ABSTRACT OF THESIS

Name of Candidate David Edward James Arnold
Address 116 Mayfield Road, Edinburgh 9.
Degree Ph.D. *Date* March, 1976.
Title of Thesis Fluorophosphine Derivatives of the Elements of Groups V and VI.

The thesis describes the attempts to form difluorophosphine derivatives of Groups V and VI elements. Preliminary exchange reactions were investigated at room temperature between bromodifluorophosphine, and silyl or germyl derivatives of the elements of these groups, the extent of reaction being followed by n.m.r. spectroscopy.

In Group VI, a series of compounds of the types $(F_2P)_2Y$ and F_2PYMH_3, ($Y = O$, S, Se or Te; $M =$ Si or Ge) were formed, for which chemical shifts (^1H, ^{19}F, ^{31}P and ^{77}Se) and coupling constants (including relative signs) were obtained. The ^{19}F spectrum of $(F_2P)_2Se$ was studied over a wide temperature range and variations in its n.m.r. parameters noted. By the same exchange route, bis(difluorophosphino)sulphide and -selenide were prepared and isolated, and characterised by mass, photoelectron, vibrational and n.m.r. spectroscopy. Various reactions of bis(difluorophosphino) selenide are described.

The exchanges of bromodifluorophosphine with the silyl derivatives of Group V elements produced (difluorophosphino)disilylphosphine, $F_2PP(SiH_3)_2$ and evidence for the formation of (difluorophosphino)-silylphosphine, $F_2PPHSiH_3$, as the only novel compounds. These were characterised by their n.m.r. parameters, and signs of coupling constants were obtained. Since no new nitrogen derivatives were formed, alternative preparative methods were tried. This led to the formation of tris(difluorophosphino) and bis(difluorophosphino)-amines, $(F_2P)_3N$ and $(F_2P)_2NH$, by the gas phase reactions of ammonia, chlorodifluorophosphine and trimethylamine. Both compounds were characterised spectroscopically, and reactions of the tertiary amine with hydrogen halides, Group VI hydrides and chlorine were carried out.

Boron trifluoride was found to react with aminodifluorophosphine, in the gas or liquid phase, to give an adduct. Upon decomposition, this adduct formed difluorophosphinoaminodifluoroborane, F_2PNHBF_2, which was characterised by its mass, photoelectron, n.m.r. and vibrational spectra. With excess aminodifluorophosphine, however, the adduct gave bis(difluorophosphino)amine and trifluoroborane-ammonia adduct.

Use other side if necessary.

The reaction of ammonia and chlorodifluorophosphine, which was known to give aminodifluorophosphine, was shown under different conditions to produce diaminodifluorophosphorane, $HPF_2(NH_2)_2$. The compound, which was also formed by reaction of ammonia and aminodifluorophosphine, was characterised spectroscopically, and its structure interpreted in terms of a trigonal bipyramid, of C_{2V} symmetry, with axial fluorine atoms.

The molecular structures of bis(difluorophosphino)selenide, tris(difluorophosphino)amine, and diaminodifluorophosphorane were determined, in the gas phase, by electron diffraction. Bis(difluorophosphino)selenide was described in terms of torsional motion of the difluorophosphino-groups about a mean C_{2V} symmetry, while tris(difluorophosphino)amine was shown to have a C_{3h} symmetry. Diaminodifluorophosphorane was found to be of C_{2V} symmetry in agreement with the spectroscopic evidence. Non-bonded distances in fluorophosphines are discussed.

The possibilities of preparing new compounds and proposals for investigating the co-ordination chemistry of species obtained in this work are presented. Molecules suitable for future electron diffraction studies are suggested. The usefulness of predicate observations in electron diffraction and of liquid-crystalline n.m.r. in the determination of fluorophosphine structures is expressed.

FLUOROPHOSPHINE DERIVATIVES
OF THE
ELEMENTS OF GROUPS V AND VI

by

David Edward James Arnold

A thesis presented for the degree of
Doctor of Philosophy in the Faculty of Science
of the University of Edinburgh, 1976

CONTENTS

GROUP VI DERIVATIVES

GROUP V DERIVATIVES

CONCLUSIONS

EXPERIMENTS

CHAPTER 9: Experimental Section

APPENDIX

ACKNOWLEDGEMENTS

I wish to express my thanks to those individuals whose help in countless ways made this work possible. To Drs. S. Cradock and A.J. Hinchcliffe, I owe a scientific debt for initiating me into the mysteries of photoelectron spectroscopy and matrix isolation techniques. Without exception, my colleagues gave practical and personal assistance, for which I am most grateful. For the provision of electron diffraction facilities at the University of Manchester Institute of Science and Technology, I am indebted to Professor D.W.J. Cruickshank, Dr. B. Beagley and Mrs. V. Ulbrecht.

Above all, I would like to thank my supervisors, Professor E.A.V. Ebsworth and Dr. D.W.H. Rankin, not only for their help and guidance with all the problems associated with this work, but also for their good humour and the many kindnesses they extended to me.

For financial support, I am grateful to the Chemistry Department for a Departmental Demonstratorship, and to the University of Edinburgh for a Watt bursary.

Finally, I am obliged to Mrs. Williams for her advice on presentation, and for typing the manuscript.

SUMMARY

The thesis describes the attempts to form difluorophosphine derivatives of Groups V and VI elements. Preliminary exchange reactions were investigated at room temperature between bromodifluorophosphine, and silyl or germyl derivatives of the elements of these groups, the extent of reaction being followed by n.m.r. spectroscopy.

In Group VI, a series of compounds of the types $(F_2P)_2Y$ and F_2PYMH_3, ($Y = O$, S, Se or Te; $M = Si$ or Ge) were formed, for which chemical shifts (^1H, ^{19}F, ^{31}P and ^{77}Se) and coupling constants (including relative signs) were obtained. The ^{19}F spectrum of $(F_2P)_2Se$ was studied over a wide temperature range and variations in its n.m.r. parameters noted. By the same exchange route, bis(difluorophosphino) sulphide and -selenide were prepared and isolated, and characterised by mass, photoelectron, vibrational and n.m.r. spectroscopy. Various reactions of bis(difluorophosphino) selenide are described.

The exchanges of bromodifluorophosphine with the silyl derivatives of Group V elements produced (difluorophosphino)-disilylphosphine, $F_2PP(SiH_3)_2$, and evidence for the formation of (difluorophosphino)-silylphosphine, $F_2PPHSiH_3$, as the only novel compounds. These were characterised by their n.m.r. parameters, and signs of coupling constants were obtained. Since no new nitrogen derivatives were formed, alternative preparative methods were tried. This led to the formation of tris(difluorophosphino) and bis(difluorophosphino)-amines, $(F_2P)_3N$ and $(F_2P)_2NH$, by the gas phase reactions of ammonia, chlorodifluorophosphine and trimethylamine. Both compounds were characterised spectroscopically, and reactions of the tertiary amine with hydrogen halides, Group VI hydrides and chlorine were carried out.

Boron trifluoride was found to react with aminodifluorophosphine, in the gas or liquid phase, to give an adduct. Upon decomposition, this adduct formed difluorophosphinoaminodifluoroborane, F_2PNHBF_2, which was characterised by its mass, photoelectron, n.m.r. and vibrational spectra. With excess aminodifluorophosphine, however, the adduct gave bis(difluorophosphino)amine and trifluoroborane-ammonia adduct.

The reaction of ammonia and chlorodifluorophosphine, which was known to give aminodifluorophosphine, was shown under different conditions to produce diaminodifluorophosphorane, $HPF_2(NH_2)_2$. The compound, which was also formed by reaction of ammonia and aminodifluorophosphine, was characterised spectroscopically, and its structure interpreted in terms of a trigonal bipyramid, of C_{2V} symmetry, with axial fluorine atoms.

The molecular structures of bis(difluorophosphino) selenide, tris(difluorophosphino)amine, and diaminodifluorophosphorane were determined, in the gas phase, by electron diffraction. Bis(difluorophosphino)selenide was described in terms of torsional motion of the difluorophosphino-groups about a mean C_{2V} symmetry, while tris(difluorophosphino)amine was shown to have a C_{3h} symmetry. Diaminodifluorophosphorane was found to be of C_{2V} symmetry in agreement with the spectroscopic evidence. Non-bonded distances in fluorophosphines are discussed.

The possibilities of preparing new compounds and proposals for investigating the co-ordination chemistry of species obtained in this work are presented. Molecules suitable for future electron diffraction studies are suggested. The usefulness of predicate observations in electron diffraction and of liquid-crystalline n.m.r. in the determination of fluorophosphine structures is expressed.

TO

Denis, Evlynn and Ann

for

Faith, Hope and Charity

"Wherever (the reader) finds that I have ventured at any small conjectures at the causes of the things that I have observed, I beseech him to look upon them only as doubtful Problems, and uncertain ghesses, and not as unquestionable Conclusions, or matters of unconfutable Science. I have produced nothing here with intent to bind his understanding to an implicit consent."

Robert Hooke
Micrographia, 1665.

INTRODUCTION

Although Moissan[1] first prepared the parent fluorophosphine, trifluorophosphine, in 1884, there was little activity in this field until the 1950s apart from sporadic reports e.g. work on bromo- and chlorofluorophosphines.[2,3] From this time on however, a lively literature has been built up and sustained with the main areas of study being phosphoramidous fluorides, alkyl-, aryl- and halogenofluorophosphines, fluorophosphites and the extensive chemistry of fluorophosphine-co-ordination complexes. Since most of these compounds are volatile liquids or gases, and many have unpleasant smells, are poisonous, pyrophoric or easily hydrolysed, much of the synthetic work has made use of vacuum line techniques or inert atmospheres.

The growth of interest in fluorophosphine chemistry has been monitored by many reviews. Schmutzler,[4] in 1965, covered general phosphorus fluorides, of which fluorophosphines form a part, and with Fild[5] in 1972 reviewed halogeno- and pseudohalogenophosphines. Kruck[6] has reported on transition metal-trifluorophosphine complexes, and Nixon[7] has discussed developments specifically in fluorophosphine chemistry up to 1970.

In spite of this considerable interest, many of the simpler fluorophosphine derivatives of main group elements remained unknown. This was particularly true of derivatives of Groups V and VI and so the principal aim of the research project became the synthetic, spectroscopic and structural investigation of simple chalcogeno- and pnictodifluorophosphines.

Despite the many dialkyl- and diarylaminodifluorophosphines reported, and the formation of the F_2PNHR group of compounds (R = Me, Et, Bu^n and Bu^t),[8,81] it was not until 1971 that Rankin prepared F_2PNH_2, and noted the presence in the mass spectrum of the further nitrogen substituted difluorophosphines, $(F_2P)_2NH$ and $(F_2P)_3N$.[9] The existence of the series $(F_2P)_2NR$ (R = Me, Et, Ph and m - ClC_6H_4)[10,11] suggested that these compounds might be prepared. Although $(F_2P)_2NR$ were synthesised by fluorination of the chloro-derivatives, attempts to obtain $(F_2P)_2NH$ and $(F_2P)_3N$ more directly were tried using halogenodifluorophosphine and ammonia, in the presence of trimethylamine. In the course of these preparations, chance reactions led to the formation of diaminodifluorophosphorane, $HPF_2(NH_2)_2$, and difluoroborylaminodifluorophosphine, F_2PNHBF_2.

In addition, the known F_2P- derivatives of phosphorus such as F_2PPF_2,[12] F_2PPH_2,[13] $(F_2P)_3P$[14] and $F_2PP(CF_3)_2$[15] coupled with the reported preparations of $F_2PNCH_3.Si(CH_3)_3$[16] and $F_2PNHSiH_3$[17] indicated that mixed difluorophosphine and silyl derivatives of Group V elements other than nitrogen might be stable. In an attempt to prepare such compounds exchange reactions between halogenodifluorophosphines and $(H_3Si)_nZH_{(3-n)}$ (Z = N and P) were tried.

Of the Group VI derivatives there was great bias towards oxygen, with a large number of the type F_2POR known (R = alkyl or aryl). The other members of the group were less favoured with only four reported compounds.

While $(F_2P)_2O$ had been well characterised,[18,19] $(F_2P)_2S$ had been discussed only in terms of its nuclear magnetic resonance spectrum with no details of preparation or characterisation published.[20,21] The other three non-oxygen derivatives were all sulphur compounds: $F_2PSPF_2(S)$[22] was formed from $(S)PF_2SH$ and $F_2PN(CH_3)_2$; F_2PSCH_3[23] from $N(CH_3)_3$, CH_3SH and F_2PCl; $F_2PSP(CF_3)_2$[24] from $(F_2P)_2S$ and $[(F_3C)_2P]_2S$. There were no known selenium or tellurium difluorophosphines. As part of an attempt to form $(F_2P)_2Se$ and $(F_2P)_2Te$ exchange reactions were tried between F_2PBr and $(H_3M)_2Y$ (M = Si and Ge; Y = O, S, Se and Te) in which several novel thio-, seleno- and tellurodifluorophosphine compounds were observed. The results of these reactions provided the impetus for the successful preparation of $(F_2P)_2Se$.

In the study of phosphorus fluorides, spectroscopic techniques such as infra red, Raman, photoelectron and mass spectroscopy have been widely used. Nuclear magnetic resonance however has been particularly important because of the 100% natural abundance of ^{31}P and ^{19}F with nuclear spin quantum number, $I = \frac{1}{2}$. For the difluorophosphines and phosphorane mentioned in this work emphasis has been given to collecting chemical shifts, coupling constants, and where possible relating the signs of these coupling constants. In some instances spectra more complicated than first order have been observed and attempts have been made to solve these. Compounds such as $(F_2P)_2S$[21] and $(F_2P)_2NR$[11] have been analysed as examples of $[A[X]_2]_2$ spin systems and the equations of Harris <u>et al.</u>[25] have been similarly applied to $(F_2P)_2Se$ and $(F_2P)_2NH$. However $(F_2P)_3N$ provided an example of a system too complicated to solve, unlike the analogous, but deceptively simple, spectrum of $(F_2P)_3P$.[14] Those parameters collected were invaluable for analytical purposes and the elucidation of structure. Some coupling constants are reported of which few examples are known, e.g. the first $^1J(^{31}P^{15}N)$ was mentioned by Cowley et al.[26] for $(F_3C)_2PNH_2$-$[^{15}N]$ as late as 1970. In such cases it is hoped that the additional information will provide a better insight into the nature of spin-spin coupling, and ultimately, bonding. Experiments have also been carried out to investigate the effect temperature has upon coupling constants, where these appear to be strongly influenced by conformation.

Finally, since many difluorophosphines are volatile, small molecules, they are ideal for gas phase molecular structure determinations, and many have been studied by microwave spectroscopy or electron diffraction. Since the early study of trifluorophosphine by Brockway and Wall[27] in 1934, the number of difluorophosphines investigated by electron diffraction alone has grown into double figures and provides much information. Furthermore, these structural data can be compared with observations and inferences drawn from vibrational and nuclear magnetic resonance spectroscopy to provide a more complete characterisation. With these aims in mind structural parameters were obtained by electron diffraction for $(F_2P)_2Se$, $(F_2P)_3N$ and $HPF_2(NH_2)_2$.

CHAPTER 1

EXCHANGE REACTIONS OF BROMODIFLUOROPHOSPHINE WITH SILYL AND GERMYL DERIVATIVES OF THE GROUP VI ELEMENTS+

Introduction

The desire to obtain difluorophosphino derivatives of the Group VI elements led to an investigation of the possibilities of exchange between F_2P groups and the silyl and germyl groups of disilyl and digermyl chalcogenides. This reaction scheme was adopted for a number of reasons, even though $(F_2P)_2O$ had been prepared previously from iododifluorophosphine and cuprous oxide.[18]

Firstly there had been several studies of exchange reactions between substituted silyl and germyl compounds[28] which at equilibrium indicated the tendency of the more electronegative groups to be bound preferentially to silicon. In one of these studies[28] germyl iodide reacted with trichlorophosphine and produced germyl chloride. No such reaction however occurred with trifluorophosphine.

Secondly, structural studies of $(F_2P)_2O$,[29] $F_2PNHSiH_3$,[17] F_2PNH_2 and $F_2PN(CH_3)_2$[30] have suggested a similarity between the bonding of phosphorus to oxygen and nitrogen, and the bonding of silicon and germanium to these elements.

And finally, it was believed that if reaction proceeded it might be possible to identify the mixed species F_2PYMH_3

+ Appendix 1 contains a paper published under the same title relating to this work.

(M = Si or Ge; Y = O, S, Se or Te) which in themselves would be of considerable interest.

1.1 Results and Discussion

During the early stages of this work several observations were made which influenced the use of starting materials and the conditions for later reactions. It was found that F_2PCl exchanged slowly with the digermyl Group VI compounds which resulted in low concentrations of mixed products, most of which were unstable over long periods at room temperature. While reactions of F_2PCl with the silyl derivatives were fast, expected products other than silyl chloride were not always seen. Consequently all the exchanges reported here made use of bromodifluorophosphine.

Consideration of the exchange rates involving sulphur, selenium and tellurium indicated a relative ordering: $Si > Ge$ and $Te > Se > S$. Also, the nature of the equilibria were such that if sufficient bromodifluorophosphine were present all silyl starting materials were used up but some germyl compounds remained. At no time however could high concentrations of F_2PYMH_3 be built up.

The oxygen systems proved to be anomalous. With disilyl oxide, F_2PBr gave only small amounts of silyl bromide over 24 hours, whereas with digermyl oxide reaction was too rapid even to observe the proton n.m.r. spectrum of starting materials. In neither system could F_2POMH_3 be detected and although MH_3Br was formed, yields of bis(difluorophosphino) oxide were lower than expected; F_3P appeared instead.

TABLE 1.1

Reactions of $(MH_3)_2Y$ and PF_2Br

Reagents PF_2Br+	Molar ratio PF_2Br : $(MH_3)_2Y$	Reaction time/s	$(MH_3)_2Y$ remaining/%	Observed products			
				MH_3Br	MH_3YPF_2	$(F_2P)_2Y$	Others
$(SiH_3)_2O$	2.5 : 1	80,000	65	✓		✓	
	3.5 : 1	80,000	55	✓		✓	
$(GeH_3)_2O$	2 : 1	600	0	✓		✓	$O{=}PF_2H$
	1 : 1	600	0	✓			PF_3
$(SiH_3)_2S$	1.8 : 1	2000	60	✓	✓	✓	
	1.8 : 1	50,000	30	✓	✓	✓	SiH_3F
$(GeH_3)_2S$	2.5 : 1	7000	100				
	2.5 : 1	180,000	80	✓	✓	✓	
$(SiH_3)_2Se$	2.5 : 1	25,000	15	✓	✓	✓	
	3 : 1	4000	30	✓	✓	✓	
	3 : 1	8000	0	✓	✓	✓	
$(GeH_3)_2Se$	2.5 : 1	8000	90	✓			
	2.5 : 1	200,000	60	✓	✓	✓	
$(SiH_3)_2Te$	1 : 1	2000	65	✓	✓	✓	Te
$(GeH_3)_2Te$	2 : 1	5000	70	✓			Te

Lastly, the products of reaction were unstable in that on standing, the sulphur and selenium systems precipitated traces of yellow solids and the tellurium system rapidly precipitated a lot of metallic tellurium. These solids did not hinder the recording of the n.m.r. spectra.

These qualitative observations indicated that the tendency in fluorophosphine-silyl exchanges was for the more electronegative atoms to be bound to silicon, whereas in fluorophosphine-germyl systems the electronegative atoms tended to be bound to the phosphorus. Since π-electron acceptor properties have been used to explain structural forms of silyl and germyl compounds, and difluorophosphine derivatives exhibit similar bonding,[30] the F_2P group appears to have a π-electron acceptor behaviour intermediate in strength between silyl and germyl groups. If this behaviour accounts for the rate and the extent of reaction, chlorodifluorophosphine would be expected to react more completely than bromodifluorophosphine with the silyl derivatives, but less completely with the germyl ones. This is largely consistent with experimental observation. Chlorodifluorophosphine reacted slowly with the germyl derivatives but products other than GeH_3Cl decomposed as rapidly as they were formed and were not seen in the n.m.r. spectra. The silyl compounds on the other hand tended to give SiH_3Cl quickly, the reactions going to completion, but with further reactions occurring giving insoluble products.

Details of the more important experiments with F_2PBr are given in Table 1.1. In addition to those products

TABLE 1.2

Chemical Shifts[(a)]

Compound	$\delta(^{1}H)$	$\delta(^{19}F)$	$\delta(^{31}P)$	$\delta(^{77}Se)$
$(SiH_3)_2O$	+ 4.56			
$(GeH_3)_2O$	+ 5.28			
$(F_2P)_2O$		- 36.7	+ 111	
$(SiH_3)_2S$	+ 4.29			
SiH_3SPF_2	+ 4.35	- 57.3	+ 229.5	
$(GeH_3)_2S$	+ 4.60			
GeH_3SPF_2	+ 4.68	- 57.1	+ 232.0	
$(F_2P)_2S$		- 64.3	+ 219.4	
$(SiH_3)_2Se$	+ 4.02			- 666.0
SiH_3SePF_2	+ 4.17	- 59.6	+ 255.4	n.o.
$(GeH_3)_2Se$	+ 4.18			- 611.5
GeH_3SePF_2	+ 4.30	- 59.5	+ 258.9	n.o.
$(F_2P)_2Se$(b)		- 66.4	+ 246.9	+ 700.8
$SiH_3)_2Te$	+ 3.59			
SiH_3TePF_2	+ 3.94	- 68.5	+ 297.0	
$(GeH_3)_2Te$	+ 3.52			
$(F_2P)_2Te$		- 72.6	+ 295.8	

Note:

n.o., not observed

(a) Refer to experimental section for shift conventions.

(b) Measured at 193K; all other spectra recorded at 300K.

listed there were small amounts of $(F_2P)_2O$ and $Y = PF_2H$ (Y = S or Se), formed if traces of water were present.

Those reactions involving oxygen compounds gave only bis(difluorophosphino) oxide and the silyl or germyl halide. In the digermyl telluride system the slow rate of formation and the rapid decomposition of fluorophosphine-tellurium compounds allowed only GeH_3Cl to be observed. GeH_3TePF_2 was not seen in the n.m.r. spectra.

1.2 Chemical Shifts

These are shown in Table 1.2 for the Group VI species studied and indicate several trends.

The proton resonances show a downfield shift when F_2P replaces an MH_3 group in $(H_3M)_2Y$. This shift, which is similar in the case of silicon or germanium for a given element Y, nevertheless varies with Y in the order: Te > Se > S, and probably reflects the electron-withdrawing character of the difluorophosphine group. The variation in the shifts could, however, be due to the changes in the geometry of the molecules, as the extent of intramolecular hydrogen bonding in a five-membered ring (I) would be very dependent upon the precise bond lengths and valence angles in the compound.

(I)

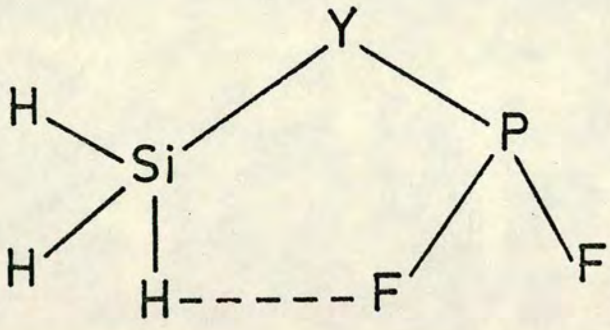


TABLE 1.3

Coupling Constants for MH_3YPF_2

Compound	T	$^1J(PF)$	$^3J(PH)$	$^4J(FH)$
SiH_3SPF_2	300	- 1298	+ 13.3	+ 2.7
GeH_3SPF_2	300	- 1285	+ 11.8	+ 3.4
SiH_3SePF_2	300	- 1286	+ 11.6	+ 2.9
GeH_3SePF_2	300	- 1287	+ 11.2	+ 3.3
SiH_3TePF_2	203		11.4	3.0
	233		10.1	2.9
	273		9.6	2.7
	300	- 1253	+ 9.3	+ 2.8

Note:

(i) T, absolute temperature

(ii) J, Hz.

The ^{19}F chemical shifts increase in the order O > S > Se > Te, a trend similar to one found for difluorohalogenophosphines,[31,32] and may be attributed to electronegativity differences. Also, for any element Y there is an ordering: $\delta[SiH_3YPF_2] \sim \delta[GeH_3YPF_2] > \delta[(F_2P)_2Y]$.

Phosphorus chemical shift values are helpful in confirming the compounds studied as derivatives of three-coordinate phosphorus fluorides.[33] The increases in the shifts as the corresponding ^{19}F shifts decrease are much as would be expected.[7] All the ^{31}P shifts are higher than those of the simple difluorohalogenophosphines with the consequence that those of the tellurium compounds are among the highest so far reported. The phosphorus atoms are presumably in some form of extreme environment.

The few selenium shifts that are given are difficult to interpret in view of the lack of comparable data. They could well be accounted for by electronegativity effects since, in a series of organo-selenium compounds[34] the electronegativity of substituents has been shown to cause shifts to high frequency.

1.3 Coupling Constants

The observed coupling constants for MH_3YPF_2 are given in Table 1.3 and show an increase in the magnitude of $^1J(PF)$ with increasing electronegativity of the element Y. Based on $^1J(PF)$ being negative,[35,36] the three bond coupling $^3J(PYMH)$ is found to be positive and greater in compounds with lighter elements Y and M.

TABLE 1.4

Coupling Constants for $(F_2P)_2Y$

Compound	T	$^1J(PF)$	$^3J(PF)$	$\lvert ^2J(PP) \rvert$	$\lvert ^4J(FF) \rvert$	$\lvert ^2J(FY) \rvert$
$(F_2P)_2O$	300	- 1365	+ 14	5	0	
$(F_2P)_2S$	300	- 1303	+ 28	274	8.5,2.5	
$(F_2P)_2Se$	293	- 1305	+ 21	232	8.8,2.8	39
	273	- 1300	+ 25	249	9.3,1.8	36
	253	- 1301	+ 24	264	10.0,1.5	36
	233	- 1297	+ 25	281	10.5,1.5	35
	213	- 1293	+ 26	300	11.4,0.9	35
	193	- 1299	+ 35	316	12.0,0.0	36
	173	- 1297	+ 28	336	12.5,0.0	36
$(F_2P)_2Te$	300	(1244)[a]	n.o.	n.o.	n.o.	n.o.

Note:

(i) n.o., not observed

(ii) T, absolute temperature

(iii) J, Hz

(a) $\lvert ^1J(PF) + {}^3J(PF) \rvert$

Figure 1.1

High frequency half of the ^{19}F n.m.r. spectrum of $(F_2P)_2Se$

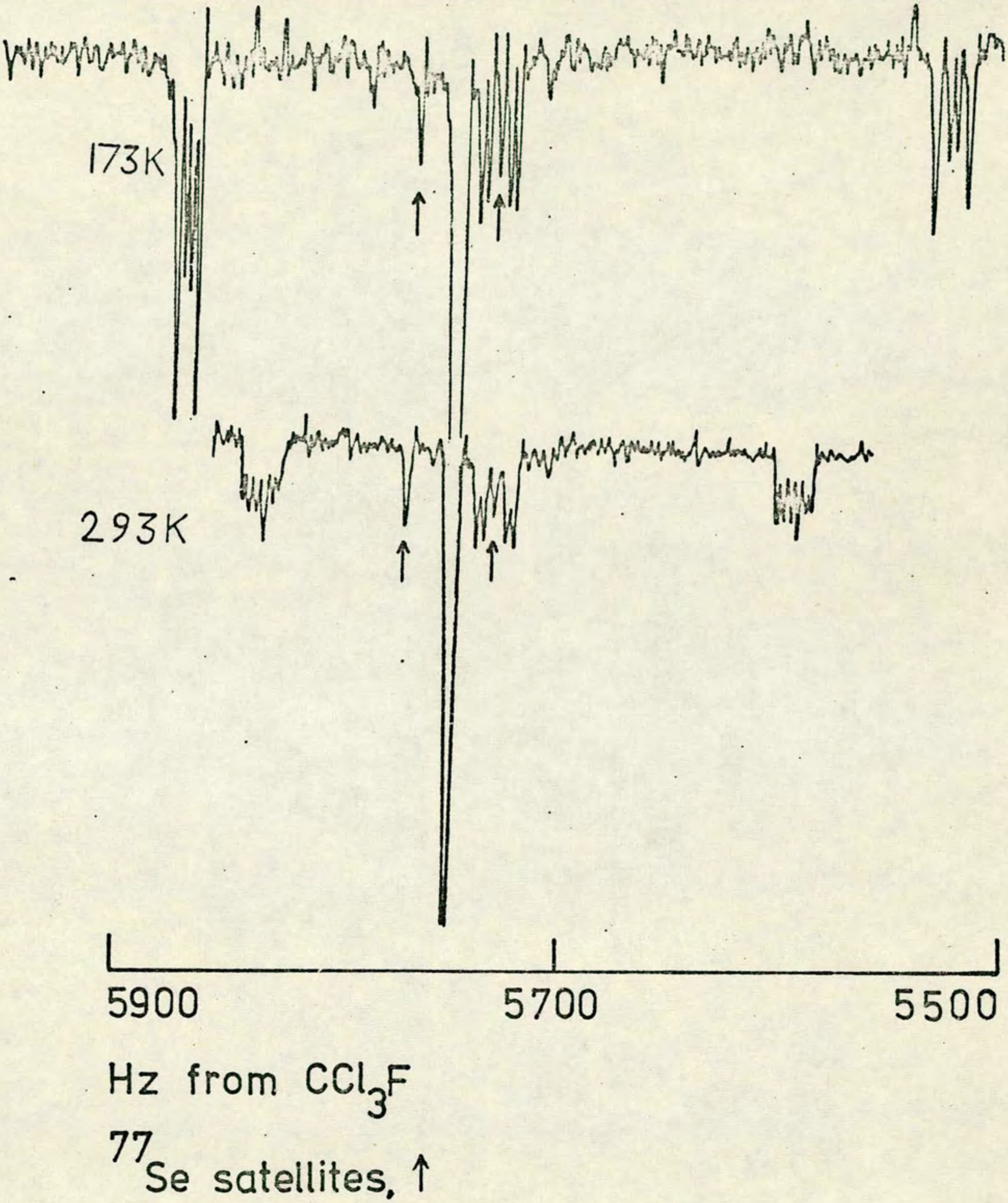


Table 1.4 shows the coupling constants for the bis(difluorophosphino) Group VI derivatives, and includes the temperature-variation of the ^{19}F spectrum of $(F_2P)_2Se$ determined at a series of temperatures covering the range 173 to 293K. While temperatures quoted may be as much as 5K in error, the relative values are correct to within 1K. The analogous behaviour of $(F_2P)_2S$ with temperature has already been described.[21]

The spectrum (Figure 1.1) of $(F_2P)_2Se$ is of second order and has been analysed, as in the case of $(F_2P)_2S$, by the method of Harris <u>et al</u>.[25] on the assumptions about the coupling constants such that: $^1J(PF)-^3J(PF) >> ^2J(PP) >> ^4J(FF)$, $^4J(FF')$. The parameters of Table 1.4 have been expressed, by least-squares fitting, as simple polynomial functions of temperatures, Table 1.5, and the results used to obtain Figure 1.2. This shows the line positions of the low-field half of the ^{19}F spectrum within, and extrapolated beyond, the temperature range studied experimentally.

Parameters found for $(F_2P)_2Se$ agree more with $(F_2P)_2S$ than with $(F_2P)_2O$,[21] where all couplings across oxygen are small by comparison with the similar ones across sulphur and selenium. Particularly, $^2J(PP)$ is only 5 Hz as opposed to over 200 Hz in the other two compounds, and no four bond fluorine-fluorine couplings are evident in $(F_2P)_2O$ whereas the other $(F_2P)_2Y$ show two such couplings which average about 6 Hz. It is these very parameters which distinguish $(F_2P)_2O$ most dramatically from the other bis-(difluorophosphino) Group VI compounds, that change most significantly with temperature.

TABLE 1.5

Temperature-Dependence of n.m.r. Parameters of $(F_2P)_2Se$

$\delta(^{19}F) = 69.05(8) - 0.009(1)\,T$ p.p.m.

$^{1}J(PF) = -1284.7\,(74) - 0.061(31)\,T$ Hz

$^{3}J(PF) = 44.2(78) - 0.077(33)\,T$ Hz

$|^{2}J(PP)| = 525.2(152) - 1.238(133)\,T + 0.00081(29)\,T^{2}$ Hz

$|^{4}J(FF)| = 4.0(7) - 0.022(3)\,T$ Hz

$|^{4}J(FF')| = 18.1(3) - 0.032(1)\,T$ Hz

$|^{2}J(SeF)| = 36(1)$ Hz

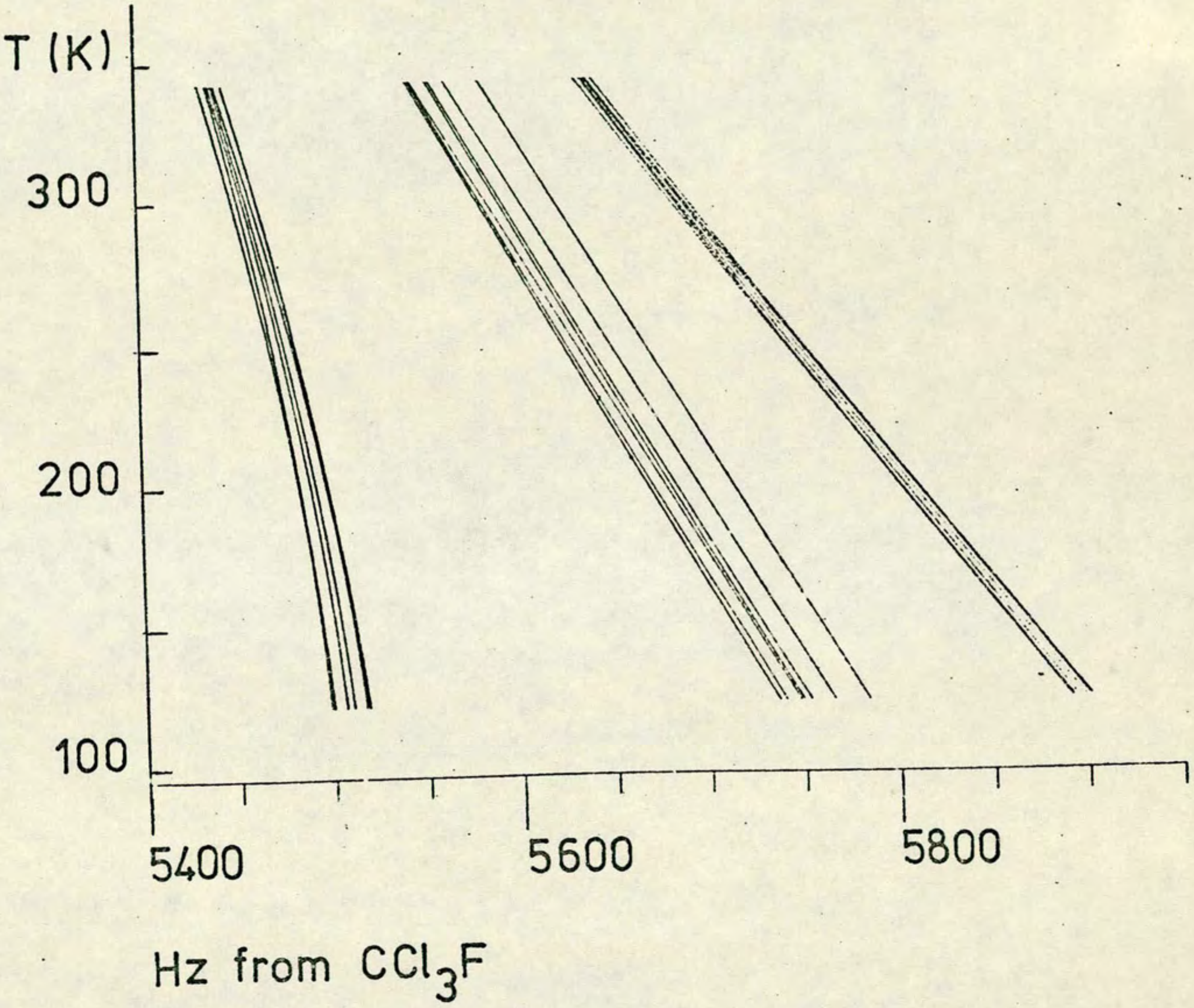
Note:

(i) Estimated standard deviations are given in parentheses.

(ii) T refers to absolute temperature.

Figure 1.2

Changes of line positions in the high frequency half of the ^{19}F spectrum of $(F_2P)_2Se$ with temperature.



It seems most probable that conformational changes are responsible. These changes could affect the long range couplings between atoms via the lone pairs of electrons present on every atom in the molecule. The wide POP angle (about 140° in the gas phase) and staggered conformation of the F_2P groups in $(F_2P)_2O$[29,37] implies fairly small interactions between lone pairs on the phosphorus atoms, and between the remote pairs of fluorine atoms. Although the phosphorus atoms would be no closer in the sulphur, selenium and tellurium compounds, the PYP angle would be narrower and a conformation that minimised long range fluorine-fluorine interactions would be adopted. Since the lone pairs on the phosphorus atoms could now come into greater direct contact, any temperature induced conformational changes would produce a larger effect on coupling constants. This interpretation although speculative, could likewise account for the variations seen in the parameters of SiH_3TePF_2 (Table 1.3).

All these species are derivatives of three co-ordinate phosphorus. However $S{=}PF_2H$[38] and $S{=}PMe_3$,[39] which are most stable in their pentavalent forms are unlike F_2PSSiH_3 and $(CF_3)_2PSH$[40] which exist exclusively with phosphorus (III) atoms. One possible way to explain the preference for the trivalent phosphorus forms is that intramolecular hydrogen bonding could stabilise the last two compounds, where four bonds separate fluorine and hydrogen atoms. An alternative explanation could involve the possibility of delocalization of the lone pair electrons of the Group VI element into the vacant d orbitals of the silicon, germanium or phosphorus atoms. For both F_2PYMH_3 and F_2PYPF_2 two such π-interactions would tend to stabilise the phosphorus (III) forms, as against the one possible phosphorus-Group VI element interaction in the corresponding phosphorus (V) derivatives.

CHAPTER 2

THE PREPARATION AND THE CHEMICAL AND SPECTROSCOPIC PROPERTIES OF BIS(DIFLUOROPHOSPHINO)-SULPHIDE AND SELENIDE, $(F_2)_2S$ and $(F_2P)_2Se$.

Introduction

The formation, on an n.m.r. tube scale, of the compounds MH_3YPF_2 and $(F_2P)_2Y$ (M = Si or Ge; Y = O, S, Se or Te) discussed in Chapter 1, prompted an interest in these compounds from the preparative point of view. Attention was concentrated on $(F_2P)_2S$ and $(F_2P)_2Se$ since $(F_2P)_2O$[18] had been successfully formed and characterised and would provide a source for comparison of the properties of bis(difluorophosphino) derivatives of the Group VI elements. It was also hoped that bis(difluorophosphino)-sulphide and -selenide might be used as starting materials, to extend the chemistry of difluorophosphines to other novel sulphur and selenium compounds.

While this work has been successful in isolating and characterising $(F_2P)_2S$ as well as $(F_2P)_2Se$, it must be noted that the former has been prepared earlier.[21] However, it has only been the subject of n.m.r. study and no details of preparation nor of its other properties have been given in the literature. For completeness, the characterisation of $(F_2P)_2S$ is included here with that of $(F_2P)_2Se$ in order to allow more fully the comparison of the series $(F_2P)_2Y$.

Results and Discussion

2.1. Preparations

The details of the various preparations described below are given in the Experimental Section, Chapter 9.

While the exchange reactions of Chapter 1 did produce $(F_2P)_2S$ and $(F_2P)_2Se$, these were slow and incomplete under the conditions used and alternative methods of preparation were sought.

Since $(F_2P)_2O$ had been formed from Cu_2O and PF_2I,[18] a reaction involving sodium selenide and PF_2Cl was tried. This however was unsuccessful, as was the attempted dehydrofluorination of a mixture of H_2Se and PF_3, with KF.

Subsequent attempts to produce $(F_2P)_2Se$ involved H_2Se and various F_2P compounds. In the formation of F_2PSCH_3,[23] trimethylamine had been used to abstract hydrogen chloride from PF_2Cl and methyl thiol. In a manner similar to this, Me_3N was reacted with a mixture of H_2Se and PF_2Br. Instead of the trimethylammonium halide of the former preparation, trimethylammonium selenide was formed and no $(F_2P)_2Se$ was produced. Despite certain similarities in the behaviour of silyl and difluorophosphine groups, and the known reaction of dimethylaminosilane with H_2Se,[41] Equation (1), no reaction took place between aminodifluorophosphine or dimethylaminodifluorophosphine and hydrogen selenide.

$$H_3SiN(CH_3)_2 + H_2Se \rightarrow [H_3SiSe][H_2N(CH_3)_2] \xrightarrow{SiH_3Br} (H_3Si)_2Se + [(CH_3)_2NH_2]Br \;\ldots\ldots\ldots\ldots (1)$$

Furthermore when $(F_2P)_3N$ and H_2Se reacted, Equation (2), they produced $(F_2P)_2NH$ and $Se{=}PF_2H$ only, unlike the analogous reaction involving $(H_3Si)_3N$,[41] Equation (3).

$$(F_2P)_3N + H_2Se \rightarrow (F_2P)_2NH + Se{=}PF_2H \quad \ldots\ldots\ldots\ldots\ldots(2)$$

$$(H_3Si)_3N + 2H_2Se \rightarrow (H_3Si)_2Se + [NH_4][SeSiH_3] \quad \ldots\ldots(3)$$

Since none of these routes gave the desired products, the exchange reactions were tried on a preparative scale. While little or no reaction occurred in the vapour phase, condensed samples of PF_2X(X=Cl or Br) with $(H_3Si)_2Se$, and PF_2Br with $(H_3Si)_2S$, gave essentially pure $(F_2P)_2Se$ and $(F_2P)_2S$:-

$$(H_3Si)_2Y + PF_2X \rightarrow F_2PYSiH_3 + H_3SiX \quad \ldots\ldots\ldots\ldots\ldots(4)$$

$$F_2PYSiH_3 + PF_2X \rightarrow (F_2P)_2Y + H_3SiX \quad \ldots\ldots\ldots\ldots\ldots\ldots(5)$$

However, in both preparations small amounts of $Se{=}PF_2H$ or $S{=}PF_2H$ arose from reactions of $(F_2P)_2Y$ with impurities in the starting materials. These impurities were predominantly hydrogen halide, used in the preparation of difluorohalogenophosphine, and hydrogen sulphide or selenide, from the formation of disilyl sulphide or selenide. Traces of moisture also gave rise to $Y{=}PF_2H$.

Both preparations were slow, taking several hours and required the silyl halide/difluorohalogenophosphine mixture to be replaced by pure difluorohalogenophosphine several times to achieve complete reaction. Also since SiH_3F and orange solid were formed by thermal decomposition of the F_2PYSiH_3 intermediate [Equation (6)], temperatures were

TABLE 2.1.

Mass Spectrum of $(F_2P)_2S$

m/e	Relative Abundance	Assignments
172	2	$[(F_2P)_2{}^{34}S]^+$
170	35	$[(F_2P)_2{}^{32}S]^+$
101	9	$[F_2P^{32}S]^+$
88	6	$[F_3P]^+$
84	4	$[FP^{34}S]^+$
82	100	$[FP^{32}S]^+$
69	100	$[F_2P]^+$
63	12	$[P^{32}S]^+$
50	7	$[FP]^+$
32	2	$^{32}S^+$
31	1	P^+

Metastable peak:

39.5 (very strong) $[(F_2P)_2{}^{32}S]^+ \longrightarrow PF_3 + [FP^{32}S]^+$

Impurities

m/e	Relative Abundance	Assignments
186	1	$[(O)PF_2SPF_2]^+$
154	2	$[(F_2P)_2O]^+$
150) 148)	4	$[F_2PBr]^+$
104	2	$[F_3PO]^+$
86	2	$[O{=}PF_2H]^+$
18	6	$[H_2O]^+$

Note:

Ionizing voltage 70 eV.

TABLE 2.2

Mass Spectrum of $(F_2P)_2Se$

m/e	Relative Abundance	Assignments
220-214	69	$[(F_2P)_2Se]^+$
151-145	28	$[F_2PSe]^+$
132-126	64	$[FPSe]^+$
113-107	20	$[PSe]^+$
88	7	$[F_3P]^+$
82-76	35	Se^+
69	100	$[F_2P]^+$
50	12	$[FP]^+$
31	2	P^+

Metastable peaks

$$\left.\begin{array}{l} 77.6\ (^{80}Se) \\ 75.9\ (^{78}Se) \end{array}\right\}\ \text{(strong)}\ [(F_2P)_2Se]^+ \longrightarrow PF_3 + [FPSe]^+$$

Impurities

236-230	2	$[(O)PF_2SePF_2]^+$
154	5	$[(F_2P)_2O]^+$
152-146	90	$[Se{=}PF_2H]^+$
86	11	$[O{=}PF_2H]^+$
18	5	$[H_2O]^+$

Note:

Ionizing voltage 70 eV.

maintained at 209K for the selenium system and 273K for the sulphur one.

$$F_2PYSiH_3 \longrightarrow H_3SiF + \frac{1}{n} \leftarrow FP\text{-}Y \rightarrow_n \text{ ....(6)}$$

2.2. Molecular Weights

The molecular weights of samples of $(F_2P)_2S$ and $(F_2P)_2Se$ were determined as 169 ± 3 g mol^{-1} (Calculated 170 g mol^{-1}), and 212 ± 4 g mol^{-1} (Calculated 217 g mol^{-1}) respectively.

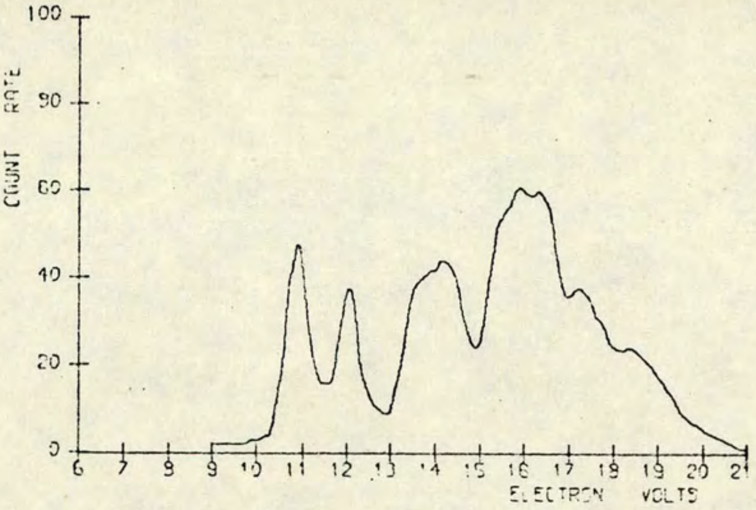
2.3. Mass Spectra

Tables 2.1 and 2.2 contain the mass spectral breakdown pattern for $(F_2P)_2S$ and $(F_2P)_2Se$ respectively. The spectra also contain impurities that have arisen from either starting materials, as in the case of PF_2Br, or from reaction of the difluorophosphine Group VI derivatives with the large amount of moisture in the mass spectrometer. In the latter case these hydrolysis products comprise either $S{=}PF_2H$ and $(O)F_2PSPF_2$, or $Se{=}PF_2H$ and $(O)F_2PSePF_2$, as well as $O{=}PF_2H$ and $(F_2P)_2O$. The presence in both spectra of $Y{=}PF_2H$ makes the breakdown routes difficult to determine. To clarify this several mass spectra of the $(F_2P)_2S$ system were taken with varying amounts of $(F_2P)_2S$ and $S{=}PF_2H$. Since $[S{=}PF_2H]^+$ was known[38] to lose H to $[PF_2S]^+$, it was essential to determine if $[PF_2S]^+$ was also arising from $[(F_2P)_2S]^+$. The results indicated that fragmentation did occur as in Equation (7).

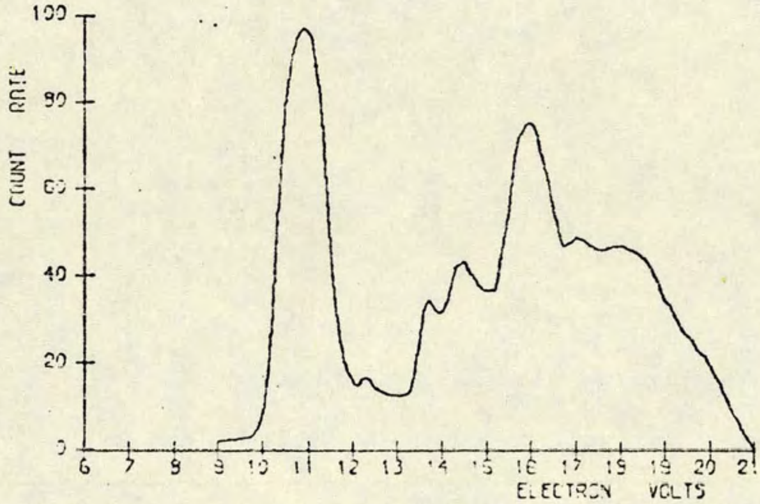
$$[(F_2P)_2S]^+ \longrightarrow PF_2 + [PF_2S]^+ \text{ ....(7)}$$

Figure 2.1

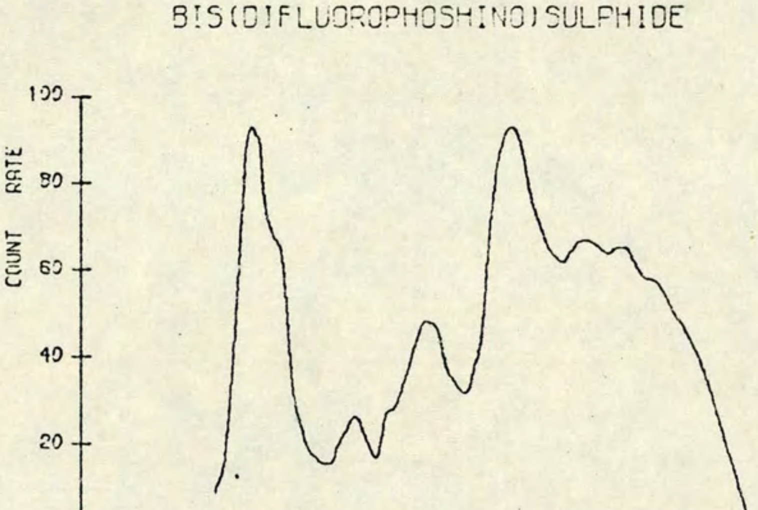
Photoelectron spectra of $(F_2P)_2O$, $(F_2P)_2S$ and $(F_2P)_2Se$.



