.9	1465.1
1468.7	1470.4
1471.2	1471.7
1475.7	1476.9
1525.7	1525.8
1530.5	1530.0
1535.9	1535.5
1544.3	1544.0
1546.5	1546.8
1548.6	1548.6
1550.5	1549.7
1554.5	1554.2
2505.6	2506.1
2510.5	2511.4
2512.9	2512.7
2517.9	2517.6
2538.4	2538.4
2542.2	2542.9
2544.5	2544.0
2548.7	2548.6
2556.1	2555.8
2561.8	2561.3
2566.8	2566.8
2572.4	2572.3
2578.1	2577.8
2586.0	2585.0
2590.1	2589.6
2592.1	2590.7
2596.2	2595.2
2617.1	2615.7
2621.7	2620.9
2623.9	2622.2
2629.0	2627.5
3578.8	3579.4
3583.0	3583.9
3585.2	3585.0
3587.0	3587.0
3589.2	3589.6
3597.7	3598.0
3603.3	3603.5
3607.8	3607.8
3657.7	3656.7
3662.3	3662.0
3664.7	3663.2
3669.3	3668.5
3671.5	3670.7
3677.1	3676.2
3688.4	3687.2