BIS(DIFLUOROPHOSPHINO)OXIDE



BIS(DIFLUOROPHOSHINO)SULPHIDE



BIS(DIFLUOROPHOSPHINO)SELENIDE

TABLE 2.3

Photoelectron Spectra of $(F_2P)_2Y$

$(F_2P)_2O^{(a)}$	$(F_2P)_2S$	$(F_2P)_2Se$	Assignments
$11.2^{(b)}$	10.8	10.2	Y lone pair
$12.4^{(b)}$	10.8	10.7	P lone pairs
11.2) 14.2)	14.5	14.1	P-Y bonding
~ 16.5	16.0	15.9	F lone pairs
17 - 19	17 - 18.5	17 - 18.5	P-F bonding

Note:

All vertical ionization potentials in eV: errors ± 0.1 eV.

(a) Reference 42

(b) See text.

The other main breakdown, which was characterised by a strong metastable peak at 39.5 m/e units, involved the loss of PF_3.

$[(F_2P)_2S]^+ \longrightarrow PF_3 + [PFS]^+$ ....(8)

Both these routes, namely loss of PF_2 and PF_3, also occurred in $(F_2P)_2Se$ but with the latter giving two metastable peaks due to the principal isotopes of selenium, ^{80}Se and ^{78}Se. The lower m/e unit ions were generated by loss of F or P from $[PF_2Y]^+$ or $[PFY]^+$.

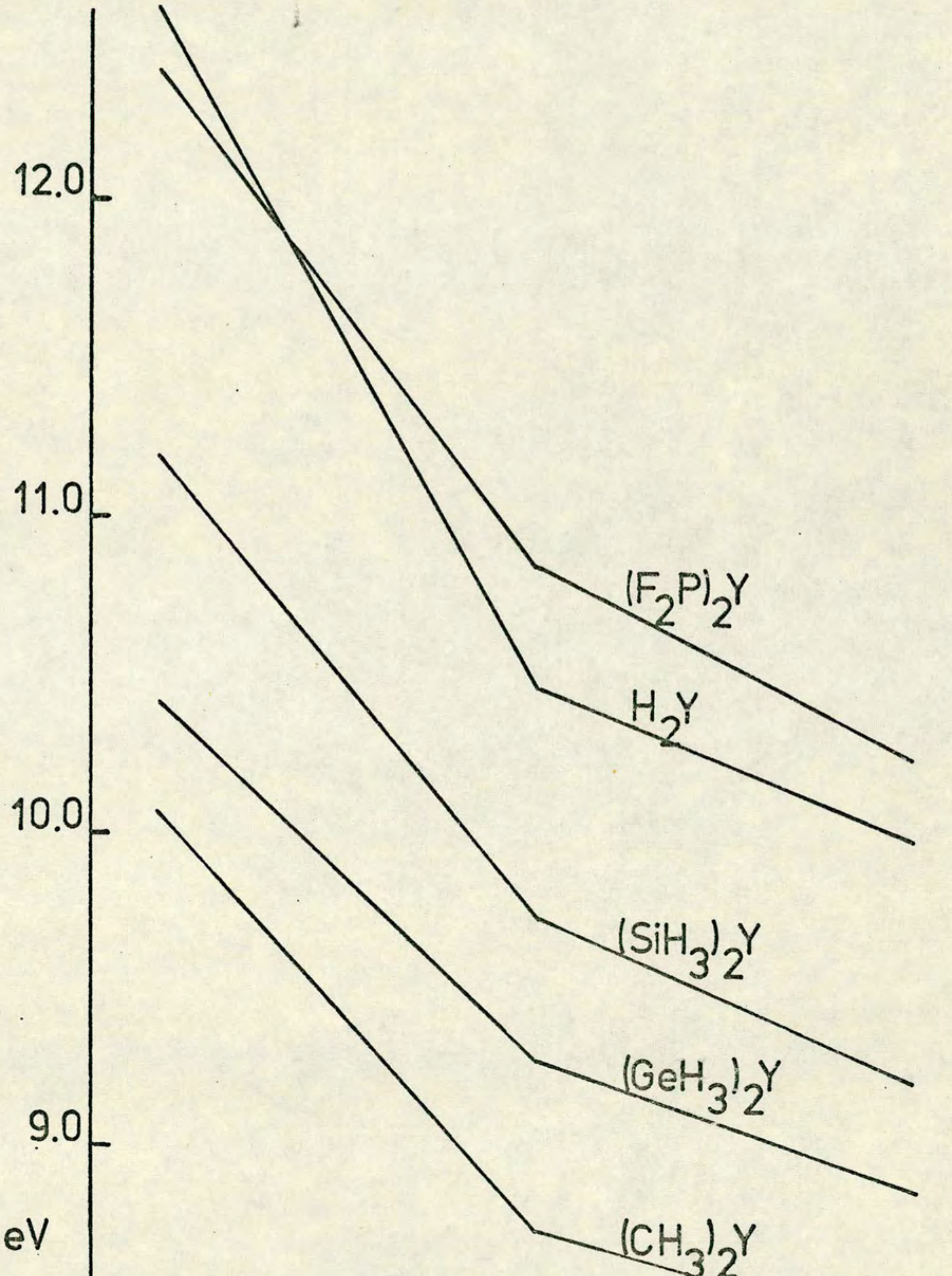
Thus the pattern seems to be dominated by facile P-Y bond cleavage, with the formation of PF_3 being particularly favoured, no ions such as $[F_2PYPF]^+$, $[F_2PYP]^+$ or $[PYP]^+$ being formed. In this respect $(F_2P)_2O$[18] differs from these other Group VI derivatives in forming $[F_2POPF]^+$.

2.4. Photoelectron Spectra

The photoelectron spectra of $(F_2P)_2Y$, including $(F_2P)_2O$[42] are depicted in Figure 2.1. and listed, with possible assignments in Table 2.3. The spectra of $(F_2P)_2S$ and $(F_2P)_2Se$ contain minute amounts of PF_3[42] and $S{=}PF_2H$ or $Se{=}PF_2H$[43] as impurities, the bands of which are very weak in the figures.

In the case of $(F_2P)_2O$, the band at 12.4 eV has been assigned previously[42] to the P 3p lone pair levels with 11.2 eV as the O 2p lone pair, perhaps with one P-O bonding level coincident. An alternative assignment is mentioned however, that due to the greater intensity of the 11.2 eV band, this could correspond to the two P lone pairs with

Figure 2.2. Group VI element lone pair ionisation potentials in some A_2Y compounds.



the one lone pair on oxygen at 12.4 eV. This latter interpretation would seem more plausible when compared to the $(F_2P)_2S$ and $(F_2P)_2Se$ spectra.

In $(F_2P)_2S$, only one intense broad band occurs below 14 eV and this must correspond to both phosphorus and sulphur lone pair levels. For $(F_2P)_2Se$, the broad bands near 10.5 eV again would seem to contain the phosphorus and the selenium lone pairs. Of these, the lower band at 10.2 eV is more intense and by analogy with $(F_2P)_2O$ could correspond to the two occupied phosphorus lone pair orbitals, leaving 10.7 eV to be the Se lone pair level. However, the presence of a band from residual $Se{=}PF_2H$ under this region may be giving more intensity to the 10.2 eV band. Furthermore, when other series of Group VI derivatives are considered the trend indicates 10.2 eV as the best fit for the Se level in $(F_2P)_2Se$. The Y lone pair levels of the H_2Y[44] and $(MH_3)_2Y$[45] (Y=O, S or Se; M=C, Si or Ge) group of compounds are depicted in Figure 2.2 alongside those of $(F_2P)_2Y$. On these grounds the P lone pairs are assigned as 10.7 eV with the Se lone pair at 10.2 eV.

For a molecule of the type $(F_2P)_2Y$ with C_{2v} symmetry the P lone pairs and the Y lone pair would have bands of a_1, b_1 and b_2 symmetry for which overlap would be possible. But although $(F_2P)_2S$ and $(F_2P)_2Se$ are assumed to tend to C_{2v}, $(F_2P)_2O$ does not have this symmetry,[29] and these assignments must therefore remain extremely tentative.

Of the remaining bands, those at 14.5 eV and 14.1 eV may correspond to the two P-S and two P-Se bonding levels.

TABLE 2.4

Vibrational Spectra of $(F_2P)_2S$

Infra red			Raman		
Gas	Solid	Matrix(a)	Liquid	Solid	Assignments
			855 w,br p	860 mw	ν (PF)
			835 w,br ? p	844 m	
840 vs,br	810 vs,br		820 w,br ? dp	814 m	
				791 m	
	618 m		631 w,p	621 w	
579 m	570 m		580 s,p	571 s	ν_s (PSP)
				558 s	δ (PF_2)
	524 w		515 m,p		
	514 w				
	507 w				
498 m			490 vw, ? dp		
	462 w			454 m	
447 ms	436 s	444 m	444 m,dp	434 m	ν_a (PSP)
407 w		407 m	408 s,p	402 m	ω (PF_2)
401 w					
	376 m	380 m			
319 m	318 m	322 m	318 vw, ? dp	319 w	ρ (PF_2)
				253 m	
			237 s,p	234 s	δ (PSP)
		130 w	125 s,dp	133 s	τ (PF_2)

Note:
(a) Not studied above 500 cm^{-1}.

s = strong, m = medium, w = weak, br = broad,
v = very, p = polarised, dp = depolarised

TABLE 2.5

Vibrational Spectra of $(F_2P)_2Se$

Infra red			Raman		
Gas	Solid	Matrix[a]	Liquid	Solid	Assignments
850 vs,br			845 vw, ? p	840 w	ν (PF)
833 sh			820 vw, dp	810 w	
	800 vs,br				
599 m	612 w		580 vw, ? p		
486 m	518 s		515 vvw, ? p		δ (PF_2)
			482 m, p	476 s	
443 m	433 ms	443 m	445 vw, dp		ν_s (PSeP)
			428 m, p		
	405 m	402 m			ω (PF_2)
	399 m		393 m, p	395 m	
368 ms,br		365 m	365 m,dp	355 s	ν_a (PSeP)
		321 m			
		292 m			
		274 m	255 w, dp	256 m	ρ (PF_2)
			215 s, p	215 s	δ (PSeP)
			95 m, dp		τ (PF_2)

Note:
(a) Not recorded above 500 cm^{-1}.

s = strong, m = medium, w = weak, br = broad,
v = very, p = polarised, dp = depolarised.

TABLE 2.6.

Vibrational modes of $(F_2P)_2Y$, with C_{2V} symmetry

	a_1	a_2	b_1	b_2
P-F stretch	/	/	/	/
P-Y stretch	/			/
PF_2 scissors	/			/
PF_2 rock		/	/	
PF_2 wag	/			/
PF_2 torsion		/	/	
PYP bend	/			

The F lone pairs and P-F bonding orbitals are at typical values.[42]

2.5. Vibrational Spectra

These are given in Tables 2.4 for $(F_2P)_2S$ and 2.5. for $(F_2P)_2Se$ and comprise the gas, solid and matrix isolated solid infra red spectra, and the solid and liquid Raman spectra. The matrix material for the infra red spectra, recorded at 8K, was argon, in which the compounds were diluted by volume approximately 800 to 1.

The vibrational spectra are very difficult to assign, since all bands are of fairly low frequency, and although the molecular symmetry is unknown there is likely to be extensive coupling of modes, the concept of group frequencies not being particularly helpful in this case. Although it is the conformation of the fluorine atoms that determines the overall molecular symmetry, initial results from an electron diffraction study of the structure of $(F_2P)_2Se$ indicate that the structure could be considered in terms of C_{2V} symmetry with some torsional distortion. On the basis that the structure does tend to C_{2V} symmetry the vibrational modes have been determined, Table 2.6, and the assignments of Tables 2.4 and 2.5 given.

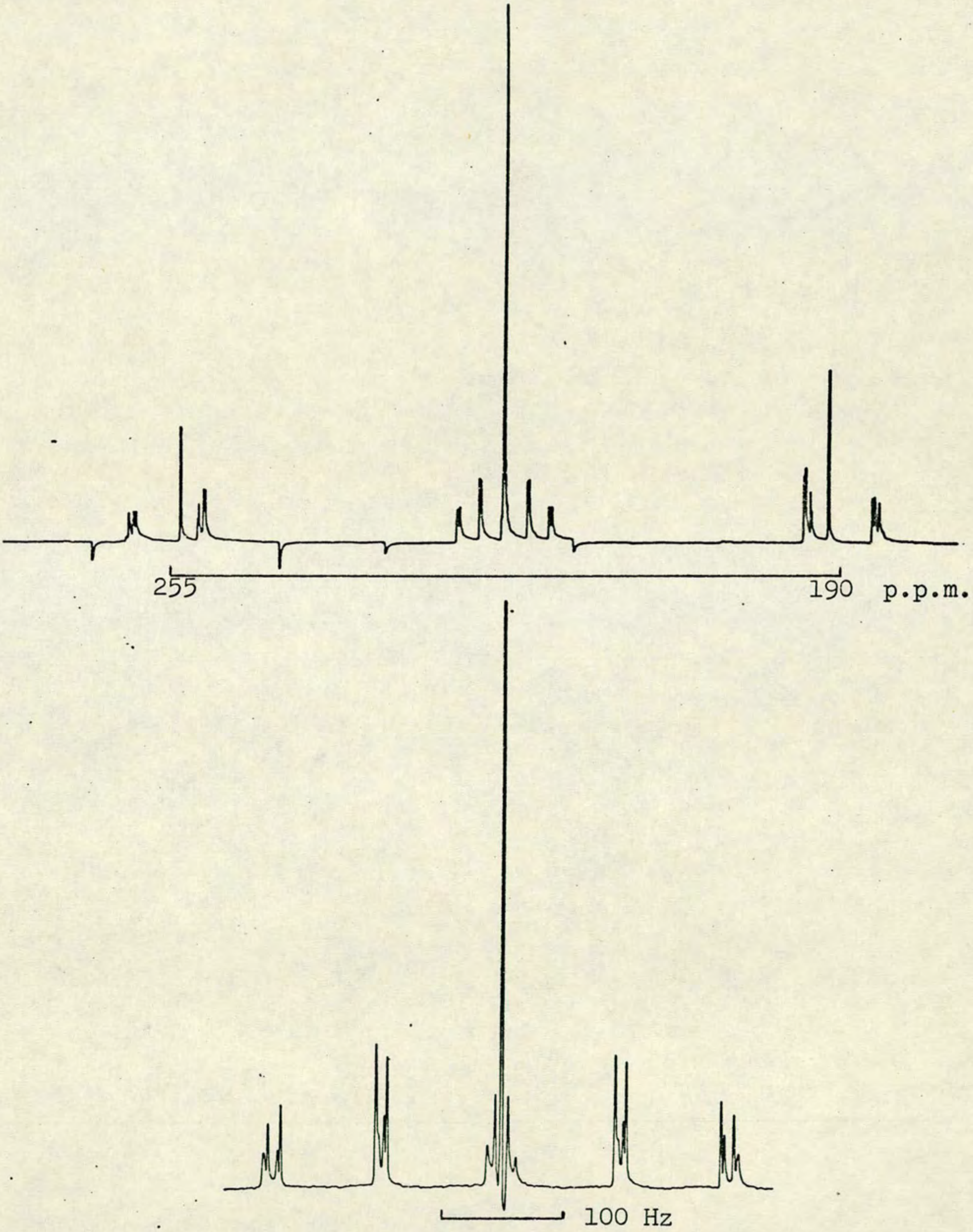
In both compounds PF stretching frequencies occur around 840 cm^{-1}. The next strongest bands in the infra red spectra of both molecules are at 447 cm^{-1} and 368 cm^{-1} and both are of medium intensity and depolarised in the liquid Raman. Thus these are assigned to the asymmetric

PSP and PSeP skeletal stretches. Bands at 125 cm^{-1} and 95 cm^{-1} in the Raman spectra could be torsional modes, whilst those at 237 cm^{-1} and 215 cm^{-1} and polarised, are probably the a_1 skeletal bends of $(F_2P)_2S$ and $(F_2P)_2Se$ respectively. Of the remaining a_1 bands, scissors and wags of the PF_2 groups are expected[46] around 500 cm^{-1} and 400 cm^{-1}. The polarised bands at 515 cm^{-1} and 408 cm^{-1}, for sulphur, and 482 cm^{-1} and 393 cm^{-1}, for selenium, are correspondingly assigned to these modes, with their analogous b_2 type vibrations being of similar energy. The skeletal PYP symmetric stretch, which could well couple strongly with any of the other a_1 modes, must be assigned to the remaining polarised band. This produces an assignment of 580 cm^{-1} in $(F_2P)_2S$ and 428 cm^{-1} in $(F_2P)_2Se$.

Comparison of the PYP skeletal stretches with the analogous stretches in other compounds containing Group VI elements is not unfavourable. The averages of the symmetric and asymmetric stretches for $(F_2P)_2S$ (512 cm^{-1}) and $(F_2P)_2Se$ (396 cm^{-1}) are in reasonable agreement not only with $(H_3Si)_2S$ (500 cm^{-1}) and $(H_3Si)_2Se$ (388 cm^{-1}),[47] but also with $[(CF_3)_2P]_2S$ (519 cm^{-1}) and $[(CF_3)_2P]_2Se$ (445 cm^{-1}).[48] These values also lie close to the observed ranges of stretching frequencies in a series of trico-ordinate phosphorus compounds containing the P-S-(C) linkage, given as 553 - 564 cm^{-1} and 440 - 492 cm^{-1}, and to the value of 350 cm^{-1}, predicted for the P-Se-(C) linkage.[49]

Figure 2.3.

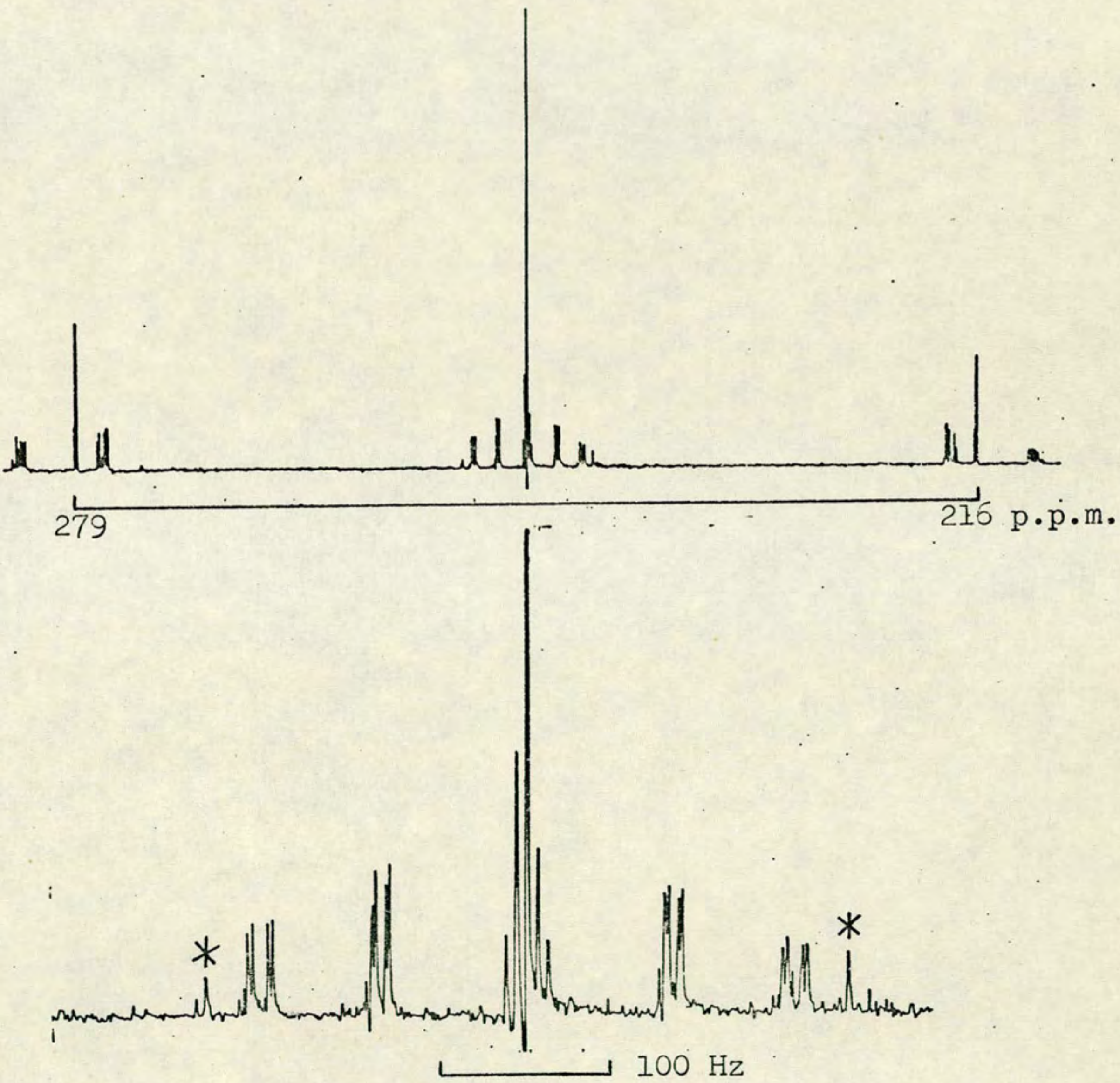
^{31}P n.m.r. spectrum of $(F_2P)_2S$



Detail of central section of spectrum.

Figure 2.4

^{31}P n.m.r. spectrum of $(F_2P)_2Se$



Detail of central section of spectrum
* = ^{77}Se satellites.

2.6. Nuclear Magnetic Resonance Spectra

The n.m.r. parameters of $(F_2P)_2S$ and $(F_2P)_2Se$ have been discussed previously in Chapter 1 and the ^{31}P spectra of these compounds are presented in Figures 2.3 and 2.4. For $(F_2P)_2Se$, one further coupling constant is given here, $^1J(^{31}P^{77}Se) = \pm 365$ Hz. This value is larger than that in Me_2PSeMe,[50] - 205 Hz, but comparable with four co-ordinate organo-phosphorus compounds containing P-Se single bonds such as $Me_2P(S)SeMe$[50] and $(C_6H_5)(t\text{-}C_4H_9)P(Se)SeMe$[51] which have $^1J(PSe)$ coupling constants of -341 Hz and ±358 Hz. respectively. The presence of the electronegative fluorines in $(F_2P)_2Se$ seems to have a similar effect in increasing the magnitude of the selenium-phosphorus coupling constant, when compared with Me_2PSeMe, to that observed for $Se = PF_2H$[52] and $Se = PPh_2H$,[53] which have $^1J(PSe)$ of -1046 Hz and -740 Hz. Consideration of P_4Se_3,[54] where the three basal phosphorus atoms have $^1J(PSe)$ of ±536 Hz compared with the value of ±263 Hz for the same coupling to the apical phosphorus, emphasises the extreme sensitivity of this coupling to substituents at both elements.

Reactions

Of the many reactions that could have been tried, only a few were attempted in an effort to gauge the scope of $(F_2P)_2S$ and $(F_2P)_2Se$ as reagents. Most of these were concentrated towards the behaviour of $(F_2P)_2Se$ to P-Se bond cleavage, none of its possible reactions as a Lewis base, such as transition metal co-ordination complex and adduct formation, being investigated.

2.7. Reaction of $(F_2P)_2S$ with $HPMe_2$

The one reaction that was undertaken with $(F_2P)_2S$ was done in an n.m.r. tube with an equimolar amount of $HPMe_2$ and the products were identified by their n.m.r. parameters. No $(F_2P)_2S$ remained, but some $HPMe_2$ ($\delta(^{31}P)$ = -99.1 p.p.m.) was left after about 30 mins at room temperature, at which time the solution was yellow with a yellow precipitate also present.

In the ^1H spectrum the principal products were identified as $S{=}PHMe_2$[55] and $Me_2P(S)PMe_2$,[56] but with $S{=}PF_2H$[52] also present, and some smaller unassigned peaks in the methylphosphine region at ca. 2δ. These compounds were observed and confirmed in the ^{31}P spectrum by their characteristic phosphorus chemical shifts. In addition, PF_3 accounted for most of the F_2P units present, and so all but one very minor product could be assigned in terms of known compounds.

This remaining one created somewhat more difficulty with two regions in the ^{31}P spectrum, +130.8 and -39.9 p.p.m., which seemed to go together since a doublet splitting of 342 Hz was present in both. At the higher frequency half of the spectrum, a triplet coupling of 1260 Hz indicated that two fluorines were bonded to this phosphorus, which at 130 p.p.m. seemed to come in the trico-ordinate F_2P- chemical shift range. These two fluorines also produced a triplet splitting of 23 Hz in the -39.9 p.p.m. part of the spectrum. In both regions there appeared to be proton coupling from CH_3-groups, which could be removed by proton noise decoupling, but the weakness of the sample and poor resolution prevented any proton couplings being measured.

Of the possible formulations for this compound, F_2PPMe_2, though agreeing with the Me_2P- $\delta(^{31}P)$ region at -40 p.p.m. does not fit for the difluorophosphine $\delta(^{31}P)$ which in PF_2H and F_2PPH_2[13] comes at +224 and +294 p.p.m. Compounds containing $(S)PMe_2$- units tend to give higher $\delta(^{31}P)$ than the -40 p.p.m. required here, e.g. $(S)PMe_2SeMe$,[50] +41.0 p.p.m., and $S{=}PMe_3$,[57] +30.9 p.p.m. Since $(S)PF_2X$ compounds give high phosphorus chemical shifts, (e.g. X=H,[54] $SSnClMe_2$,[58] $SSiMe_3$;[58] $\delta(^{31}P)$=62, 98 and 88 p.p.m.) $(S)PF_2PMe_2$ produces the best approximation to the parameters, therefore, with P^{III}-P^{V} bonding giving the high $^1J(PP)$ of 342 Hz, but which assumes a phosphorus chemical shift for the $(S)PF_2$- unit of 131 p.p.m. Obviously further information is needed to identify this particular compound.

From the diversity of products it seems that several reactions are taking place involving not only the initial reagents, but also products formed. The reaction is certainly more complicated than expected, viz. simple P-S bond cleavage to give $S{=}PF_2H$ and F_2PPMe_2, since neither of these were found. Extension to H_2PMe and PMe_3 may be of interest for both $(F_2P)_2S$ and $(F_2P)_2Se$.

Reactions of $(F_2P)_2Se$

2.8. Reaction of $(F_2P)_2Se$ with HX(X = Cl, Br, and CN)

With hydrogen halides, $(F_2P)_2Se$ gave quantitative yields according to Equation (9);

$$F_2PSePF_2 + HX \longrightarrow PF_2X + Se{=}PF_2H \text{ .... } (9)$$

This is in agreement with the behaviour of HBr towards $(F_2P)_2O$[19] where it was postulated P-O bond cleavage was followed by rapid rearrangement of F_2POH to the more stable $O{=}PF_2H$, but contrasts with the trifluoromethyl analogues where reaction simply gives $(CF_3)_2PX$ and $(CF_3)_2PYH$ (Y=O,[59] S[60] or Se[61]). The fluoro- and trifluoromethyl-compounds, $X_2P(S)SPX_2$,[62] undergo a similar P^{III}-S bond cleavage but the thiol moiety so formed cannot rearrange.

$$(S)PX_2SPX_2 + HCl \longrightarrow (S)X_2PSH + PX_2Cl \text{ ....} (10)$$

$$(X = F \text{ or } CF_3)$$

No reaction took place between $(F_2P)_2Se$ and HCN.

2.9. Reaction of $(F_2P)_2Se$ with ZH_3 (Z = N, P or AS)

While it was hoped that successive reactions of the type in Equations (11), (12) and (13) would occur, only ammonia reacted to give a small amount of F_2PNH_2. With PH_3 and AsH_3 even after 50 hours at room temperature no products were observed. As expected there was no reaction between F_2PNH_2 and $(F_2P)_2Se$.

$$(F_2P)_2Se + ZH_3 \longrightarrow F_2PZH_2 + Se{=}PF_2H \text{ ....} (11)$$

$$(F_2P)_2Se + F_2PZH_2 \not\longrightarrow (F_2P)_2ZH + Se{=}PF_2H \text{ ....} (12)$$

$$(F_2P)_2Se + (F_2P)_2ZH \not\longrightarrow (F_2P)_3Z + Se{=}PF_2H \text{ ......} (13)$$

$$(Z = N \text{ only})$$

Presumably the hydrides were not acidic enough, nor the formation of $Se{=}PF_2H$ a strong enough driving force, to allow reaction.

2.10. Reaction of $(F_2P)_2Se$ with H_2Y (Y = O, S, Se or Te)

By analogy with the hydrogen halides, reaction was expected to proceed by Equation (14)

$$(F_2P)_2Se + H_2Y \longrightarrow Se{=}PF_2H + Y{=}PF_2H \quad \text{...........(14)}$$

All H_2Y reacted to give $Se{=}PF_2H$, but with H_2O and H_2Te further reactions prevented the observation of $O{=}PF_2H$ and $Te{=}PF_2H$. In the former case the ^{31}P spectrum indicated PF_3, and a compound with a doublet, $^1J(PH)$ of ca. 780 Hz, but the signals were broad and ill-resolved. The ^1H spectrum showed no coupling of this magnitude but four broad peaks centred at 9.43 δ with couplings of ca. 80 Hz. Thus decomposition or further reaction occurred while the observations were being made. It has been reported by Centofanti *et al.*[65] and Charlton *et al.*[38] that decomposition follows the path:-

$$2\ O{=}PF_2H \longrightarrow PF_3 + FPO_2H_2 \quad \text{..................(15)}$$

and that further reaction can produce $O{=}PH(OH)_2$.

Since previous attempts to form $Te{=}PF_2H$[63] had resulted only in PH_3 and Te, a reaction between H_2Te and $(F_2P)_2Se$ was attempted at reduced temperature. No reaction occurred on warming from 200K to 273K; above this, rapid deposition of black metallic tellurium took place and $Se{=}PF_2H$, PH_3 and PF_5 were identified. No $(F_2P)_2Se$ remained. The presence of PF_5 indicates that reaction other than reduction of $Te{=}PF_2H$ is taking place, perhaps involving HF attack on $Se{=}PF_2H$ or $(F_2P)_2Se$.

For the H_2S and H_2Se systems reaction was slow, going to completion only after about one hour at ambient temperatures.

Since these reactions might involve the formation of intermediates of the type F_2PYH, a low temperature n.m.r. study was tried using H_2Se and $(F_2P)_2Se$. No evidence for the existence of F_2PSeH was found, rearrangement, if it is such, being rapid even at 200K.

2.11. Reaction of $(F_2P)_2Se$ with CH_3YH (Y = O or S)

From the behaviour of HX and H_2Y, reaction could be expected to give $Se{=}PF_2H$ and F_2PYCH_3. And since F_2POCH_3[4] and $O{=}PF_2(CH_3)$,[64] and also F_2PSCH_3[23] and $S{=}PF_2(CH_3)$[65] are known to be stable to interconversion, if formed, F_2POCH_3 and F_2PSCH_3 should not rearrange. In fact both reactions do follow Equation (16), rapidly in the case of methanol, with no $(F_2P)_2Se$ left after only a few minutes, but more slowly with CH_3SH, reagents still remaining after an hour at room temperature.

$$(F_2P)_2Se + HYCH_3 \longrightarrow Se{=}PF_2H + F_2PYCH_3 \quad \ldots\ldots.(16)$$
$$(Y = O \text{ or } S)$$

In addition to the major products both reactions contained a trace of $F_2POC_2H_5$,[65] from ethanol (an impurity in the $CHCl_3$ n.m.r. lock) reacting with $(F_2P)_2Se$. Extension to other alkyl- or aryl-alcohols may therefore provide a general route to F_2POR (and use of RSeH to the novel $RSePF_2$ group of compounds). Also observed in the ^{31}P spectrum of the methanol system was a minor product consisting of a doublet of doublets of quartets whose chemical shift and coupling constants appeared to fit the formulation, $Se{=}PFH(CH_3)$. How this could have arisen is unknown.

TABLE 2.7

N.m.r. parameters of the $(F_2P)_2Se/CH_3YH$ reaction products$^{(a)}$

Reactants	Products	δ(H)	$\delta(CH_3)$	δ(P)	$^1J(PF)$	$^1J(PH)$	$^2J(HF)$	$^2J(PH)$	$^3J(PH)$	$^3J(HH)$	$^4J(FH)$
1. $(F_2P)_2Se$	F_2POCH_3	-	3.88	112.4	1290	-	-	-	8.3	-	0.0
+ CH_3OH	$Se = PF_2H$	8.85	-	78.1	1193	705	91	-	-	-	-
	$Se = PFH(CH_3)^{(b)}$	n.o.	n.o.	80.5	1135	675	n.o.	15.0	-	n.o.	-
2. $(F_2P)_2Se$	F_2PSCH_3	-	2.49	237.1	-1290	-	-	-	+7.4	-	+2.0
+ CH_3SH	$Se = PF_2H$	n.o.	-	78.9	1219	721	91	-	-	-	-
	$F_2POC_2H_5^{(b)}$	n.o.	n.o.	114.3	1315	-	-	-	7.5	-	n.o.

(a) See Experimental section for chemical shift conventions

(b) See text.

n.o.; not observed.

The various n.m.r. parameters of the reaction products are given in Table 2.7, with the relative signs of coupling constants of F_2PSCH_3 (related to $^1J(PF)$ which was assumed negative[35,36]) determined by spin-tickling experiments, $^1H-[^{19}F]$ and $^1H-[^{31}P]$. The details are given in the Experimental section. Signs could not be related in F_2POCH_3, $^4J(FH)$ being zero.

The MH_3SPF_2 system (M=Si or Ge) has slightly larger $^3J(PH)$ and $^4J(FH)$ than the corresponding methyl analogue, and it is interesting to speculate whether F_2PSCH_3 will exhibit temperature dependent behaviour similar to that seen in $F_2PTeSiH_3$ (cf. Table 1.3).

The formation of F_2POCH_3 and F_2PSCH_3 has an obvious parallel with the reaction of CH_3OH or CH_3SH with $(S)PF_2SPF_2$[22] which also involved cleavage of the $P^{III}-S$ bond, but in which none of the expected F_2PYCH_3 was detected.

$$(S)PF_2SPF_2 + HYCH_3 \longrightarrow (S)PF_2SH + [F_2PYCH_3] \quad ....(17)$$
$$(Y = O \text{ or } S)$$

2.12. Reactions of $(F_2P)_2Se$ with $HM(CO)_5$ (M = Mn or Re)

The products of these reactions, identified by their n.m.r. parameters were PF_2H and $Se{=}PF_2H$, with either an orange precipitate, in the case of manganese, or a white precipitate, in the case of rhenium. In both cases, reaction was rapid, with some $(F_2P)_2Se$ remaining.

These data can be rationalised as another example of the general HX reaction, with formation of an $F_2PM(CO)_5$ intermediate, followed by its reaction with $HM(CO)_5$

TABLE 2.8

N.m.r. parameters(a) of the products of reaction between $(F_2P)_2Se$ and Cl_2

	Product	δ(P)	δ(F)	$^1J(PF)$	$^1J(PSe)$	$^2J(FSe)$	Comments
1.	PF_2Cl_3	-8.6		1083			
			119.5	1083			
2.	$Se=PF_2Cl$	46.5		1304	1200		
			-2.4	1304		165	
3.	PF_3Cl_2	-25.7		1087			
			31.5	1075			
4.	PF_4Cl	-50.1		1030			
			-23.5	1032			
5.	$PFCl_4$	-23.4		1020			
			133.1	1012			
6.	$Se=PF_2X$(b)	52.5		1240	n.o.		Triplet
			-12.6	1246		n.o.	Doublet
7.	? (b)	-102.0	n.o.				Singlet
8.	PF_3	n.o.	-36.8	1401			
9.	?	n.o.	-45.7	1171			Doublet
10.	PF_5	n.o.	-67.3	967			

n.o. = not observed.

(a) See experimental section for chemical shift conventions.

(b) See text.

$(F_2P)_2Se + HM(CO)_5 \longrightarrow [F_2PM(CO)_5] + Se{=}PF_2H$ ....(18)

$[F_2PM(CO)_5] + HM(CO)_5 \longrightarrow M_2(CO)_{10} + PF_2H$ ....(19)

[ ] = not observed

Thus $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ would correspond to the orange and white precipitates,[66] though these were not isolated and identified as such. At no time however was the postulated intermediate, $F_2PM(CO)_5$, observed.

2.13. Reaction of $(F_2P)_2Se$ with Cl_2

$(F_2P)_2Se$ and Cl_2 were reacted in the ratio 1:2 in the expectation of obtaining oxidation products of the F_2P moiety. The reaction was fast at room temperature, the solution becoming dark yellow and a black precipitate forming. No $(F_2P)_2Se$ remained unreacted and at least 10 products were formed. Of these, there were four main ones, with PF_2Cl_3 being of greatest intensity in the ^{31}P and ^{19}F spectra. The others were PF_3Cl_2, PF_4Cl and the novel compound $Se{=}PF_2Cl$. All remaining products were much less abundant. Table 2.8 lists the data for the compounds in descending order of amount as judged from the spectra.

The assignment of the major product was straightforward except for $Se{=}PF_2Cl$, but selenium-77 satellites in both ^{31}P and ^{19}F spectra and the trends in the fluorine and phosphorus chemical shifts for the series $O{=}PF_2X$, $S{=}PF_2X$ and $Se{=}PF_2X$ ($X{=}H$[52] or Cl[31,67]) supported this interpretation. The couplings $^1J(PSe)$ and $^2J(FSe)$ are larger than those found in $Se{=}PF_2H$[52] (viz. -1046 Hz and

-99.6 Hz) and $^1J(PSe)$ is well above the typical range for organo-selenophosphoryl compounds,[51] ca. 950 - 650 Hz, where for example, $Se{=}P(OMe)_3$[53] has a particularly high $^1J(PSe)$ of -963 Hz. If, as it seems, increasing the electronegativity of the substituents on phosphorus increases $^1J(PSe)$, then $Se{=}PF_3$ may provide a maximum value.

Of the minor products, one had a high positive phosphorus shift which indicated an $Se{=}PF_2X$ compound, but was too weak for selenium satellites to be seen. Another, a singlet, had a particularly low phosphorus shift (-102.0 p.p.m.), but could not be attributed to PCl_5 (-80 p.p.m.).

The effect of chlorine on the trifluoromethyl analogue $[(CF_3)_2P]_2Se$,[61] gives $P(CF_3)_2Cl_3$ and $P(CF_3)_2Cl$ as the major products, with selenium being deposited. For $(F_2P)_2Se$, a similar route would yield PF_2Cl_3 but with rearrangement of the intermediate F_2PSeCl to the more stable $Se{=}PF_2Cl$ taking place rather than elimination of selenium.

$$(F_2P)_2Se + Cl_2 \longrightarrow PF_2Cl + [F_2PSeCl] \xrightarrow{Cl_2} PF_2Cl + Se{=}PF_2Cl \quad \ldots(20)$$

[ ]=not observed

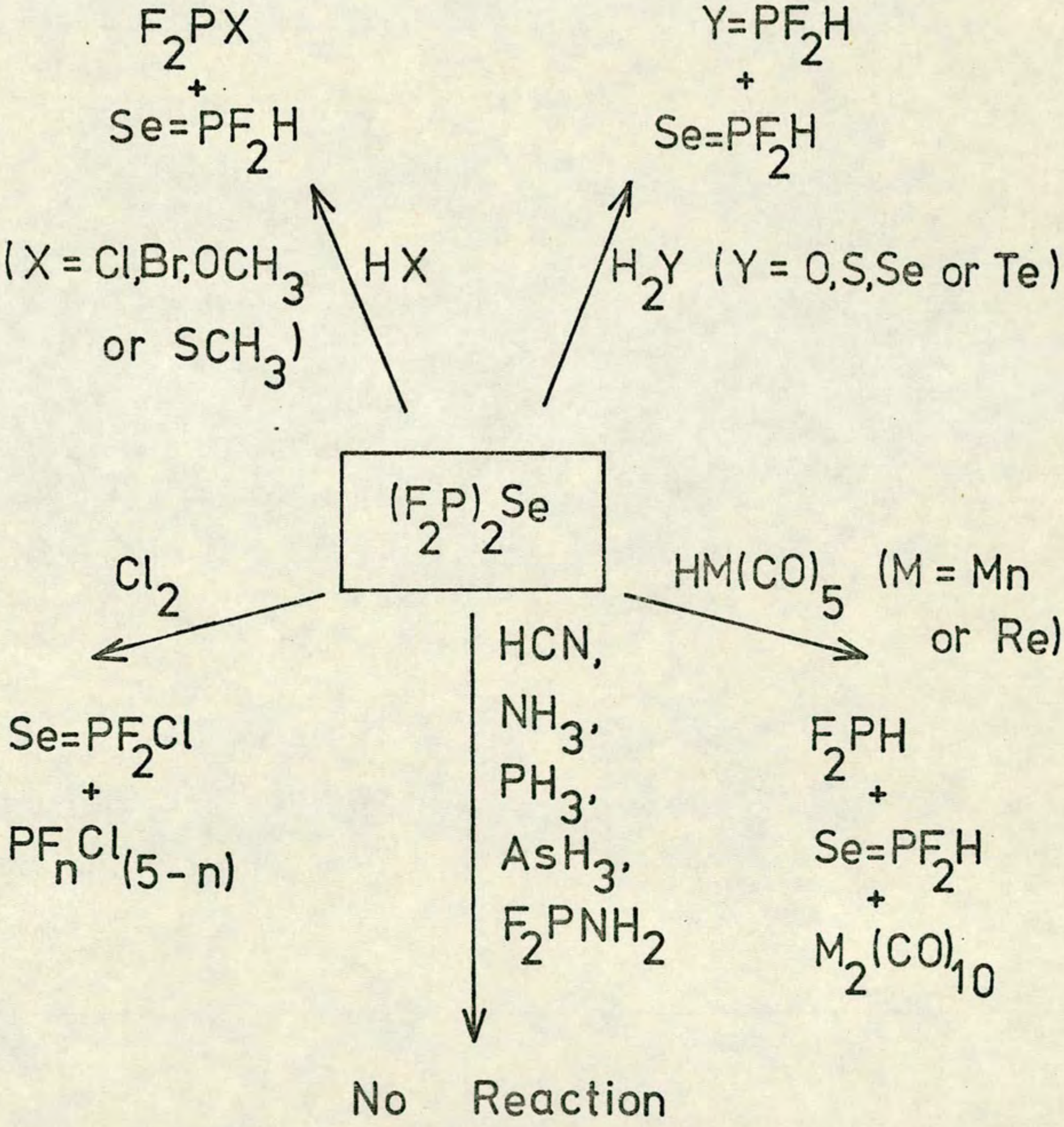
While phosphorus-selenium bond cleavage by chlorine accounts for the two main products, the range of others implies that disproportionation and further chlorine oxidations must be occurring to an appreciable extent.

2.14. Reaction of $(F_2P)_2Se$ with $Y{=}PF_2H$ (Y = S or Se)

In the course of some reactions, $(F_2P)_2S$ or $(F_2P)_2Se$ was present with either $S{=}PF_2H$ or $Se{=}PF_2H$. In neither case was reaction observed.

Summary of Reactions

Figure 2.5 depicts those reactions attempted for $(F_2P)_2Se$ involving P-Se bond breaking by various acidic hydrogen containing molecules. There is no reason to suppose that $(F_2P)_2S$ would be any less reactive.



CHAPTER 3

EXCHANGE REACTIONS BETWEEN BROMODIFLUOROPHOSPHINE AND SILYL DERIVATIVES OF GROUP V ELEMENTS

Introduction

The measure of success obtained with exchange reactions involving the Group VI elements suggested the extension of this type of reaction to Group V compounds. Of these, several difluorophosphine derivatives viz. F_2PNH_2,[9] F_2PPH_2,[13] F_2PPF_2[12] and $(F_2P)_3P$,[14] and one mixed silyldifluorophosphine derivative, $F_2PNHSiH_3$,[17] were already known. Although not prepared by an exchange process, the existence of the latter was particularly encouraging in that it showed mixed compounds of this type could be formed, and were stable.

$3F_2PNH_2 + 2SiH_3Br \longrightarrow PF_2Br + NH_4Br + 2F_2PNHSiH_3$ ....(1)

However, one potential route to further-substituted difluorophosphine derivatives of nitrogen can be eliminated since silylaminodifluorophosphine was prepared in the presence of PF_2Br, and exchange of a silyl for a difluorophosphine group does not take place.

$F_2PNHSiH_3 + PF_2Br \not\longrightarrow F_2PNHPF_2 + SiH_3Br$ .... (2)

Despite this, the susceptibility of silicon-phosphorus bonds to cleavage by phosphorus-halogen bonds has been shown in the reaction of $(H_3Si)_3P$ with trihalogenophosphines.[68] PBr_3 and PCl_3 both react to give elemental phosphorus and silyl halide: PF_3 however, does not react with $(H_3Si)_3P$.

TABLE 3.1

$PF_2X/(H_3Si)_nZ\ H_{(3-n)}$ Reaction Products

No.	Reactants	Molar Ratio	Solvents	Products		
	PF_2Br +	PF_2X:Reactant				
1.	$N(SiH_3)_3$	3:1	a	SiH_3Br SiH_2F_2 SiH_4		Orange solid
2.	$HN(SiH_3)_2$	2:1	b	SiH_3Br $N(SiH_3)_3$	$F_2PNHSiH_3$	White solid
3.	$P(SiH_3)_3$	3:1	b	SiH_3Br	$F_2PP(SiH_3)_2$	Yellow solid
4.	$HP(SiH_3)_2$	2:1	b	SiH_3Br	PH_3 H_2PSiH_3 $F_2PPHSiH_3$ $F_2PP(SiH_3)$	Yellow solid
5.	H_2PSiH_3	2:1	b	SiH_3Br	PH_3 F_2PPH_2	Yellow solid
6.	PH_3, $N(CH_3)_3$	3:1:3	a	none observed		Brown-Yellow solid
7.	PF_2Cl +					
	SiH_3Cl, NH_3	2:1:4	None	SiH_3F $N(SiH_3)_3$	PF_3 F_2PNH_2 $F_2PNH.SiH_3$	White solid

Note:
(a) TMS/C_6D_6/CCl_3F (b) C_6H_6/C_6D_6/ CCl_3F

TABLE 3.2

Silyl and Difluorophosphine Derivatives of Ammonia and Phosphine

(a) Nitrogen

$\underline{NH_3}$

$\underline{F_2PNH_2}$ H_2NSiH_3

$(F_2P)_2NH^+$ $\underset{-\,-\,-\,-\,-\,-}{\underline{F_2PNH.SiH_3}}$ $\underline{HN(SiH_3)_2}$

$(F_2P)_3N^+$ $(F_2P)_2NSiH_3{}^{\neq}$ $F_2PN(SiH_3)_2{}^{\neq}$ $\underline{N(SiH_3)_3}$

(b) Phosphorus

$\underline{PH_3}$

$\underset{-\,-\,-\,-}{\underline{F_2PPH_2}}$ $\underline{H_2PSiH_3}$

$(F_2P)_2PH$ $\underset{-\,-\,-\,-\,-\,-}{F_2PPH.SiH_3}$ $\underline{HP(SiH_3)_2}$

$\underline{(F_2P)_3P}$ $(F_2P)_2PSiH_3$ $\underset{-\,-\,-\,-\,-}{F_2PP(SiH_3)_2}$ $\underline{P(SiH_3)_3}$

Note:

________ Compounds already known

– – – – – Compounds observed as products, this work.

+ Subsequently prepared, cf. Chapter 4.

≠ Subsequently prepared, J. Wright, personal communication.

3.1. Results and Discussion of Reactions

The reactions attempted are summarised in Table 3.1, and all except the one between ammonia and a chlorosilane-chlorodifluorophosphine mixture were carried out in n.m.r. tubes. All products were identified by n.m.r. spectroscopy. Experimental details are presented in Chapter 9.

The table shows that in all cases where exchange was possible SiH_3Br was produced. All systems also gave solids, indicating that in general, products were not stable over long periods. Rates of exchange varied such that the $HN(SiH_3)_2$ and $HP(SiH_3)_2$ systems were the only ones with no starting material remaining after about one hour at room temperatures; the other systems were much slower. For those reactions in which exchange did occur, it involved the substitution of only one silyl group, even with excess bromodifluorophosphine present. The compounds observed in the course of this work, and those previously known, are indicated in Table 3.2. which shows all possible products from these reactions.

Both trisilylamine and trisilylphosphine were slow to react, with the former after 9 days giving no new silyl-nitrogen compounds, but a large amount of bright orange solid and bromosilane. The ^{31}P spectrum indicated only PF_2Br.

Although slow, $P(SiH_3)_3$ did react, and after 9 days had gone an estimated 85% to completion of Equation (3).

$$P(SiH_3)_3 + PF_2Br \longrightarrow F_2PP(SiH_3)_2 + SiH_3Br \text{ .... } (3)$$

TABLE 3.3

N.m.r. parameters[(a)] of some Silyl- and Difluorophosphino-Phosphine Derivatives

			Compound		
	$F_2PP'(SiH_3)_2$	$F_2PP'H.SiH_3$	$F_2PP'H_2$	$HP'(SiH_3)_2$	$P'(SiH_3)_3$
$\delta(H)$	-	n.o.	2.27	0.50	-
$\delta(SiH_3)$	3.82	n.o.	-	3.72	3.93
$\delta(F)$	-84.3	n.o.	-87.9	-	-
$\delta(P)$	288.7	291.3	292.5	-	-
$\delta(P')$	-211.7	-168.0	-137.6	-322.3	-375
$^1J(PF)$	-1225	1200	1185	-	-
$^1J(PP')$	-301	255	213	-	-
$^1J(P'Si)$	±38	n.o.	-	n.o.	+42.2
$^1J(P'H)$	-	n.o.	187.5	+186	-
$^2J(P'F)$	+70	78	82	-	-
$^2J(P'H)$	+17.0	n.o.	-	+17.0	-16.9[(e)]
$^2J(PSi)$	±24	n.o.	-	-	-
$^2J(PH)$	-	n.o.	16.5	-	-
$^3J(PH)$	+9.1	n.o.	-	-	-
$^3J(HF)$	-	n.o.	22.0	-	-
$^3J(HH)$	-	n.o.	-	+5.1	-
$^4J(FH)$	+2.5	n.o.	-	-	-
References			(b)	(c)	(d)

Note:

(a) For chemical shift conventions see experimental section.

(b) Reference 13.

(c) Reference 70.

(d) Reference 71.

(e) See text.

Despite the length of reaction time and the excess of PF_2Br (one PF_2 for every silyl group in $P(SiH_3)_3$), no further difluorophosphine substitution into $F_2PP(SiH_3)_2$ took place. This is in accordance with the reaction of PF_2Br with tris(trimethylsilyl)amine to give only bis(trimethylsilyl)difluorophosphino-amine.[69] It is possible that the presence of the PF_2 group affects the reactivity of the remaining Group V element-silicon bonds. It is more likely that steric factors, such as crowding of the central phosphorus or nitrogen atom, are dominant. The latter interpretation is made particularly favourable by the tendency of PF_2 groups to adopt structures maximising $H\cdots F$ interactions, as in the case of $F_2PNHSiH_3$.[17] This would cause more crowding in the F_2P substituted molecules than the unsubstituted $N(SiMe_3)_3$ or $P(SiH_3)_3$.

The novel compound (difluorophosphino)-disilylphosphine was characterised by its n.m.r. parameters, the magnitude and signs of which were determined by direct observation and spin-tickling experiments. Details of the parameters are given in Table 3.3., and of the experiments in Table 9.3.1. in the experimental section. The signs of coupling constants, which formed a self-consistent set, were related on the assumption that $^1K(PF)$ was negative.[35,72] Generally these agreed well in magnitude and sense with those in analogous systems. One difference however was $^2J(PH)$ which in $P(SiH_3)_3$ had been found to be negative.[71] Consequently, spin-tickling experiments were performed on $HP(SiH_3)_2$ (Table 9.3.2.)which confirmed the findings in $F_2PP(SiH_3)_2$, even though the signs in the former were related on the separate assumption that $^{1}K(PH)$ was positive.[73] The disparity with the findings in $P(SiH_3)_3$ may be due to neglect in that work of the negative gyromagnetic ratio for silicon, which when taken into account makes $^{2}J(PH)$ and $^{4}J(HH)$ positive, all other signs remaining as before. As those signs were based on $^{1}K(SiH)$ being positive, the $^{2}J(PH)$ has been found to have the same sign in three different compounds on three separate assumptions.

The long range couplings $^{3}J(PH)$ and $^{4}J(FH)$ in $F_2PP(SiH_3)_2$ are of the same sign, and similar in size, to those in $F_2PNHSiH_3$[74] and in F_2PYSiH_3 (Y = S, Se and Te).

When $HN(SiH_3)_2$ reacted it did so rapidly to form $F_2PNHSiH_3$, and bromosilane with which further reaction occurred to give $N(SiH_3)_3$.

$$HN(SiH_3)_2 + PF_2Br \longrightarrow F_2PNHSiH_3 + SiH_3Br \text{ .... } (4)$$

$$4HN(SiH_3)_2 + SiH_3Br \longrightarrow 3N(SiH_3)_3 + NH_4Br \text{ .... } (5)$$

The comparable $HP(SiH_3)_2$ reaction was not so straightforward. Although exchange as in Equation (4) did take place, the hitherto unknown $F_2PPHSiH_3$ was detected only in very low concentration, preventing its complete n.m.r. characterisation. To account for this, and the other products, it is possible that the SiH_3Br formed reacted further with $F_2PPHSiH_3$ to give $F_2PP(SiH_3)_2$, and that any HBr liberated could cleave Si-P bonds to H_2PSiH_3 and PH_3.

$$HP(SiH_3)_2 + PF_2Br \longrightarrow F_2PPHSiH_3 + SiH_3Br \text{ .... } (6)$$

Lack of intensity, and peaks arising from $F_2PP(SiH_3)_2$ and

TABLE 3.4.

^{15}N and ^{31}P Chemical Shifts(a) of Silyl- and Difluorophosphino-Group V Derivatives

	δ(Z)		Reference	
Compound	δ(^{15}N)	δ^{31}(P)	N	P
ZH_3	-21	-243	75	
H_2ZSiH_3		-278		
F_2PZH_2	21	-138	74	13
$HZ(SiH_3)_2$	-69	-322	74	
$F_2PZH.SiH_3$	14	-168	74	
$(F_2P)_2ZH$	86			
$Z(SiH_3)_3$	-80	-375	74	
$F_2PZ(SiH_3)_2$		-212		
$(F_2P)_2ZSiH_3$				
$(F_2P)_3Z$	139	46(b)		14

Note:

(a) For chemical shift conventions see experimental section.

(b) Calculated from reference 14, which gives $\delta(P)_{PF_2} - \delta(P)$ = 245 p.p.m.
Typical $\delta(P)_{PF_2}$ assumed 291 p.p.m. (from F_2PPH_2, $F_2PP(SiH_3)_2$ and $F_2PPHSiH_3$)

H_2PSiH_3 in the ^1H spectrum prevented parameters, other than those given in Table 3.3., from being measured for $F_2PPHSiH_3$.

Silylphosphine underwent slow reaction to give the expected exchange product F_2PPH_2. Phosphine, the major decomposition product of F_2PPH_2 was also observed.

$H_2PSiH_3 + PF_2Br \longrightarrow F_2PPH_2 + SiH_3Br$ .... (7)

In the vigorous reaction between PH_3, PF_2Br and $N(CH_3)_3$ no products other than brown-yellow solids were detected. The remaining reaction, involving a mixture of chlorosilane and chlorodifluorophosphine with ammonia, gave as major products F_2PNH_2, $N(SiH_3)_3$ and $F_2PNHSiH_3$; no other mixed amines were formed which contained both SiH_3 and F_2P groups.

3.2. Chemical Shifts

The ^{15}N and ^{31}P chemical shifts of the silyl- and difluorophosphino- Group V derivatives are given in Table 3.4. Presented graphically, Figures 3.1. and 3.2., these indicate some striking trends into which the new compounds, $F_2PPHSiH_3$ and $F_2PP(SiH_3)_2$, fit.

For $\delta(^{15}N)$ and $\delta(^{31}P)$, replacement of a hydrogen atom by a silyl group produces a shift to low frequency, characteristic of silyl compounds, and observed also for silyl derivatives of ^{19}F,[76] ^{77}Se, and ^{125}Te.[77] Additional F_2P units however, produce large steady increases in frequency, indicative of deshielding, of ca. 50 p.p.m. for $\delta(^{15}N)$ and ca. 100 p.p.m. for $\delta(^{31}P)$. This is perhaps due to the electronegativity of the F_2P group affecting the

Figure 3.1. ^{15}N chemical shifts of some difluorophosphino- and silyl-amines

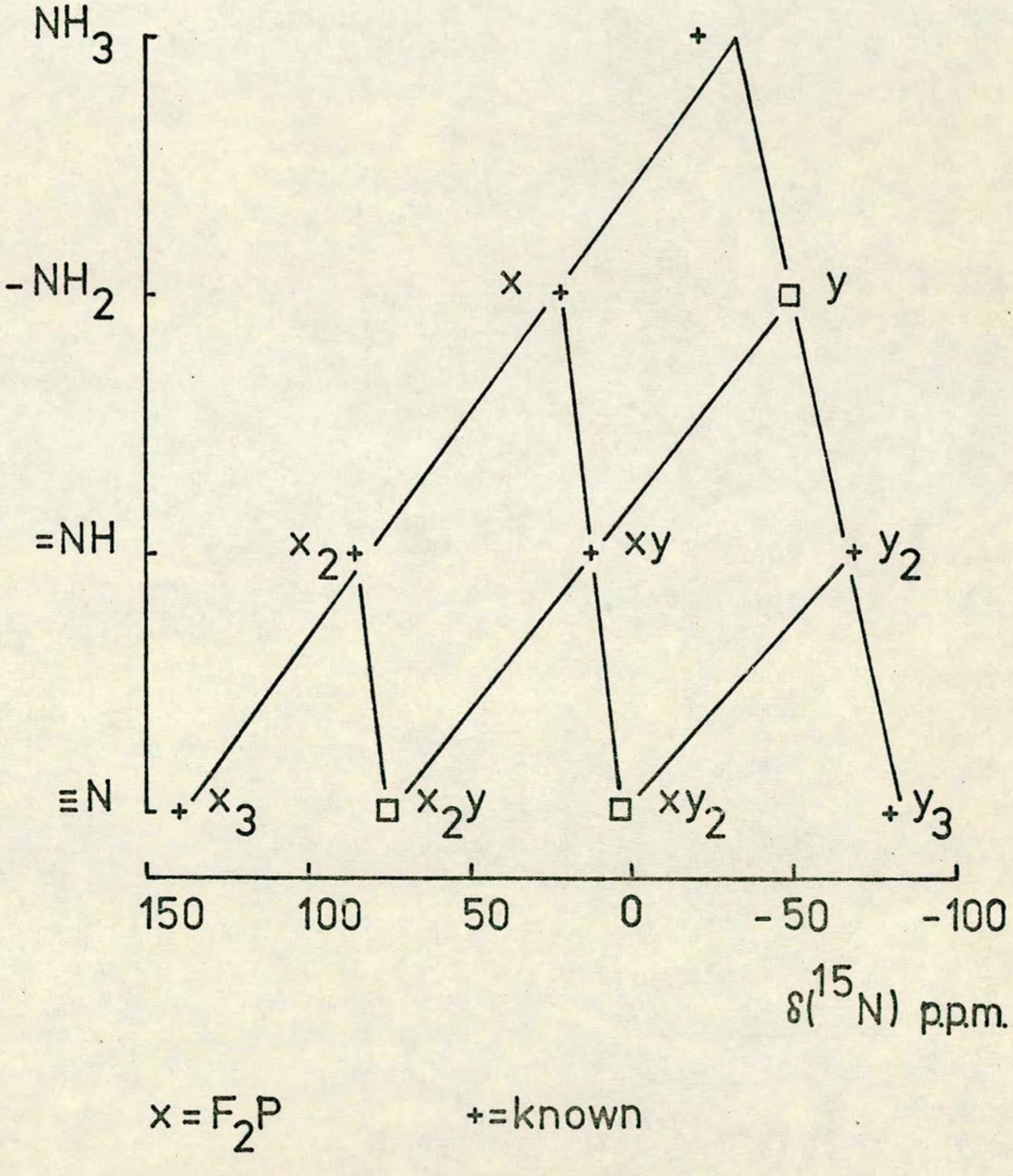
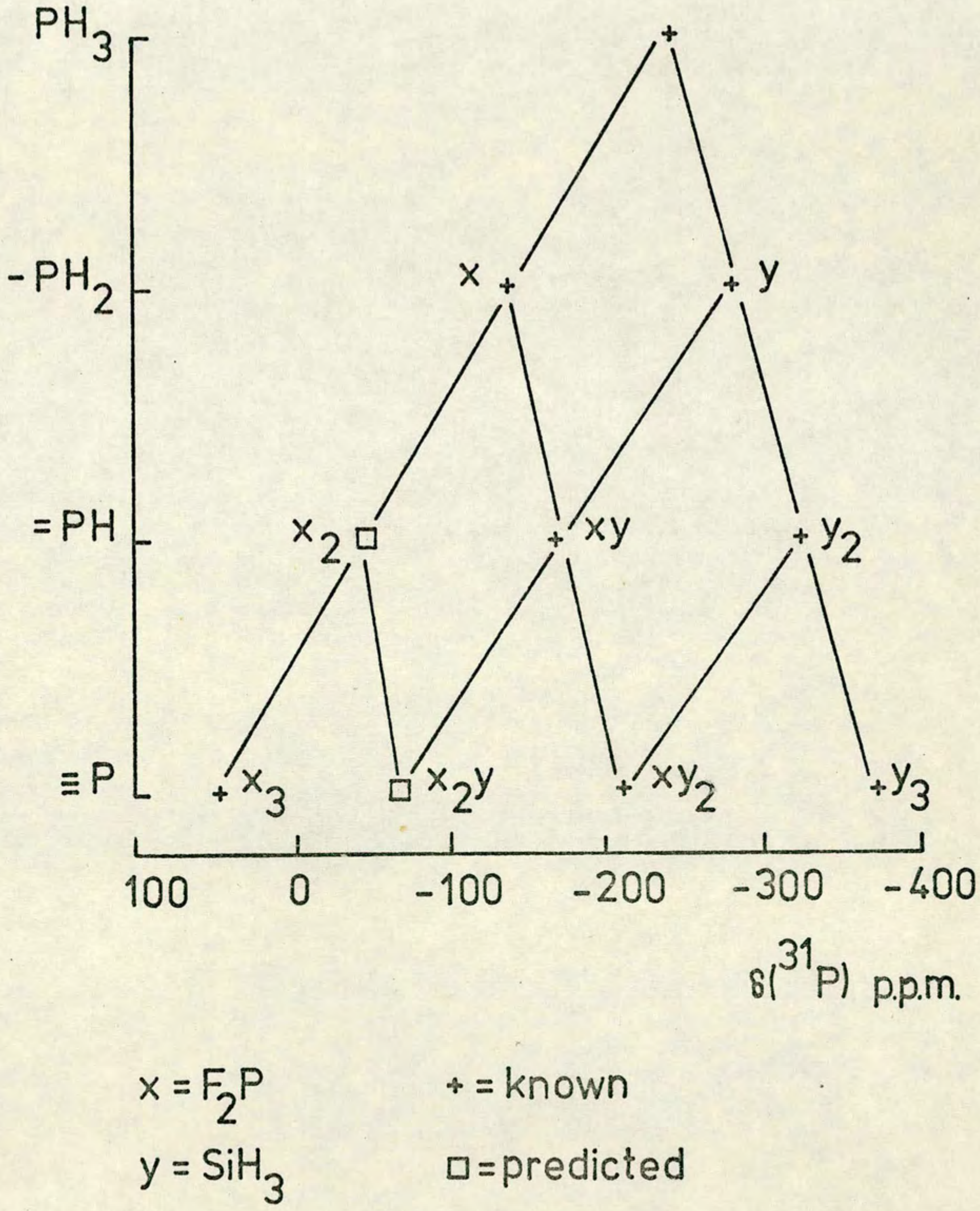


Figure 3.2. ^{31}P chemical shifts of some difluorophosphino- and silyl-phosphines



paramagnetic term in the chemical shift which is thought to dominate the total screening constant for $\delta(^{15}N)$ and $\delta(^{31}P)$.[75,78] These steady changes make it possible to predict, within a few p.p.m., the chemical shifts of those compounds as yet undiscovered.

CHAPTER 4

THE PREPARATION AND PROPERTIES OF BIS(DIFLUOROPHOSPHINO)- AND TRIS(DIFLUOROPHOSPHINO)-AMINES, $(F_2P)_2NH$ AND $(F_2P)_3N$

Introduction

Since the exchange reactions discussed in the previous chapter failed to produce novel difluorophosphino-amines, more direct routes to these compounds were investigated. Although ammonia and halodifluorophosphines had been shown to react in the gas phase to give aminodifluorophosphine, F_2PNH_2,[9,79] further reaction to the secondary and tertiary amines, $(F_2P)_2NH$ and $(F_2P)_3N$, was slow and incomplete. The reaction is similar in this respect to that of ammonia and chlorobis(trifluoromethyl)phosphine which gives only primary amine, unless a base, trimethylamine, is added, when secondary amine is formed. To produce the tertiary amine, $[(F_3C)_2P]_3N$, it is necessary to go by way of the anion $[(F_3C)_2P]_2N^-$.[80] In an adaption of this method, namely the reactions of bromo- or chlorodifluorophosphine with ammonia in the presence of trimethylamine, it was found that by carefully controlling the conditions both secondary and tertiary difluorophosphino-amines could be prepared without recourse to the $[(F_2P)_2N]^-$ anion. The choice of trimethylamine was made because of its suitable volatility, and the need for a non-protonic base which would not cleave P-N bonds. The importance of the latter point is demonstrated by the ease with which methylamine reacts with $(F_2P)_2NCH_3$ to form F_2PNHCH_3.[81]

Results and Discussion

4.1. Preparation

The investigation into the preparation of the secondary and tertiary difluorophosphino-amines was difficult and time-consuming since the volatilities of all three amines, and of NMe_3, were so similar that separation by trap-to-trap distillation was impossible. Reaction schemes using methyllithium, or potassium phosphide, in an attempt to produce the $[(F_2P)_2N]^-$ anion failed, as did the use of 2,6-dimethyl-pyridine as an alternative base to NMe_3. The following methods were the best ones found of preparing and isolating these compounds.

Bis- and tris(difluorophosphino)-amines were prepared from either ammonia or aminodifluorophosphine. For the preparations of the teritary amine that used NH_3, it is possible to describe the gas-phase reaction by Equation [1]

$$NH_3 + 3PF_2Cl + 3NMe_3 \longrightarrow (F_2P)_3N + 3[Me_3NH]Cl \;\ldots\ldots\; [1]$$

However, ammonium chloride will also be formed to some extent, and therefore if NH_3, PF_2Cl, and NMe_3 are used in the ratio 1:3:3, complete conversion of the NH_3 to $(F_2P)_3N$ or $[NH_4]Cl$ will take place and some NMe_3 and PF_2Cl will remain unreacted. In practice, no NMe_3 was recovered, but primary and secondary difluorophosphino-amines were present. While additional NMe_3 and PF_2Cl would be expected to increase the proportion of tertiary amine in the products, it was found that as the initial NMe_3:NH_3 ratio was increased beyond 3:1, so the total yield of amines decreased. It was necessary therefore to prepare a mixture of amines and to estimate the extent to which reaction had occurred, usually by infra-red spectroscopy. Then to add more PF_2Cl (about 1.5 per N-H bond remaining) followed by more NMe_3 (about 1.0 per N-H bond). This procedure was repeated until reaction to tris(difluorophosphino)-amine was essentially complete. If any NMe_3 remained unreacted, it was removed by adding boron trifluoride which gave a solid involatile adduct with NMe_3, but did not appear to form a stable adduct at room temperature with $(F_2P)_3N$.

An alternative method, which gave less complicated mixtures of products, and was therefore easier to regulate, started with aminodifluorophosphine, and initially used reagents in the proportions of Equation [2]:

$$F_2PNH_2 + 2PF_2Cl + 2NMe_3 \longrightarrow (F_2P)_3N + 2[Me_3NH]Cl \quad .... \quad [2]$$

The subsequent stages were exactly as in the former method, except that it was usually possible to gauge quantities so that use of BF_3 was unnecessary.

Study of the reactions of $(F_2P)_3N$ with various hydrides showed that the secondary amine could be prepared in a pure form by removal of one F_2P group with a hydrogen halide. This seemed to be the best method of obtaining small amounts of really pure amine, and was the one adopted for the preparation of $(F_2P)_2ND$.

A more direct route started with aminodifluorophosphine, chlorodifluorophosphine, and trimethylamine in the ratio 1:2(excess):1, Equation [3]

$$F_2PNH_2 + PF_2Cl + NMe_3 \longrightarrow (F_2P)_2NH + [Me_3NH]Cl \quad .... \quad [3]$$

This yielded a mixture of primary, secondary and tertiary amines in a ratio of approximately 30:65:5. When BF_3 was added to this mixture, F_2PNH_2 decomposed (cf. Chapter 5), leaving a mixture of secondary and tertiary amines, inseparable by distillation. Alternatively, a hydrogen halide could be added to the mixture, destroying F_2PNH_2 and converting $(F_2P)_3N$ to $(F_2P)_2NH$.

4.2. Reactions of $(F_2P)_3N$

These were undertaken to determine the usefulness of $(F_2P)_3N$ as a preparative intermediate, and eventually led to the best method of preparation of $(F_2P)_2NH$. Reaction with hydrogen halides was rapid for chloride and bromide, but slower for iodide, and resulted in cleavage of only one P-N bond per molecule, even when excess hydrogen halide was used.

$$(F_2P)_3N + HX \longrightarrow (F_2P)_2NH + PF_2X \quad (X = Cl, Br, I) \; ... \; [4]$$

A small amount of white solid was formed, indicating that further reaction did occur to a limited extent. However, as reaction of F_2PNH_2 with HX is fast, no other volatile products were observed. This rather surprising behaviour, with F_2PNH_2 and $(F_2P)_3N$ being reactive, and $(F_2P)_2NH$ being inert, is similar to that observed in the analogous series of $(CF_3)_2P$- compounds,[80] but contrasts sharply with the reactivity of $(F_2P)_2NR$ towards hydrogen chloride.[82]

Group VI hydrides reacted in a manner similar to the hydrogen halides, but the presumed intermediates F_2P-Y-H rearranged rapidly to the phosphorus (v) forms, Y = PF_2H.

TABLE 4.1

N.m.r. parameters of difluorophosphino-amines[(a)]

	$F_2P^{15}NH_2$	$(F_2P)_2{}^{15}NH$	$(F_2P)_3{}^{15}N$
$\delta(^1H)$	+3.23(2)	+4.38(2)	-
$\delta(^{19}F)$	-58.1(2)	-62.0(1)	-62.3(3)
$\delta(^{31}P)$	+147.5(1)	+144.4(1)	+150.3(1)
$\delta(^{15}N)$	+21.4(2)	+86.3(3)	+139.0(1)
$^1J(PF)$	-1200(1)	-1253(1)	(-)1224(1)[(b)]
$^1J(PN)$	+72.5(3)	+78.9(3)	+87.0(3)
$^1J(NH)$	-80.4(4)	-74.7(2)	-
$^2J(PH)$	+18.8(2)	+13.6(2)	-
$^2J(NF)$	-6.4(4)	-3.6(2)	±2.5(4)
$^2J(PP')$	-	±154(1)	(c)
$^3J(FH)$	+12.8(4)	+11.2(2)	-
$^3J(PF')$	-	+21.0(5)	(c)
$^4J(FF')$	-	±5.4(5)	(c)
$^4J(FF'')$	-	±5.4(5)	(c)

Note:

Values of J are given in Hz. Estimated standard deviations are quoted in parentheses.

(a) Solutions in C_6D_6:Me_4Si, ratio 1:1, at 308K. See experimental section for chemical shift conventions.

(b) $|{}^1J(PF) + 2\,{}^3J(PF')|$.

(c) Not determined due to complexity of spectra. See text.

As the remaining hydrogen is no longer acidic, further reaction did not occur.

$(F_2P)_3N + H_2Y \longrightarrow (F_2P)_2NH + Y{=}PF_2H \quad (Y = O, S, Se, Te)$ .. [5]

For selenium, the reaction was clean, and gave just the expected products. For sulphur, $(F_2P)_2NH$ was obtained in high yield, but $S{=}PF_2H$ decomposed. For oxygen, both products underwent decomposition reactions, and PF_3 was the main volatile product. For tellurium, the secondary amine remained intact, but the other products were PH_3, PF_3 and elemental tellurium. No $Te{=}PF_2H$ was observed.

The reaction of $(F_2P)_3N$ with chlorine seemed to involve P-N bond cleavage since PF_2Cl was the only main product. Other minor compounds remained unidentified in the n.m.r. spectra.

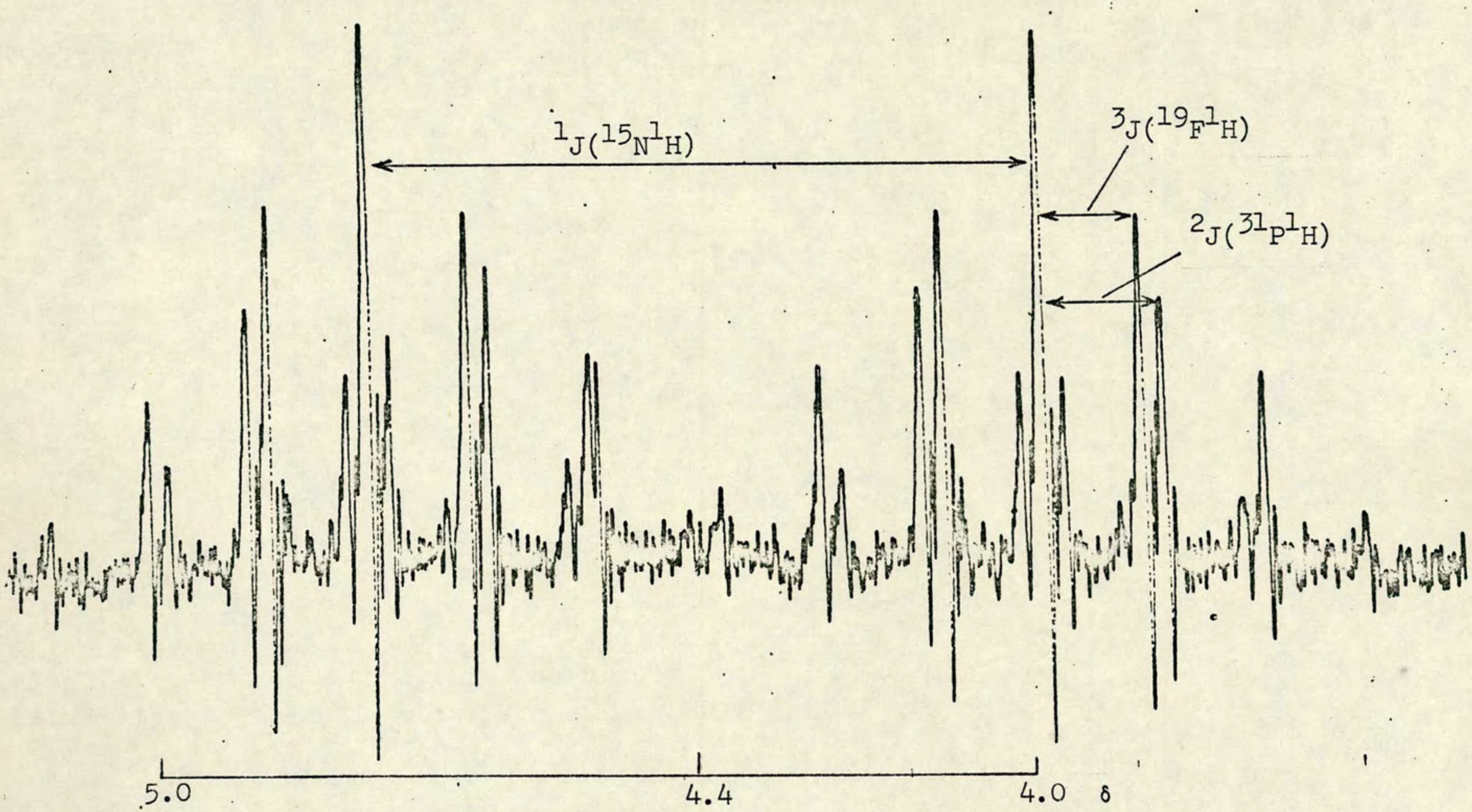
4.3. Spectroscopic Properties

In compounds such as the difluorophosphino-amines, there is the possibility that the nitrogen atoms have a planar arrangement of ligands. The spectroscopic studies were therefore intended to give some indication of whether this was so, as well as to assist in the routine characterisation of the new compounds.

N.m.r. parameters are listed in Table 4.1, together with those of F_2PNH_2, and were obtained mainly by direct observation of ^1H, ^{19}F and ^{31}P spectra. Information about the ^{15}N spectra and signs of coupling constants were obtained by heteronuclear double resonance experiments, (listed in Tables 9.4.1. and 9.4.2.). The ^{15}N chemical

Figure 4.1

^{1}H n.m.r. spectrum of $(F_2P)_2{}^{15}NH$



shift of $(F_2P)_3N$ was found by selective noise-decoupling of the ^{15}N spectrum while observing the $^{31}P^{15}N$ splitting in the ^{31}P spectrum, after the manner of Birdsall et al.[83]

The ^1H spectrum of $(F_2P)_2{}^{15}NH$ appeared to be of the first order, the resonance being split by ^{15}N, ^{31}P and ^{19}F into a doublet of triplets of quintets, (Figure 4.1); the ^{15}N spectrum similarly seemed to be first order. The ^{19}F and ^{31}P spectra, however, were of the second order, and showed long range PF and FF couplings. The spectra were analysed in terms of an $[A[X]_2]_2MQ$ spin system,[25] assuming that M and Q caused only first order splittings of the A and X spectra. On cooling, the ^{19}F spectrum became more complex, mainly due to changes in the long range $^4J(FF)$, which were no longer equal. The only other coupling constant to change significantly was $^2J(PP)$ which varied from 181 Hz at 223K to 154 Hz at 308K.

The ^{19}F and ^{31}P spectra of $(F_2P)_3{}^{15}N$ were complex, and full analysis for the $[A[X]_2]_3M$ spin system was impossible. However, it would appear that the long range $^4J(FF)$ couplings are significant, probably of the same order of magnitude as in the secondary amine.

Most of the observed parameters were as expected, an exception being ^{31}P chemical shifts, which differed by small but significant amounts, the order being $(F_2P)_2NH < F_2PNH_2 < (F_2P)_3N$. The ^{15}N resonance was shifted to high frequency on replacement of hydrogen by F_2P groups. This probably reflects the electronegativity of the groups, rather than any π-bonding involving the nitrogen lone pair of electrons, as replacement of hydrogens by SiH_3 groups results in a small low frequency shift.[74]

The smaller absolute value of $^1J(^{15}N^1H)$ in $(F_2P)_2NH$ than in F_2PNH_2 is surprising as this is normally associated with a smaller s-orbital contribution to the nitrogen-hydrogen bond.[84] Increasing the number of F_2P groups should, if anything, increase the s-orbital contribution to the remaining N-H bonds. However, $^1J(NH)$ may also be affected by other factors, such as the presence nearby of electronegative atoms.

The magnitudes and signs of the $^1J(^{31}P^{15}N)$ couplings are consistent with those few that have been determined previously.[26,74]

The small value of $^2J(PP)$ in $(F_2P)_2NH$, and the probable smaller value in $(F_2P)_3N$, are perhaps the most unexpected parameters. A number of alkyl- and aryl-bis(difluorophosphino)amines have been studied, and the values of $^2J(PP)$ in these all lie between 370 and 450 Hz.[11] Moreover, the magnitude of variation in $^2J(PP)$ with temperature in $(F_2P)_2NH$ is similar to that in $(F_2P)_2NR$.[21,85] It seems possible that this coupling constant is very sensitive not only to the intervening atom and its ligands, but also to the conformation adopted by the F_2P groups, perhaps being related to the extent to which the phosphorus lone pairs interact. The small value found for $(F_2P)_2O$[18] could therefore be related to the very wide angle at oxygen in this molecule,[29] while the much smaller angles likely in $(F_2P)_2S$ and $(F_2P)_2Se$ would account for the large and temperature dependant $^2J(PP)$ values in these compounds.[21,77]

TABLE 4.2.

Vibrational spectra (cm^{-1}) of $(F_2P)_3N$

	Raman		
I.r. (gas)	(liquid)	(CCl_3F solution)	Assignment
1880 vw			2 x 939
1750 vw			939 + 816, 912 + 838
1167 w			816 + 363
1075 w			2 x 542
1045 w			816 + 234
1004 mw			542 + 468
939 vs	936 w,dp	937 m	ν (PN)
912 vs	905 w,p	907 m	
878 w,sh			
863) P 858) Q vs	874 m,p	869 s	ν (PF)
843) P 838) Q vs	837 s,p	(a)	
833) R			
816 vs	805 m,dp	~805 m	
706 w			363 + 345
	558 vs,p	557 vs	ν (PN)
542 m	537 vs,p	(a)	
509 vw			363 + 142
503 vw			
468 m	467 m,p	466 m	$\delta(PF_2)$ and $\delta(P_3N)$
450 m	447 m,dp	442 m	
	421 ms,p	422 ms	
	404 ms,p		
366) P			$\omega(PF_2)$
363) Q ms	389 vw,p	(a)	
359) R			
345 s	347 vw,?	(a)	
295 m	295 vw,p	293 w	$\rho(PF_2)$
	251 s,p	(a)	$\delta(P_3N)$
	234 vs,p	231 s	
	142 m,?	145 s	$\tau(PF_2)$

Note:

s = strong, m = medium, w = weak, v = very, sh = shoulder, p = polarised, dp = depolarised.

(a) Obscured by CCl_3F.

TABLE 4.3.

Vibrational spectra (cm^{-1}) of $(F_2P)_2NH$ and $(F_2P)_2ND$

I.r. (gas)		Raman		
H	D	H(liquid)	H(solid)	Assignment
3373 m	2502 w			$\nu(NH)$
3333 m	2472 w	3322 w	3313 w	
1248 ms	1066 m			$\delta(NH)$
1210 ms	1044 m			
	941 vs			
919 s	914 s	920 w	ca. 930 w	$\nu_{asym}(PNP)$
863 s	888 s	880 vs	885 vs	$\nu(PF)$?$\delta(NH)$
830 vs	838 vs	830 m	838 s	
823)	832 vs, sh			
816) vs	816 vs	797 s	792 s	
810)				
747 m	741 m	743 m	775 s	$\nu_{sym}(PNP)$
		669 m		
566 m	571 vw	593 w		
	542 w			
508 vw	508 w	510 m		? 2 x 264
	470 vw			
444 m	449 w	430 s	430 w	$\delta(PF_2)$
427 w, sh				
361 m	360 m, sh			$\omega(PF_2)$
323 w	350 m		325 m	
291 w	296 w	295 w	280 w	$\rho(PF_2)$
		264 vs	265 m	$\delta(PNP)$
		240 vw		
		150 m	170 w	$\tau(PF_2)$

Note:

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

Infra-red and Raman data for $(F_2P)_3N$ and $(F_2P)_2NH$ are presented in Tables 4.2. and 4.3.

Possible point groups for $(F_2P)_3N$ are C_{3h}, C_{3v}, C_3, C_s or C_1. Any of these could be consistent with a planar P_3N skeleton, and in the case of C_{3h} this is essential. The C_{3h} structure would give rise to 12 Raman-active fundamentals, four of which would be polarised, and 9 infra-red active fundamentals. It is immediately obvious from Table 4.2. that this is not consistent with the observed spectra. Similarly, on the basis of the number of polarised Raman bands, the C_{3v} and C_3 structures can be eliminated. This leaves only C_s and C_1 symmetries, or possibly a mixture of conformers. Any conclusion about which of these possibilities is correct depends on assignment of the skeletal vibrations. These may, of course, be mixed with the vibrations of the F_2P groups, but as bands occur in the regions normally expected for difluorophosphines, it is likely that the concept of skeletal vibrations is a useful one.

After assignment of F_2P group vibrations, three sets of bands remain unassigned; in the regions 1000-900 cm^{-1}, about 550 cm^{-1}, and about 250 cm^{-1}. A planar P_3N skeleton could well have stretching vibrations in the higher frequency regions, and a deformation in the lowest region, by analogy with trisilylamine.[86] The effect of the F_2P groups would be to lower the skeletal symmetry from D_{3h}. An overall C_s structure would allow the asymmetric skeletal stretch to be split into a' and a" components, both Raman active, one polarised and one depolarised.

Figure 4.2

Possible structures of $(F_2P)_3N$

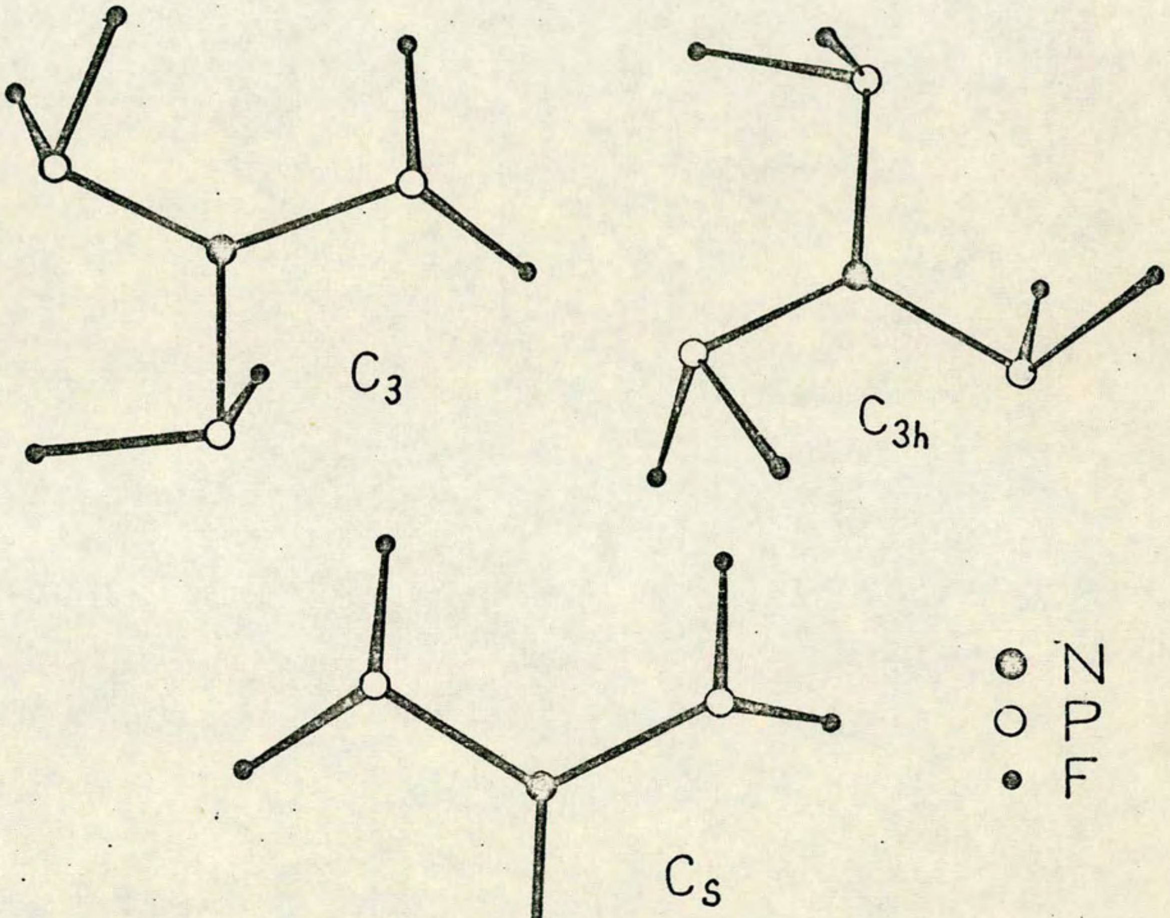
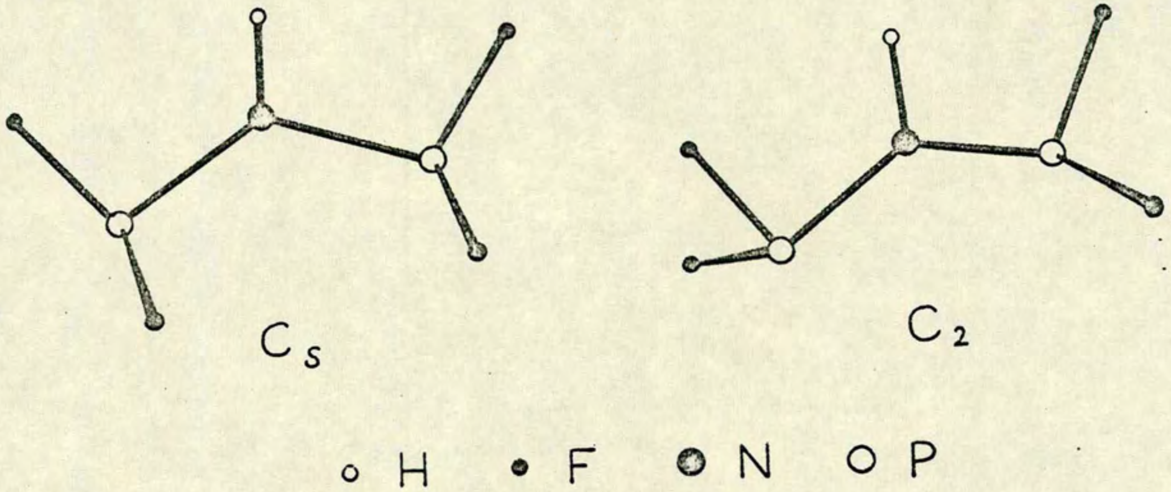


Figure 4.3

Possible conformations of $(F_2P)_2NH$



Broken lines represent possible H···F interactions.

The symmetric stretch would remain as a single fundamental, but would become infra-red allowed.

The Raman spectrum of the liquid phase, however, includes bands at both 558 and 537 cm^{-1}. These frequencies are rather high for F_2P deformations, the only other reasonable assignment. Neither band can be accounted for in terms of Fermi resonance, as there is just one corresponding band in the infra-red spectrum, and the two Raman bands have distinctly different widths and degrees of polarisation. These vibrations, and those at 251 and 234 cm^{-1} therefore are tentatively assigned to skeletal vibrations of different conformers of $(F_2P)_3N$, one probably of C_s symmetry, and one of another symmetry, possibly C_3. The bands at 905 and 936 cm^{-1} are also assigned as skeletal modes, but these could both arise from a single conformer. Use of models of the molecule shows that the structures likely to minimise fluorine-fluorine interactions are those with C_s and C_3 or C_{3h} symmetry (Figure 4.2.) and the spectra have therefore been assigned in terms of these structures.

The conformation of the F_2P groups also affects the point group of $(F_2P)_2NH$. Studies of H···F interactions in this type of molecule,[17] indicate that the most stable conformations would have C_s and C_2 symmetry, with two H···F interactions in each case (Figure 4.3.). Observation of two N-H deformation frequencies near 1200 cm^{-1} in the gas phase infra-red spectrum suggests strongly that two conformers are indeed present in the gas phase.

As with $(F_2P)_3N$, a number of bands can readily be assigned to vibrations of the F_2P groups. The three bands

TABLE 4.4.

Mass Spectra

$(F_2P)_3N$

m/e	Intensity	Assignment
221	32	$[(F_2P)_3N]^+$
202	1.2	$[(F_2P)_2N(PF)]^+$
171	0.3	$[F_2P)_2NF]^+$
152	4	$[(F_2P)_2N]^+$
133	53	$[(F_2P)N(PF)]^+$
114	27	$[(FP)N(PF)]^+$
107	6	$[PF_4]^+$ and $[P_3N]^+$
95	0.5	$[(FP)NP]^+$
88	46	$[PF_3]^+$
69	100	$[PF_2]^+$
66.5	<0.1	$[(F_2P)N(PF)]^{2+}$
50	9	$[PF]^+$
47.5	<0.1	$[(FP)NP]^{2+}$
45	1.0	$[PN]^+$
34.5	0.5	$[PF_2]^{2+}$
31	1.3	P^+
Metastable		
58.1	weak	$[(F_2P)N(PF)]^+ \rightarrow [PF_3]^+ + PN$
80.0	strong	$[(F_2P)_3N]^+ \rightarrow [(F_2P)N(PF)]^+ + PF_3$

$(F_2P)_2NH$

m/e	Intensity	Assignment
153	90	$[(F_2P)_2NH]^+$
152	53	$[(F_2P)_2N]^+$
134	7	$[(F_2P)NH(PF)]^+$
133	21	$[(F_2P)N(PF)]^+$
114	2	$[(F_2P)NP]^+$
88	10	$[PF_3]^+$
81	5	$[P_2F]^+$
69	100	$[PF_2]^+$
65	70	$[(FP)NH]^+$
50	6	$[PF]^+$
47.5	0.1	$[(FP)NP]^{2+}$
46	48	$[PNH]^+$
34.5	<0.1	$[PF_2]^{2+}$
32.5	<0.1	$[(FP)NH]^{2+}$
31	1	P^+
20	2	$[HF]^+$
Metastable		
115.6	weak	$[(F_2P)_2NH]^+ \rightarrow [(F_2P)N(PF)]^+ + HF$
151.0	medium	$[(F_2P)_2NH]^+ \rightarrow [(F_2P)_2N]^+ + H$

between 790 and 890 cm^{-1} will include P-F stretching modes, but the remaining N-H deformations (presumably two bands, one for each conformer) may also lie in this region. Bands at 920, 745 and 265 cm^{-1} have been assigned to skeletal modes, although these may be strongly coupled with F_2P vibrations. Frequencies observed for $(F_2P)_2ND$ are generally consistent with this assignment, although a strong band rather surprisingly appears at 941 cm^{-1}. This may be a P-F or P-N stretching mode raised in frequency by coupling with an N-D deformation.

Details of the mass spectra of $(F_2P)_3N$ and $(F_2P)_2NH$ are presented in Table 4.4. It seems that the most important breakdown path for the tertiary amine involves the following reaction sequence:

$$[(F_2P)_3N]^+ \longrightarrow [(F_2P)N(PF)]^+ + PF_3 \;\ldots\ldots\; [6]$$

$$[(F_2P)N(PF)]^+ \longrightarrow [PF_3]^+ + PN \;\ldots\ldots\ldots\ldots\; [7]$$

Other reactions involving F_2P or F, and in one case a rearrangement, occur giving rise to the ion $[(F_2P)_2NF]^+$, which must contain either an N-F bond, or a four co-ordinate phosphorus atom.

The ion $[(F_2P)N(PF)]^+$ is also formed by loss of HF from the parent ion of $(F_2P)_2NH$.

$$[(F_2P)_2NH]^+ \longrightarrow [(F_2P)N(PF)]^+ + HF \;\ldots\ldots\ldots\; [8]$$

However, in this case, there are probably at least three other routes by which the parent ion can dissociate:

TABLE 4.5.

Photoelectron spectra

F_2PNH_2	$(F_2P)_2NH$	$(F_2P)_3N$	Assignment
10.9	11.3	11.2	N 2p lone pair
11.5	11.9	12.2	P 3p lone pairs
	12.3	12.5	
15.4	15.6	15.8(a)	PN, NH bonding
	16.0		
16.7	16.8		F 2p lone pairs
	17.4	17.4	
17.9	18.5	18.7	PF bonding

Note:

Vertical ionisation potentials in eV; ± 0.1 eV.

(a) Intense, broad band.

$$[(F_2P)_2NH]^+ \longrightarrow [(F_2P)_2N]^+ + H \text{ .... [9]}$$

$$[(F_2P)_2NH]^+ \longrightarrow [(F_2P)NH(PF)]^+ + F \text{ .... [10]}$$

$$[(F_2P)_2NH]^+ \longrightarrow [(FP)NH]^+ + PF_3 \text{ .... [11]}$$

The last of these routes yields the ion $[(FP)NH]^+$, one which has been observed in F_2PNH_2 to be particularly readily formed.[9]

Some details of the He(I) photoelectron spectra of the three difluorophosphino-amines are given in Table 4.5. There is a general increase in binding energy with increasing replacement of hydrogen atoms by F_2P groups. The fact that the nitrogen lone pair level in the tertiary amine is slightly lower in energy than in the secondary amine, probably reflects a change in the amount of interaction of this level with the phosphorus lone pair levels. This interaction in turn depending on the orientations of the phosphorus groups.[42]

CHAPTER 5

PREPARATION AND PROPERTIES OF DIFLUOROPHOSPHINOAMINODIFLUOROBORANE, F_2PNHBF_2

Introduction

In the work of the previous chapter, boron trifluoride was used as a means of removing trimethylamine from reaction mixtures which contained mono-, bis-, and tris(difluorophosphino)-amines. It was observed that the boron trihalide also reacted with aminodifluorophosphine to form an involatile white solid. Further investigation of this reaction indicated that formation of the solid was the last stage of a reaction which initially gave a new volatile compound. By careful control of conditions, this compound was isolated and identified as difluorophosphinoaminodifluoroborane, F_2PNHBF_2.

Results and Discussion

5.1. Preparation

F_2PNHBF_2 was prepared by both gas and liquid phase reactions of F_2PNH_2 and BF_3. The yield and purity of the product depended greatly upon the conditions and ratio of reagents used, and also varied appreciably within each particular set of conditions, perhaps due to local excesses of reagent. It was also found that excess aminodifluorophosphine led to the formation of bis(difluorophosphino)-amine, $(F_2P)_2NH$.

The preparation of F_2PNHBF_2 can best be described, Equation [1], by adduct formation, followed by loss of hydrogen fluoride.

$F_2PNH_2 + BF_3 \longrightarrow F_2PNH_2.BF_3 \longrightarrow F_2PNHBF_2 + HF$ .... [1]

Although no attempt was made to identify the adduct, by a low temperature n.m.r. study for example, its presence was indicated by the observation that on warming a mixture of the reagents from 77 to 209 K, no volatile compounds were formed despite both starting materials and F_2PNHBF_2 being volatile at this temperature. Hydrogen fluoride, a product of Equation [1], was not observed directly, nor was silicon tetrafluoride, the product of its action upon glass. However, PF_3 was a by-product in each preparation and its formation can be rationalised in the following terms;

$F_2PNH_2 + HF \longrightarrow PF_3 + NH_3$ .... [2]

The ammonia so formed can react with BF_3 to give an adduct, or with HF in the presence of BF_3 to produce ammonium tetrafluoroborate. A simple representation of the overall reaction would therefore correspond to Equation [3].

$3F_2PNH_2 + 3BF_3 \longrightarrow 2F_2PNHBF_2 + PF_3 + [NH_4]BF_4$ ...... [3]

To maximise the yield it was necessary to use a threefold excess of BF_3 and to carry out the reaction in the gas phase. This was the method favoured for the preparation of F_2PNDBF_2 and $F_2P^{15}NHBF_2$. Attempts to improve yields by the use of hydrogen fluoride abstractors, such as potassium fluoride and aluminium metal,[87] were unsuccessful.

The adducts of BF_3 with ammonia and the difluorophosphino-amines can be placed in the following order of stability;

$NH_3.BF_3 > F_2PNH_2.BF_3 > (F_2P)_2NH.BF_3 \sim (F_2P)_3N.BF_3$

The primary amine adduct was undissociated at 209K, whereas those of the secondary and tertiary amines were weak enough to allow separation of these amines from BF_3 by low temperature fractionation. Relative stabilities of these adducts almost certainly accounted for the principal side reaction which occurred when the ratio $BF_3:F_2PNH_2$ fell below 3:1.

$F_2PNH_2.BF_3 + F_2PNH_2 \longrightarrow (F_2P)_2NH + NH_3.BF_3$ ...... [4]

In fact, if the ratio $F_2PNH_2:BF_3$ exceeded 2:1, Equation [4] was the only reaction giving a volatile product. However, a 50:50% mixture of F_2PNH_2 and $(F_2P)_2NH$ in a 2:1 ratio with BF_3 produced only $(F_2P)_2NH$; further substitution to tris-(difluorophosphino)amine did not take place.

$(F_2P)_2NH.BF_3 + F_2PNH_2 \not\longrightarrow (F_2P)_3N + NH_3.BF_3$ .... [5]

The details of these experiments are given in the experimental section, Chapter 9.

5.2. Properties of F_2PNHBF_2

The compound was sufficiently stable in the gas phase to allow study of its spectroscopic properties, but as liquid underwent rapid decomposition, yielding the trifluorides of boron and phosphorus, and a white solid. On gently warming this solid, F_2PNHBF_2 was regenerated with more BF_3 and PF_3, and eventually some involatile white material remained. In this behaviour F_2PNHBF_2 closely resembled F_2BNH_2.[88] As both compounds have Lewis acid and

TABLE 5.1

Mass spectrum of F_2PNHBF_2 (a)

m/e	Rel. abundance	Assignment (b)
133	92	$[^{11}M]^+$
132	17	$[^{10}M]^+, [^{11}M-H]^+$
131	1	$[^{10}M-H]^+$
114	5	$[^{11}M-F]^+$
113	4	$[^{10}M-F]^+, [^{11}M-HF]^+$
112	<1	$[^{10}M-HF]^+$
94	8	$[^{11}M-HF_2]^+$
93	2	$[^{10}M-HF_2]^+$
88	10	$[PF_3]^+$
84	5	$[(F_2P)NH]^+$
69	100	$[F_2P]^+$
68	4	$[^{11}BF_3]^+$
67	1	$[^{10}BF_3]^+$
65	12	$[(FP)NH]^+$
64	2	$[(FP)N]^+$
50	6	$[FP]^+$
49	10	$[^{11}BF_2]^+$
48	2	$[^{10}BF_2]^+$
46	17	$[PNH]^+$
45	2	$[PN]^+, [(F^{11}B)NH]^+$
44	<1	$[(F^{10}B)NH]^+, [(F^{11}B)N]^+$
31	1	P^+
20	1	$[HF]^+$

Note: (a) Recorded at an ionising voltage of 70 eV.
(b) $^{11}M = F_2PNH^{11}BF_2$, $^{10}M = F_2PNH^{10}BF_2$.

Lewis base properties, it is possible that the first solid formed was a cyclic or polymeric adduct, $\leftarrow NH(PF_2)BF_2 \rightarrow_n$, and the involatile solid, polymerous material, consisting of $\leftarrow NHPF \rightarrow$ and $\leftarrow NHBF \rightarrow$ units produced by loss of BF_3 or PF_3 molecules. This liquid phase instability made a study of some properties impossible, and characterisation more difficult and less complete than normal.

The molecular weight in the gas phase [Found 132.2 ± 2.9; Calculated for HBF_4NP, 132.8 g mol^{-1}], and the exact mass of the parent ion [Found 132.9874; Calculated for $^{1}H^{11}B^{19}F_4{}^{14}N^{31}P$, 132.9876] were in agreement with the proposed formulation.

Further details of the mass spectrum, Table 5.1, indicated initial loss of hydrogen, or fluorine atoms, or even larger units. In contrast with the $[PF]^+$ and $[PN]^+$ ions, there were no detectable $[BF]^+$ or $[BN]^+$ ions. From the spectrum, there was little evidence to show fluorine was lost preferentially from phosphorus or from boron. In addition to the spectral pattern of F_2PNHBF_2, a peak of unit relative abundance was observed which corresponded to the ion, $[(F_2PNH)_2BF]^+$. This compound might have arisen in the manner of Equation [6].

$$F_2PNHBF_2 + F_2PNH_2 \longrightarrow (F_2PNH)_2BF + HF \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad [6]$$

5.3. Vibrational Spectra

The gas phase infra-red and solid phase Raman spectra of F_2PNHBF_2, which are given in Table 5.2, provide good evidence for the suggested identity of the compound. In particular, bands at 3400 and 1205 cm^{-1} imply that there is

TABLE 5.2

Vibrational spectra of F_2PNHBF_2

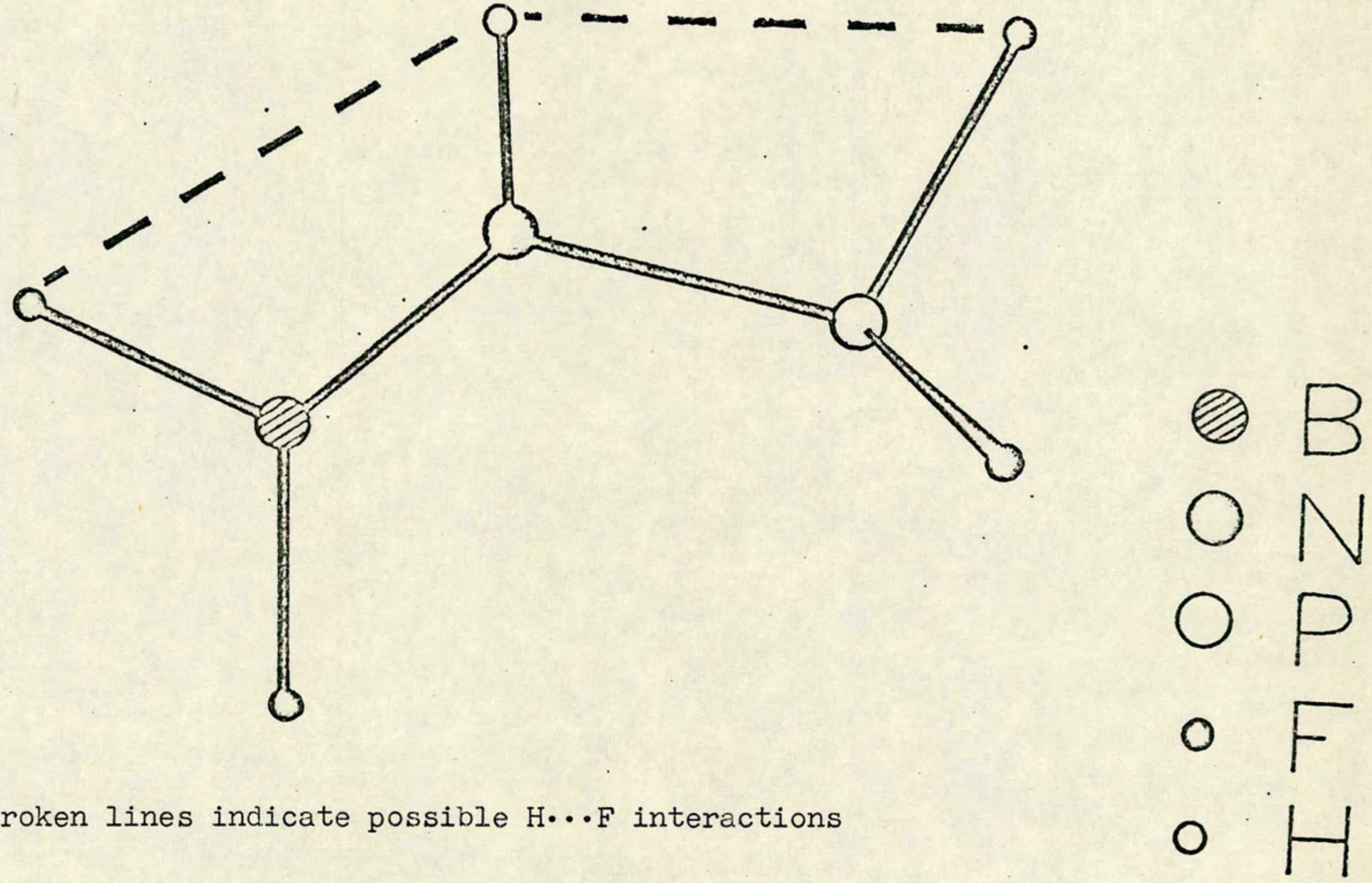
I.r. (gas)		Raman (solid)	
F_2PNHBF_2	F_2PNDBF_2	F_2PNHBF_2	Assignment
3400 m	2530 m	3386 m	ν(NH) or ν(ND)
1494) 1489) s 1485)			$\nu_{asym}(F_2BN)$
1446) 1441) vs	1445 vs		
1404 vs	1415 vs, br	1410 w, br	
1355 w	1359 w		
1205 m	1055 m		δ(NH) or δ(ND)
		995 w	δ(NH)
952 m	954 w	961 w, br	ν(PNB)
851)		877 s	ν(PF)
848) s	860 s		
845)		842 vs	
809 vs	814 s	786 m 772 m	
	780 s		δ(ND)
678 m	672 m	659 w, br	ν(PNB)
592 m	590 w	604 w, br	$\delta(NBF_2)$, $\delta(PF_2)$, and $\tau(BF_2)$
541 m	530 w		
508 w			
434 w		434 w	
396 m, br	395 m	401 m	
356 w		331 m	
296 w, br	290 w	294 m	
		260 w	δ(PNB)
		156 w	$\tau(PF_2)$

Note:

vs = very strong, s = strong, m = medium,
w = weak, br = broad.

Figure 5.1

Possible structure of F_2PNHBF_2



Broken lines indicate possible H•••F interactions a secondary amine present; bands between 1400 and 1500 cm^{-1} suggest the presence of a species containing fluorine bound to three co-ordinate boron; and absorptions between 800 and 900 cm^{-1}, and below 500 cm^{-1}, are consistent with a difluorophosphino-amine, rather than a phosphorus (V) species.

The highest possible point group for F_2PNHBF_2 is C_s, generating 12 a' and 6 a" vibrational modes. By analogy with the structures of other NBF_2 containing molecules,[88,89] the $PNBF_2$ unit is expected to be planar, whilst the maximisation of H···F interactions[17,30] would make one P-F bond also lie in the plane, giving overall C_1 symmetry. However, the only difference, spectroscopically, between C_s and C_1 point groups is that in the latter case all modes would be polarised in the Raman spectrum, instead of just the a' modes of a C_s molecule. In the absence of polarisation data the spectra were therefore interpreted in terms of, and were consistent with, the higher symmetry.

Moreover, the spectra were entirely consistent with there being only one conformer present in the gas phase, in marked contrast with $F_2PNHSiH_3$[17] and $(F_2P)_2NH$. This is not surprising, however, when the possibilities of H···F interaction, Figure 5.1, are considered. Delocalisation of nitrogen lone pair electrons into a boron 2p orbital may also affect the conformation, by reducing the degree of phosphorus - nitrogen lone pair - lone pair interaction.

The bands at 3400 and 1205 cm^{-1}, which shifted to 2530 and 1055 cm^{-1} on deuteriation, were assigned to the N-H stretch and N-H in-plane deformation of a secondary amine. Other assignments in Table 5.2 were much more tentative, and assumed

TABLE 5.3

N.m.r. parameters for $F_2P^{15}NHBF'_2$ $^{(a)}$

$\delta(^1H)$	+4.44(5)
$\delta(^{19}F)$	-62(1)
$\delta(^{19}F')$	-116(1)
$\delta(^{31}P)$	+150(1)
$^1J(^{31}P^{19}F)$	1240(10)
$^1J(^{31}P^{15}N)$	70(10)
$^1J(^{15}N^1H)$	77(1)

Note: (a) Recorded at 273K in $C_6D_6/CHCl_3$. Error limits in parentheses.
For chemical shift conventions refer to the experimental section.
Chemical shifts, δ, are in p.p.m., coupling constants, J, in Hz.

TABLE 5.4.

Photoelectron spectrum of F_2PNHBF_2

Vertical I.P.$^{(a)}$	Assignment
11.5	N lone pair
12.3	P lone pair
15.3	P-N, N-H, B-N bonding
15.9	
16.6	
17.2	F lone pairs
18.0	P-F bonding
ca. 18.7 (broad)	B-F bonding

Note: (a) In eV; ± 0.1 eV.

TABLE 5.5.

Ionisation potentials of some difluorophosphino- and difluoroboryl-amines$^{(a)}$

Compound	N lone pair	P lone pair	Ref.
$(CH_3)_2NPF_2$	9.6	10.5	42
$(CH_3)_2NBF_2$	9.7	-	93
F_2PNH_2	10.9	11.5	42
F_2PNHPF_2	11.3	12.1	This work
F_2PNHBF_2	11.5	12.3	This work

Note: (a) Vertical I.P. in eV; ± 0.1 eV.

considerable mixing of bond stretching and deformation modes. Those bands between 1400 and 1500 cm^{-1} were correlated with the B-F asymmetric stretches of $^{11}BF_3$ and $^{10}BF_3$, but with the degeneracy lifted by replacement of one fluorine by nitrogen. The "symmetric" NBF_2 vibration, corresponding to the band at 890 cm^{-1} in BF_3, was assumed to mix with the P-N stretch, also expected in this region and also of a' symmetry, to give bands at 952 and 678 cm^{-1}. Remaining bands in this region were the P-F stretches, and the out-of-plane N-H deformation which appeared at 780 cm^{-1} on deuteriation.

The specific assignment of deformations in the region below 700 cm^{-1} proved to be too difficult, except for those suggested by consideration of the spectra of $F_2BN(CH_3)_2$,[90] and $(F_2P)_2NH$ and $(F_2P)_3N$.

5.4. N.m.r. spectra

The determination of the n.m.r. parameters quoted in Table 5.3 was made unusually difficult for two reasons. Firstly, the compound was unstable when in the liquid phase, or in solution. And secondly, the spectral lines were broadened by coupling to quadrupolar nuclei. While the use of $F_2P^{15}NHBF_2$ removed the problem due to ^{14}N, it was not possible to broad-band decouple ^{11}B with the available equipment. Neither could ^{15}N or ^{11}B chemical shifts be obtained by heteronuclear double resonance experiments while observing either the ^{1}H or ^{31}P spectrum. However, those parameters obtained were fully consistent with the proposed formula. Particularly, the ^{19}F chemical shifts confirmed the presence of a difluorophosphino-amine,[91] and fluorine bonded to three co-ordinate boron.[92] Although the error margin in $^{1}J(^{31}P^{15}N)$ precludes further comment, both this and $^{1}J(^{15}N^{1}H)$ are comparable with the analogous couplings in mono-, bis-, and tris(difluorophosphino)-amines.

5.5. Photoelectron spectrum

Table 5.4 records the details of the He (I) photoelectron spectrum of F_2PNHBF_2, the first two bands of which were assigned to nitrogen and phosphorus lone pair levels, based on results from earlier studies of difluorophosphino-nitrogen compounds.[42] These same two ionisation potentials for several F_2P and F_2B containing amines are presented in Table 5.5. It can be seen that both lone pair levels depend mainly on the number of fluorine containing substituents, and that replacement of F_2P for F_2B has little effect. This may only reflect the electronegativities of the two groups. Another possibility is that the extent of overlap of the nitrogen lone pair orbital with the vacant boron 2p orbital is matched by the overlap of the nitrogen lone pair and vacant phosphorus 3d orbitals.

CHAPTER 6

PREPARATION AND CHARACTERISATION OF DIAMINODIFLUOROPHOSPHORANE, $HPF_2(NH_2)_2$

6.1. Preparation

During the preparation of F_2PNHBF_2, from F_2PNH_2 and BF_3, difficulty was experienced in having to remove $(F_2P)_2NH$ from reaction mixtures. Although due to a side-reaction, it was thought at first that $(F_2P)_2NH$ was present in the F_2PNH_2, and to prevent this, F_2PNH_2 was prepared using a slight excess of ammonia. Upon fractionation this sample was found to contain a novel compound, whose subsequent characterisation showed it to be $HPF_2(NH_2)_2$.

From this chance observation further preparations from F_2PNH_2 or PF_2Cl, and ammonia were successful. Although a simplification, reactions proceed by oxidative addition of NH_3 to F_2PNH_2 according to Equations [1] and [2], in 25% or 40% yields (based on difluorophosphine taken).

$$F_2PNH_2 + NH_3 \longrightarrow HPF_2(NH_2)_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad [1]$$

$$PF_2Cl + 3NH_3 \longrightarrow HPF_2(NH_2)_2 + [NH_4]Cl \quad \ldots\ldots\ldots \quad [2]$$

These two routes meant that suitable preparations could give selectively deuteriated compounds which, despite a certain amount of scrambling of hydrogen and deuterium, were helpful in vibrational assignments.

$$F_2PNH_2 + ND_3 \longrightarrow \text{"}DPF_2(NH_2)(ND_2)\text{"} \quad \ldots\ldots\ldots\ldots\ldots \quad [3]$$

$$F_2PND_2 + NH_3 \longrightarrow \text{"}HPF_2(ND_2)(NH_2)\text{"} \quad \ldots\ldots\ldots\ldots\ldots \quad [4]$$

Footnote: refer to p. 123(a) for additional references to phosphorus compounds with P–H bonds

TABLE 6.1

Some Physical Properties of $HPF_2(NH_2)_2$

(1) Colourless liquid at 298 K.

(2) Exact Mass of $[HPF_2(NH_2)_2]^+$;
102.015741 (observed), 102.015839 (calculated).

(3) Vapour pressure; 6 ± 1 torr at 292 K.

(4) Melting point; 270.0 ± 0.5 K.

(5) Molecular weight; 101.4 ± 3.4 g mol^{-1} (observed),
102.0 g mol^{-1} (calculated).

TABLE 6.2

Mass Spectra of $HPF_2(NH_2)_2$

	Relative Abundance			
m/e	at 13 eV	at 70 eV	Assignments	
102	3	1		$[HPF_2(NH_2)_2]^+$
101		13	$[PF_2(NH_2)_2]^+$,	$[HPF_2(NH_2)(NH)]^+$
86	37	100		$[HPF_2(NH_2)]^+$
85	22	80	$[PF_2(NH_2)]^+$,	$[HPF_2(NH)]^+$
84		5	$[PF_2(NH)]^+$,	$[HPF_2N]^+$
83	1	25	$[PF_2N]^+$,	$[HPF(NH_2)_2]^+$
82	100	16	$[PF(NH_2)_2]^+$,	$[HPF(NH_2)(NH)]^+$
81		4	$[PF(NH_2)(NH)]^+$,	$[HPF(NH)_2]^+$
78	6	1	$[PFN_2]^+$	
69		42	$[PF_2]^+$	
67		1		$[HPF(NH_2)]^+$
66	3	44	$[PF_2(NH_2)]^+$,	$[HPF(NH)]^+$
65		4	$[PF(NH)]^+$,	$[HPFN]^+$
62	3	2	$[P(NH_2)(NH)]^+$,	$[HP(NH)_2]^+$
50		3	$[PF]^+$	
47		1	$[PNH_2]^+$,	$[HP(NH)]^+$
46		21	$[PNH]^+$	
45		2	$[PN]^+$	
33		1	$[NF]^+$	
31		1	P^+	
20		3	$[HF]^+$	
16		3	$[NH_2]^+$	

Metastable ions

49.7 $[PF_2(NH_2)]^+ \longrightarrow HF + [PF(NH)]^+$

52.5 $[HPF(NH_2)_2]^+ \longrightarrow NH_3 + [PF(NH_2)]^+$

55.4 $[HPF_2(NH_2)]^+ \longrightarrow NH_3 + [PF_2]^+$

Results and Discussion

Table 6.1 shows some physical properties, and Table 6.2 the mass spectrum with assignments, of $HPF_2(NH_2)_2$.

6.2. Mass Spectrum

Lack of intensity of the parent ion seems common in fluorophosphoranes and $HPF_2(NH_2)_2$ was no exception. For H_2NPF_4[94] and $(H_2N)_2PF_3$[95] no parent ions were observed. Neither were they seen in HPF_4 or H_2PF_3[96] where it was suggested that the stability of phosphonium ions, such as $[PF_4]^+$ and $[HPF_3]^+$, may be responsible. The recent preparation of $[Me_2PF_2]^+[PF_6]^-$[97] seems to give support to this view.

Fragmentation from H_2NPF_4 produced ions such as $[HNPF_4]^+$, $[PF_4]^+$, and $[H_2NPF_3]^+$, whilst $(H_2N)_2PF_3$ gave $[H_2NPF_3]^+$, $[HNPF_3]^+$, $[PF_3]^+$, and $[H_2NPF_2]^+$. Similar breakdown routes were seen in $HPF_2(NH_2)_2$ with loss of H,F, and HF, NH_2 and NH_3 being most important.

However, the ability to lose a proton bound to phosphorus or nitrogen made assignment particularly difficult. The presence of ions at 86 and 83 m/e units, which are most likely to be $[HPF_2(NH_2)]^+$ and $[HPF(NH_2)_2]^+$, indicated NH_2 and F loss from the parant ion not involving H-P bond cleavage.

$$[HPF_2(NH_2)_2]^+ \longrightarrow NH_2 + [HPF_2(NH_2)]^+ \; \ldots\ldots\ldots \; [5]$$

$$[HPF_2(NH_2)_2]^+ \longrightarrow F + [HPF(NH_2)_2]^+ \; \ldots\ldots\ldots \; [6]$$

These fragments in turn gave rise to metastable peaks at 55.4 and 52.5 m/e when ammonia was eliminated.

$$[HPF_2(NH_2)]^+ \longrightarrow NH_3 + [PF_2]^+ \; \ldots\ldots\ldots\ldots\ldots \; [7]$$

$$[HPF(NH_2)_2]^+ \longrightarrow NH_3 + [PF(NH)]^+ \text{ .... } [8]$$

A third metastable peak at 49.7 m/e could have arisen from HF elimination from $[HPF_2(NH)]^+$, but since it is also seen in the mass spectrum of pure F_2PNH_2,[9] it most probably occurs by Equation [9]:

$$[F_2PNH_2]^+ \longrightarrow HF + [FP(NH)]^+ \text{ .... } [9]$$

At 12 eV the intensity of the parent ion was greater than at 70 eV, and the main pattern was produced by NH_2 and HF loss. From 12 to 13 eV corresponded to the appearance potential of the 101 m/e fragment.

In both spectra the 82 m/e peak was strong, perhaps due to the stability of $[FP(NH_2)_2]^+$. Harman and Sharp[8] have shown that molecules of this type can be formed by reaction of primary amine with difluorophosphines.

$$3RNH_2 + 2RNHPF_2 \longrightarrow 2(RNH)_2PF + [RNH_3]^+[HF_2]^- \text{ ..... } [10]$$

If Equation [10] is regarded as HF abstraction, then formation of $[FP(NH_2)_2]^+$ by elimination of HF from $[HPF_2(NH_2)_2]^+$ is not unreasonable.

6.3. N.m.r. Spectra

From the parameters, it was apparent that $HPF_2(NH_2)_2$ was stereochemically rigid on the n.m.r. time scale at room temperature, with the fluorines axial in a trigonal bipyramid in agreement with the "apicophilicity" series of Cavell *et al.*[98] Although no intramolecular re-arrangement was taking place, rotation about the P-N bonds was making all amino protons equivalent. A sample was prepared containing

Figure 6.1 ^{1}H n.m.r. spectrum of $HPF_2(^{15}NH'_2)_2$

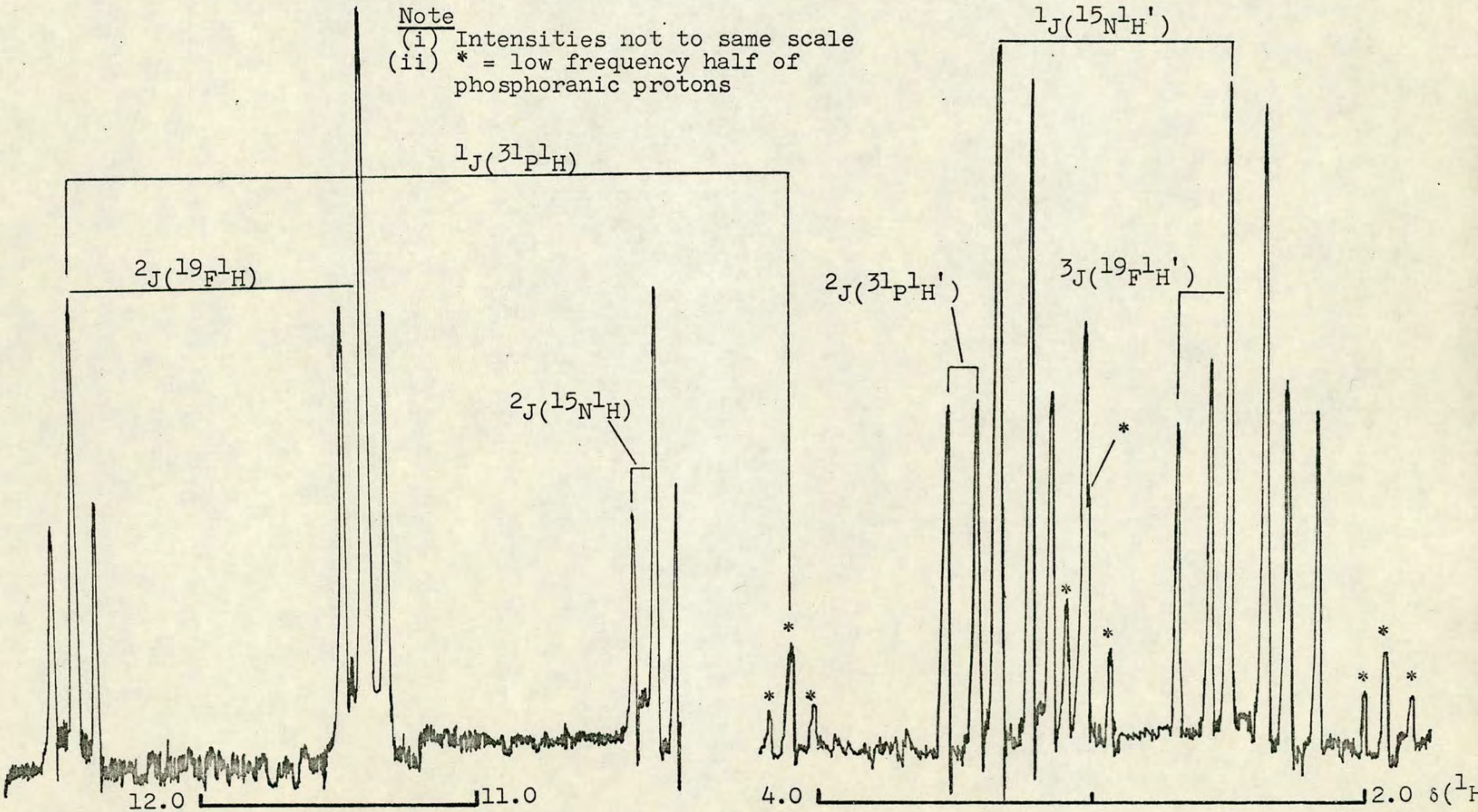


Figure 6.2

^{19}F n.m.r. spectrum of $HPF_2(^{15}NH'_2)_2$

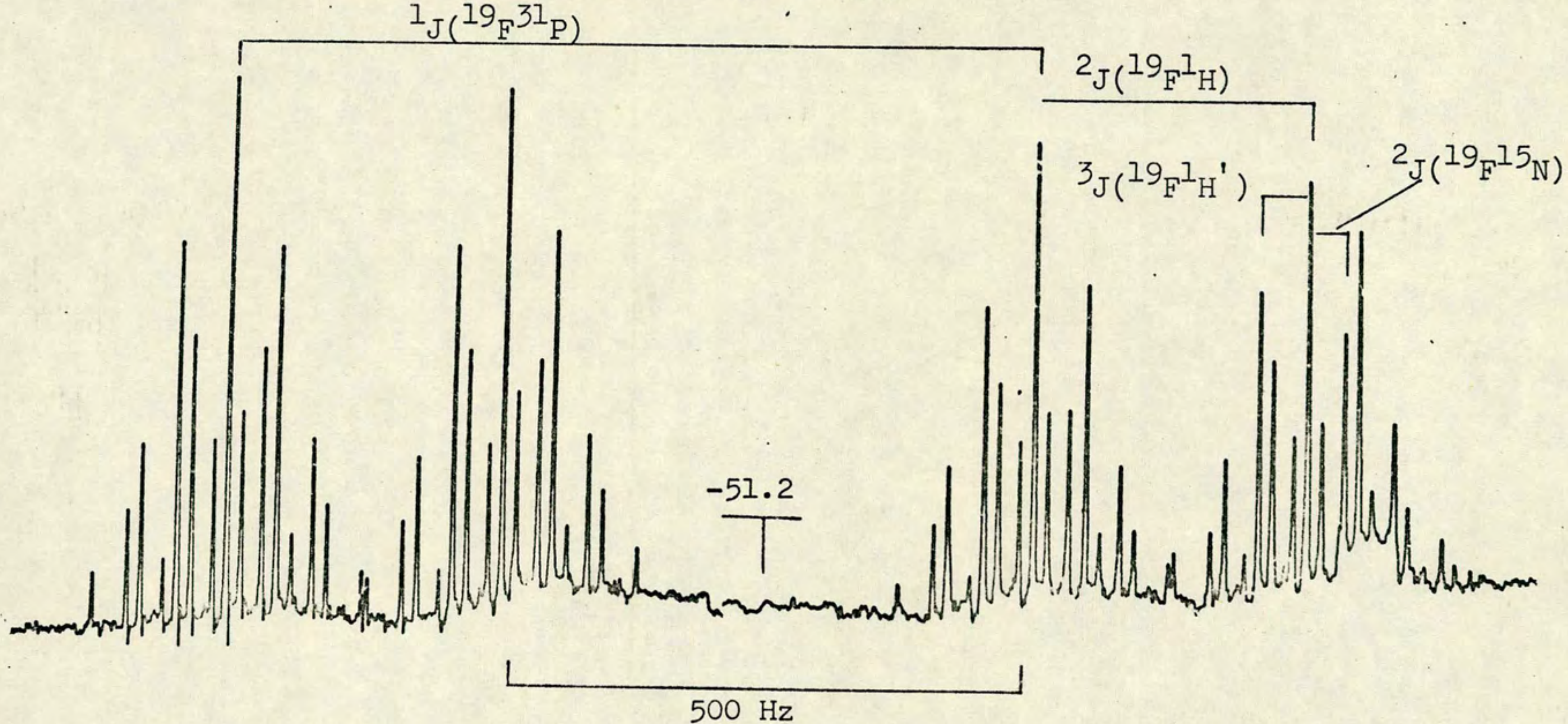


Figure 6.3

^{31}P n.m.r. spectrum of $HPF_2(^{15}NH'_2)_2$

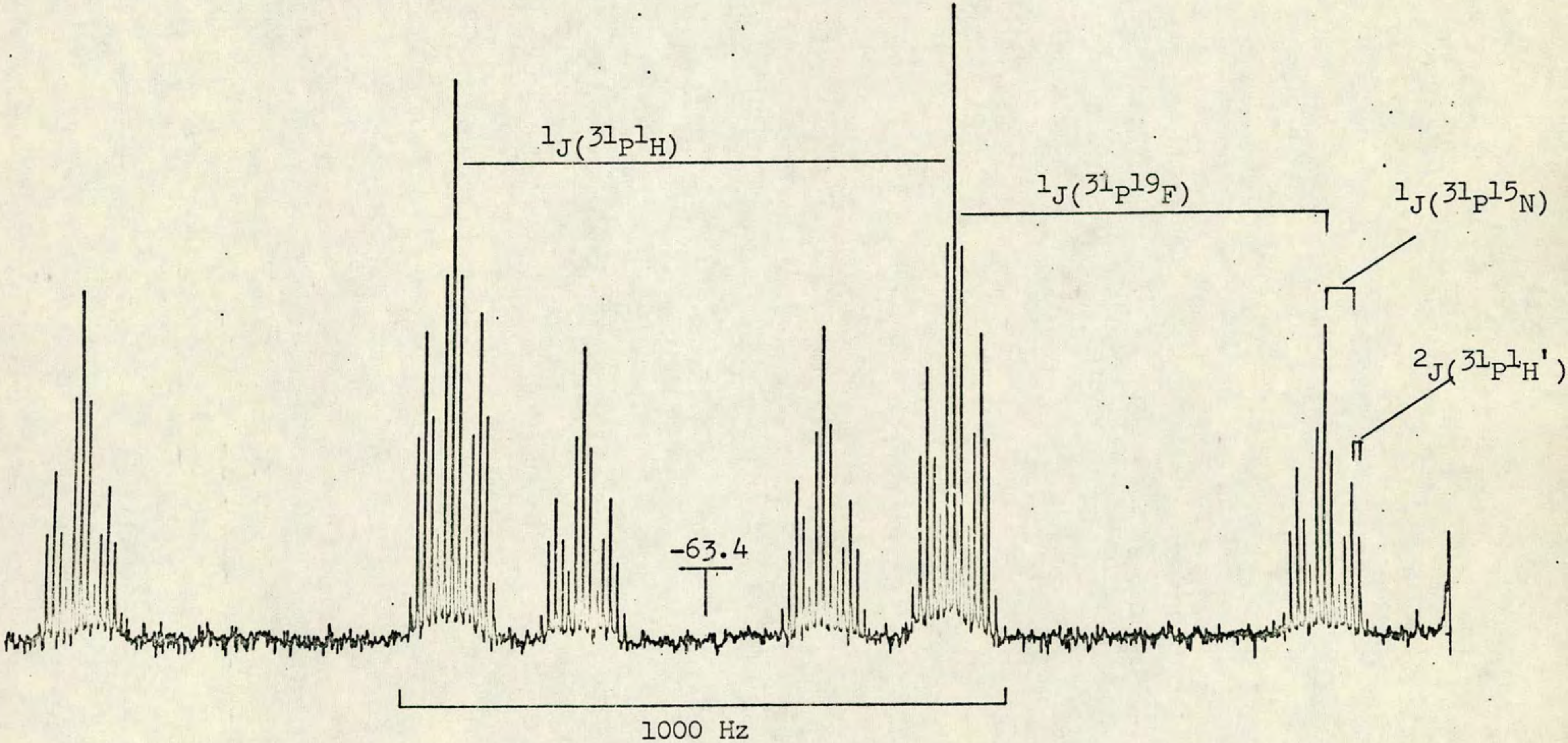


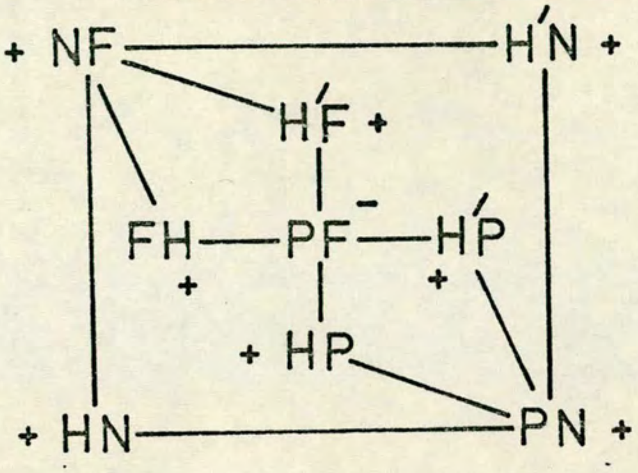
TABLE 6.3

Double Resonance Experiments for $HPF_2(^{15}NH'_2)_2$

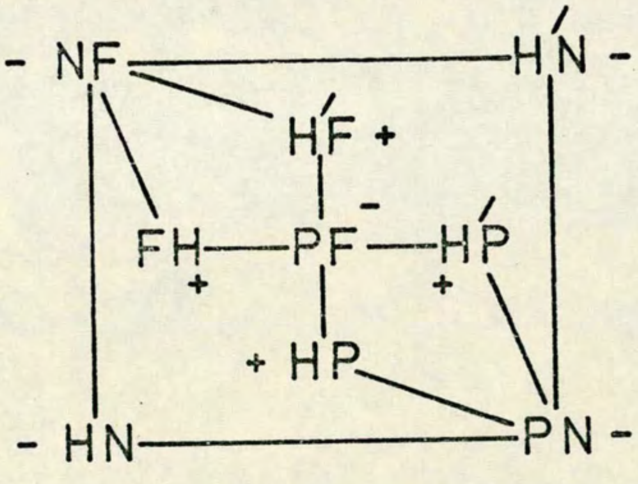
Experiment	Coupling Constants related		Relative Signs
$^{1}H-(^{15}N)$	$^{2}K(^{19}F^{1}H)$	$^{2}K(^{19}F^{15}N)$	Equal
	$^{1}K(^{31}P^{1}H)$	$^{1}K(^{31}P^{15}N)$	Equal
$^{1}H-(^{19}F)$	$^{2}K(^{15}N^{1}H)$	$^{2}K(^{19}F^{15}N)$	Equal
	$^{1}K(^{31}P^{1}H)$	$^{1}K(^{31}P^{19}F)$	Opposite
$^{1}H-(^{31}P)$	$^{2}K(^{19}F^{1}H)$	$^{1}K(^{31}P^{19}F)$	Opposite
	$^{2}K(^{15}N^{1}H)$	$^{1}K(^{31}P^{15}N)$	Equal
$^{1}H'-(^{15}N)$	$^{3}K(^{19}F^{1}H')$	$^{2}K(^{19}F^{15}N)$	Equal
	$^{2}K(^{31}P^{1}H')$	$^{1}K(^{31}P^{15}N)$	Equal
$^{1}H'-(^{19}F)$	$^{1}K(^{15}N^{1}H')$	$^{2}K(^{19}F^{15}N)$	Equal
	$^{2}K(^{31}P^{1}H')$	$^{1}K(^{31}P^{19}F)$	Opposite
$^{1}H'-(^{31}P)$	$^{3}K(^{19}F^{1}H')$	$^{1}K(^{31}P^{19}F)$	Opposite
	$^{1}K(^{15}N^{1}H')$	$^{1}K(^{31}P^{15}N)$	Equal

Figure 6.4

Signs of Coupling Constants in $HPF_2(^{15}NH'_2)_2$ related by Double Resonance Experiments



Reduced coupling constants, K



Coupling constants, J

Note:
Solid lines indicate which coupling constants were related by experiments (Table 6.3) + or - refer to signs based on negative $^1K(PF)$.

TABLE 6.4

N.m.r. parameters(a) of $HPF_2(^{15}NH'_2)_2$ and analogous compounds

Parameter	Compounds							
	$HPF_2(^{15}NH'_2)_2$	HPF_4	H_2PF_3	$HPF_2(NH'CH_3)_2$	$F_4P^{15}NH'_2$	$F_4P^{15}NH'CH_3$	$F_3P(^{15}NH'_2)$	$F_3P(NH't\text{-}C_4H_9)_2$
Temp. (K)	273	133	183	298	298	193	233	298
$\delta(^1H)$	7.23	7.0	7.1	6.5				
$\delta(^1H')$	2.89			3.2	n.o.	3.3	3.14	2.5
$\delta(^{15}N)$	28.6			n.o.	n.o.	n.o.	n.o.	n.o.
$\delta(^{19}F_{axial})$	-51.2	-27.4	-31.0	-62	-56.7	-60,-70(b)	-51.3	-47
$\delta(^{31}P)$	-63.4	-53.6	-24.1	n.o.	n.o.	n.o.	-58.6	n.o.
$^1J(^{31}P^1H)$	+836.0	1115	865	837				
$^1J(^{31}P^{19}F_{ax})$	-619.1	941	n.o.	655	760	755,770(b)	665	726
$^1J(^{15}N^1H')$	-85.0			n.o.	90.3	n.o.	87.5	n.o.
$^1J(^{31}P^{15}N)$	-45.0			n.o.	n.o.	n.o.	-81.5	n.o.
$^2J(^{19}F_{ax}{}^1H)$	+109.1	148	105	118				
$^2J(^{19}F_{ax}{}^{15}N)$	-14.0			n.o.	23.8	n.o.	n.o.	n.o.
$^2J(^{31}P^1H')$	+11.8			n.o.	17.7	~21	+14.5	n.o.
$^2J(^{15}N^1H)$	-8.3			n.o.				
$^3J(^{19}F_{ax}{}^1H')$	+19.7			n.o.	~42	27.6	41.5,1.0(c)	16.4
References		96,101	91,96,102	8	94	103,104	95,105,106,107	104

$^3J(^1H^1H')$, $^3J(^{15}N^1H')$, and $^4J(^1H'^1H')$ < 0.5 Hz. in $HPF_2(^{15}NH_2)_2$

(a) For chemical shift conventions see experimental section; δ in p.p.m., J in Hz.

(b) Due to non-equivalence of axial fluorines.

(c) At 298 K average $^3J(^{19}F_{ax}{}^1H') = +20.7$ Hz.; reference 105

n.o. = not observed

^{15}N atoms in both amine groups. Firstly, since few parameters involving ^{15}N couplings in compounds of this type had been determined, and secondly to eliminate the problem of ^{14}N quadrupolar broadening.

With this sample the spectra in Figures 6.1, 6.2, and 6.3 were obtained, from which the parameters were taken. The couplings $^{3}J(HPNH)$, $^{3}J(^{15}NPN^{1}H)$ and $^{4}J(HNPNH)$ were not observed and so the spectra were of first order. The relative signs of couplings constants and the ^{15}N chemical shift were determined, while observing the proton spectrum, in a series of spin-tickling experiments. Corrected frequencies from these experiments are presented in the experimental section. Those experiments performed, Table 6.3, provided enough information to relate the signs of all coupling constants in a self-consistent manner. This could be done separately for phosphoranic and amino protons, and jointly, since both sets have $^{1}J(PF)$, $^{1}J(PN)$, and $^{2}J(NF)$ in common. Figure 6.4 indicates these relationships in terms of the coupling constant, J, and the reduced coupling constant, K, taking into account the negative value of the ^{15}N gyromagnetic ratio. On the assumption that $^{1}K(PF)$ is always negative[35,72] these results agree with the independent observation of $^{1}K(^{15}N^{1}H)$ being positive.[99,100]

Comparison of the parameters with those for analogous compounds, Table 6.4, shows close agreement, and although no ^{15}N chemical shifts seem to have been measured, the value of 28.6 p.p.m. for $HPF_2(^{15}NH_2)_2$, and 21.4 p.p.m. for $F_2P^{15}NH_2$[74] are similar. Since few $^{1}J(^{31}P^{15}N)$ have been reported, the significance of the value here cannot be

Figure 6.5. ^1H spectrum of the amino protons of $HPF_2(^{15}NH_2)_2$

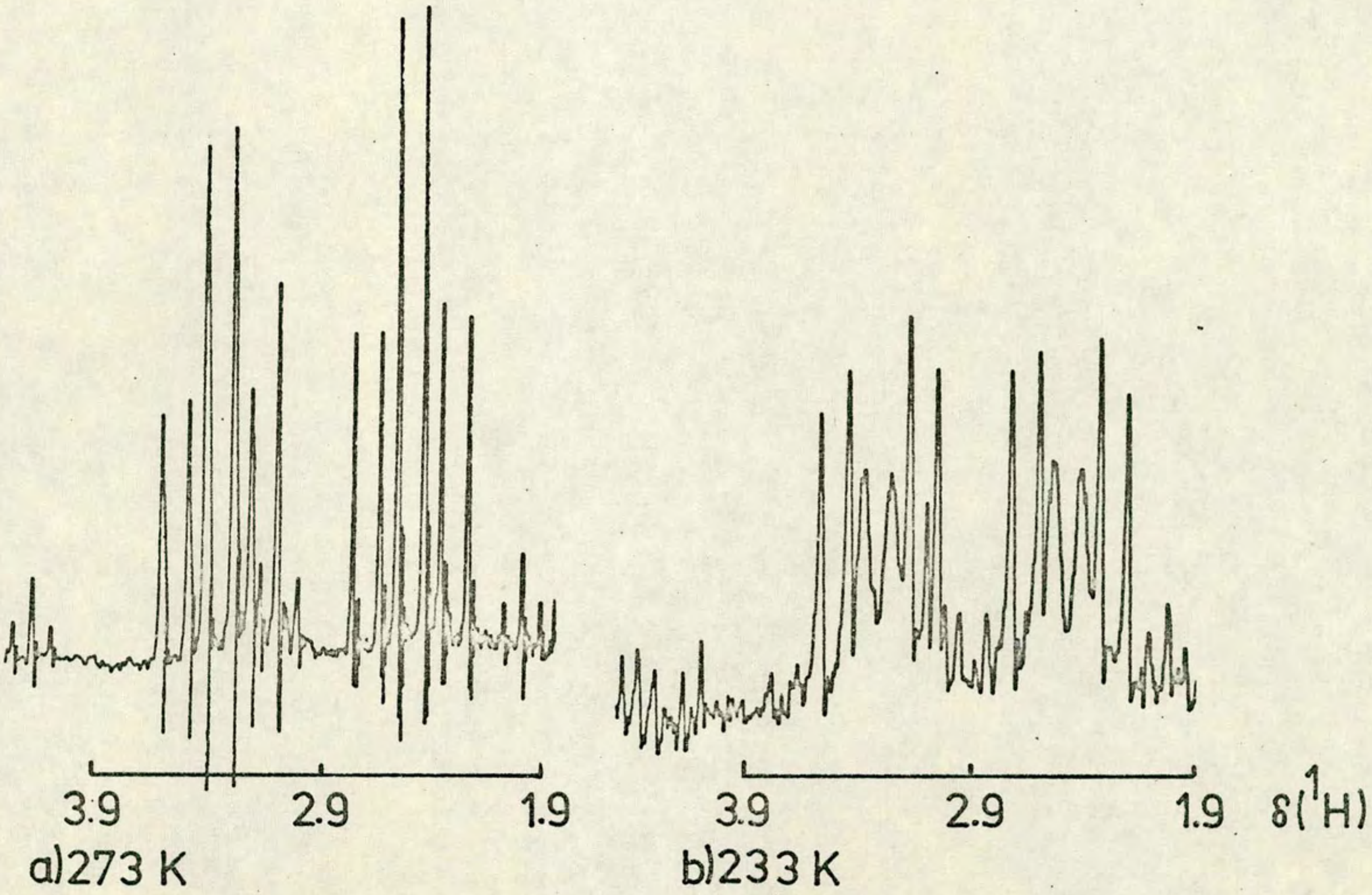
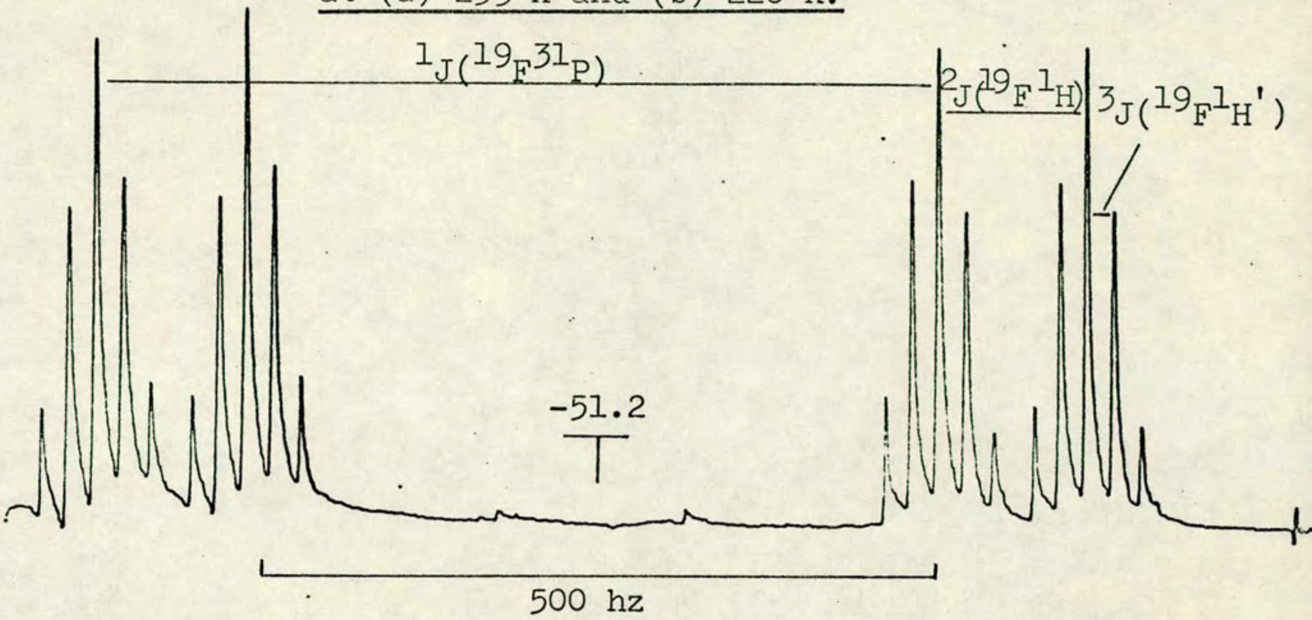
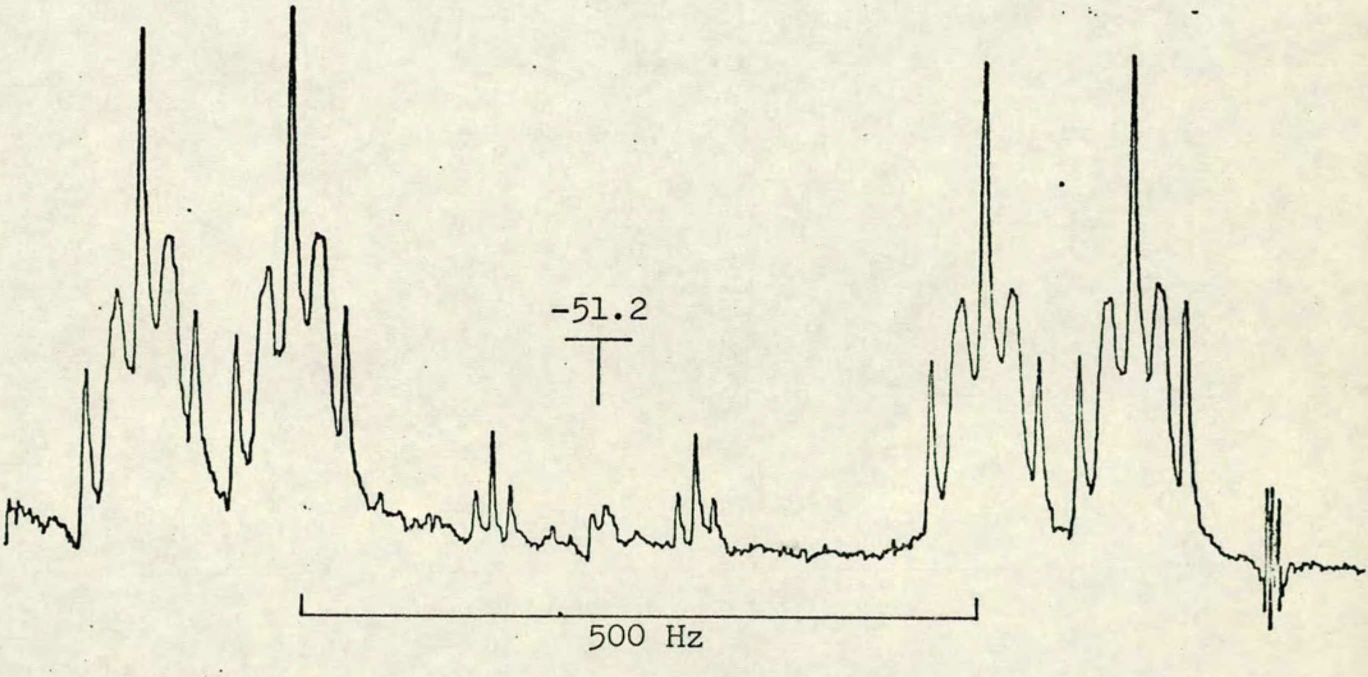


Figure 6.6

^{15}N decoupled, ^{19}F n.m.r. spectrum of $HPF_2(^{15}NH'_2)_2$ at (a) 253 K and (b) 226 K.



(a) 253 K



(b) 226 K

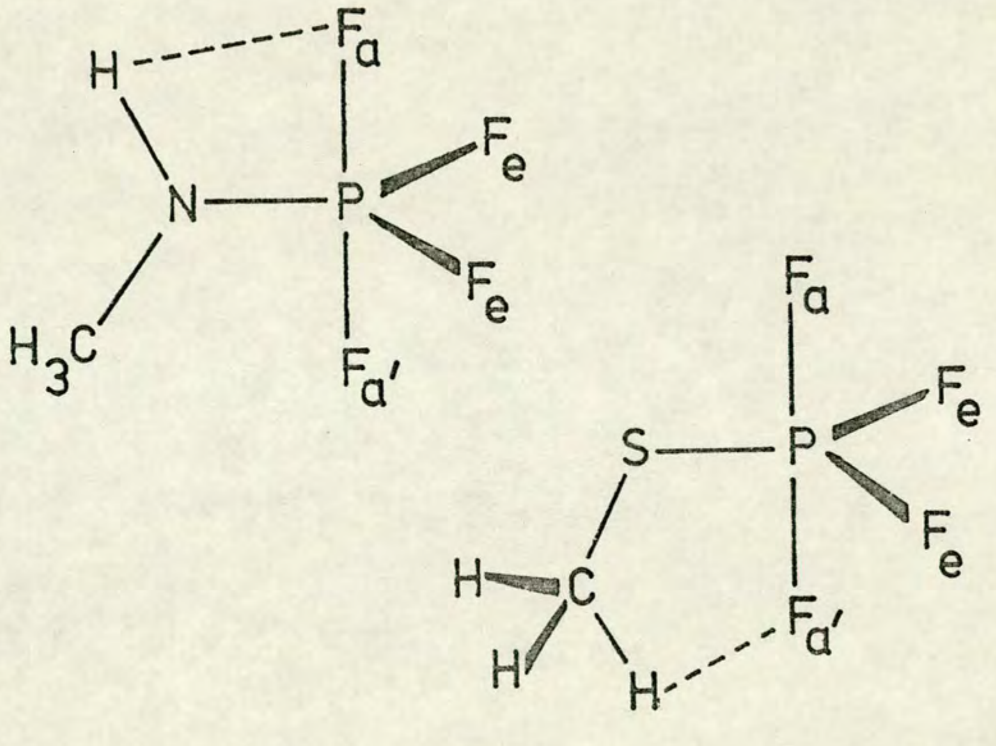
assessed except to say that by comparison with $F_3P(^{15}NH_2)_2$, $F_3P{=}^{15}NP'F_2$, and $(F_3C)_2P^{15}NH_2$, which have values of -81.5, -53.2 ($^1J(PN)$) and +93.8 ($^1J(P'N)$, and +52.6 Hz respectively,[107] this coupling constant is as sensitive to the type of ligands at phosphorus as to the co-ordination number.

The slow intramolecular re-arrangement which makes $HPF_2(NH_2)_2$ appear stereochemically rigid at ambient temperatures is also observed in $F_3P(NH_2)_2$.[94] For various phosphoranes, including F_4PNH_2, the barrier to intramolecular ligand exchange by a Berry pseudorotation has been calculated to be high due to P-N π-interaction.[108] It is also suggested that on reducing the number of electronegative ligands from four, the exchange barrier increases. This is attributed to the preference of the transitory state, a square pyramid, for electronegative ligands in the four basal positions. It seems reasonable, therefore, that with two P-N π-contributions, and only two fluorine atoms, $HPF_2(NH_2)_2$ will have a ligand exchange barrier as high, if not higher, than $F_3P(NH_2)_2$.

The rotation about the P-N bond which averages couplings to the hydrogen atoms has been slowed sufficiently at 233 K in $F_3P(NH_2)_2$[106] to see two different $^2J(F_{ax}H)$ couplings, 41.5 and 10 Hz. An attempt to do this with $HPF_2(NH_2)_2$ failed when the solvents froze at 223 K before the P-N rotation had been slowed enough. However, both proton and fluorine spectra did show changes with temperature, Figures 6.5. and 6.6, similar to those observed in $F_3P(NH_2)_2$.

That the structures adopted by $HPF_2(NH_2)_2$ and $F_3P(NH_2)_2$ are trigonal bipyramids, with the amino groups lying in the plane of the axial fluorines, is supported on two counts. First, it has been shown that this produces the most stable configuration for F_4PNH_2[108] by optimising P-N π-bonding, and second, it maximises H···F interactions which are known to be significant in these types of molecules. In F_4PSCH_3[109] and F_4PNHCH_3[103] for example, the low temperature structures, influenced by these effects, produce different axial fluorine environments and coupling constants.

Figure 6.7.



6.4. Vibrational Spectra

The frequencies, intensities, band shapes (where these are clear), states of polarisation and suggested assignments are presented in Tables 6.5, 6.6 and 6.7, for the molecule, with and without deuteriation. For $DPF_2(NH_2)(ND_2)$ and $HPF_2(ND_2)(NH_2)$ mixing of hydrogen and deuterium has occurred, but the intended form has been

TABLE 6.5

I.r.(gas) Spectra of $HPF_2(NH_2)_2$

$HPF_2(NH_2)_2$	'$HPF_2(ND_2)(NH_2)$'	'$DPF_2(NH_2)(ND_2)$'	$DPF_2(ND_2)_2$	Assignment	
3595 3587 3578 m A	3585 m A	3586 vw A		ν (NH)	See text
	3531 m	3536 3526 m		ν D(NH)	
3476 3471 3464(sh) m C,B	3474 m C,B			ν (NH)	
		2920 vw,br		?	
	2680 w	2686 m,br	2678 m	ν (ND)	See text
	2608 m	2600 m,br	2611 vw	ν H(ND)	
	2540 vw	2540 m,br	2541 m	ν (ND)	
2514 2504 2502 m ?C	2500 m ?C	2500 m ?C		See text	
2449 2437 2425 m C	2436 m C	2435 m C		ν (PH)	
		1810 vw,br	1825 w ?C	See text	
		1770 vw,br	1786 m C	ν (PD)	
1564 1557 s	1557 m,br	1560 m,br		δ_s (NH_2)	
	1406 m,br	1408 s		δ_s (NHD)	
1300 vw,br				?	
1240 w,br	1240 vw			δ_p(NH_2)	
	1195 m,br	1198 s	1204 s	δ_s (ND_2)	
	1095 m,br	1090 m		δ_p (NHD)	
1017 1010 s B	1010 s,br	1008 s			
	930 w	925 w	935 s	δ_p (ND_2)	ν_a(PN_2)
879 w C	876 w *	885 *	854 s		
844 835 vw	834 m *	845 835 m,br *		δ (PH)	ν_s(PN_2)
	810 vw *		829 vw 816 vw	?	
782 m A				δ_w (NH_2)	
730 s A	731 s A	722 s A	716 s A	ν_a (PF_2)	
658 m A				δ (PH)	
	611 w	610 w		? δ (PD), δ_w (ND_2)	
582 w C	580 w C	580 w C	580 w C	ν_s (PF_2)	
519 m ?A	512 m	509 m	505 m	δ (PF_2N_2)	
437 w				?	
420 m,br	415 406 w,br	410 w		δ (PF_2N_2)	
383 m C				δ (PF_2N_2)	
359 m ?A	364 360 w			τ (NH_2)	
303 ms C	309 m C			δ (PF_2N_2)	
	294 m ?C	295 m C		?	
	214 w			τ (PF_2N_2)	

Legend for Tables 6.5, 6.6 and 6.7:- All frequencies in cm^{-1}: s = strong; m = medium; w = weak; v = very; sh = shoulder. A, B and C refer to band shapes (6.5). p = polarised; dp = depolarised (6.6). (a) and (b) (6.7), no bands observable below 300 cm^{-1} and 450 cm^{-1}, respectively. * = spikey, ill-defined region.

TABLE 6.6

Raman (liquid) spectra of $HPF_2(NH_2)_2$

$HPF_2(NH_2)_2$	'$HPF_2(ND_2)(NH_2)$'	'$DPF_2(NH_2)(ND_2)$'	$DPF_2(ND_2)_2$	Assignment	
3546 w,br dp	3540 vw ?				ν(NH) See text
	3490 w p	3485 vw p		ν D(NH)	
3440 m p	3440 m p	3435 vw p			
		2645 w dp	2645 w dp		ν(ND) See text
	2580 m p	2575 w p		ν H(ND)	
2522 m p	2520 m p	2515 m p	2515 m p	See text	
2450 m p	2445 m p	2435 w p		ν(PH)	
	1815 w,br p	1815 m p	1815 m p	See text	
	1780 w,br p	1780 m p	1775 m p	ν(PD)	
1580 w,br dp	1575 vw,br ?			$\delta_s(NH_2)$	
1249 m,br dp	1245 m dp	1240 w,br dp		$\delta_p(NH_2)$	
		1190 w,br p	1185 w,br p	$\delta_s(ND_2)$	
			1090 w ?	$\delta_p(NHD)$	
930 m dp	930 s dp			$\delta_w(NH_2)$	
		895 m,br ? dp	905 w ?	$\delta_p(ND_2)$	
889 vs p	885 s p			$\nu_s(PN_2)$	
	840 s p	830 vs p	825 s p		
	705 w dp	695 m dp	695 m dp	$\delta_w(ND_2)$	
			625 w,br p	?	
			605 w,br p	?	
561 m p	560 s p	555 m p	555 m p	$\nu_s(PF_2)$	
516 m dp	515 m dp	505 m dp	500 m dp	$\delta(PF_2N_2)$	
454 m dp	455 w ?			$\tau(NH_2)$	
	430 vw ?	425 w,br ?		?	
248 m dp	248 s dp	235 m dp	230 m dp	$\tau(PF_2N_2)$	

TABLE 6.7

I.r. and Raman (solid) spectra of $HPF_2(NH_2)_2$

$HPF_2(NH_2)_2$		$DPF_2(ND_2)_2$			
I.r.(solid)$^{(a)}$	Raman(solid)	I.r.(solid)$^{(b)}$	Raman(solid)	Assignment	
3518 3508 s	3531 w			ν (NH) See text	
	3516 w				
3417 s	3416 m				
		2630 m	2642 w 2628 w		ν (ND) See text
		2560 w		ν H(ND)	
		2500 m	2502 w		
2502 m	2518 m			See text	
2428 m	2448 m			ν (PH)	
		2380 w		?	
		2030 w,br		?	
		1980 w,br		?	
		1820 m	1822 w	See text	
		1780 m	1785 w	ν (PD)	
1569 s	1586 w,br 1571 w,br	1585 w,br		δ_s (NH_2)	
		1425 m		δ_s (NHD)	
1241 w	1234 w			δ_p (NH_2)	
		1210 m	1194 w	δ_s (ND_2)	
		1090 w		δ_p (NHD)	
1029 s					
	996 vw,br 935 m	950 915(sh) s	900 w	$\delta_w(NH_2)$ δ_p (ND_2)	ν_a (PN_2)
882 m	884 vs	880(sh) 840 s	840 m 821 s	ν_s (PN_2)	
			697 m	δ_w (ND_2)	
676 s,br		660 vs		ν_a (PF_2)	
612 vw	616 vw,br	610 w		δ (PH)	
	591 vw,br			?	
548 vw	561 w,br	545 m	541 m	ν_s (PF_2)	
503 w	506 m	495 s	489 m	δ (PF_2N_2)	
	461 m			τ (NH_2)	
	446 w		445 w	δ (PF_2N_2)	
397 w	407 m		401 w	δ (PF_2N_2)	
350 vw				τ (NH_2)	
			298 w	δ (PF_2N_2)	
	240 m		221 m	τ (PF_2N_2)	
	120 w			?	

TABLE 6.8

Vibrational Modes of $HPF_2(NH_2)_2$, point group C_{2V}

	a_1	a_2	b_1	b_2
ν (NH)	/	/	/	/
ν (PN)	/			/
ν (PF)	/		/	
ν (PH)	/			
δ (PH)			/	/
δ (PF_2N_2)	//		/	/
$\delta_s(NH_2)$	/			/
$\delta_w(NH_2)$		/	/	
$\delta_\rho(NH_2)$	/			/
τ (NH_2)		/	/	
τ (PF_2N_2)		/		
I.r. band shape	C	-	A	B

TABLE 6.9

NH and ND stretching frequencies of Diaminodifluorophosphorane

	Symmetry class	I.r. (cm^{-1})		Raman (cm^{-1})	
		(gas)	(solid)	(liquid)	(solid)
$HPF_2(NH_2)_2$					
ν (NH)	b_1	3587	3513	3546	3516
	a_2	–	–		3531
	a_1	3476	3417	3440	3416
	b_2	3468			
$DPF_2(ND_2)_2$					
ν (ND)	b_1	2678	2630	2645	2628
	a_2	–	–		2642
	a_1	2541	2500	2515	2502
	b_2				

retained to an extent sufficient to help with assignments, e.g. $HPF_2(ND_2)(NH_2)$ shows only a P-H stretch while $DPF_2(NH_2)(ND_2)$ gives both P-H and P-D stretches. Also useful is the presence of the NHD group which has an effect intermediate between NH_2 and ND_2 vibrations.

From the data available it is clear that interaction with neighbouring linkages occurs, causing bands to be mass sensitive and making assignments to a particular stretch or deformation less meaningful. In particular, the 1000-800 cm^{-1} region has many bands of the same symmetry class where mixing of modes could be taking place. The observation of bands of A, B and C shape in the spectra of the gas phase samples is consistent with the n.m.r. evidence that the molecule adopts a structure with C_{2V} symmetry.[110] Assignments have therefore been made on this assumption, Table 6.8.

From the vibrational data, NH stretches can be selected by frequency and band-shape, additional information being provided by deuteriation. As well as $\nu(NH)$ in NH_2 groups, there is an intermediate vibration from this stretch in NHD units. A similar effect is observed for $\nu(ND)$. When NH and ND stretching regions in $HPF_2(NH_2)_2$ and $DPF_2(ND_2)_2$ are compared, Table 6.9, it is possible to assign all four vibrational species. The a_1 and b_2 modes, which involve symmetric stretching of the NH_2 groups, are assumed to be of similar energy, but are identifiable by their i.r. band shapes and different degrees of Raman polarisation.

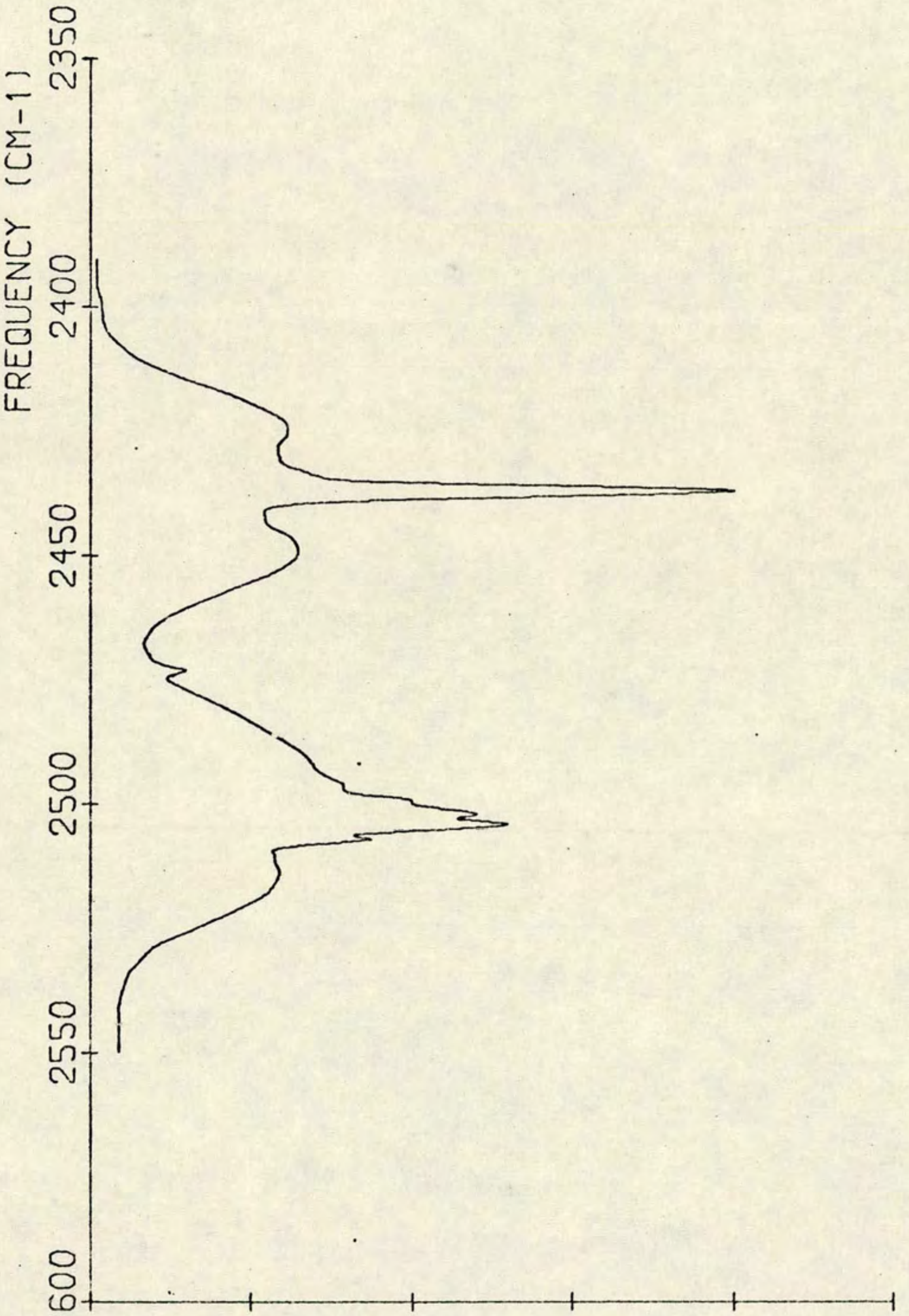
Deformations of the amino groups are observed at ca. 1560 and 1200 cm^{-1}, shifting to 1410 and 1090 cm^{-1} on partial deuteriation, and to 1200 and 935 cm^{-1} on complete deuteriation, and assigned to scissors and rocking modes, by analogy with other amine compounds, such as hydrazine.[111]

Of the large number of bands below 1000 cm^{-1}, those at 879 and 582 cm^{-1} are Raman polarised with a C band-shape, and correspond to the symmetric P-N and P-F stretches, respectively. The corresponding asymmetric stretches are more difficult to place. A strong i.r. band at 1014 cm^{-1} has a B-contour expected for a b_2 species, such as the asymmetric P-N stretch, and occurs within a range of known P-N stretches, 1053-873 cm^{-1}.[46] This band does move on deuteriation, as does the symmetric P-N stretch, being an indication of the sensitivity of these stretches to substitution at nitrogen. For the asymmetric P-F stretch, the 730 cm^{-1} vibration is most plausible, moving little on isotopic substitution and having an A band-shape. Both P-N and P-F asymmetric stretches although strong in the i.r., are too weak to be observed in the Raman spectra. Analogy of the P-F axial stretches with the values in PF_5, PF_3Cl_2 and PF_2Cl_3[112] is not unfavourable, and bands at 712 and 548 cm^{-1} in $F_3P(NH_2)_2$,[95] though not assigned as such, are comparable.

The presence of a_2 bands only in the Raman, makes it possible to assign the PF_2N_2 and NH_2 torsions to 248 and 454 cm^{-1} respectively. The remaining a_2 species, the amino group wag, can be assigned as 930 cm^{-1}, shifting to 695 cm^{-1} on deuteriation. This band is absent from both solid and gas phase i.r. spectra. Unfortunately, the corresponding NHD mode cannot be detected, the strong P-N stretch obscuring the region concerned.

Figure 6.8

PH stretching region of the infra red spectrum of gaseous $HPF_2(NH_2)_2$



Unassigned frequencies between 900 and 600 cm^{-1}, at 840, 782 and 658 cm^{-1} should correspond to the two PH deformations and the remaining NH_2 group wag. Since all three bands are too weak to be seen in the Raman, and isotopic shifts are no help, the weakest band at 844 and 836 cm^{-1} must be ascribed to the b_2 PH deformation giving a B band-shape. The other two bands both have A contours. Comparison with hydrazine places the NH_2 wag at 782 cm^{-1}, leaving the PH deformation (b_1 mode) at 658 cm^{-1}.

Below 600 cm^{-1}, PF_2N_2 group deformations may occur at 308 (a_1 mode), 519 (b_1 mode) and 420 cm^{-1} (b_2 mode). These frequencies conform to the expected band-shapes, and are relatively undisturbed by deuteriation effects. The remaining vibrations at 383 and 359 cm^{-1} must then be the a_1 skeletal deformation, and b_1 amino group torsion.

This assignment has so far made no mention of the single P-H stretch expected at 2460-2310 cm^{-1} for five co-ordinate phosphorus compounds.[46] That two, medium intensity, C band-shape, Raman polarised bands are seen in the P-H and P-D stretching region cannot readily be explained. Of these two bands, the lower frequency one seems to have an i.r. band-shape more like the other C-types. It is more intense and also falls within the known range. For these reasons, the P-H stretch is assigned at 2437 cm^{-1}, and P-D stretch at 1786 cm^{-1}; Figure 6.8 indicates these factors.

What then causes this extra band? Conformation could be responsible, but both n.m.r. and electron diffraction evidence point conclusively to a single trigonal bipyramidal

TABLE 6.10

Vibrational Assignments$^{(a)}$ of $HPF_2(NH_2)_2$ and $DPF_2(ND_2)_2$

	a_1		a_2		b_1		b_2	
	H	D	H	D	H	D	H	D
ν (NH or ND)	3476	2541	3531 (b)	2642	3587	2678	3468	2541
ν (PN_2)	879	829					1014	854
ν (PF_2)	582	580			730	716		
ν (PH or PD)	2437	1786						
δ (PH or PD)					658	n.o.	840	n.o.
δ (PF_2N_2)	383 308	n.o. n.o.			519	505	420	n.o.
δ_s (NH_2 or ND_2)	1560	1204					1560	1204
δ_w (NH_2 or ND_2)			930 (c)	695	782	n.o.		
δ_p (NH_2 or ND_2)	1240	935					1240	935
τ (NH_2 or ND_2)			454 (c)	n.o.	359	n.o.		
τ (PF_2N_2)			248 (c)	230				

NOTE: All frequencies in cm^{-1}; n.o. = not observed.

(a) I.r. (gas phase) frequencies, unless stated otherwise.

(b) Raman (solid phase) frequencies.

(c) Raman (liquid phase) frequencies.

structure of C_{2V} symmetry. Any effect therefore would have to result from amino group conformations, which seems unlikely to produce a 70 cm^{-1} shift in P-H stretching frequency. This is also made implausible since both HPF_4 and DPF_4 exhibit two P-H and two P-D stretches.[96] Interpretation of this observation in HPF_4[113] is by a combination band, but unfortunately this does not also account for the extra band in DPF_4. It is interesting to note that $HPF_2(NHR)_2$, (R = Me, Et and Bu^n),[8] all show two bands between 2502 and 2414 cm^{-1}, whereas F_4PNHCH_3[103] and $F_3P(NH_2)_2$,[95] although containing ligands common to these other phosphoranes, do not show a combination band. Thus a P-H or P-D band seems essential, and a combination band with its intensity enhanced by Fermi resonance could be responsible for the ghost band. However, no binary combinations of a_1 symmetry fall into the correct regions, the nearest being $\delta(NH_2) + \nu_s(PN_2)$ (1560 + 879 = 2439 cm^{-1}), and $\delta(ND_2) + \nu_s(PF_2)$ (1204 + 580 = 1784 cm^{-1}). Consequently, it seems that the additional band is a product of Fermi resonance enhancing the intensity of a combination of vibrational modes, which belong solely to the HPF_2X_2 skeleton.

A summary of the assignments suggested for $HPF_2(NH_2)_2$ is given in Table 6.10.

6.5. Photoelectron Spectrum

Figure 6.9 illustrates the He(I) photoelectron spectrum of diaminodifluorophosphorane, the vertical ionisation potentials and assignments of which are presented in Table 6.11.

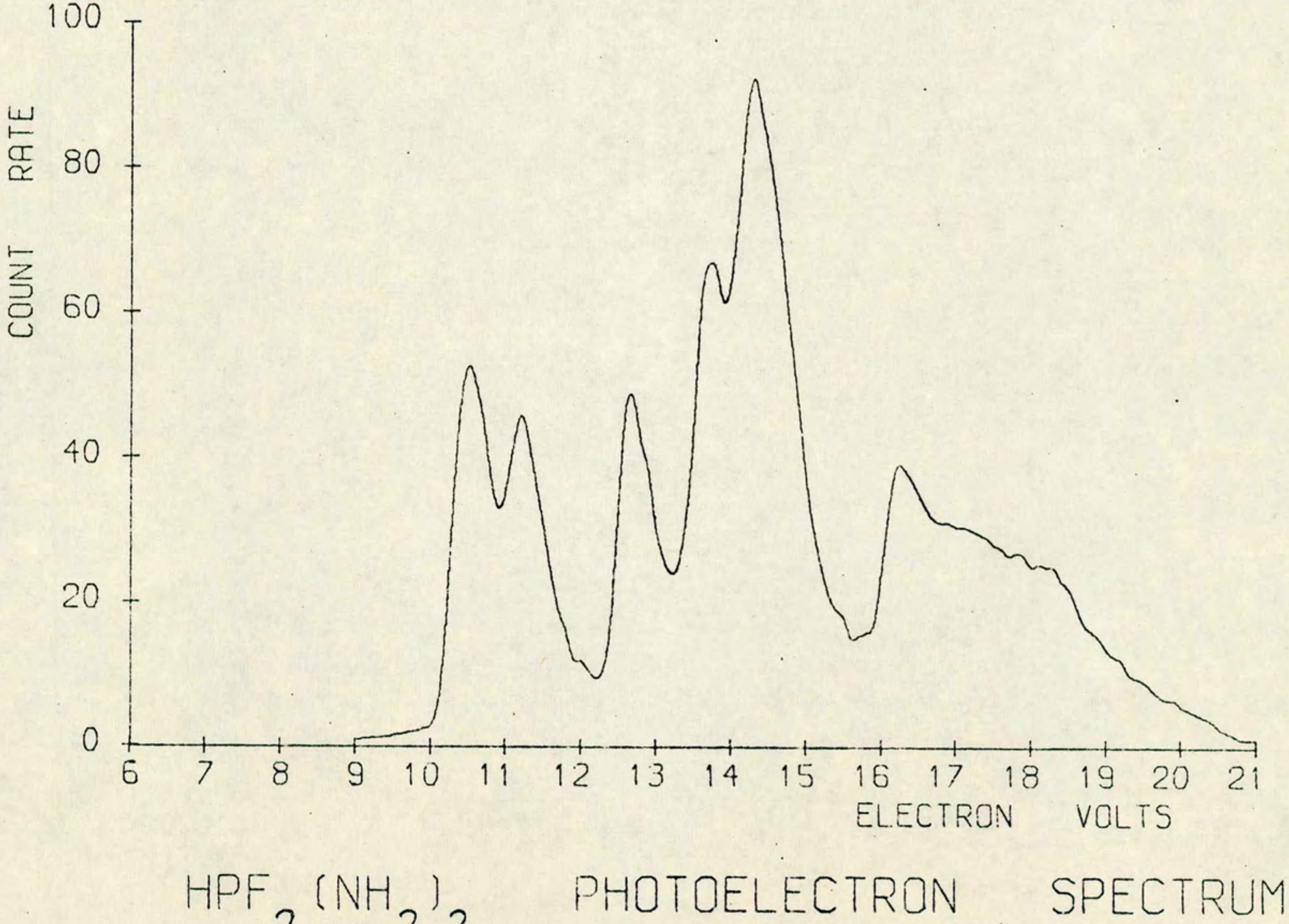
TABLE 6.11

He(I) Photoelectron Spectrum of $HPF_2(NH_2)_2$

Ionisation potential	Assignment
10.7 11.4	N lone pairs
12.9	P-H bonding
13.9	P-N bonding
14.5	P-N, N-H bonding
16.5	F lone pairs
17 - 18	P-F bonding

All ionisation potentials in eV; ± 0.1 eV.

Figure 6.9. Photoelectron spectrum of Diaminodifluorophosphorane



Features of the spectrum include the two nitrogen lone pair bands, which have a separation of 0.7 eV, and two P-N bonding levels at 13.9 and 14.5 eV, with N-H bonding also appearing under the intense, broad band at 14.5 eV. These compare with values for F_2PNH_2 of 10.9 eV for the nitrogen lone pair level, and the higher ionisation potential of 15.4 eV for P-N and N-H bonding levels.[42] Fluorine lone pairs and P-F bonding orbitals occur at characteristic values for three[42] and five co-ordinate phosphorus compounds.[114] The P-H bonding level at 12.9 eV lies closer to that of PH_3 (12.5 - 15.0 eV)[115] than PF_2H(15.1 eV).[42]

6.6. Reactions

Only two reactions were attempted. In the first, F_2PNH_2 was formed when PF_2Cl was reacted with $HPF_2(NH_2)_2$ in the presence of NMe_3, which acted as a hydrogen halide abstractor.

$$HPF_2(NH_2)_2 + PF_2Cl + NMe_3 \longrightarrow 2F_2PNH_2 + [Me_3NH]Cl \;....[11]$$

Secondly, with hydrogen chloride, only PF_2Cl and unreacted $HPF_2(NH_2)_2$ were observed. Reaction of HCl would seem to be faster with F_2PNH_2 than $HPF_2(NH_2)_2$, and proceed according to Equation [12] and [13].

$$HPF_2(NH_2)_2 + HCl \longrightarrow F_2PNH_2 + [NH_4]Cl \;.........\; [12]$$

$$F_2PNH_2 + HCl \longrightarrow PF_2Cl + [NH_4]Cl \;..............\; [13]$$

Details of these reactions are given in the experimental section.

CHAPTER 7

ELECTRON DIFFRACTION GAS PHASE MOLECULAR STRUCTURE DETERMINATION OF $(F_2P)_2Se$, $(F_2P)_3N$ and $HPF_2(NH_2)_2$

7.1. BIS(DIFLUOROPHOSPHINO)SELENIDE

The structure of bis(difluorophosphino)oxide has been the subject of two recent electron diffraction (ED) studies. While the earlier one interpreted the data in terms of one fixed conformer,[29] the later study suggested a model which involved an appropriately weighted mixture of four conformers of C_1, C_2, C_s and C_{2V} symmetries.[37] Although differing in overall conformation and bonded distances, both investigations produced wide POP angles, about 140° on average, and P-O bond lengths short in comparison with the Shomaker-Stevenson predicted value of 1.71Å.[116] The similarity of these parameters with those of the analogous silyl and germyl compounds, in which d-orbital participation in bonding to oxygen has been suggested,[117,118] led to the proposal of $(p \rightarrow d)$ π-bonding in the phosphorus-oxygen bond.[29] Since the silyl and germyl derivatives of the other Group VI elements gave bond lengths close to predicted values, and angles little different from those in the methyl analogues, it was concluded that $(p \rightarrow d)$ π-bonding was not sterically important in the sulphur and selenium compounds.[119] The structure of $(F_2P)_2Se$ has therefore been determined to see if such behaviour is also observed in the difluorophosphino-derivative.

In addition to those factors affecting the P-Se bond length and PSeP angle, the overall conformation, as determined by the orientations of the F_2P groups, is of considerable interest. Particularly so with regard to the influence of lone pair-lone pair interactions between fluorine atoms and phosphorus atoms, their effect on conformation and such properties as the temperature sensitive coupling, $^2J(PP)$, observed in n.m.r. experiments.

7.2. Molecular Models and Refinements

Because the difficulties in the structural determination of $(F_2P)_2O$ due to overlap of the bonded distances were not present in $(F_2P)_2Se$ (r(PSe) = 2.273Å $\gg$ r(PF) = 1.573 Å), the major problem was that of conformation. This was tackled by use of two models. The simple model, (A), which produced a single fixed conformer, involved the P-F and P-Se bonded distances, angles FPF, FPSe, PSeP and two twist angles, and eleven non-bonded distances of which four were P···F and four long range F···F distances. The twist angles, one for each F_2PSe unit, described the rotations about the P-Se bonds and were defined to be zero when the bisector of the FPF angle was trans with respect to the further P-Se bond.

Assuming C_{2V} symmetry, the bonded distances and their amplitudes of vibration, angles FPSe and PSeP, and the amplitude of vibration of the F···Se distance refined satisfactorily. However, the radial distribution curve, P(r)/r, contained a small peak at 2.01 Å, due to the P=Se bonded distance in $Se{=}PF_2H$,[120] an impurity which arises readily from reaction of $(F_2P)_2Se$ with traces of moisture.

A series of refinements was therefore carried out with different percentages of $Se=PF_2H$ contributing to the calculated intensity curves. Plots of R factor against percentage impurity for each camera height gave minima corresponding to 27 and 15% $Se=PF_2H$ in the 25 and 50 cm data sets respectively. Scale factors for each data set (equal to the product of the amount of impurity and the scale factor at that amount) and known parameters for $Se=PF_2H$[120] were then used to calculate theoretical intensity data which were subtracted from the experimental intensity data. These corrected intensity data were used in all subsequent refinements (Figures 7.2 and 7.3).

Having established the parameters of the PSeP backbone of the molecule, the conformation was investigated for C_2 and C_s symmetries, the twist angles covering the range of angles 0 to 180°. On the assumption that the non-bonded P···F and long F···F distances must be greater than the sum of their Van der Waals radii, and from relative values of the R factor, the possibility of twist angles greater than 80° was eliminated. Refinements within this range produced rotational dependent distances between 4.0 and 6.0 Å. Although the experimental radial distribution curve appeared to have prominent peaks at the 4.0 to 5.0 Å region, all attempts to fit these exactly to P···F, or combinations of P...F and F···F distances, failed. The single most favourable conformer had C_2 symmetry with a twist angle of ca. 20°, which when fixed allowed the FPF angle to refine.

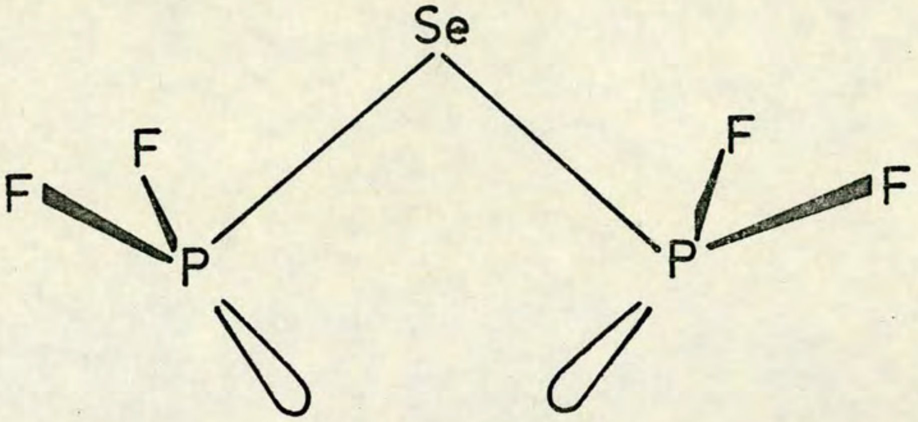
This proved to be the limit of the simple model, and hereafter it was necessary to use a second model, (B). This was done for two reasons. Firstly, what appeared as peaks between 4.0 and 5.0 Å would have had amplitudes of vibration unreasonably small for such distances, and were in fact background ripples superimposed on an envelope in the radial distribution curve. Secondly, this envelope was taken as an indication of torsional motion of the F_2P groups about the P-Se bonds, giving rise to a series of torsional-dependent distances.

Model (B) contained the same parameters as (A) except for those more appropriately defined by torsional displacements. These parameters were δ, an angle which replaced the two twist angles and represented the root mean squared amplitude of the F_2P group torsion from C_{2V} symmetry; and the P···F and long F···F distances which were dependent on δ. The model described the effect of torsional motion by a summation of weighted fixed conformers. To obtain these conformers, each F_2P group torsion was assumed to be independent, and harmonic. The probability distribution of both F_2P groups was therefore;[121]

$$p \ (\phi_1, \phi_2) = Q^{-1} \exp\left\{ -(\phi_1^2 + \phi_2^2)/2\,\delta^2 \right\} \ldots\ldots\ [1]$$

where Q was a normalisation factor, and ϕ_1 and ϕ_2 were the angular displacements of the F_2P groups from C_{2V} symmetry (Figure 7.1).

Figure 7.1



C_{2V}

$(\phi_1 = \phi_2 = 0^{\circ})$

To produce a satisfactory distribution of torsion dependent distances, values of ϕ_1 and ϕ_2 were selected to be equal to 0, $\pm 2\,\delta/3$, $\pm 4\,\delta/3$ and $\pm 2\,\delta$. Thus from an angular r.m.s. amplitude of torsional rotation, δ, it was possible to calculate distances corresponding to pairs of torsional angles, ϕ_1 and ϕ_2, and to weight these by the appropriate probability term, $p(\phi_1,\phi_2)$. In all, there were 16 different instantaneous conformations from the combinations of the seven possible values of each ϕ. The number of different torsional-dependent distances from model (B) was therefore large; 7 P···F and 56 F···F. The problem of the unwieldy number of F···F distances was overcome by the use of 28 distances covering the range 3.20 to 5.90 Å in 0.10 Å steps. Calculated F···F distances that fell within ± 0.05 Å of any of these steps were weighted and assigned to that particular step. For example, if an individual F···F distance was calculated as 4.24 Å, it was said to occur at 4.20 Å; likewise

TABLE 7.1

Weighting functions, correlations parameters, and scale factors

Compound	Camera height (mm)	Δs	$s_{min.}$	s_1	s_2	$s_{max.}$	P/h	Scale factor	Wavelength (Å)
$(F_2P)_2Se$	250	0.40	6.00	8.00	25.00	29.20	0.1990	0.635 ± 0.020	0.05660
	500	0.20	3.00	5.50	12.50	15.80	0.4945	0.612 ± 0.027	0.05660
$(F_2P)_3N$	190	0.40	3.20	6.00	30.00	35.20	0.3839	0.748 ± 0.011	0.05852
	580	0.20	1.00	3.50	10.50	13.40	0.4876	0.838 ± 0.013	0.05847
$HPF_2(NH_2)_2$	250	0.40	6.00	9.00	26.00	30.00	0.4379	0.741 ± 0.009	0.05660
	500	0.20	1.80	4.50	12.50	16.00	0.4977	0.844 ± 0.013	0.05660

TABLE 7.2

$(F_2P)_2Se$: Least-Squares Correlation Matrix (x 1000)

r 1	r 2	∠ 1	∠ 2	∠ 3	u 1	u 2	u 4	u 5	k 1	k 2	
1000	-21	-93	-82	33	20	10	-18	9	24	6	r 1
	1000	417	-514	-212	187	83	133	114	268	196	r 2
		1000	-722	-658	337	-159	-35	175	483	359	∠ 1
			1000	256	-332	-2	-194	-332	-475	-378	∠ 2
				1000	-66	88	358	-132	-101	-29	∠ 3
					1000	297	308	65	710	374	u 1
						1000	236	32	407	194	u 2
							1000	172	424	357	u 4
								1000	95	76	u 5
									1000	463	k 1
										1000	k 2

TABLE 7.3

Molecular Parameters of $(F_2P)_2Se$(a)

		Distance (Å)	Amplitude (Å)
(A) Independent Distances			
r 1	(P - F)	1.573(3)	0.047(5)
r 2	(P - Se)	2.273(5)	0.057(5)
(B) Dependent Distances			
d 3	(F···F)	2.421(35)	0.078 (tied to u 2)
d 4	(F···Se)	2.953(47)	0.130 (9)
d 5	(P···P)	3.341(97)	0.112(27)
d 6	(P···F)	3.83 (9)	0.15(F)
d 7	(P···F)	4.04 (10)	
d 8	(P···F)	4.22 (8)	
d 9	(P···F)	4.39 (12)	
d 10	(P···F)	4.51 (7)	
d 11	(P···F)	4.61 (11)	
d 12	(P···F)	4.66 (9)	
d 13 - d 40	(F···F)	3.20-5.90	0.20(F)
(C) Angles (°)			
∠ 1	(F - P - F)	100.6(11)	
∠ 2	(F - P - Se)	98.7(4)	
∠ 3	(P - Se - P)	94.6(8)	
∠ 4	R.m.s. torsional amplitude, δ	20.0(F)	

N.B.

Fixed parameters marked (F)

(a) Refer to text for definition of torsional-dependent distances P···F and F···F in terms of δ.

Figures 7.2 and 7.3

Intensity Data of $(F_2P)_2Se$

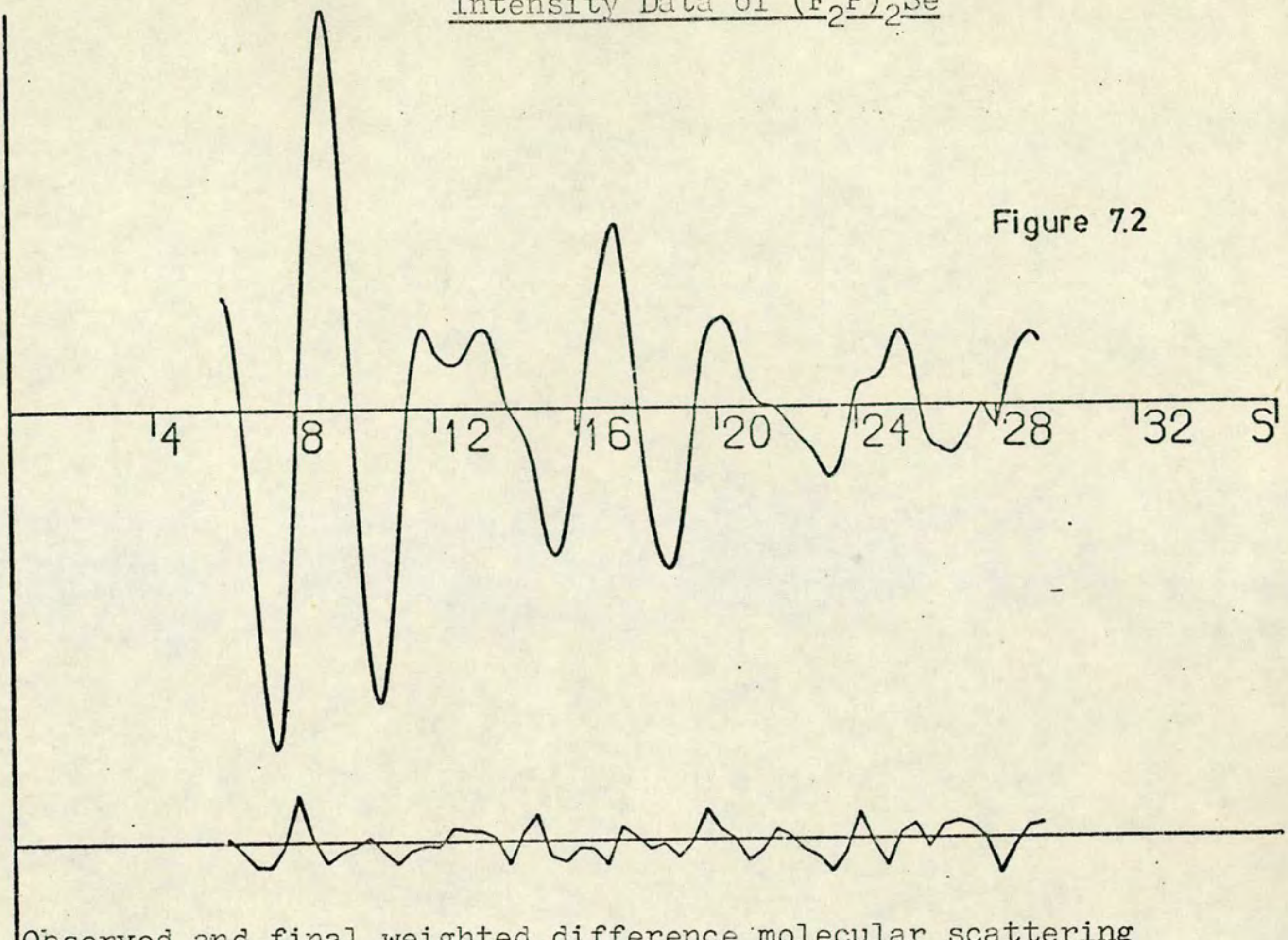


Figure 7.2

Observed and final weighted difference molecular scattering intensities for nozzle-to-plate distances of 250 mm (Figure 7.2) and 500 mm (Figure 7.3).

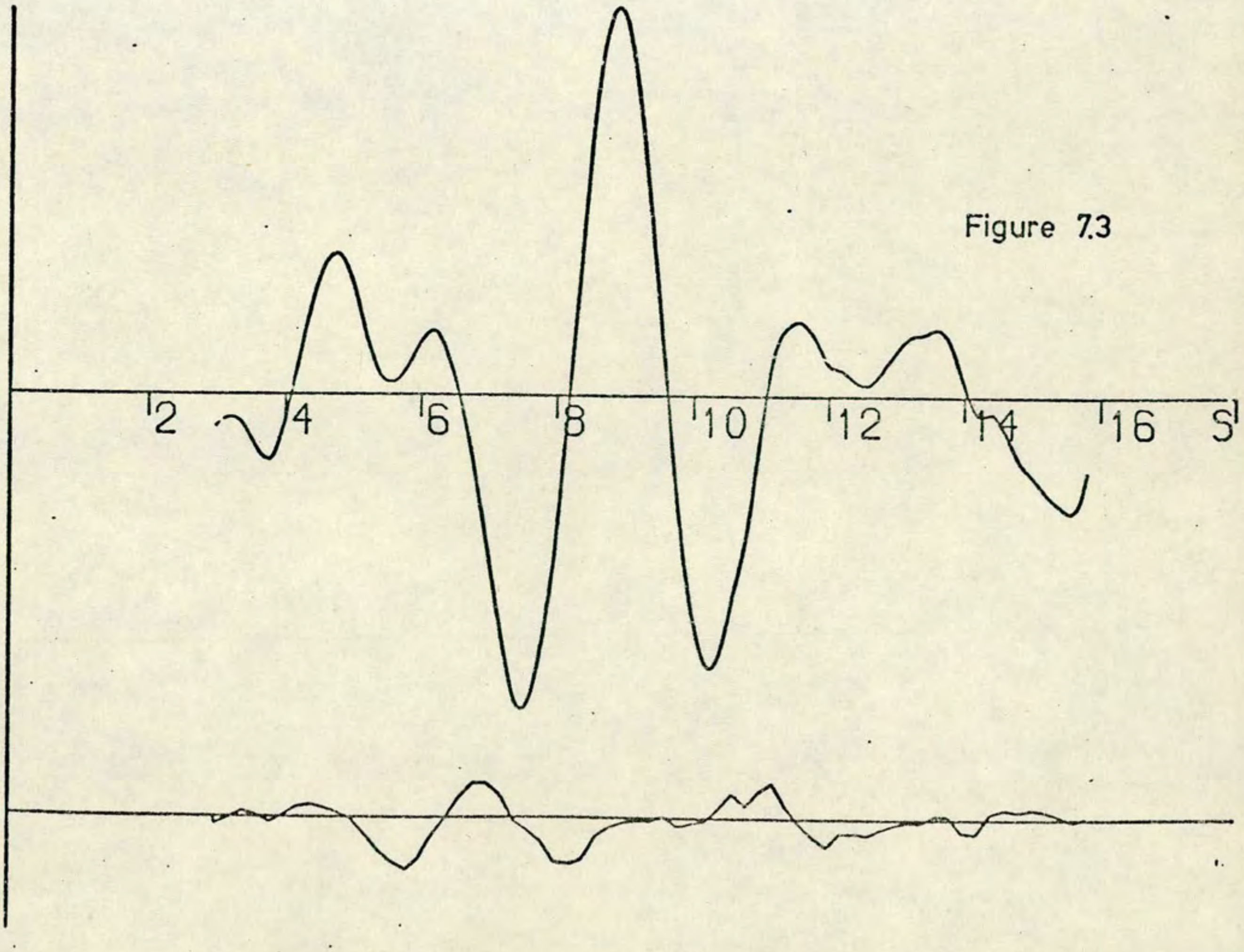


Figure 7.3

Figures 7.4 and 7.5

Radial Distribution Curves of $(F_2P)_2Se$

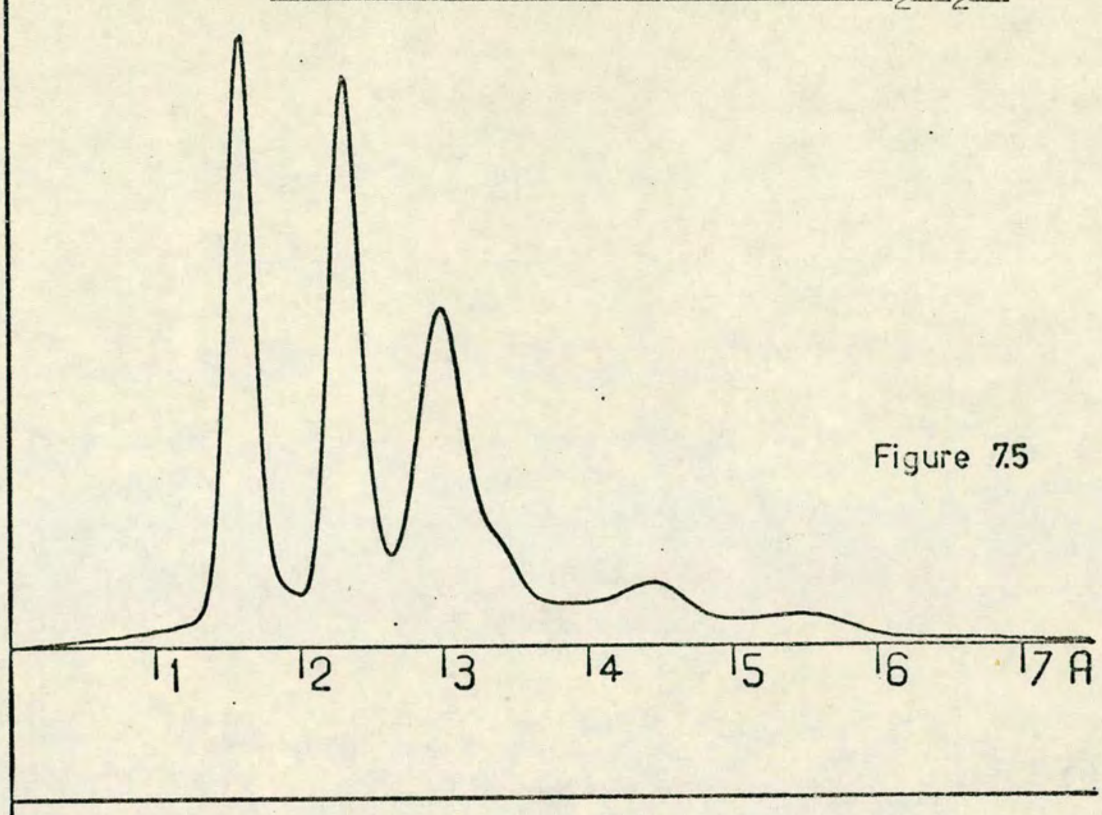


Figure 7.5: Radial distribution curve calculated from the $(F_2P)_2Se$ parameters of Table 7.3.

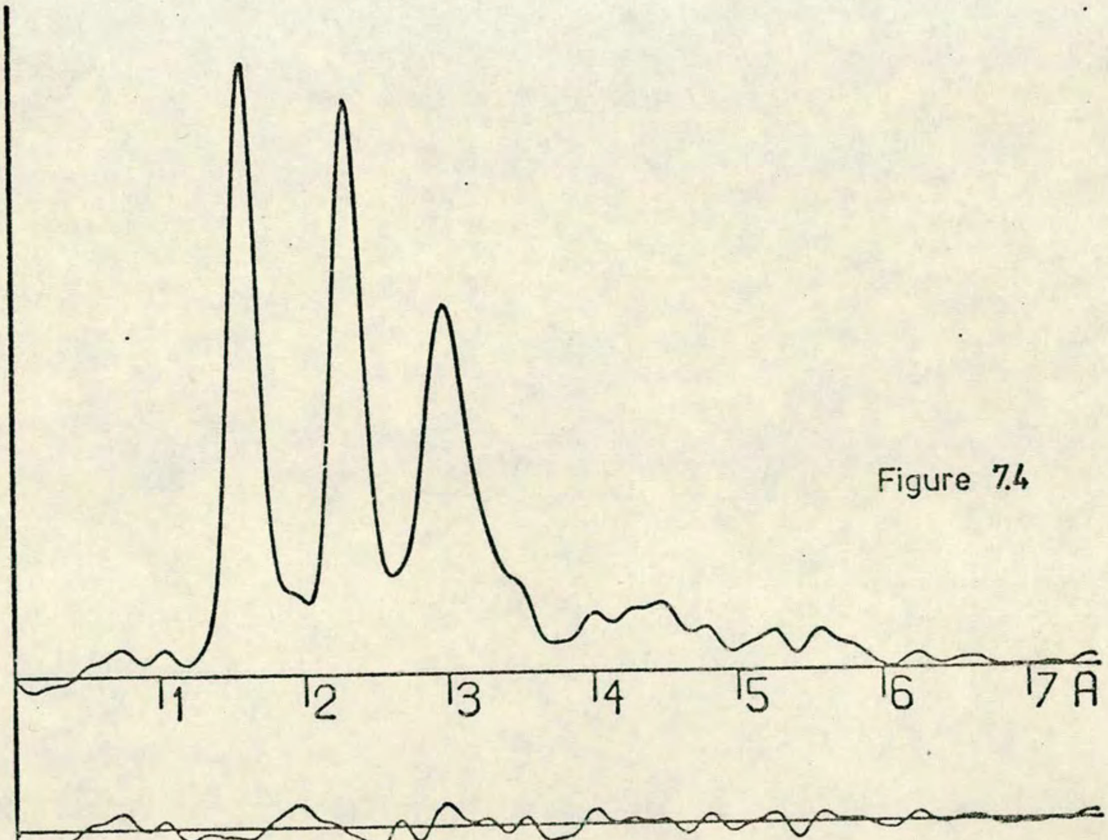


Figure 7.4: Observed and difference radial distribution curves, $P(r)/r$, for $(F_2P)_2Se$

$s \exp(-0.0030s^2)/(z_P - f_P)(z_F - f_F)$

for a distance of 4.16 Å. The errors implicit in this approach were believed to be small in the calculated intensity curves representing the torsional motion of $(F_2P)_2Se$.

Results from model (A) were taken as the starting point of model (B) refinements. All parameters that had refined with the simpler model also did so with model (B). The vibrational amplitudes of distances affected by torsional motion, P···F and long F···F, were given the same value for all conformational components of the particular distance. Refinement of the r.m.s. amplitude of torsion was not possible, but an R factor loop with fixed δ values in the range 8 to 28° indicated a minimum at 20 ± 4°, with 50% confidence.[122] With δ fixed at 20°, two further amplitudes of vibration were refined; those of the P···P distance, and of the short F···F distance which was tied to the amplitude of the P-Se distance in the ratio 1:0.73.[123] Refinement of more parameters than those nine described was not possible, giving a final R_G = 0.158 for the torsional model (B), significantly better than 0.179, achieved with the single conformer model (A).

The parameters of model (B) are given in Table 7.3, while the elements of the correlation matrix, and the weighting function, correlation parameters and scale factor information are presented in Tables 7.2 and 7.1. For comparison, Figures 7.4 and 7.5 are the experimental radial distribution curve, and the radial distribution curve calculated from the parameters of Table 7.3.

It must be stressed that the structure found for

TABLE 7.4

Bond lengths and angles in some A_2Y Group VI derivatives[(a)]

		r (A - Y)			
Y	A	Experimental	Calculated[(b)]	∠ AYA	Reference
O	CH_3	1.416	-	111.5	128
	SiH_3	1.634	1.749	144.1	117
	GeH_3	1.766	1.829	125.6	118
	F_2P	1.533	1.702	145.1	29
		1.631		135.2	37
Se	CH_3	1.943	-	96.8	129
	SiH_3	2.273	2.274	96.6	134
	GeH_3	2.344	2.352	94.5	119
	F_2P	2.273	2.229	94.6	

(a) Distance in Å; angles in degrees.

(b) See text.

$(F_2P)_2Se$, namely C_{2V} symmetry with torsional motion of the F_2P groups having a r.m.s. amplitude of 20°, assumes harmonic motion of the F_2P groups as expressed by Equation [1]. This assumption may not be entirely valid due to the possibility of physical interaction of the lone pairs on the phosphorus atoms making the zero twist position, C_{2V} symmetry, energetically less favoured than at small displacement angles. If this were so, the function relating the potential energy of hindered rotation to torsional angle displacements (and thus their probabilities at a particular displacement angle) could approximate to a quartic expression, with the ground state of torsional motion lying either above or below the energy hump at zero displacement. Above this hump, harmonic motion would be an adequate approximation, but below, the F_2P groups would spend most time displaced from C_{2V} symmetry. In this situation the F_2P groups could adopt either C_2 or C_s symmetries. No attempt has been made, however, to investigate this more complicated interpretation, the present intensity data not being of sufficient quality.

7.3. Discussion

Table 7.4 contains some bond lengths and angles of Group VI derivatives with which to compare the P-Se bond length and PSeP angle found for $(F_2P)_2Se$. The predicted bond lengths have been calculated from the tetrahedral covalent radii derived from bond lengths in C_2H_6,[124] CH_3SiH_3,[125] CH_3GeH_3,[126] F_2PCH_3,[127] $(CH_3)_2O$[128] and $(CH_3)_2Se$.[129] The values for $(F_2P)_2Se$ are consistent with those of $(MH_3)_2Se$, (M = C, Si or Ge), in indicating the unimportance of multiple bonding in the stereochemistry of these selenium compounds. Another estimate of the P-Se bond length, from the Shomaker-Stevenson rule,[116] gives a value of 2.24 Å, also significantly shorter than the value found.

The conformation of the F_2P groups, expressed in terms of several rotameric forms, is a much more satisfactory description of the structure than a single frozen conformer. The r.m.s. torsional angle, δ, in $(F_2P)_2Se$ compares with $(F_2P)_2NCH_3$ ($11.6 \pm 4.3^\circ$ at 298 K)[130] and F_2PPF_2 ($16.7 \pm 4.0^\circ$),[131] both investigated in a similar manner.

The relationship between δ and the potential constant (Equation [2] below) also implies the temperature dependence of δ; $\delta \propto T^{\frac{1}{2}}$. The structure of $(F_2P)_2NCH_3$ was obtained at 238 and 298 K when a difference of only 1.2° was observed. The larger value of δ at 298 K in $(F_2P)_2Se$ may be sufficient to see a significant change, since raising the temperature to 373 K should increase δ by 2.4°. However, it is first necessary to obtain a greater degree of accuracy in the existing value by better quality intensity data.

Another implication of the conformation is the near right angle at selenium, and the extent to which the phosphorus lone pairs are directed towards each other. In F_2PPF_2 they are trans,[131] and in $(F_2P)_2NCH_3$ the wide PNP angle (115.9°)[130] considerably reduces any interaction. Studies of the behaviour of coupling constants with temperature in F_2PPF_2 and $(F_2P)_2NCH_3$ indicate only small changes in $^2J(PP)$, the most sensitive coupling constant, over a 100 K range; 2 Hz in the former and 10 Hz in the latter.[21] This contrasts sharply with $(F_2P)_2Se$ where, over the same temperature range $^2J(PP)$ varies by 100 Hz. It seems possible that the mechanism responsible for this behaviour is through-space interaction of phosphorus-phosphorus lone pairs, made more effective at lower temperatures by a reduction in the torsional amplitude of the F_2P groups.

7.4. Torsional Frequency of the Difluorophosphino Group

Knowledge of δ allows an estimate to be made of the torsional frequency. Since harmonic torsion angle displacements are assumed ($V_\phi = k_\phi \phi^2/2$, where V_ϕ is the potential barrier to rotation) the potential constant, k_ϕ, is related to the r.m.s. amplitude by Equation [2];[130,132,133]

$$k_\phi = kT/\delta^2 \quad \text{(J)} \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots \;[2]$$

The torsional frequency, ν, can then be calculated from Equation [3] where I_r represents the reduced moment of inertia about the P-Se bond.

$$\nu = (k_\phi/I_r)^{\frac{1}{2}} \,/\, 2\pi \quad \text{(Hz)} \;\ldots\ldots\ldots\ldots \;[3]$$

The experimental section contains details of this calculation which produced a frequency of 34 cm^{-1} at 298 K for $(F_2P)_2Se$. This value is considerably lower than the 260 ± 50 cm^{-1} found for the torsional frequency about the P-N bond in $(F_2P)_2NCH_3$.[130] Recalculation of this frequency using the published value of δ suggested that moments were taken about the N-C and not the P-N bond. If this were so, a torsional frequency of ca. 60 cm^{-1} is obtained, in more reasonable agreement with the value for $(F_2P)_2Se$. Both frequencies are capable of measurement by infra red interferometric methods.

7.5. TRIS(DIFLUOROPHOSPHINO)AMINE

Structural studies of difluorophosphino compounds containing bonds to three co-ordinate nitrogen atoms include a number of interesting problems. These centre round the possible co-planarity of the ligands to nitrogen, and the extent to which the P-N bond possesses multiple-bond character through the use of d-orbitals on the phosphorus atom. An electron diffraction (ED) study of F_2PNH_2 and $F_2PN(CH_3)_2$ found non-planarity of the PNX_2 group with angles of 35° and 32° between the P-N bond and the NX_2 plane.[30] A microwave investigation, however, concluded that in both $F_2PN(CH_3)_2$[135] and F_2PNH_2[136] there was co-planarity of the ligands to nitrogen: an X-ray study of the former supported this interpretation.[137] The recent ED structure determination of $(F_2P)_2NCH_3$[130] reported a planar P_2NC arrangement, and in common with the other investigations, a P-N bond length short by comparison with the sum of the covalent single-bond radii.

$(F_2P)_3N$ is consequently of interest in relation to these problems and when compared with the earlier studies. In addition, conformations of the molecule, determined by positions of the F_2P groups, will also be of considerable importance.

7.6. Molecular Models

Models were designed to elucidate the problems outlined previously, viz:-

(a) possible co-planarity of the P_3N skeleton.

(b) variety of conformers with symmetries C_{3h}, C_{3V}, C_3, C_s or C_1.

To this end F_2P groups were treated as units with a plane of symmetry and identical parameters. With this restriction the structure was defined in terms of the two bonded distances, and the angles FPF, FPN, PNP and three twist angles; eight parameters in all. The twist angles, one for each F_2P group, were measured from the bisectors of the FPF angle; e.g. when all three twist angles were either $+90^\circ$ or -90°, with angle FPN 120°, the point group was C_{3V}. The maximum possible number of different dependent P···F and non-geminal F···F distances was twelve in each case. For symmetries higher than C_1 there were fewer different distances, some of which were degenerate. Symmetry constraints could be applied to the twists so that different conformations could be investigated. These constraints were:

(A) all twists equal. As such, twists of 0° or $\pm 90^\circ$ were particular cases, C_{3h} or C_{3V}, of the general C_3 symmetry. This gave rise to four groups, each of degeneracy three, for P···F and F···F distances alike.

(B) C_s symmetry with two twists subtending equal, but opposite sign, angles at the mirror plane bisecting the third F_2P group which has a twist angle of $\pm 90^\circ$. This produced six groups of different P···F and seven different F···F distances.

(C) all twists equal, but one of opposite sign. A particular case of C_1 symmetry having four P···F distances and eight F···F distance different.

(D) all twist independent. C_1 symmetry with twelve different P···F and twelve different F···F distances.

Figures 7.6 and 7.7

Intensity Data of $(F_2P)_3N$

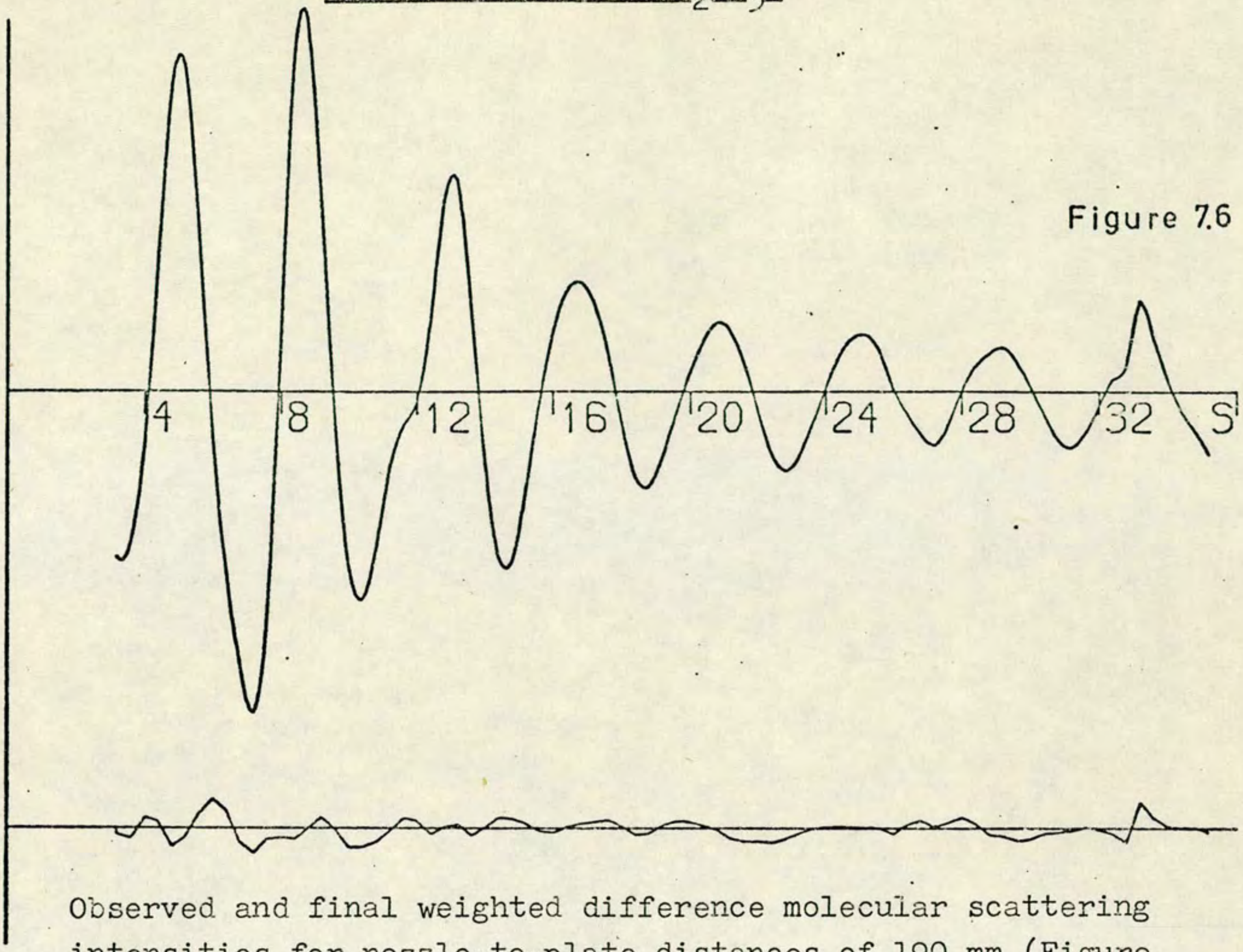


Figure 7.6

Observed and final weighted difference molecular scattering intensities for nozzle-to-plate distances of 190 mm (Figure 7.6) and 580 mm (Figure 7.7).

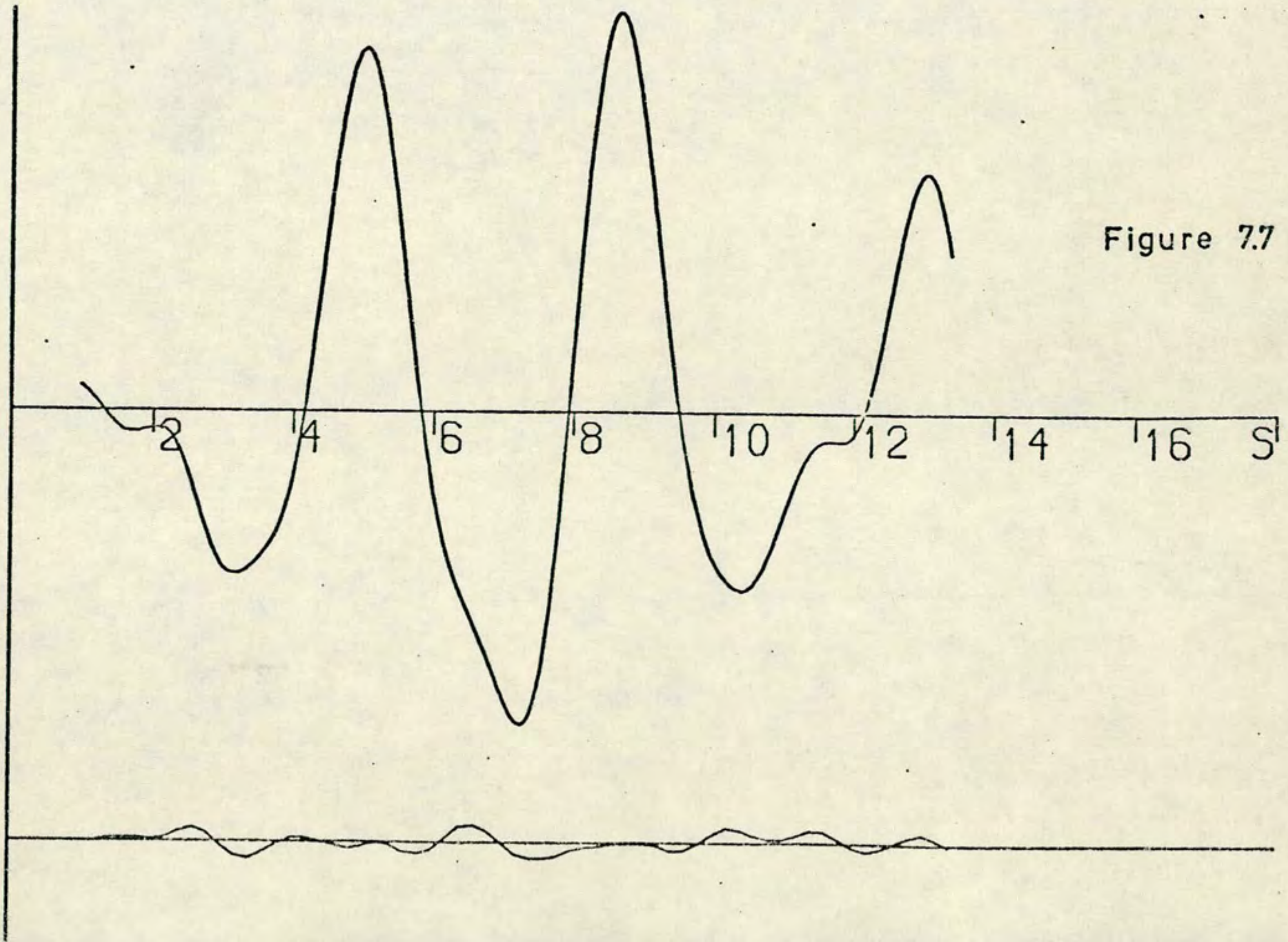
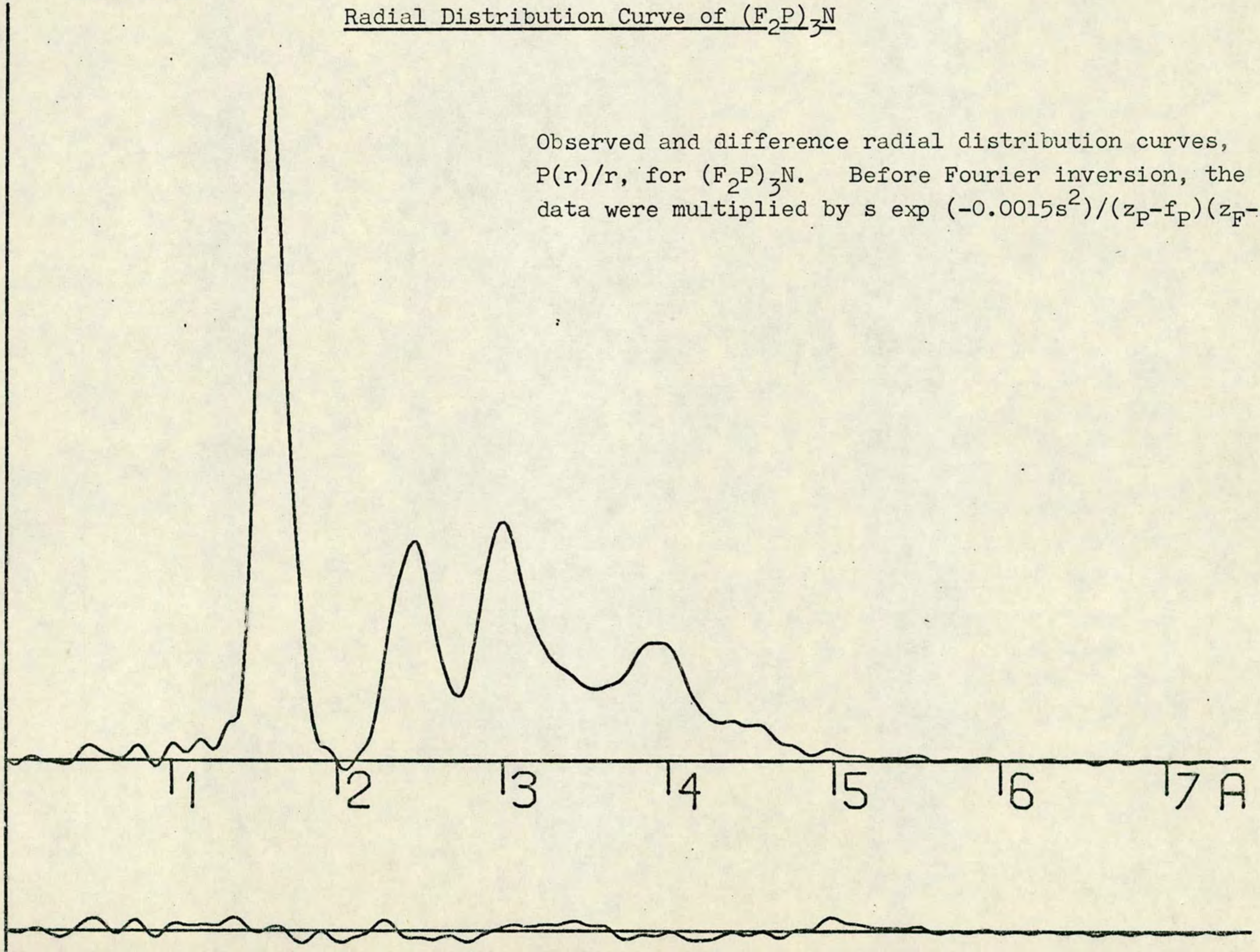


Figure 7.7

Figure 7.8

Radial Distribution Curve of $(F_2P)_3N$

Observed and difference radial distribution curves, $P(r)/r$, for $(F_2P)_3N$. Before Fourier inversion, the data were multiplied by $s \exp(-0.0015s^2)/(z_P-f_P)(z_F-f_F)$



7.7. Refinements

Reference to the radial distribution curve, P(r)/r, for $(F_2P)_3N$ (Figure 7.8) indicates that the P_3N skeleton was well defined by the peaks at ca. 1.6, 2.5 and 3.0 Å, which contain respectively, the P-F and P-N bonded distances, the geminal F...F and F···N, and the P···P non-bonded distances. From these peaks it was possible to refine the bonded distances, the angles FPN and FPF, and the amplitudes of vibration of the P-F, F···N, and P···P distances. As the P-F and P-N distances were similar, their amplitudes were constrained so that the P-N amplitude was 1.08 times that of the P-F amplitude. Similarly the geminal F···F distance amplitude was constrained to be 0.87 times that of the F···N. These ratios were derived from calculated mean amplitudes of vibration in difluoro(isocyanato)- and difluoro(isothiocyanato)-phosphine,[138] and from refined amplitudes in other aminodifluorophosphines.[30,130,139] All these parameters refined to reasonable values.[123]

These parameters, however, gave no information about molecular conformation, which was determined by the P···F and F···F distances greater than 3.0 Å.

With angle PNP fixed at 120°, and using model (A) which gave overall C_3 symmetry, refinements were carried out on fixed twist angles in the range 0 to 16°. A minimum R_G value was found at ca. 10°. The twist angle was allowed to refine, and remained steady at this value, not being heavily correlated with any of the other seven refining parameters. This gave four sets of P···F distances. The amplitudes of vibration of those at 3.0 and 3.2 Å were tied together with a ratio of unity and allowed to refine, as were the amplitudes of those sets at 3.9 and 4.0 Å. The F···F distances also occurred in four sets at 3.7 and 4.0 Å, and 4.3 and 4.6 Å. However, only the amplitudes of vibration of the two longest F···F distance groups, when tied together with unit ratio, refined satisfactorily. The other two, occurring underneath the stronger P···F peak, did not refine well, and their amplitudes were left fixed at a reasonable value, 0.20 Å. Since the PNP angle had remained fixed at 120°, an R factor loop was carried out on this angle between 118 and 120° in 0.20° steps. At each step the angle was fixed, but with the above mentioned ten parameters refining. It was found that over the 2° decrease in PNP angle, the twists decreased by approximately 6°, to 4°. However, a best fit was found at 120°, and the angle was fixed at this value. Refinement to convergence gave R_G = 0.102 for the C_3 model.

Model (B) was then used to investigate the possibilities of C_s symmetry. Initially, the PNP angle was fixed at 120°, and all parameters other than the amplitudes of the P···F and F···F distances were refined as before. Refinements were carried out with two twist angles from 10 to -90°, the third twist angle, that of the F_2P group on the plane of symmetry, remaining at 90° throughout. The three twist angles therefore covered the range (-90, -90, + 90°) to (+170, +10, +90°). With this symmetry one of the F···F distances was always very short (although not always between the same pair of fluorine atoms) giving a maximum of 2.6 Å at (-109, -71, +90°). The shortest F···F distance in model (A) was 3.7 Å. The lowest R_G value was achieved at (-170, -10, +90°) but produced an F···F distance of only 2.2 Å. Consequently, subsequent refinements were done with the twist angles that maximised the shortest F···F distance since this was the most plausible physical structure with C_s symmetry. As in model (A) the amplitudes of vibration of groups of P···F distances were refined, but those of F...F distances did not. The PNP angle was again varied between 118 and 120°, moving two F_2P groups towards and away from the third, i.e., with twists (-109, -71, +90°) and (+109, +71, -90°). Both alterations gave a minimum R factor at 118.9°, σ = 0.6°.[122] However, since this was only 0.220, the C_s model could be rejected with virtually absolute confidence.

Since model (A) had produced the best fit, distortions from its C_3 symmetry were studied using model (C). It was found that there was a significant improvement with this model, the twist angles (-10, -10, +10°) and all other parameters as for (A) refining with acceptable values to produce a converged R_G = 0.095.

Model (D) was then used which allowed independent movement of the three twist angles. This was done to ensure that there were no more-favoured conformations, either between C_3 symmetry (+10, +10, +10°)and C_1 symmetry (-10, -10, +10°), or away from C_1 symmetry towards C_s symmetry (-109, -71, +90°). In the latter case, refinements were carried out starting either with twists at (-10, -10, +10°) or (+10, +10, -10°). The twist angles were changed in small steps in the ratios -100:-60:+80, or -120:-80:+100, which would bring the structure towards C_s symmetry. All such shifts produced much less favourable results. In the former

TABLE 7.5

$(F_2P)_3N$: Least Squares Correlation Matrix (x 1000)

r 1	r 2	∠ 1	∠ 2	∠ 4	u 1	u 4	u 5	u 7	u 9	u 14	k 1	k 2	
1000	407	-20	-145	33	14	-17	29	26	151	-27	56	31	r 1
	1000	-146	-302	177	183	-67	46	140	591	-29	421	268	r 2
		1000	128	-787	30	718	-116	-745	-114	-99	13	47	∠ 1
			1000	-692	-43	-322	-133	-583	-487	-396	-111	-75	∠ 2
				1000	-15	-287	133	900	336	321	13	-13	∠ 4
					1000	139	125	28	164	0	611	287	u 1
						1000	-95	-284	93	95	186	151	u 4
							1000	177	-113	105	176	86	u 5
								1000	210	376	68	36	u 7
									1000	106	320	270	u 9
										1000	-6	0	u 14
											1000	313	k 1
												1000	k 2

TABLE 7.6

Molecular Parameters of $(F_2P)_3N$

	Distance (Å)	Amplitude (Å)
(A) Independent Distances		
r 1 (P - F)	1.574(3)	0.034(3)
r 2 (P - N)	1.712(4)	0.037 (tied to u 1)
(B) Dependent Distances		
d 3 (F ... F)	2.374(15)	0.070 (tied to u 4)
d 4 (F ... N)	2.499(18)	0.081(11)
d 5 (P ... P)	2.965(10)	0.102(6)
d 6 (P ... F)	2.997(15)	0.203 (tied to u 7)
d 7 (P ... F)	3.195(36)	0.203(17)
d 8 (P ... F)	3.846(16)	0.150 (tied to u 9)
d 9 (P ... F)	4.014(28)	0.150(20)
d 10 (F ... F)	3.618(21)	0.200 (F)
d 11 (F ... F)	3.634(23)	
d 12 (F ... F)	3.991(54)	
d 13 (F ... F)	4.012(36)	
d 14 (F ... F)	4.297(20)	0.183(17)
d 15 (F ... F)	4.440(24)	0.183 (tied to u 14)
d 16 (F ... F)	4.534(41)	0.183 (tied to u 14)
d 17 (F ... F)	4.619 (33)	0.183 (tied to u 14)
(C) Angles (^{o})		
∠ 1 (F - P - F)	97.9(12)	
∠ 2 (F - P - N)	98.9(7)	
∠ 3 (P - N - P)	120.0(F)	
∠ 4 Twist 1$^{(a)}$	-10.4(13)	
∠ 5 Twist 2	-10.4(F)	
∠ 6 Twist 3	10.4(F)	

(a) See text

Fixed parameters marked (F)

TABLE 7.7

ED Parameters[(a)] of some Aminodifluorophosphines

	Bond length		Angles				
Compound	r(P-F)	r(P-N)	$\angle$ FPF	$\angle$ FPN	$\angle$ PNP	$\angle$ PNX	Reference
F_2PNH_2	1.581	1.661	95.3	101.0	-	119	30
$F_2PNHSiH_3$	1.574	1.657	100.8	95.6	-	127.9	17
$F_2PN(CH_3)_2$	1.589	1.684	99	97	-	118.3	30
$(F_2P)_2NCH_3$	1.583	1.680	95.1	99.6	115.9	122.0	130
$(F_2P)_3N$	1.574	1.712	97.9	98.9	120.0	-	

(a) Distances in Å; angles in degrees.

case, no combination of twist angles produced a better fit than that found using model (C). A structure with twists (-10, 0, +10°) gave $R_G = 0.099$, marginally better than the best for C_3 symmetry. However, since model (C) gave $R_G = 0.095$, better than 99.5% confidence can be placed in this structure on the R factor ratio test.[122]

The parameters given in Table 7.6 therefore refer to those found using model (C) as the most probable fixed conformation of $(F_2P)_3N$. Table 7.1 contains values of the weighting functions, correlation parameters and scale factors, while Table 7.5 gives the correlation matrix of refined parameters.

7.8. Discussion

The P-N bond length in $(F_2P)_3N$, (1.712 Å), is short compared with the value of 1.762 Å calculated from the Shomaker-Stevenson rule,[116] or 1.769 Å in $H_3NPO_3^-$, regarded as a 'normal' single bond length.[140] Comparison with related aminodifluorophosphines, however, (Table 7.7) indicates that this bond is significantly longer in $(F_2P)_3N$ than in the other compounds. While this may result from involvement of the nitrogen lone pair with three bonds, as against two in $(F_2P)_2NCH_3$, and one in $F_2PN(CH_3)_2$ and F_2PNH_2, steric factors may also be important. It is interesting to note the similarity of $(F_2P)_3N$ and $(F_2P)_2NCH_3$ with their silyl analogues which are also planar at nitrogen. The Si-N bond lengths decrease from $(H_3Si)_3N$ (1.738 Å)[141] to $(H_3Si)_2NCH_3$ (1.726 Å),[142] a process which is accompanied by a widening of the SiNSi angle to 125.4°. This last change contrasts with $(F_2P)_2NCH_3$, where the PNP angle narrows to 115.9°.[130] Since the factors affecting the silylamines have been interpreted in terms of (p $\rightarrow$ d) π-bonding, it seems reasonable to assume that involvement of the d-orbitals on phosphorus influences both P-N bond length and planarity of ligands at nitrogen.

The conformation of $(F_2P)_3N$ represents the most probable fixed orientations of the F_2P groups, assuming independent torsions around the P-N bonds. Since there appears no physical reason why a barrier to torsional motion should exist at zero twist angle, and harmonic oscillation of the F_2P groups around zero would make this position most probable,[143] a simple harmonic approximation would not describe the torsional behaviour adequately. This torsion seems to be represented best by a most probable displacement of 10° from C_{3h} symmetry, for which twists (-10, -10, +10°) or (+10, +10, -10°) would be three times more likely than (-10, -10, -10°) or (+10, +10, +10°). Perhaps the approach adopted in the structure determination of $(F_2P)_2Se$, in which the F_2P group torsional displacements from a mean position were described in terms of an angular root mean squared amplitude, might be applied to $(F_2P)_3N$. Such an investigation should produce a r.m.s. amplitude of about 10° from C_{3h} symmetry. However, in view of the structure found in this study, it may be necessary to introduce anharmonicity into the potential function describing the F_2P group torsions, so as to increase the probabilities of the angular displacements with respect to zero displacement. Since this would give greater weight to conformations with non-zero displacements, and the structure would be represented by a summation of probability weighted instantaneous molecular conformations, it may represent more accurately the torsional motion of the F_2P groups about C_{3h} symmetry.

7.9. DIAMINODIFLUOROPHOSPHORANE

The characterisation of diaminodifluorophosphorane described in Chapter 6 indicated that the molecule had C_{2V} symmetry with the fluorines axial in a trigonal bipyramidal molecule. The effect on the n.m.r. spectra of reducing the temperature showed hindered rotation of the amino groups about the P-N bonds, and a preference for the NH_2 group and the fluorine atoms to be co-planar. This ED study was carried out to investigate these observations, and to provide further structural information about five co-ordinate pentavalent phosphorus compounds, few of which have been studied.

7.10. Molecular Model

The model was a particularly simple one which assumed C_{2V} symmetry, with the planes of the amino groups perpendicular to the HPN_2 plane and the C_2 axis along the H-P bond. No provision was made to investigate either rotation of the NH_2 groups about the P-N bonds, or non-coplanarity at nitrogen, since these effects would be determined by non-bonded distances involving hydrogen atoms, of little influence in the ED experiment. The seven independent parameters that

TABLE 7.8

$HPF_2(NH_2)_2$: Least-Squares Correlation Matrix (x 1000)

r 2	r 3	r 4	∠ 1	∠ 2	u 4	u 11	u 12	u 13	k 1	k 2	
1000	-832	80	-479	339	-11	-145	139	144	102	57	r 2
	1000	-130	394	-379	0	151	-137	-181	-87	-31	r 3
		1000	-37	-180	-31	92	-45	15	79	32	r 4
			1000	-899	-5	244	-268	149	-155	-174	∠ 1
				1000	20	-250	264	-128	134	145	∠ 2
					1000	25	20	-1	95	33	u 4
						1000	-50	-122	274	186	u 11
							1000	-51	131	103	u 12
								1000	-1	-110	u 13
									1000	107	k 1
										1000	k 2

TABLE 7.9

Molecular Parameters of $HPF_2(NH_2)_2$

	Distance (Å)	Amplitude (Å)
(A) Independent Distance		
r 1 $(P-H_1)$	1.430 (F)	0.085 (F)
r 2 $(P-F_1)$	1.643 (5)	0.043 (F)
r 3 $(P-N_1)$	1.640 (5)	0.043 (F)
r 4 (N_1-H_2)	0.993 (11)	0.055 (19)
(B) Dependent Distances		
d 5 $(F_1...H_1)$	2.165 (12)	0.080 (F)
d 6 $(N_1...H_1)$	2.645 (10)	0.090 (F)
d 7 $(H_1...H_2)$	3.209 (13)	0.200 (F)
d 8 $(P...H_2)$	2.303 (11)	0.100 (F)
d 9 $(F_1...H_2)$	2.284 (12)	0.150 (F)
d 10 $(F_1...H_3)$	3.296 (20)	0.150 (F)
d 11 $(F_1...N_1)$	2.328 (10)	0.073 (5)
d 12 $(F_1...F_2)$	3.285 (12)	0.037 (12)
d 13 $(N_1...N_2)$	2.873 (16)	0.111 (27)
d 14 $(N_1...H_4)$	3.426 (19)	0.170 (F)
d 15 $(H_2...H_3)$	1.720 (19)	0.100 (F)
d 16 $(H_2...H_4)$	3.743 (21)	0.200 (F)
d 17 $(H_2...H_5)$	4.119 (26)	0.200 (F)
(C) Angles (°)		
∠ 1 (H_1-P-F_1)	89.3 (8)	
∠ 2 (H_1-P-N_1)	118.8 (5)	
∠ 3 $(P-N_1-H_2)$	120.0 (F)	

Fixed parameters marked (F).

defined the structure were therefore the bonded distances H-P, P-F, P-N and N-H, and the angles HPF, HPN and PNH.

7.11. Refinements

The radial distribution curve, P(r)/r, of $HPF_2(NH_2)_2$ (Figure 7.11) showed that the principal scattering distances in the molecule, P-F and P-N, came together at ca. 1.64 Å. Attempts to refine these distances and their amplitudes of vibration made the latter become unreasonably small, and caused the former to separate under the peak contour. Since the non-bonded F···F peak could be clearly seen at ca. 3.28 Å, the P-F distance must have a minimum value of 1.64 Å. The amplitudes of vibration of the P-N and P-F distances were therefore fixed at reasonable values[123] allowing refinement of these distances. As the N-H, F···N and F···F distances were well resolved, the angles HPN and HPF, the N-H distance, and the amplitudes of vibration of the distances N-H, F···F and F···N all refined. The remaining geometrical parameters, the P-H distance and PNH angle, were not well defined. Lowest R factors were obtained with values of 1.43 Å and 120°, and these were used in subsequent refinements. Finally the amplitude of vibration of the N···N distance was found to refine despite the fact that the peak was not prominent in P(r)/r. Under these conditions refinements converged to give a final R_G = 0.096.

The parameters found for $HPF_2(NH_2)_2$ are presented in Table 7.9, and Figure 7.12 depicts the structure. Tables 7.1

Intensity Data of $HPF_2(NH_2)_2$

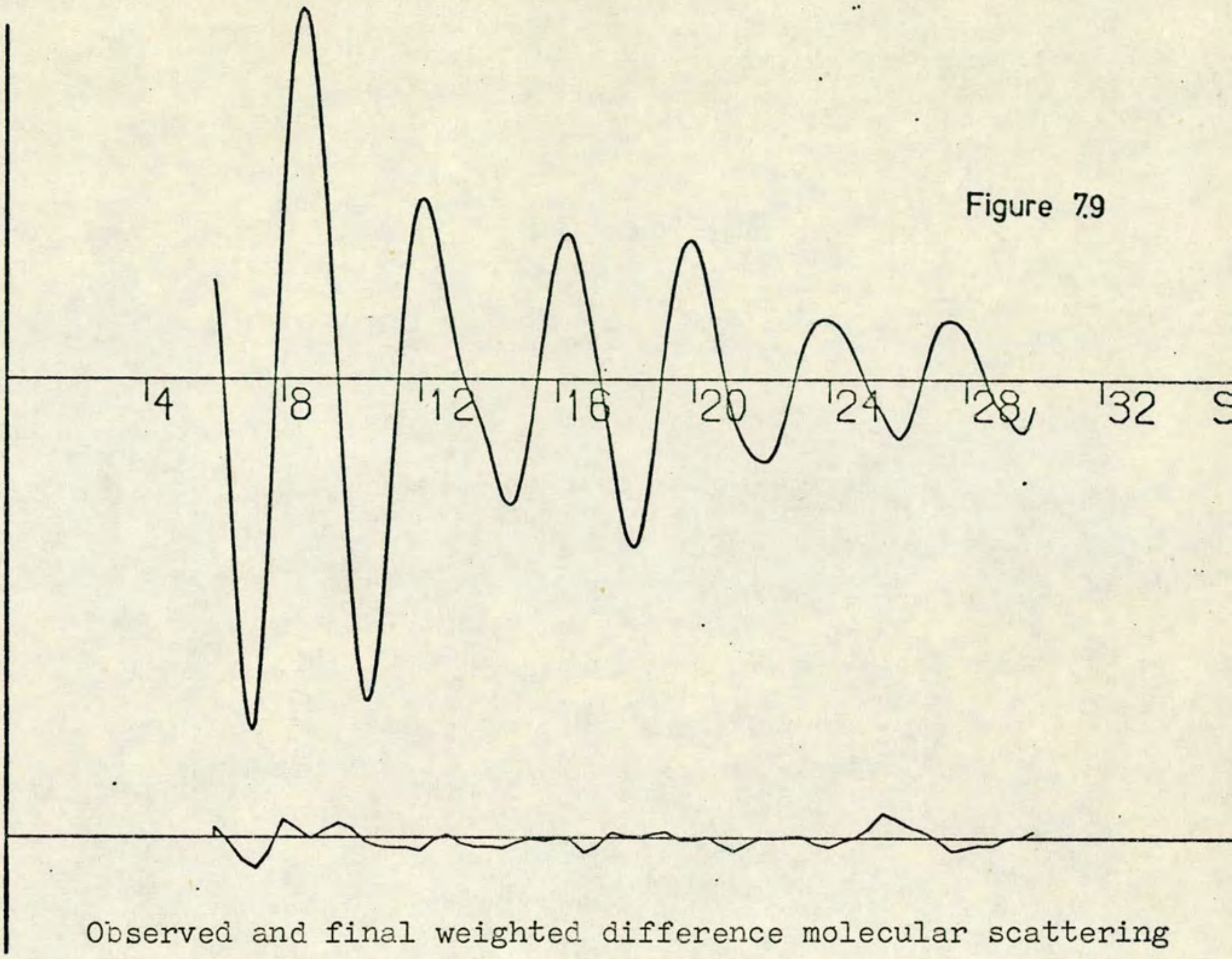


Figure 7.9

Observed and final weighted difference molecular scattering intensities for nozzle-to-plate distances of 250 mm (Figure 7.9) and 500 mm (Figure 7.10)

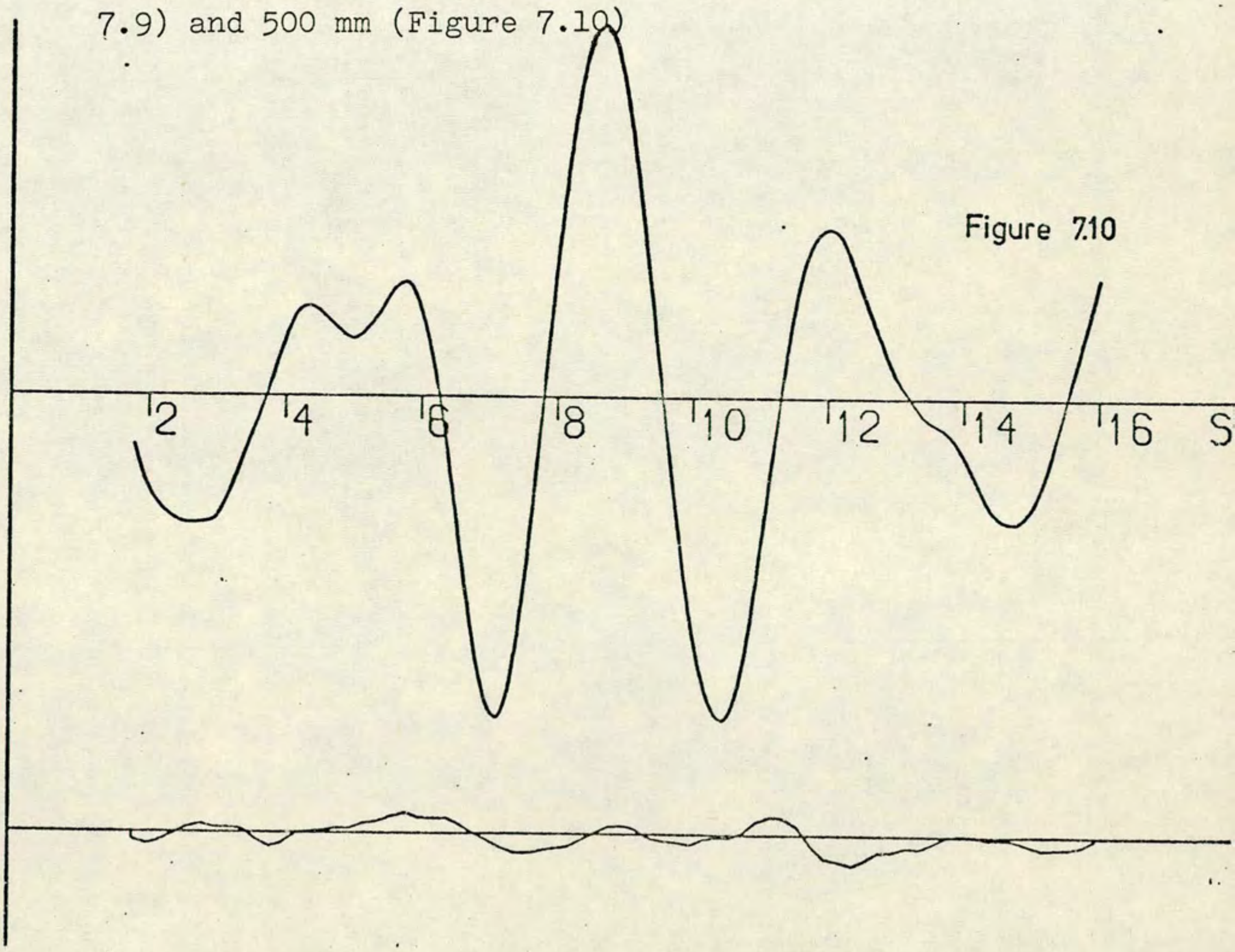


Figure 7.10

Figure 7.11

Radial Distribution Curve of $HPF_2(NH_2)_2$

Observed and difference radial distribution curves, $P(r)/r$, for $HPF_2(NH_2)_2$, showing contributions due to the non-bonded distances F···N, N···N and F···F. Before Fourier inversion, the data were multiplied by $s \exp(-0.015s^2)/(z_P-f_P)(z_F-f_F)$

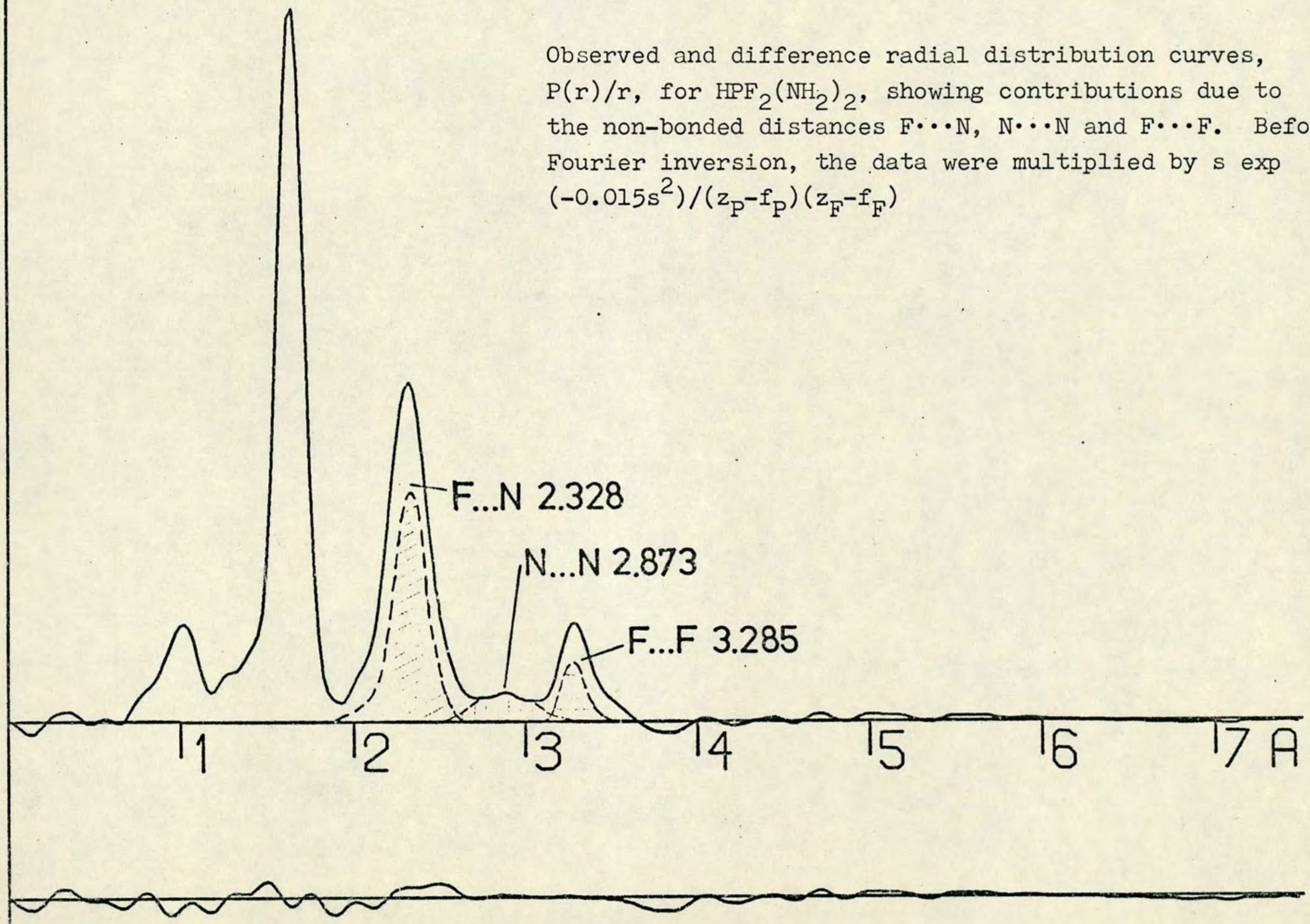


Figure 7.12

Proposed gas phase conformation of $HPF_2(NH_2)_2$

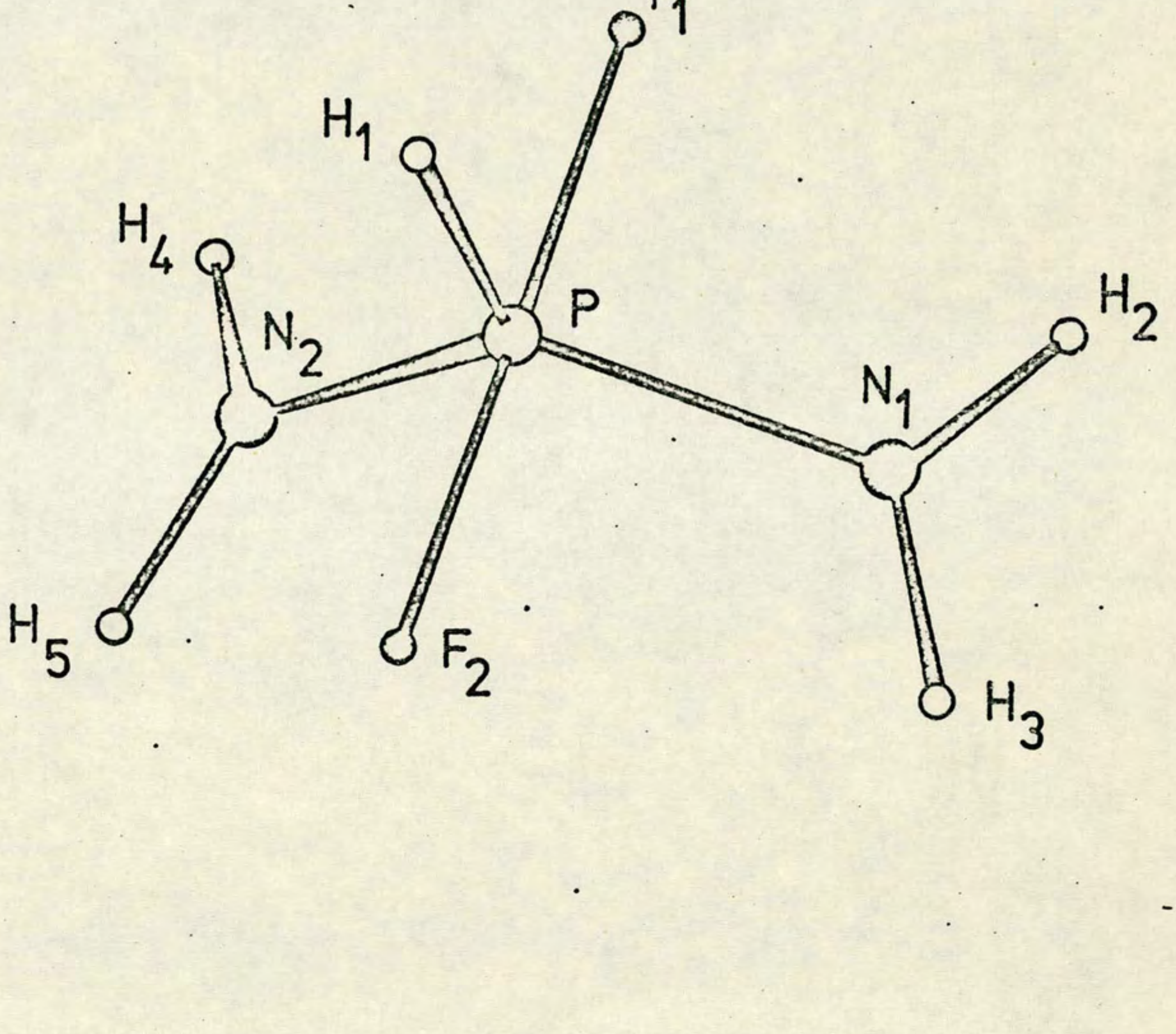


TABLE 7.10

Bond Lengths and Angles[(a)] in some Fluorophosphoranes

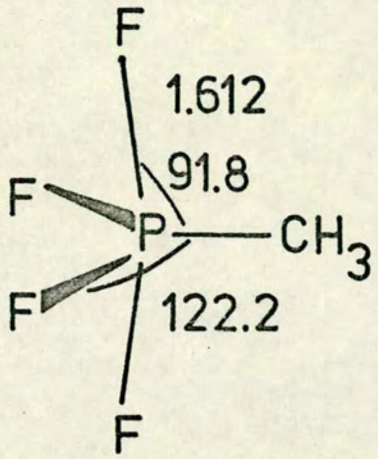
Compound	X	Y	r(P-F_{ax})	∠($F_{ax}PX_{eq}$)	∠($X_{eq}PY_{eq}$)	Reference
PF_5	F	F	1.577	90	120	144
HPF_4[(b)]	H	F	1.594	90	124	145
CH_3PF_4	C	F	1.612	91.8	122.2	146
$(CH_3)_2PF_3$	F	C	1.643	89.9	118.0	146
$(CH_3)_3PF_2$	C	C	1.685	90	120	147
$HPF_2(NH_2)_2$	H	N	1.643	89.3	118.8	

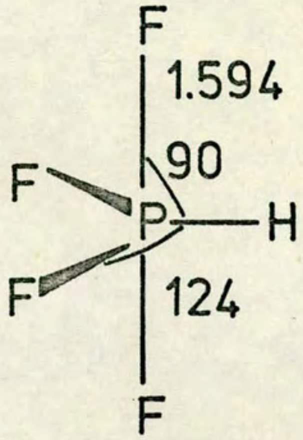
(a) Bond lengths in Å; angles in degrees.

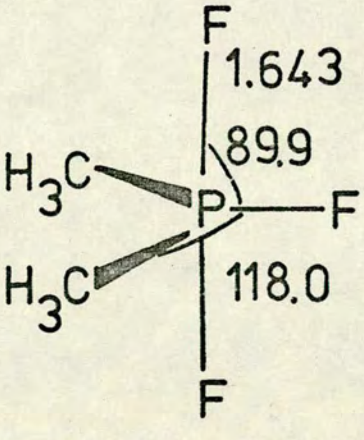
(b) Microwave values, all other ED.

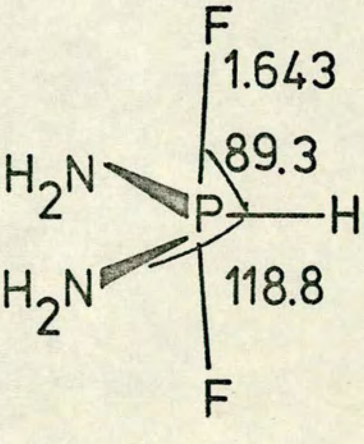
Figure 7.13

Bond angles and distances in some Fluorophosphoranes









Angles in degrees; distances in Å.

and 7.8 contain weighting functions, correlation parameters and scale factors, and the correlation matrix. Intensity curves are represented in Figures 7.9 and 7.10. The parameters of Table 7.9 were also used to calculate theoretical P(r)/r showing contributions due to the non-bonded distances F···F, F···N, and N···N. Figure 7.11 clearly demonstrates the compatability of the experimental and theoretical observations, and provides assurance for the assumptions about molecular geometry.

7.12. Discussion

Table 7.10 contains bond lengths and angles in some fluorophosphoranes. The values for $HPF_2(NH_2)_2$ are unexceptional and there is a particular similarity with $(CH_3)_2PF_3$.[146] The P-N bond length at 1.64 Å is 0.02 Å less than in F_2PNH_2,[30] not unreasonable when compared with the 0.01 Å difference in P-C bond length between F_2PCH_3[127] and $F_2P(CH_3)_3$.[147] The small distortions from regular trigonal bipyramidal geometry seem steric in origin, and not attributable to electronegativity effects. This can be seen in the displacement of axial and equatorial groups away from the least electronegative group, CH_3, in CH_3PF_4 and $(CH_3)_2PF_3$,[146] whereas in $HPF_2(NH_2)_2$, displacement is towards the least electronegative group and away from the NH_2 groups (Figure 7.13). Insofar as this is valid, inclusion in a series of fluorophosphoranes of the isoelectronic SF_4[148] allows ligands to be arranged in an approximate order of their distorting effect upon this geometry:

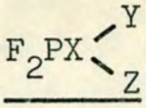
lone pair > NH_2 ~ CH_3 > F ~ H.

7.13. Non-Bonded Distances in Fluorophosphines

In a series of substituted ethylenes and carbonyl derivatives, Bartell observed that while bond lengths were determined by valence forces, bond angles in crowded molecules were governed mainly by non-bonded van der Waals forces between nearest neighbour atoms.[149] From these non-bonded contact distances, 'hard sphere' radii for atoms bonded to a common central atom were obtained, the sum of two such radii giving a distance of minimum approach for the two atoms concerned. For example, the sum of fluorine and chlorine 'hard sphere' radii derived from half the F···F distance in $CH_2=CF_2$ and Cl···Cl distance in $CH_2=CCl_2$, would give a reasonable estimate of the F···Cl distance in $CH_2=CFCl$. Although these radii related to a carbon central atom, the ideas have been extended to other central atoms, in silyl derivatives of nitrogen,[150] and several fluorophosphine and fluorophosphoryl compounds.[151] In the latter case, only the fluorine 'hard sphere' radius was found from the non-bonded F···F distance in F_2P moieties. From the non-bonded distances in these compounds, Tables 7.11 and 7.12, many other radii can be obtained however, both with, and without phosphorus as the central atom, Table 7.13. The 'hard sphere' radii values with a particular central atom seem constant, irrespective of their source, as in the case of silicon obtained from H_3SiN_3 and $(H_3Si)_2NCN$,[150] 1.57 Å, and from $F_2PNHSiH_3$, 1.58 Å. Consequently, they can be used in conjunction with bond lengths, predicted from electronegativity-corrected covalent radii, to give estimates of valence

TABLE 7.11

Non-bonded Distances in some Difluorophosphino-Compounds



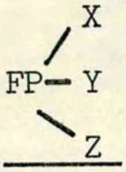
$F_2PX\begin{smallmatrix}\nearrow Y \\ \searrow Z\end{smallmatrix}$

			Distance (Å)					
X	Y	Z	F...F	F...X	P...Y	P...Z	Method[a]	Reference
H	–	–	2.406	2.233	–	–	MW	152
CH_3	–	–	2.398	2.570	–	–	MW	127
C	N	–	2.365	2.545	2.956	–	MW/ED	151,153
N	H	H	2.337	2.504	2.339	–	MW/ED	136,30
N	H	SiH_3	2.436	2.395	2.310	3.034	ED	17
N	CH_3	CH_3	2.420	2.456	2.692	–	MW/ED	135,30
N	PF_2	CH_3	2.340	2.492	2.851	2.767	ED	130
N	PF_2	PF_2	2.368	2.498	2.965	–	ED	
N	$CNPF_2$	–	2.451	2.378	2.682	–	ED	139
N	CO	–	2.358	2.480	2.675	–	ED	138
N	CS	–	2.384	2.447	2.743	–	ED	138
O	CH_3	–	2.340	2.456	2.653	–	MW	154
O	PF_2	–	2.420	2.378	2.925	–	ED	29,37
Se	PF_2	–	2.421	2.953	3.341	–	ED	
F	–	–	2.364	–	–	–	MW/ED	155,156
Cl	–	–	2.352	2.754	–	–	MW/ED	157,158
Br	–	–	2.386	2.896	–	–	ED	158
I	–	–	2.439	3.132	–	–	ED	158
P	H	H	2.398	2.884	2.640	–	MW	159
P	F	F	2.415	2.900	–	–	ED	131

(a) Where both microwave (MW) and electron diffraction (ED) data have been obtained, ED values are quoted.

TABLE 7.12

Non-bonded Distances in some Fluorophosphino- and Fluorophosphoryl Compounds



			Distances (Å)					
X	Y	Z	F...X	F...Y	F...Z	X...Y	Method[a]	Reference
Cl	Cl	-	2.762	-	-	3.127	ED	158
Br	Br	-	2.910	-	-	3.410	ED	158
O	H	F	2.529	2.275	2.354	2.420	MW	160
O	F	F	2.521	2.355	-	-	MW/ED	161,162
S	F	F	2.912	2.350	-	-	MW	161
Se	H	F	3.051	2.271	2.365	2.923	ED	120

(a) Where both microwave (MW) and electron diffraction (ED) data have been obtained, ED values are quoted.

TABLE 7.13

Hard Sphere Radii derived from Fluorophosphine and Fluorophosphoryl Compounds

Hard sphere radii (Å)	Central atom C[(a)]	N	O	P	Se
H	0.92	0.88		1.07	
C	1.25	1.26	1.19	1.37	
N	1.14	-	-	1.27	
O	1.13	-	-	1.28	
F	1.08	-	-	1.19	
Si	-	1.58	-	1.68[(b)]	
P	-	1.45	1.46	1.70	1.67
S	-	-	-	1.72	
Cl	1.44	-	-	1.57	
Se	-	-	-	1.81	
Br	-	-	-	1.71	
I	-	-	-	1.94	

(a) Values from reference 149.

(b) Derived from $P(SiH_3)_3$, reference 163.

angles. This information, and the effect of van der Waals forces upon dihedral angles, therefore provides a reasonable basis for predictions about molecular structure.

CHAPTER 8

CONCLUSIONS AND FUTURE WORK

Although the number of known difluorophosphino-derivatives of Groups V and VI has been extended, large areas of Main Group chemistry still remain relatively unexplored. Group IV compounds, for example, are not known beyond the large number for carbon. Of these, the perfluorovinylfluorophosphines,[164] and the recent preparations of vinyldifluorophosphine[165] and propynyldifluorophosphine,[166] are particularly interesting. Suggested reactive and stereochemical likeness between silyl and difluorophosphino species[30,139] implies $F_2PC \equiv CX$, other than $X = CH_3$, may be formed, since many $H_3SiC \equiv CX$ are known.[167] In addition, the recent formation of $(F_3C)_2PSiH_3$[168] indicates that the difluorophosphine analogue may be stable, fluoro- and trifluoromethyl compounds also being similar in many respects.[50,60,61] Although the nitrogen derivatives $(F_2P)_2NH$ and $(F_2P)_3N$ were prepared, attempts to form novel mixed silyl(difluorophosphino)amines by exchange routes were unsuccessful. In view of the observation of $F_2PP(SiH_3)_2$, it seemed unlikely that the nitrogen containing analogues were intrinsically unstable. Subsequent attempts to form such species by reactions making use of trimethylamine have vindicated this belief, resulting in the isolation of both the silyl and germyl compounds, $(F_2P)_2NMH_3$ and $F_2PN(MH_3)_2$.[169] $F_2PP(GeH_3)_2$ has also been prepared, in a similar manner to that of $F_2PP(SiH_3)_2$.[170] As for the bis(difluorophosphino)-Group VI derivatives, these may provide useful routes to other compounds, particularly by the facile acidic hydrogen cleavage of the phosphorus-Group VI element bonds. Moreover, recent improved methods of preparation of both $(F_2P)_2S$ and $(F_2P)_2Se$, using either bis(tri-n-butyltin)-sulphide or -selenide, makes them readily available starting materials.[171]

While it was beyond the scope of this work to investigate the complex-forming capabilities of the novel compounds, the molecules $(F_2P)_2S$, $(F_2P)_2Se$ and $(F_2P)_2NH$ are all capable of acting as bidentate ligands, co-ordinating through phosphorus, to give transition-metal complexes similar to $RN(PF_2)_2Mo(CO)_4$.[172] It may even be possible to use $(F_2P)_3N$ as a tridentate ligand. Developments have shown that using norbornadiene molybdenum tetracarbonyl and cycloheptatriene molybdenum tricarbonyl, complexes are in fact formed. By reaction at these co-ordinated ligands other new complexes could well be generated, since examples of P-C,[81] P-F[173] and P-N[174] bond cleavage in co-ordinated fluorophosphines are well known. In addition, reactions involving boranes and trihaloboranes could be studied, since there is the possibility of co-ordination through Group V or VI elements, as well as phosphorus atoms. In particular, any complex with $(F_2P)_2S$ or $(F_2P)_2Se$ would be most interesting in comparison with the behaviour of $(F_2P)_2O$. This forms only a monoborane adduct, $F_2POPF_2.BH_3$,[7] attributed to reduction in the base strength of the unco-ordinated phosphorus via a π-system involving oxygen, a mechanism likely to be absent in the sulphur and selenium analogues. Furthermore, hydrogen halide cleavage of the Group VI element bond to the uncoordinated phosphorus atom in such adducts may result in the complexes, $HSPF_2.BH_3$ and $HSePF_2.BH_3$. Uncomplexed, F_2PSH and F_2PSeH are unstable with respect to rearrangement to $S{=}PF_2H$ and $Se{=}PF_2H$. In this context it is interesting to note that reaction of bromomanganese pentacarbonyl with $S{=}PR_2H$ (R = Me, Et or Ph), results in elimination of a carbonyl group and rearrangement of the thiophosphoryl to form $(HS)PR_2Mn(CO)_4Br$.[175]

The volatility of difluorophosphines makes them ideal for gas phase molecular structure determinations. Although electron diffraction (ED) studies have been carried out on only three molecules, others, such as $(F_2P)_2S$, $F_2PP(SiH_3)_2$ and F_2PNHBF_2 would also be worth investigating. The P-S bond length, PSP angle, and amplitude of the F_2P torsion in $(F_2P)_2S$ would not only be interesting parameters in themselves, but also in comparison with $(F_2P)_2O$[29,37] and $(F_2P)_2Se$. Also, since the torsion of the F_2P group is temperature dependent, structures determined at large enough temperature differences may be expected to show significant differences in this parameter. With both $(F_2P)_2S$ and $(F_2P)_2Se$, recent studies have shown this to be so.[120,171] $F_2PP(SiH_3)_2$ could be studied from the point of view of changes in bond distances and angles from $P(SiH_3)_3$, when F_2P replaces an SiH_3 group. Also of interest is the orientation of the F_2P moiety, particularly since the isolation of $F_2PP(GeH_3)_2$, and the determination of its ED structure, indicates crowding of the ligands to the central phosphorus atom, with the possibility of H•••F interactions affecting the overall conformation.[120,170] Of most concern in F_2PNHBF_2 would be the position of the difluorophosphino group and the supposed planarity of the $PNHBF_2$ skeleton, as well as the B-N bond length. This distance is important due to the π-acceptor character of the BF_2 moiety being in competition for the nitrogen lone pair electrons with the postulated d-orbital interaction of phosphorus. In $F_2BN(SiH_3)_2$, it was concluded that the B-N bond length was unexceptional for these two three co-ordinate atoms, and that the BF_2 group had about the same π-acceptor capacity as an SiH_3 group.[176] Again due to stereochemical similarities between SiH_3 and F_2P groups,[30,139] a B-N bond distance similar to that in $F_2BN(SiH_3)_2$, and not appreciably shortened, may be found in F_2PNHBF_2.

In addition to ED, microwave (MW) studies on several of these molecules could also be carried out. The recent developments in ED, whereby predicate observations are used in the least-squares refinements of molecular structure,[177] make combined MW and ED investigations particularly useful. However, the predicate observations can be any set of structural parameters obtained by other techniques, not only MW, but also X-ray, vibrational analysis, or liquid-crystalline n.m.r. Knowledge of parameters in analogous systems, or non-bonded distance estimates may also be used, the predicate observations being weighted as to their reliability. Although deviations from the predicate values are allowed, the extent depends upon their weighting. Therefore care must be exercised to prevent undue bias when interpreting the data aided by preconceptions held about the structural parameters. Despite this proviso, the method can be particularly powerful by easing high correlations between pairs of overlapping peaks in the radial distribution curve, and thus assisting resolution.

Structural information about fluorophosphines may also be obtained from their n.m.r. spectra in the nematic phase of liquid-crystalline solvents. Since the earliest references by Saupe and Englert,[178,179] both the theory,[180,181] and reviews of developments[182,183] in this technique have appeared. Although only angles or ratios of molecular distances may be obtained, the method complements ED since both experiments determine internuclear distances averaged over molecular vibrations. Furthermore, if two distances were similar and produced overlapping peaks in the ED radial distribution curve, knowledge of the ratio of these distances from liquid-crystalline n.m.r. would enable them to be resolved. The P-F and P-N bond lengths in aminodifluorophosphines are one such case. There is still, of course, a difference in the phase in which the parameters would be obtained. However, results from PH_3,[184] and PF_3,[185] are in good agreement with gas phase MW and ED data. Despite theoretical limitations, such as the vibrational motion of the molecule and anisotropies in indirect couplings, the determination of liquid phase structures by n.m.r. is extremely useful. Applied to the 100% abundance of spin $\frac{1}{2}$ nuclei in fluorophosphines it could prove invaluable.

CHAPTER 9

EXPERIMENTAL SECTION

1. SYNTHETIC METHODS

The volatile compounds were handled in a standard Pyrex-glass vacuum system fitted with greased ground-glass, and Sovirel polytetrafluoroethylene taps. Apiezon N and L greases were used on glass taps and joints. Apparatus with Sovirel taps, and detachable from the vacuum line, was used for off-line experiments. The amounts of volatile compounds, and molecular weights, were calculated from gas volumes, assuming Boyle's Law. Separation of materials was effected at convenient temperatures using slush baths of liquid nitrogen or solid carbon dioxide in a suitable solvent.[186] Commercially available solvents for use in n.m.r. tube reactions were purified as follows and stored under vacuum: CCl_3F, C_6D_6 and $(CH_3)_4Si$ were spectroscopically pure; C_6H_6 was distilled off sodium; CH_2Cl_2 and C_6H_{12}(cyclohexane), distilled through flamed-out molecular sieve; $CHCl_3$, shaken with activated alumina and distilled. Other solvents were either pure enough for use, like tetramethylenesulphoxide, or were purified by standard methods. NH_3 and $(C_2H_5)_2O$ were stored over sodium wire, then distilled; $(CH_3)_2O$ was distilled off $LiAlH_4$ and fractionated in vacuo; and diglyme was shaken with potassium and anthracene until dark blue, then distilled.

Starting materials for reactions were prepared as outlined below, their purity being checked spectroscopically.

	Compound	Preparation	Reference
(1)	Cl_2PNMe_2	PCl_3 + $HNMe_2$	187
(2)	F_2PNMe_2	(1) + SbF_3, or NaF/TMSO	187
(3)	F_2PX	(2) + HX(X = Cl, Br or I)	187
(4)	F_2PNH_2	(3) + NH_3	9, 79
(5)	GeH_3Br	GeH_4 + HBr + $AlBr_3$	188
(6)	$(GeH_3)_2O$	(5) + $Pb(OH)_2$	45
(7)	$(GeH_3)_2Y$	(5) + $(SiH_3)_2Y$(Y = S, Se or Te)	28, 189
(8)	SiH_3Br	$PhSiCl_3$ + $LiAlH_4$, then HBr	190
(9)	SiH_3Cl	(8) + $HgCl_2$ (streaming)	86
(10)	$(SiH_3)_3N$	(9) + NH_3	191
(11)	$(SiH_3)_2NH$	(9) + NH_3	74
(12)	$(SiH_3)_2O$	(9) + H_2O	45
(13)	$(SiH_3)_2Y$	(10) + H_2Y(Y = S, Se or Te), then(8)	41
(14)	$(SiH_3)_3P$	(8) + KPH_2	192
(15)	$(SiH_3)_2PH$	(14) + $LiCH_3$, then H_2S	193
(16)	$(SiH_3PH_2$	(8) + KPH_2	192
(17)	DBr	PBr_3 + D_2O	186
(18)	H_2Y	Al_2Y_3 + aqueous HCl(Y = Se or Te)	186
(19)	ND_3	D_2O + NH_4Cl, then CaO, repeatedly	17
(20)	PH_3	H_3PO_3 + heat	66
(21)	AsH_3	As_2O_3 + KBH_4	186
(22)	HCN	NaCN + H_2SO_4	186
(23)	$HMn(CO)_5$	$NaMn(CO)_5$ + H_3PO_4	194
(24)	$HRe(CO)_5$	$NaRe(CO)_5$ + H_3PO_4	195

All other compounds were either commercial products, or prepared by standard methods.

2. INSTRUMENTATION

Infra red spectra were recorded on a Perkin-Elmer 225 grating spectrometer (4000 - 200 cm^{-1}), a Grubb Parsons Spectromajor (8500 - 400 cm^{-1}), or a Beckmann RIIC FS720 interferometer (400 - 50 cm^{-1}), using gas cells equipped with CsI, KBr or polythene windows. Raman spectra were obtained using a Cary 83 spectrophotometer with argon-ion 488 nm laser excitation, mass spectra with a double-focusing A.E.I. MS902 spectrometer, and ultra violet photoelectron spectra with a Perkin-Elmer PS16 spectrometer having He(I) excitation (21.22 eV). Assistance in running and interpreting photoelectron spectra was given by Dr. S. Cradock. Also helpful were reviews concerned with the spectra of related molecules.[196,197] The ^{1}H, ^{19}F and ^{31}P n.m.r. spectra were observed on Varian Associates HA100 and deuterium locking XL100 spectrometers operating at 100.0, 94.1 and 40.5 MHz respectively, and equipped with variable temperature control.[198,199] Heteronuclear double-resonance experiments involving irradiation of ^{1}H, ^{11}B, ^{13}C, ^{15}N, ^{19}F, ^{29}Si or ^{77}Se were carried out using either a Schlumberger FS30 frequency synthesiser (for the HA100[200]) or the Gyrocode decoupler of the XL100 instrument. Since the frequencies of the synthesiser and HA100 spectrometer were generated independently, these were monitored periodically to ensure consistency to at least one part in 10^7. Decoupling frequencies could then be used to calculate chemical shifts. To do this, the frequency was corrected, after the manner of McFarlane and White,[199] to its value in a field such that the proton resonance of $(CH_3)_4Si$ was exactly 100 MHz.

The chemical shift (δ) was then given by:-

$$\delta = \frac{\Xi_c - \Xi_s}{\Xi_s} \times 10^6 \quad \text{(p.p.m.)}$$

where Ξ_c and Ξ_s were the corrected frequency of the sample, and the standard frequency. The chemical shift was therefore positive to high frequency of the standard. Those standards used are presented below:-

Compound	Nucleus	Standard Frequency, Ξ_s (Hz)
$(CH_3)_4Si$	^{1}H	100 000 000
$(CH_3O)_3B$	^{11}B	32 084 657
$(CH_3)_4Si$	^{13}C	25 144 995
$(CH_3)_4N^+I^-$	^{15}N	10 133 352
CCl_3F	^{19}F	94 093 963
$(CH_3)_4Si$	^{29}Si	19 867 183
H_3PO_4	^{31}P	40 480 746
$(CH_3)_2Se$	^{77}Se	19 071 433

In the interpretation of chemical shifts, reviews of ^{15}N,[75] ^{19}F,[91,201] and ^{31}P[202] n.m.r. data were of particular value.

Electron diffraction data were collected photographically on Kodak Electron Image and Agfa Gevaert Replica 23 plates, using Balzers' KD.G2 instruments,[203] with rotating sector, at the University of Manchester Institute of Science and Technology ($(F_2P)_2Se$ and $HPF_2(NH_2)_2$), and the University of Oslo ($(F_2P)_3N$). The electron wavelength was determined directly by measurement of the accelerating voltage, and also from the diffraction patterns of benzene and solid ZnO (at Oslo). For $(F_2P)_2Se$ and $HPF_2(NH_2)_2$, nozzle-to-plate distances of 250 and 500 mm were used with the samples maintained at 228 K and room temperature (RT) respectively, and the nozzle at RT. Nozzle-to-plate distances of 190 and 580 mm, with sample and nozzle temperatures of 235 K and RT, were obtained for $(F_2P)_3N$. A Joyce-Loebl automatic microdensitometer was used to convert the data to digital form, which was handled by established methods and programmes[30,204,205] on the ICL 4/75 computer at the Edinburgh Regional Computer Centre. The complex scattering factors of Schäfer, Yates and Bonham[206] have been used. Distances quoted were r_a values, corresponding to the centres of gravity of peaks in the radial distribution curve, P(r)/r.[121,143] Errors in distances, amplitudes of vibration, and angles have been increased to allow for systematic errors.[121] A general account of procedures in the electron diffraction study of gases has been given by Davis.[207]

3. EXPERIMENTAL DETAILS

All reactions were carried out under vacuum in clean, dry apparatus. Products other than those in n.m.r. tubes were purified by trap-to-trap fractional condensation. Identification was made by infra red and n.m.r. spectroscopy.

1.1. Exchange Reactions of F_2PBr with $(MH_3)_2Y$; (M = Si or Ge), (Y = O, S, Se or Te)

Reactions were followed by n.m.r. spectroscopy in 1:1 mixtures of C_6H_{12} (cyclohexane) and CCl_3F as both solvents, and proton and fluorine lock signals. $(MH_3)_2Y$ (ca. 0.2 mmol) in the solvents (ca. 0.7 ml) was treated at RT with the appropriate ratio of F_2PBr (ca. 0.2 - 0.7 mmol) for whichever product was to be studied. Reaction times varied from minutes to several weeks.

Preparations and Reactions of $(F_2P)_2S$ and $(F_2P)_2Se$

Experiments 2.1 to 2.7 and 2.10, and 2.8, were unsuccessful attempts to form $(F_2P)_2Se$, and $(F_2P)_2S$.

2.1. Reaction of F_2PBr, H_2Se and NMe_3:-

In a clean, dry double-bulb apparatus of 1000 and 100 ml capacity, NMe_3 (4.0 mmol) was injected into a mixture of F_2PBr (5.0 mmol) and H_2Se (2.0 mmol). Five minutes after the immediate formation of clouds of (yellow-orange) solid, the only volatile products were PF_3 (2.1 mmol) and F_2PBr (0.9 mmol).

2.2. Reaction of PF_3, H_2Se and KF:-

PF_3 (5 mmol) and H_2Se (2 mmol) were condensed onto excess, dry KF in a greaseless tap ampoule. No reaction had occurred after 30 minutes at RT, the reactants being recovered without loss.

2.3. Reaction of F_2PNH_2 and H_2Se:-

No reaction occurred between F_2PNH_2 (2 mmol) and H_2Se (2 mmol) either in the gas of liquid phases.

2.4. Reaction of F_2PNH_2, H_2Se and NMe_3:-

Vapour phase reaction between NMe_3 (1.0 mmol), and H_2Se (2.0 mmol) and F_2PNH_2 (2.0 mmol) gave white solid, which turned green-yellow on standing, and PF_3 (0.1 mmol) and unreacted F_2PNH_2 (0.2 mmol) as the only volatile products.

2.5. Reaction of F_2PNMe_2 and H_2Se:-

When gaseous H_2Se (0.8 mmol) and F_2PNMe_2 (0.8 mmol) were mixed, no reaction occurred over 5 minutes. Co-condensation, and warming to RT produced only a trace of PF_3, a little solid, and unreacted starting materials.

2.6. Reaction of F_2PCl with Na_2Se:-

(i) F_2PCl (2.0 mmol) was condensed onto freshly prepared Na_2Se (5.0 mmol), whereupon red solid, and a volatile mixture of $O{=}PF_2H$, F_2PCl, $(F_2P)_2O$ and PF_3 (0.5 mmol) was formed. A further addition of F_2PCl (2.0 mmol) returned F_2PCl and PF_3 (1.2 mmol).

(ii) F_2PCl (4.0 mmol) and Na_2Se (2.0 mmol) in dry diglyme gave after 10 minutes at RT; $O{=}PF_2H$ (0.2 mmol), F_2PCl, $(F_2P)_2O$ and PF_3 (1.0 mmol). Further F_2PCl (2.0 mmol) after 15 minutes gave PF_3 (1.4 mmol) and a mixture of $O{=}PF_2H$ and PCl_3 (0.3 mmol).

2.7. Reaction of $(F_2P)_3N$ and H_2Se:-

Co-condensed $(F_2P)_3N$ (0.5 mmol) and H_2Se (1.5 mmol) yielded yellow solid, PF_3 (0.4 mmol), unreacted H_2Se (0.7 mmol), and an $(F_2P)_2NH$, $Se{=}PF_2H$ mixture (ca. 0.5 mmol). When SiH_3Br was allowed to stand over the solid for 12 hours at 195 K, a mixture of SiH_3Br and SiH_3F was recovered.

2.8. Reaction of F_2PCl and $(SiH_3)_2S$:-

In a Sovirel tap ampoule (ca. 300 ml) $(SiH_3)_2S$ (7.2 mmol) and F_2PCl (38.0 mmol) reacted for 24 hours at 195 K and 12 hours at 209 K, but gave no $(F_2P)_2S$.

2.9. Preparation of $(F_2P)_2S$:-

$(SiH_3)_2S$ (7.2 mmol) and F_2PBr (16.0 mmol) were reacted in a Sovirel tap ampoule (ca. 300 ml) for 2 and 17.5 hours at 209 and 195 K, respectively. With the ampoule at 195 K, volatiles were condensed out to reveal an F_2PBr, SiH_3Br mixture. The mixture (16.0 mmol) and fresh F_2PBr (16.0 mmol) were returned to the ampoule and reacted for 63 and 28.5 hours at 195 and 209 K. Fractionation at this stage indicated an H_3SiS-species was still present. The SiH_3Br, F_2PBr mixture was removed, and pure F_2PBr (5.0 mmol) added, for 29.5, 16.5 and 5 hours at 195, 209 and 273 K, respectively. Again fractionation showed H_3SiS- and so further reaction was effected at 273 K for 15 hours with another pure F_2PBr sample (10.0 mmol).

Finally, fractionation yielded pure $(F_2P)_2S$ (3.8 mmol, 54% on $(SiH_3)_2S$ taken) involatile at 195 K, SiH_3Br, unreacted F_2PBr, and some $S{=}PF_2H$ and SiH_3F. A little yellow solid remained in the reaction vessel.

2.10 Reaction of F_2PBr and $(SiH_3)_2Se$, vapour phase:-

Gaseous F_2PBr (1.5 mmol) and $(SiH_3)_2Se$ (0.5 mmol) failed to react over 15 minutes at RT, and were recovered without loss.

2.11 Preparation of $(F_2P)_2Se$:-

In a Sovirel tap ampoule (ca. 300 ml), $(SiH_2)_2Se$ (8.8 mmol) was reacted with occasional shaking with F_2PCl (19.0, 19.0 and 2.8 mmol) for 4 and 2 hours at 209 K and 13 hours at 195 K. Before each addition of fresh F_2PCl the reaction vessel was maintained at 195 K and the SiH_3Cl, F_2PCl mixture, volatile at this temperature, was condensed out. In the latter case, the F_2PCl reacted to completion, only pure SiH_3Cl (2.8 mmol) being recovered. As the reaction was incomplete, the SiH_3Cl, F_2PCl mixture (38.0 mmol) was returned to the ampoule and given a further 5 and 17 hours at 209 and 195 K.

Fractionation of the product yielded pure $(F_2P)_2Se$ (4.6 mmol, 52% on $(SiH_3)_2Se$ taken) involatile at 195 K, unreacted F_2PCl, SiH_3Cl, and traces of $Se{=}PF_2H$, SiH_3F and PF_3. A little yellow solid remained in the reaction vessel.

2.12. Preparation of $(F_2P)_2Se$:-

A Sovirel tap ampoule (ca. 300 ml) was charged with $(SiH_3)_2Se$ (8.6 mmol) and F_2PBr (47.0 mmol) and allowed to react, with periodic shaking, for 5 hours at 209 K, and 84 hours at 195 K at which temperature F_2PBr and SiH_3Br were condensed out. Pure F_2PBr (10.0 mmol) was returned to the reaction vessel for 22 hours at 209 K and 27 hours at 195 K before being removed, and further F_2PBr (4.5 mmol) added. Reaction continued at 209 K for 7 hours. Between additions of fresh F_2PBr the products were fractionated to assess the extent of reaction. At completion, the products were

$(F_2P)_2Se$ (7.1 mmol, 83% on $(SiH_3)_2Se$ taken) involatile at 195 K, unreacted F_2PBr, SiH_3Br, traces of $Se{=}PF_2H$ and SiH_3F, and some involatile yellow solid.

TABLE 9.2.1

Preparations of $(F_2P)_2S$ and $(F_2P)_2Se$: Reaction Conditions

Reactants (mmol)				Total Reaction Times (hours)			Yield[a]
$(SiH_3)_2S$	$(SiH_3)_2Se$	F_2PCl	F_2PCl	273K	209K	195K	(%)
-	8.8	40.8	-	-	11	30	52
-	8.6	-	61.5	-	34	111	83
7.2	-	38.0	-	-	12	24	0
7.2	-	-	47.0	20	47	110	54

(a) Yield based on amount $(SiH_3)_2Y$ taken.

2.13. Molecular Weights of $(F_2P)_2S$ and $(F_2P)_2Se$:-

	Volume (ml)	Pressure (mm)	Temp. (K)	Weight (g)	Molecular weight (g) Obs.	Calc.
$(F_2P)_2S$	336.2	73.0	292.6	0.2270	169±3	170
$(F_2P)_2Se$	336.2	73.5	293.5	0.2864	212±4	217

2.14. Reaction of $(F_2P)_2S$ and $HPMe_2$:-

Equimolar (ca. 0.2 mmol)amounts of materials were reacted in an n.m.r. tube containing a 3:4:3 solvent mixture of C_6D_6, $CHCl_3$ and CCl_3F. ^1H, ^{31}P, and ^{31}P-(^1H) spectra were recorded.

2.15. Reaction of $(F_2P)_2Se$ and HX; (X = Cl, Br or CN):-

With HBr or HCl, co-condensed equimolar amounts (ca. 0.2 mmol) of $(F_2P)_2Se$ and hydrogen halide when warmed to RT gave $Se{=}PF_2H$ (0.2 mmol) and F_2PCl (0.2 mmol).

With HCN, no reaction occurred in liquid or vapour phases.

2.16. Reaction of $(F_2P)_2Se$ with ZH_3, or F_2PNH_2; (Z = N, P or As):-

N.m.r. tube reactions using between 0.1 and 0.4 mmol of starting materials with solvents C_6D_6, $CHCl_3$ and CCl_3F (3:4:3) gave the following products:-

	Reactants +	Molar Ratio $[(F_2P)_2Se/ZH_3]$	Products
$(F_2P)_2Se$			
	NH_3	3.0	PF_3, $Se{=}PF_2H$, F_2PNH_2
	PH_3	3.0	None
	AsH_3	1.6	None
	F_2PNH_2	1.0	None

2.17. Reaction of $(F_2P)_2Se$ and H_2Y; (Y = O, S, Se or Te):-

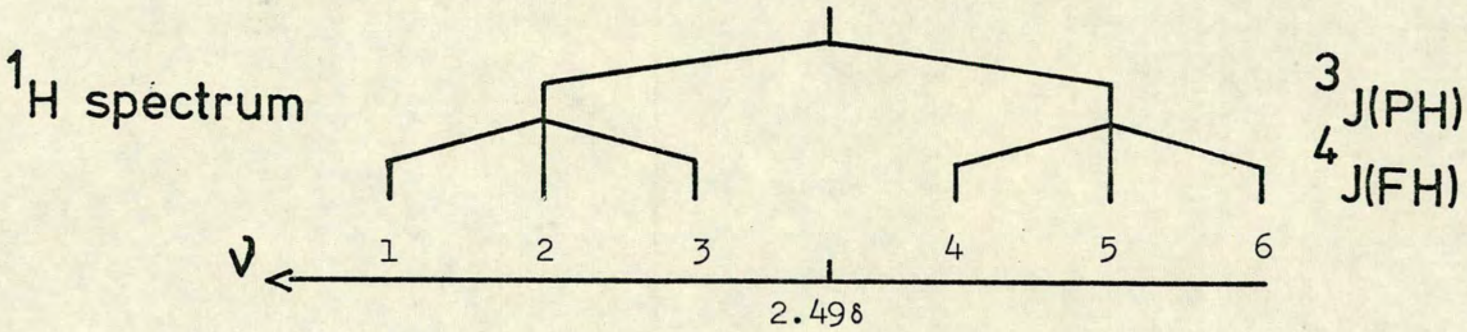
N.m.r. tube reactions using equal amounts of reagents (0.2 mmol) were carried out with $(CH_3)_4Si$, C_5D_6 and CCl_3F as solvents. Products were identified by their ^1H and ^{31}P spectra. Additionally, the H_2Se and H_2Te reactions were followed over the temperature range 198 to 303 K with a C_5D_6, CCl_3F (1:2) solvent mixture.

2.18. Reaction of $(F_2P)_2Se$ with CH_3YH; (Y = O or S):-

Reagents (0.2 mmol) were reacted in n.m.r. tubes with C_6D_6, $CHCl_3$ (1:2) solvents at RT, and ^1H and ^{31}P spectra recorded.

Figure 9.2.1

F_2PSCH_3 : signs of coupling constants



Experiment	^1H line	Ξ (Hz)	Signs related	Chemical shifts (p.p.m.)
$^1H - (^{31}P)$	1	40 488 925	$^4J(^{19}F^1H)$, $^1J(^{19}F^{31}P)$	$\delta(^{31}P) = 233$
	2	40 490 188	opposite	
$^1H - (^{19}F)$	1	94 086 616	$^3J(^{31}P^1H)$, $^1J(^{19}F^{31}P)$	$\delta(^{19}F) = -71$
	4	94 087 949	opposite	

Data from the F_2PSCH_3 relative sign determination are given in Figure 9.2.1. The corrected frequencies, ⌸ , correspond to the centres of the methyl quartet in the ^{19}F and ^{31}P spectra.

2.19. Reaction of $(F_2P)_2Se$ and $HM(CO)_5$; (M = Mn or Re):-

N.m.r. tube reactions at RT, with C_6D_6 and $(CH_3)_4Si$ (1:2) as solvents, were carried out with $(F_2P)_2Se$ (ca. 0.3 - 0.4 mmol) and $HM(CO)_5$, the amount of which was only estimated to be equimolar due to its involatility. Reaction gave an orange (Mn) or a white (Re) precipitate and products identified by ^1H and ^{31}P spectra as $Se{=}PF_2H$ and F_2PH.

2.20. Reaction of $(F_2P)_2Se$ with Cl_2:-

$(F_2P)_2Se$ (0.3 mmol) and Cl_2 (0.6 mmol) were reacted in C_6D_6 and $(CH_3)_4Si$ (1:2) as solvents, and ^{19}F and ^{31}P spectra recorded. At RT, the solution rapidly became dark yellow and a black precipitate formed.

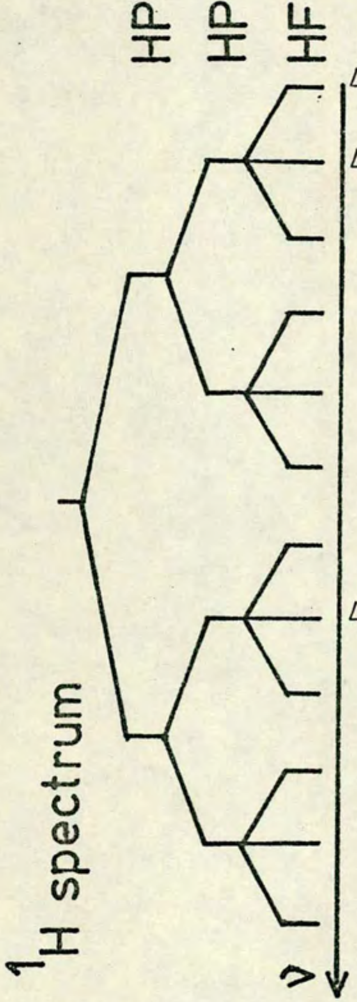
3.1. Exchange Reactions between F_2PBr and the Silyl Derivatives of Group V Elements:-

Reactions 1-6 of Table 3.1 were carried out in n.m.r. tubes using between 0.1 and 0.3 mmol of silyl-amine or -phosphine. Products were identified by direct observation of ^1H, ^{19}F and ^{31}P spectra.

In reaction 7, a gaseous mixture (2.9 mmol) of SiH_3Cl and F_2PCl (1:2) was added to NH_3 (3.9 mmol). Immediately, dense white clouds (NH_4Cl) were formed. After 15 minutes,

Figure 9.3.1

$F_2PP'(SiH_3)_2$; heteronuclear double resonance experiments



$^1H-(^{31}P)$

▭	Parameters
40 493 797 40 492 572	HF, FP equal $^1J(PF)$= 1225
40 492 572 40 492 272	HP', P'P opposite $^1J(PP')$= 300 $\delta(^{31}P)$ = 228.4

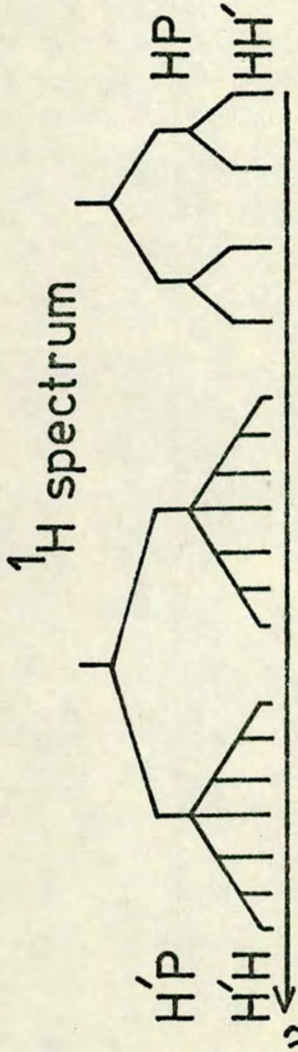
$^1H-(^{31}P')$

▭	Parameters
40 472 247 40 472 317	HF, FP' equal $^2J(P'F)$ = 70
40 472 317 40 472 016	HP, PP' opposite $^1J(P'P)$ = 301

$^1H-(^{19}F)$

▭	Parameters
94 086 844 94 085 622	HP, PF opposite $^1J(PF)$ = 1222
94 086 844 94 086 914	HP', P'F equal $^2J(P'F)$ = 70

Figure 9.3.2. $(H_3Si)_2PH'$; hetero- and homonuclear double resonance experiments.



^{1}H-(^{31}P), ^{1}H'-(^{31}P)				^{1}H-(^{1}H'), ^{1}H'-(^{1}H)	
▭	Signs	Parameters	Oscillator frequency	Signs	Parameters
40 467 607 40 467 791 40 467 607 40 467 791	HH', H'P equal	^{1}J(H'P) = 184 δ(^{31}P) = -322.3	2514 2702	HP, PH' equal	^{1}J(H'P) = 188
40 467 777 40 467 795 40 467 813 40 467 777 40 467 795 40 467 813	HH', HP equal	^{2}J(HP) = 18	2943 2960	H'P, PH equal	^{2}J(HP) = 17

fractionation yielded a sample (1.1 mmol) comprising F_2PNH_2, $F_2PNHSiH_3$ and $N(SiH_3)_3$ involatile at 177 K, and another (0.6 mmol) of F_2PCl, SiH_3Cl, SiH_3F and a trace of PF_3, volatile at this temperature.

3.2. Double Resonance Experiments of $F_2PP(SiH_3)_2$ and $(SiH_3)_2PH$:-

Details of these experiments are contained in Figures 9.3.1 and 9.3.2.

Preparations and Reactions of $(F_2P)_2NH$ and $(F_2P)_3N$

Reactions 4.1 - 4.3 were unsuccessful attempts to form bis- and tris(difluorophosphino)amines.

4.1. Reaction of F_2PBr, F_2PNH_2 and 2,6 dimethylpyridine:-

Equal amounts (4 mmol) of reagents were condensed and warmed to RT, whereupon brown solid was formed with PF_3 as the only volatile product.

4.2. Reaction of F_2PNH_2 with methyllithium:-

F_2PNH_2 and $LiCH_3$ (1.5 mmol each) reacted in diethylether at 227 K to give CH_4 (ca. 0.8 mmol). Addition of F_2PBr (1.5 mmol) gave only a small amount of PF_3.

4.3. Reaction of F_2PNH_2 and KPH_2:-

To a freshly prepared sample of KPH_2 (ca. 3.5 mmol) was added F_2PNH_2 (1.0 mmol). PH_3 (0.5 mmol) was evolved, but no further reaction occurred on addition of F_2PBr (3.5 mmol).

4.4. Preparation of $(F_2P)_3N$:-

This was achieved in apparatus consisting of two bulbs, of about 2 l and 100 ml capacity, linked by a Sovirel tap. The reaction was done in three stages, with the apparatus being cleaned and dried between each stage, and final drying done by allowing SiH_3Br or SiH_3Cl to stand in the bulbs for a few minutes.

In the first stage, the small bulb was filled with NMe_3 (4.5 mmol) and the large one with an F_2PNH_2 (2.0 mmol) and F_2PCl (5.0 mmol) mixture. The connecting tap was opened to allow the pressures to equalise (admitting ca. 4 mmol of NMe_3), and closed again. Clouds of white trimethylammonium chloride were formed. After 40 minutes, volatile products were removed and fractionated. The fraction retained at 195 K but passing 209 K consisted of 1.6 mmol (80% based on F_2PNH_2 taken) of a mixture of F_2PNH_2, $(F_2P)_2NH$ and $(F_2P)_3N$.

Secondly, NMe_3 (1.05 mmol) was added from the small bulb to F_2PCl (3.2 mmol) and the mixed amines (1.6 mmol) in the 2 l bulb. After 45 minutes, the volatile products were fractionated to yield ca. 1.4 mmol of tertiary amine containing some secondary amine (about 90% based on amines taken).

Finally, the second step was repeated so that the ratios of difluorophosphino-amines:F_2PCl:NMe_3 was 1.0:2.0:0.5. This time the fraction retained at 195 K but passing 209 K was essentially pure $(F_2P)_3N$. The yield over the three stages was 65% based on F_2PNH_2 used.

The molecular weight of the product was found to be

221 ± 3 g. (calculated 221 g), and the vapour pressure was given by the expression, log p (mm) = -1625/T + 7.911. ΔH_{vap} was 31.20 kJ mol^{-1}, ΔS_{vap} was 99.4 J mol K^{-1}, and the extrapolated boiling point was 314 K.

4.5. Preparation of $(F_2P)_2NH$:-

HBr (0.2 mmol) was added from an 100 ml bulb to $(F_2P)_3N$ (0.2 mmol) in a 2 ℓ bulb. A small amount of white solid was formed. Volatile products, separated by fractional condensation, were $(F_2P)_2NH$ (0.1 mmol, 50%, retained at 195 K) and F_2PBr (0.16 mmol, 80%, retained at 143 K). Determination of vapour pressures was not possible, but the molecular weight was found to be 158 ± 5 g. (calculated 153 g). [Subsequent reactions have shown this preparation to be equally effective on larger scale samples.]

4.6. Reaction of $(F_2P)_3N$ with HX; (X = Cl, Br or I):-

Reactions were carried out in the liquid phase, condensing reagents together and allowing them to warm to RT, or in the gas phase, using a double-bulb apparatus. In a typical reaction, $(F_2P)_3N$ (0.2 mmol) and HI (0.4 mmol) were co-condensed and warmed to RT. A small amount of white solid formed. The volatile products, separated by fractionation were $(F_2P)_2NH$ (0.15 mmol, 75% on amine taken), F_2PI (0.11 mmol, 55%) and excess HI. In general, yields of $(F_2P)_2NH$ were higher for gas phase reactions than liquid phase ones, and the use of excess hydrogen halide reduced this yield. F_2PNH_2 was not observed in any of these reactions.

4.7. Reaction of $(F_2P)_2NH$ with HCl:-

When $(F_2P)_2NH$ and HCl were condensed together (ratio 1:1 or 1:2) and allowed to warm to RT, no white solid formed, and the reagents were recovered unchanged.

4.8. Reaction of $(F_2P)_3N$ and H_2O:-

The reagents (0.2 mmol of each) were mixed in the gas phase and allowed to stand for 10 minutes. No solid material was formed. Fractionation of the products caused decomposition to white solid, $(F_2P)_2NH$ (0.07 mmol, 35% of amine) and PF_3 (0.11 mmol).

4.9. Reaction of $(F_2P)_3N$ with H_2S:-

$(F_2P)_3N$ and H_2S reacted slowly (10 minutes or longer) in the gas phase to give $(F_2P)_2NH$ in high yields (ca. 85%) and a trace of PF_3 as the only volatile products. The involatile residue was a colourless liquid or film of solid.

4.10. Reaction of $(F_2P)_3N$ with H_2Se:-

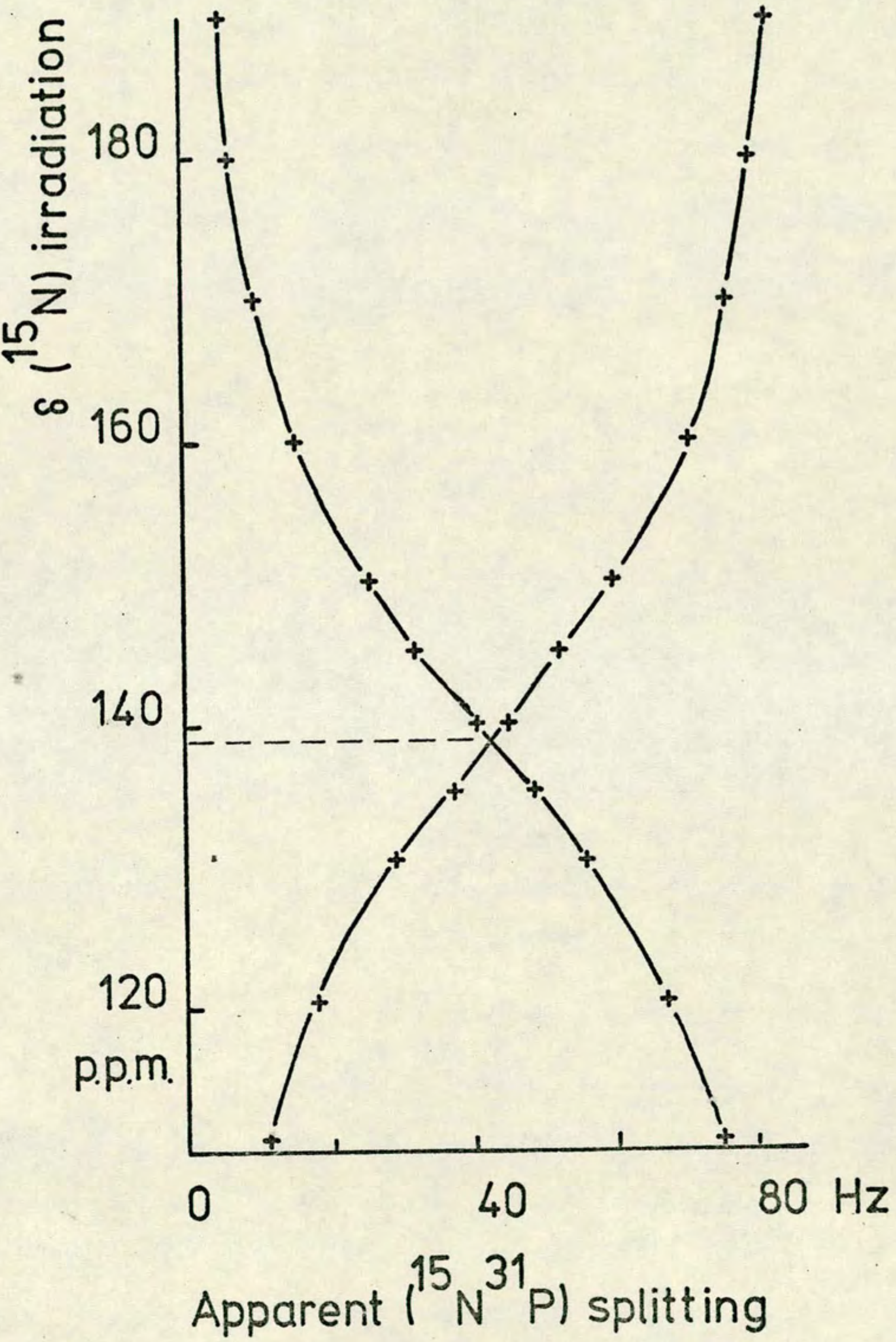
$(F_2P)_3N$ (0.2 mmol) and H_2Se (0.6 mmol) were condensed together and warmed to RT. The volatile products were $(F_2P)_2NH$ (0.12 mmol, 60%), $Se{=}PF_2H$ (0.06 mmol), PF_3 (0.05 mmol) and unreacted H_2Se.

4.11. Reaction of $(F_2P)_3N$ and H_2Te:-

$(F_2P)_3N$ (0.2 mmol) and H_2Te (0.25 mmol) were allowed to react in an n.m.r. tube containing C_6D_6, $(CH_3)_4Si$ (1:2) solvents at about 200 K. The products observed were

Figure 9.4.1

Determination of $\delta(^{15}N)$ in $(F_2P)_3{}^{15}N$ by ^{31}P-(^{15}N) heteronuclear noise-decoupling[(a)]



Broken line gives $\delta(^{15}N)$ of $(F_2P)_3{}^{15}N$ (139.0 p.p.m.) at the position of zero ($^{15}N^{31}P$) splitting.

(a) 50% XL100 Decoupler power

$(F_2P)_2NH$, PH_3, PF_3 and elemental tellurium.

4.12. Reaction of $(F_2P)_3N$ with Cl_2:-

$(F_2P)_3N$ (0.2 mmol) and Cl_2 (0.3 mmol), when mixed in an n.m.r. tube containing C_6D_6 and $(CH_3)_4Si$ solvents (1:2) at RT, gave F_2PCl as the only major product.

4.13. Nuclear Magnetic Double Resonance Experiments

(i) For $(F_2P)_3{}^{15}N$, $\delta(^{15}N)$ was found by observing the doublet splitting in the ^{31}P spectrum, caused by the $^1J(^{15}N^{31}P)$ coupling, while irradiating with 50% decoupler power at selected frequencies in the ^{15}N spectrum. Figure 9.4.1 depicts the results of this experiment.

(ii) For $(F_2P)_2{}^{15}NH$, the experiments performed to relate the signs of coupling constants are given below.

TABLE 9.4.1

$(F_2P)_2{}^{15}NH$ Double Resonance Experiments

Experiment	Coupling Constants Related	Relative Signs
$^1H-\{^{15}N\}$	$^3K(^1H^{19}F)/^2K(^{15}N^{19}F)$	Equal
	$^2K(^1H^{31}P)/^1K(^{15}N^{31}P)$	Opposite
$^1H-\{^{19}F\}$	$^1K(^1H^{15}N)/^2K(^{15}N^{19}F)$	Equal
	$^2K(^1H^{31}P)/^1K(^{31}P^{19}F)$	Opposite
$^1H-\{^{31}P\}$	$^1K(^1H^{15}N)/^1K(^{15}N^{31}P)$	Opposite
	$^3K(^1H^{19}F)/^1K(^{31}P^{19}F)$	Opposite

Preparations of F_2PNHBF_2

All preparations involved the reaction of F_2PNH_2 (1 - 3 mmol) with BF_3, the products for several reactions

TABLE 9.5.1

Products of Reaction of F_2PNH_2 and BF_3

Reaction Conditions		Molar Ratio $[BF_3/F_2PNH_2]$	Total Yield of amines[a]	Estimated F_2PNHBF_2(%)[b]	Estimated $(F_2P)_2NH$(%)[b]
5.1		1.0	0.75	80	-
		1.6	0.35	50	-
5.2		1.0	0.50	80	20
5.3		1.0	0.25	25	65
		1.3	0.50	80	-
5.4		1.0	0.60	80	-
	(c)	2.0	0.70	90	-
		3.0	0.50	95	-
	(c)	3.0	0.80	90	-
5.5		0.9	0.50	50	40
		0.5	0.30	0	60
		0.5	0.10	10	80
		0.3	0.30	0	50
5.6		0.5	0.40	0	95

N.B. (a) Yield of F_2PNH_2, F_2PNHBF_2 and $(F_2P)_2NH$ based on reactant F_2PNH_2 as unity.

(b) Estimate of compound in total yield from infra red spectra.

(c) Reaction time 15 minutes, all others 5 minutes.

being given in Table 9.5.1. The most successful method was 5.4 below, using a 3:1 ratio of BF_3 to F_2PNH_2.

5.1. Reaction of F_2PNH_2 with BF_3, liquid phase:-

Reactants were condensed together and allowed to warm to RT, producing white solid, and volatiles consisting of difluorophosphino-amines, retained at 177 K, and PF_3 and unreacted BF_3.

5.2. Reaction of F_2PNH_2 and BF_3 over aluminium:-

As 5.1, but with the reaction vessel containing an excess of aluminium turnings.

5.3. Reaction of F_2PNH_2 and BF_3 over potassium fluoride:-

As 5.1, but with an excess of finely-divided, dry KF in the reaction vessel.

5.4. Reaction of F_2PNH_2 and BF_3, gas phase:-

BF_3 was allowed to expand from an 100 ml bulb into a 2 ℓ bulb containing F_2PNH_2. A cloud of white solid formed which settled slowly onto the bulb walls. After about 15 minutes the volatile products were fractionated, F_2PNHBF_2 being retained at 177 K.

Preparations of $(F_2P)_2NH$

5.5. Reaction of F_2PNH_2 and BF_3, liquid phase:-

As 5.1, with the reactant ratios those of Table 9.5.1.

5.6. Reaction of an $(F_2P)_2NH$, $(F_2P)_3N$ mixture with BF_3:-

A mixture of $(F_2P)_2NH$ and $(F_2P)_3N$ (1:1) was reacted with BF_3 after the manner of 5.1, above.

Preparations and Reactions of $HPF_2(NH_2)_2$

6.1. Preparation of $HPF_2(NH_2)_2$ from F_2PNH_2 and NH_3:-

F_2PNH_2 and NH_3 (2.0 mmol each) were co-condensed in a dry, evacuated ampoule (100 ml) fitted with a Sovirel tap. Warming to RT produced some white solid. After 10 minutes, products were fractionated to yield $HPF_2(NH_2)_2$ (0.49 mmol, 0.050 g, 25% on F_2PNH_2 taken) retained at 227 K, and a small amount of PF_3 and unreacted F_2PNH_2.

6.2. Preparation of $HPF_2(NH_2)_2$ from F_2PCl and NH_3:-

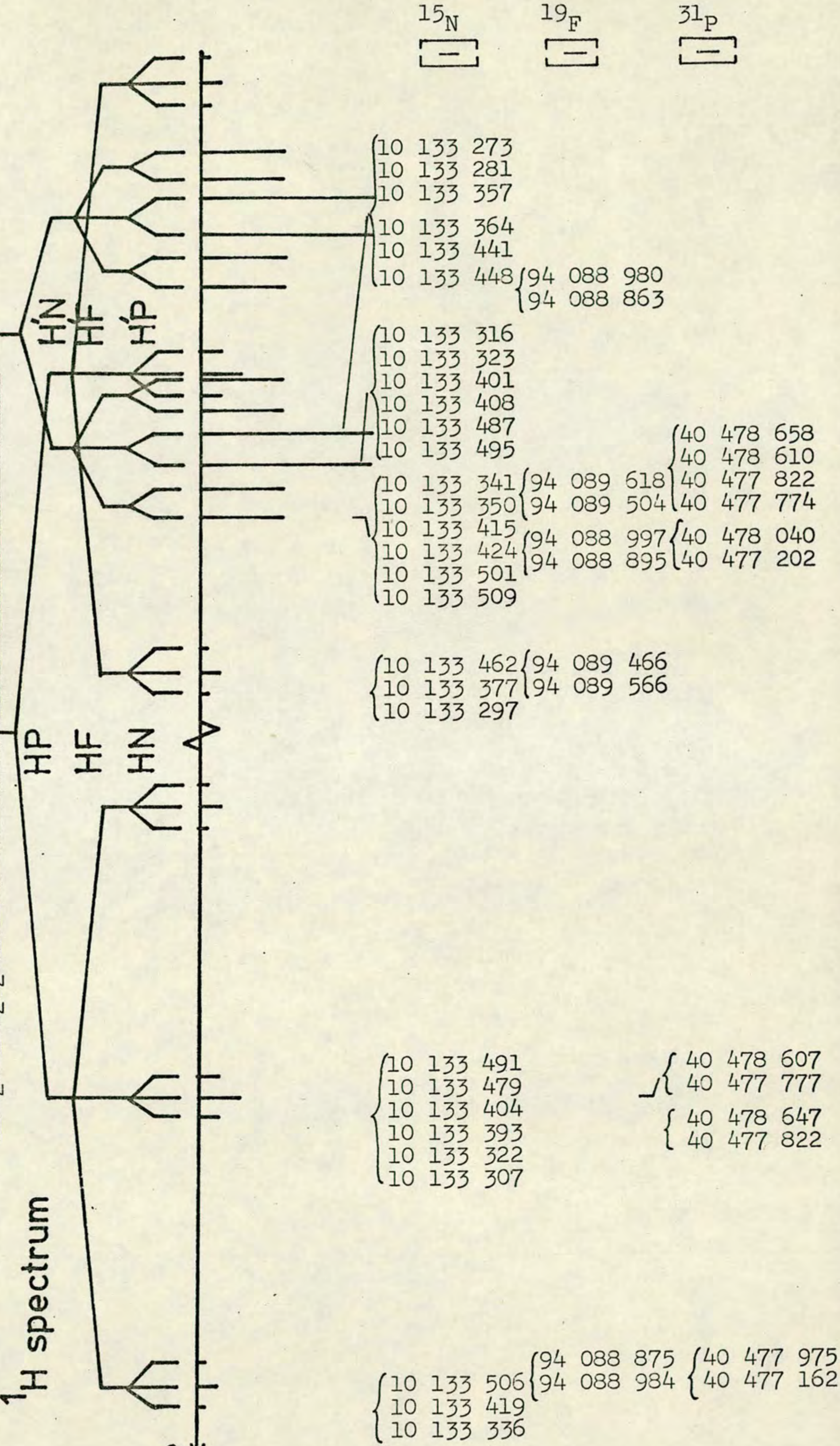
In a typical experiment, NH_3 (8.4 mmol) expanded from an 100 ml bulb into a 1 ℓ bulb containing F_2PCl (2.8 mmol), with the immediate formation of white solid. After 3 minutes, volatile products were condensed out of the reaction vessel, over the course of an hour, and fractionated. Retained at 227 K was a sample of $HPF_2(NH_2)_2$ (1.17 mmol, 0.119 g, 42% on F_2PCl taken), at 177 K was F_2PNH_2 containing a trace of $HPF_2(NH_2)_2$ (0.1 mmol), and at 77 K was a mixture (0.3 mmol) of PF_3 and unreacted NH_3.

6.3. Preparation of Deuteriated $HPF_2(NH_2)_2$.

Prior to reaction the vacuum system was flushed with D_2O, pumped out for several hours, then flushed with silylhalide which again was pumped out.

Figure 9.6.1

$HPF_2(^{15}NH'_2)_2$; Heteronuclear double resonance experiments



The compounds $DPF_2(ND_2)_2$, "$HPF_2(ND_2)(NH_2)$" and "$DPF_2(NH_2)(ND_2)$" were prepared as in 6.1 and 6.2 above from F_2PCl (3.3 mmol) and ND_3 (10.0 mmol), F_2PND_2 (1.0 mmol) and NH_3 (1.5 mmol), and F_2PNH_2 (1.0 mmol) and ND_3 (1.5 mmol), respectively. To maintain purity yields were not taken.

6.4. Reaction of $HPF_2(NH_2)_2$, F_2PCl and NMe_3:-

$HPF_2(NH_2)_2$ (0.4 mmol) reacted in the gas phase with F_2PCl (2.8 mmol) and NMe_3 (1.4 mmol) for 5 minutes giving white solid, F_2PNH_2 (0.8 mmol), and some unreacted F_2PCl.

6.5. Reaction of $HPF_2(NH_2)_2$ and HCl:-

Equimolar amounts (0.2 mmol) of HCl and $HPF_2(NH_2)_2$ when co-condensed and warmed to RT yielded some involatile white solid, F_2PCl (0.05 mmol) and unreacted $HPF_2(NH_2)_2$ (0.10 mmol). No F_2PNH_2 was detected.

6.6. Nuclear Magnetic Double Resonance Experiments:-

These were carried out on a sample of $HPF_2(^{15}NH_2)_2$ (0.4 mmol) with a C_6D_6, $CHCl_3$ (2:3) mixture as solvents and locks. Figure 9.6.1 gives the corrected frequencies of the main lines in the ^{15}N, ^{19}F and ^{31}P spectra associated with a particular resonance in the ^{1}H spectrum.

7.1. Calculation of the Torsional Frequency of the Difluorophosphine Group in $(F_2P)_2Se$:-

The torsional frequency was calculated from the theory of references 130, 132 and 133 as expressed by:-

$$k_\phi = kT/\delta^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{[1]}$$

where; k_ϕ is the potential constant (J)

k is Boltzmann's constant (1.3805×10^{-23} J K^{-1})

T is temperature (298 K)

δ is r.m.s. torsional amplitude ($\frac{20}{180} \times \pi$ radians)

AlsO:-

$$\nu = (k_\phi/I_r)^{\frac{1}{2}}/2\pi \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{[2]}$$

where; ν is the torsional frequency (Hz)

I_r is the reduced moment of inertia about the P-Se bond calculated (in a.m.u.-Å²) from the axis connecting the centres of gravity of the F_2P and $SePF_2$ units ($50.1 \times 1.660 \times 10^{-47}$ kg m²)

Since 1 Hz = 3.33564×10^{-11} cm^{-1}, equation [2] readily gives the torsional frequency of 34 cm^{-1}.

REFERENCES

1. H. Moissan, Compt. Rendus, (1884), 99, 655.
2. H.S. Booth and S.G. Frary, J. Amer. Chem. Soc. (1939), 61, 2934.
3. H.S. Booth and A.R. Bozarth, J. Amer. Chem. Soc. (1939), 61, 2927.
4. R. Schmutzler, Adv. Fluorine Chem. (1965), 5, 31.
5. M. Fild and R. Schmutzler in 'Organic Phosphorus Compounds', ed. G.M. Kosolapoff and L. Maier, Wiley-Interscience, New York, 1972, vol. 4.
6. T. Kruck, Angew. Chem., Int. Ed., (1967), 6, 53.
7. J.F. Nixon, Adv. Inorg. Chem. Radiochem., (1970), 13, 363.
8. J.S. Harman and D.W.A. Sharp, J. Chem. Soc.(A), (1970), 1935.
9. D.W.H. Rankin, J. Chem. Soc.(A), (1971), 783.
10. J.F. Nixon, J. Chem. Soc.(A), (1968), 2689.
11. J.F. Nixon, J. Chem. Soc.(A), (1969), 1087.
12. F.A. Johnson and R.W. Rudolph, J. Chem. Phys., (1967), 47, 5449.
13. R.W. Rudolph and H.W. Schiller, J. Amer. Chem. Soc., (1968), 90, 3581.
14. D. Solan and P.L. Timms, Chem. Comm., (1968), 1540.
15. H.W. Schiller and R.W. Rudolph, Inorg. Chem., (1971), 10, 2500.
16. J.S. Harman, M.E. McCartney, and D.W.A. Sharp, J. Chem. Soc.(A), (1971), 1547.
17. D.E.J. Arnold, E.A.V. Ebsworth, H.F. Jessep, and D.W.H. Rankin, J.C.S. Dalton, (1972), 1681.
18. R.W. Rudolph, R.C. Taylor, and R.W. Parry, J. Amer. Chem. Soc., (1966), 88, 3729.
19. L.F. Centofanti and R.W. Parry, Inorg. Chem., (1968), 7, 1005.
20. R.A. Newmark and A.D. Norman, Chem. Comm., (1969), 893.
21. R.W. Rudolph and R.A. Newmark, J. Amer. Chem. Soc. (1970), 92, 1195.

22. T.L. Charlton and R.G. Cavell, Inorg. Chem., (1969), 8, 2436.

23. R. Foester and K. Cohn, Inorg. Chem., (1972), 11, 2590.

24. R.G. Cavell and A.R. Sanger, J. Inorg. Nuclear Chem. Letters, (1973), 9, 461.

25. R.K. Harris, J.R. Woplin, R.E. Dunmur, M. Murray and R. Schmutzler, Ber. Bunsenges. Phys. Chem., (1972), 76, 44.

26. A.H. Cowley, J.R. Schweiger and S.L. Manatt, Chem. Comm., (1970), 1491.

27. L.O. Brockway and F.T. Wall, J. Amer. Chem. Soc., (1934), 56, 2373.

28. K. Moedritzer and J.R. Van Wazer, Inorg. Chem., (1966), 5, 547; S. Cradock and E.A.V. Ebsworth, J. Chem. Soc.(A), (1967), 1226.

29. D.E.J. Arnold and D.W.H. Rankin, J. Fluorine Chem., (1973), 2, 405.

30. G.C. Holywell, D.W.H. Rankin, B. Beagley, and J.M. Freeman, J. Chem. Soc.(A), (1971), 785.

31. A. Müller, E. Niecke, and O. Glemser, Z. Anorg. Chem., (1967), 350, 256.

32. R.W. Rudolph, J.G. Morse and R.W. Parry, Inorg. Chem., (1966), 5, 1464.

33. J.F. Nixon and R. Schmutzler, Spectrochim. Acta, (1964), 20, 1835.

34. W. McFarlane and R.J. Wood, J.C.S. Dalton, (1972), 1397.

35. J.A. Pople and D.P. Santry, Mol. Phys. (1964), 8, 1.

36. A.V. Cunliffe, E.G. Finer, R.K. Harris and W. McFarlane, Mol. Phys., (1967), 12, 497.

37. L. Vilkov and L.S. Khaikin, Topics Current Chem., (1975), 53, 50, and references therein.

38. T.L. Charlton and R.G. Cavell, Inorg. Chem. (1967), 6, 2204.

39. F. Seel and K.D. Velleman, Chem. Ber., (1972), 105, 406.

40. R.C. Dobbie and B.P. Straughan, Spectrochim. Acta, (1971), 27A, 255.

41. S. Cradock, E.A.V. Ebsworth and H.F. Jessep, J.C.S. Dalton, (1972), 359.

42. S. Cradock and D.W.H. Rankin, J.C.S. Faraday II, (1972), 68, 940.

43. S. Cradock, Unpublished observations.

44. C.R. Brundle and D.W. Turner, Proc. Roy. Soc., (1968), A, 307, 27.

45. S. Cradock and R.A. Whiteford, J.C.S. Faraday II, (1972), 68, 281.

46. D.E.C. Corbridge, Topics Phosphorus Chem., (1969), 6, 235.

47. E.A.V. Ebsworth, R. Taylor and L.A. Woodward, Trans. Faraday Soc., (1959), 55, 211.

48. R.C. Dobbie, M.J. Hopkinson and B.P. Straughan, J. Mol. Struct., (1974), 23, 141.

49. R.A. Chittenden and L.C. Thomas, Spectrochim. Acta, (1964), 20, 1679.

50. W. McFarlane and J.A. Nash, Chem. Comm., (1969), 913.

51. W.J. Stec, A. Okruszek, B. Uznanski, and J. Michalski, Phosphorus, (1972), 2, 97.

52. D.W.W. Anderson, E.A.V. Ebsworth, G.D. Meikle and D.W.H. Rankin, Mol. Phys., (1973), 25, 381.

53. W. McFarlane and D.S. Rycroft, J.C.S. Chem. Comm., (1972), 902.

54. R.A. Dwek, R.E. Richards, D. Taylor, G.J. Penney and G.M. Sheldrick, J. Chem. Soc.(A), (1969), 935.

55. L. Maier, Helv. Chim. Acta, (1966), 49, 1249.

56. R.K. Harris and R.G. Hayter, Canad. J. Chem. (1964), 42, 2282.

57. L. Maier in 'Organic Phosphorus Compounds', ed. G.M. Kosolapoff and L. Maier, Wiley-Interscience, New York, 1972, vol. 4.

58. D.W. McKennon and M. Lustig, Inorg. Chem., (1971), 10, 406.

59. J.E. Griffiths and A.B. Burg, J. Amer. Chem. Soc., (1962), 84, 3442.

60. R.G. Cavell and H.J. Emeléus, J. Chem. Soc., (1964), 5825.

61. R.C. Dobbie and M.J. Hopkinson, J. Fluorine Chem., (1974), 3, 367.

62. R.G. Cavell, T.L. Charlton and A.A.Pinkerton, Chem. Comm., (1969), 424.

63. L.F. Centofanti and R.W. Parry, Inorg. Chem., (1970), 9, 744.

64. R. Schmutzler, J. Chem. Soc. (1965), 5630.

65. G.S. Reddy and R. Schmutzler, Z. Naturforsch., (1970), B, 25, 1199.

66. F.A. Cotton and G.W. Wilkinson 'Advanced Inorganic Chemistry', second edition, Wiley-Interscience, London, 1966, and references therein.

67. H.G. Horn and A. Müller, Z. Anorg. Chem., (1966), 346, 266.

68. E.A.V. Ebsworth, C. Glidewell, and G.M. Sheldrick, J. Chem. Soc.(A), (1969), 352.

69. E. Niecke and W. Flick, Angew. Chem., Int. Ed., (1973), 12, 585.

70. C. Glidewell and G.M. Sheldrick, J. Chem. Soc.(A), (1969), 350.

71. K.D. Crosbie and G.M. Sheldrick, Mol. Phys., (1971), 20, 317.

72. R.R. Dean and W.McFarlane, Chem. Comm., (1967), 840.

73. S.L. Manatt, G.L. Juvinall, R.I. Wagner and D.D. Elleman, J. Amer. Chem. Soc., (1966), 88, 2689.

74. D.W.W. Anderson, J.E. Bentham and D.W.H. Rankin, J.C.S. Dalton, (1973), 1215.

75. M. Witanowski and G.A. Webb, Ann. Reports N.M.R. Spectroscopy, (1972), 5A, 395.

76. E.A.V. Ebsworth and J.J. Turner, J. Phys. Chem., (1963), 67, 805.

77. D.E.J. Arnold, J.S. Dryburgh, E.A.V. Ebsworth and D.W.H. Rankin, J.C.S. Dalton, (1972), 2518.

78. R.M. Lynden-Bell and R.K. Harris, 'Nuclear Magnetic Resonance Spectroscopy', Nelson, Belfast, 1969, and references therein.

79. J.E. Smith and K. Cohn, J. Amer. Chem. Soc., (1970), 92, 6185.

80. A.B. Burg and J. Heners, J. Amer. Chem. Soc., (1965), 87, 3092.

81. C.G. Barlow, R. Jefferson and J.F. Nixon, J. Chem. Soc.(A), (1968), 2692.

82. J.F. Nixon, Chem. Comm., (1967), 669.

83. B. Birdsall, N.J.M. Birdsall, and J. Feeney, J.C.S. Chem. Comm., (1972), 316.

84. G. Binsch, J.B. Lambert, B.W. Roberts and J.D. Roberts, J. Amer. Chem. Soc., (1964), 86, 5564.

85. E. Niecke and J.F. Nixon, Z. Naturforsch., (1972), B, 27, 467.

86. E.A.V. Ebsworth, J.R. Hall, M.J. Mackillop, D.C. McKean, N. Sheppard and L.A. Woodward, Spectrochim. Acta, (1958), 13, 202.

87. G.I. Drozd, S.Z. Ivin, V.V. Sheluchenko, B.I. Tetel'baum, G.M. Luganskii, and A.D. Varshavskii, Zh. Obshch. Khim. (1967), 37, 1343.

88. F.J. Lovas and D.R. Johnson, J. Chem. Phys., (1973), 59, 2347.

89. A.G. Robiette, G.M. Sheldrick, W.S. Sheldrick, B. Beagley, D.W.J. Cruickshank, J.J. Monaghan, B.J. Aylett and I.A. Ellis, Chem. Comm., (1968), 909.

90. A.J. Banister, N.N. Greenwood, B.P. Straughan and J. Walker, J. Chem. Soc., (1964), 995.

91. C.H. Dungan and J.R. Van Wazer, 'Compilation of Reported ^{19}F N.M.R. Chemical Shifts', Wiley-Interscience, New York, 1970, and references therein.

92. G. Elter, O. Glemser and W. Herzog, J. Organometallic Chem., (1972), 36, 257.

93. H. Bock and W. Fuss, Chem. Ber., (1971), 104, 1687.

94. A.H. Cowley and J.R. Schweiger, J.C.S. Chem. Comm., (1972), 560.

95. M. Lustig and H.W. Roesky, Inorg. Chem., (1970), 9, 1289.

96. P.M. Treichel, R.A. Goodrich and S.B. Pierce, J. Amer. Chem. Soc., (1967), 89, 2017.

97. M. Brownstein and R. Schmutzler, J.C.S. Chem. Comm., (1975), 278.

98. R.G. Cavell, D.D. Poulin, K.I. The, and A.J. Tomlinson, J.C.S. Chem. Comm., (1974), 19.

99. W. McFarlane and R.R. Dean, J. Chem. Soc.(A), (1968), 1535.

100. A.J.R. Bourn and E.W. Randall, Mol. Phys., (1964), 8, 567.

101. A.H. Cowley and R.W. Braun, Inorg. Chem. (1973), 12, 491.

102. J.W. Gilje, R.W. Braun and A.H. Cowley, J.C.S. Chem. Comm., (1974), 15.

103. J.S. Harman and D.W.A. Sharp, Inorg. Chem., (1971), 10, 1538.

104. J.S. Harman and D.W.A. Sharp, J. Chem. Soc.(A), (1970), 1138.

105. A.H. Cowley and J.R. Schweiger, Chem. Comm., (1970), 1492.

106. E.L. Muetterties, P. Meakin and R. Hoffman, J. Amer. Chem. Soc., (1972), 94, 5674.

107. J.R. Schweiger, A.H. Cowley, E.A. Cohen, P.A. Kroon, and S.L. Manatt, J. Amer. Chem. Soc., (1974), 96, 7122.

108. A Strich and A. Veillard, J. Amer. Chem. Soc., (1973), 95, 5574.

109. S.C. Peake and R. Schmutzler, J. Chem. Soc.(A), (1970), 1049.

110. R.M. Badger and L.R. Zumwalt, J. Chem. Phys., (1938), 6, 711.

111. K. Namoto, 'Infra red Spectra of Inorganic and Coordination Compounds', Wiley, New York, 1963, and references therein.

112. J.E. Griffiths, R.P. Carter Jnr., and R.R. Holmes, J. Chem. Phys., (1964), 41, 863.

113. R.R. Holmes and C.J. Hora Jnr., Inorg. Chem., (1972), 11, 2506.

114. D.W. Goodman, M.J.S. Dewar, J.R. Schweiger and A.H. Cowley, Chem. Phys. Letters, (1973), 21, 474.

115. G.R. Branton, D.C. Frost, C.A. McDowell and I.A. Stenhouse, Chem. Phys. Letters, (1970), 5, 1.

116. V. Shomaker and D.P. Stevenson, J. Amer. Chem. Soc., (1941), 63, 37.

117. A. Almenningen, O. Bastiansen, V. Ewing, K. Hedburg, and M. Traetteberg, Acta Chem. Scand., (1963), 17, 2455.

118. C. Glidewell, D.W.H. Rankin, A.G. Robiette, G.M. Sheldrick, B. Beagley and S. Cradock, J. Chem. Soc.(A), (1970), 315.

119. J.D. Murdoch, D.W.H. Rankin and C. Glidewell, J. Mol. Struct., (1971), 9, 17.

120. D.W.H. Rankin, Unpublished observations.

121. H.M. Seip in 'Molecular Structure by Diffraction Methods', ed. G.A. Sim and L.E. Sutton, The Chemical Society, London, 1973, Vol. 1, and references therein.

122. W.C. Hamilton, Acta Cryst., (1965), 18, 502.

123. S.J. Cyvin, 'Molecular Vibrations and Mean Square Amplitudes', Universitetsforlaget, Oslo, 1968.

124. L.S. Bartell and H.K. Higginbotham, J. Chem. Phys., (1965), 42, 851.

125. R.W. Kilb and L. Pierce, J. Chem. Phys., (1957), 27, 108.

126. V.W. Laurie, J. Chem. Phys., (1959), 30, 1210.

127. E.G. Codding, R.A. Creswell and R.H. Schwendeman, Inorg. Chem., (1974), 13, 856.

128. K. Kimura and M. Kubo, J. Chem. Phys., (1959), 30, 151.

129. J.F. Beecher, J. Mol. Spectroscopy, (1966), 21, 414.

130. E. Hedburg, L. Hedburg and K. Hedburg, J. Amer. Chem. Soc., (1974), 96, 4417.

131. H.L. Hodges, L.S. Su, and L.S. Bartell, Inorg. Chem., (1975), 14, 599.

132. W.G. Fately, R.K. Harris, F.A. Miller and R.E. Witanowski, Spectrochim. Acta, (1965), 21, 231.

133. K. Hagen and K. Hedburg, J. Amer. Chem. Soc., (1973), 95, 1003.

134. A. Almenningen, L. Fernholt and H.M. Seip, Acta Chem. Scand., (1968), 22, 51.

135. P. Forti, D. Damiani and P.G. Favero, J. Amer. Chem. Soc., (1973), 95, 756.

136. A.H. Britten, J.E. Smith, P.L. Lee, K. Cohn and R.H. Schwendeman, J. Amer. Chem. Soc., (1971), 93, 6772.

137. E.D. Morris and C.E. Nordman, Inorg. Chem., (1969), 8, 1673.

138. D.W.H. Rankin and S.J. Cyvin, J.C.S. Dalton, (1972), 1277.

139. D.W.H. Rankin, J.C.S. Dalton, (1972), 869.

140. E. Hobbs, D.E.C. Corbridge and B. Raistrick, Acta Cryst., (1953), 6, 621.

141. B. Beagley and A.R. Conrad, Trans. Faraday Soc., (1970), 66, 2740.

142. C. Glidewell, D.W.H. Rankin, A.G. Robiette and G.M. Sheldrick, J. Mol. Struct., (1969), 4, 215.

143. A.G. Robiette in 'Molecular Structure by Diffraction Methods', ed. G.A. Sim and L.E. Sutton, The Chemical Society, London, 1973, vol. 1 and references therein.

144. K.W. Hansen and L.S. Bartell, Inorg. Chem., (1965), 4, 1775.

145. S.B. Pierce and C.D. Cornwell, J. Chem. Phys., (1968), 48, 2118.

146. L.S. Bartell and K.W. Hansen, Inorg. Chem., (1965), 4, 1777.

147. H. Yow and L.S. Bartell, J. Mol. Struct., (1973), 15, 209.

148. W.M. Tolles and W.D. Gwinn, J. Chem. Phys., (1962), 36, 1119.

149. L.S. Bartell, J. Chem. Phys., (1960), 32, 827.

150. C. Glidewell and A.G. Robiette, Chem. Phys. Letters, (1974), 28, 290.

151. P.L. Lee, K. Cohn and R.H. Schwendeman, Inorg. Chem. (1972), 11, 1917.

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

153. G.C. Holywell and D.W.H. Rankin, J. Mol. Struct., (1971), 9, 11.

154. R.H. Schwendeman, E.G. Codding and C.E. Jones, Inorg. Chem. (1974), 13, 178.

155. A. Mirri, J. Chem. Phys., (1967), 47, 2823.

156. Y. Morino, K. Kuchitsu and T. Moritani, Inorg. Chem., (1969), 8, 867.

157. A.H. Brittain, J.E. Smith and R.H. Schwendeman, Inorg. Chem., (1972), 11, 39.

158. J.A. Salthouse, Unpublished observations.

159. R.L. Kuczkowski, H.W. Schiller and R.W. Rudolph, Inorg. Chem., (1971), 10, 2505.

160. L.F. Centofanti and R.L. Kuczowski, Inorg. Chem., (1968), 7, 2582.

161. Q. Williams, J. Sheridan and W. Gordy, J. Chem. Phys., (1952), 20, 164.

162. T. Moritani, K. Kuchitsu, and Y. Morino, Inorg. Chem., (1971), 10, 344.

163. B. Beagley, A.G. Robiette and G.M. Sheldrick, J. Chem. Soc.(A),(1968), 3002.

164. A.H. Cowley and M.W. Taylor, J. Amer. Chem. Soc., (1969), 91, 1929.

165. E.L. Lines and L.F. Centofanti, Inorg. Chem. (1974), 13, 1517.

166. E.L. Lines and L.F. Centofanti, Inorg. Chem., (1973), 12, 598.

167. C. Eaborn and R.W. Bolt in 'Organometallic Compounds of the Group IV Elements', ed. A.G. MacDiarmid, Marcel Dekker, New York, 1968, Vol. 1, and references therein.

168. L. Maya and A.B. Burg, Inorg. Chem., (1975), 14, 698.

169. J.G. Wright, Unpublished observations.

170. D.J. Hutchison, Unpublished observations.

171. E.R. Cromie, Unpublished observations.

172. T.R. Johnson and J.F. Nixon, J. Chem. Soc. (S), (1969), 2518.

173. C.A. Udovich, R.J. Clark and H. Haas, Inorg. Chem., (1969), 8, 1066.

174. T. Kruck, M. Hofler, H. Jung and H. Blume, Angew. Chem., Int. Ed., (1969), 8, 522.

175. E. Lindner and H. Dreher, J. Organometallic Chem., (1973), 55, 347.

176. A.G. Robiette, G.M. Sheldrick and W.S. Sheldrick, J. Mol. Struct., (1970), 5, 423.

177. L.S. Bartell, D.J. Romenesko and T.C. Wong in 'Molecular Structure by Diffraction Methods', ed. G.A. Sim and L.E. Sutton, The Chemical Society, London, 1975, vol. 3, and references therein.

178. A. Saupe, Z. Naturforsch., (1964), A, 19, 161.

179. G. Englert and A. Saupe, Z. Naturforsch., (1964), A, 19, 172.

180. A.D. Buckingham and J.A. Pople, Trans. Faraday Soc., (1963), 59, 2421.

181. L.C. Snyder, J. Chem. Phys., (1965), 43, 4041.

182. P. Diehl and P.M. Hendrichs in 'Nuclear Magnetic Resonance', ed. R.K. Harris, The Chemical Society, London, 1972, vol. 1, and references therein.

183. P. Diehl and W. Niederberger in 'Nuclear Magnetic Resonance', ed. R.K. Harris, The Chemical Society, London, 1974, vol. 3, and references therein.

184. H. Spiesecke, Z. Naturforsch., (1970), A, 25, 650.

185. N. Zumbulyadis and B.P. Dailey, Mol. Phys., (1973), 26, 777.

186. G. Brauer, 'Handbook of Preparative Inorganic Chemistry', Academic Press, London, 1963 and 1965, Vols. I and II, and references therein.

187. J.G. Morse, K. Cohn, R.W. Rudolph, and R.W. Parry, Inorg. Synth., (1967), 10, 147.

188. L.M. Dennis and P.R. Judy, J. Amer. Chem. Soc., (1929), 51, 2321.

189. S. Cradock, E.A.V. Ebsworth and D.W.H. Rankin, J. Chem. Soc.(A), (1969), 1628.

190. G. Fritz and D. Kummer, Z. Anorg. Chem., (1961), 308, 105.

191. A. Stock and K. Somieski, Ber., (1921), 54, 740.

192. F. Amberger and H.D. Boeters, Chem. Ber., (1964), 97, 1999.

193. W.J. Savage, Ph.D. Thesis, Edinburgh, 1975.

194. R.B. King and F.G.A. Stone, Inorg. Synth., (1963), 7, 198.

195. W. Beck, W. Hieber and G. Braun, Z. Anorg. Chem., (1961), 308, 23.

196. R.L. DeKock and D.R. Lloyd, Adv. Inorg. Chem. Radiochem., (1974), 16, 66, and references therein.

197. H. Bock and B.G. Ramsey, Angew. Chem., Int. Ed., (1973), 12, 734, and references therein.

198. T.C. Farrar and E.D. Becker, 'Pulse and Fourier Transform NMR', Academic Press, New York and London, 1971.

199. W. McFarlane and R.F.M. White, 'Techniques in High Resolution Nuclear Magnetic Resonance Spectroscopy', Butterworths, London, 1972.

200. A. Charles and W. McFarlane, Mol. Phys., (1968), 14, 299.

201. R. Fields in 'Annual Reports in N.M.R. Spectroscopy', ed. E.F. Mooney, 1975, 5A.

202. M. Grayson and E.J. Griffith, ed., Topics Phosphorus Chem., (1967), 5, and references therein.

203. B. Beagley, A.H. Clark and T.G. Hewitt, J. Chem. Soc. (A), (1968), 658.

204. D.W.H. Rankin, Ph.D. Thesis, Cambridge, 1969.

205. D.M. Bridges, G.C. Holywell, D.W.H. Rankin and J.M. Freeman, J. Organometallic Chem., (1971), 32, 87.

206. L. Schäfer, A.C. Yates and R.A. Bonham., J. Chem. Phys., (1971), 55, 3055.

207. M.I. Davis, 'Electron Diffraction in Gases', Marcel Dekker Inc., New York, 1971.

208. J.F. Nixon and J.R. Swain, J. Chem. Soc.(A), (1970), 2075, and references therein.

209. M. Sanchez, J.-F. Brazier, D. Houalla, and R. Wolf, Bull. Soc. Chim., France, (1967), 3930.

210. M. Sanchez, R. Wolf, R. Burgada, and F. Mathis, Bull. Soc. Chim., France, (1968), 773.

211. T. Reetz and J.F. Powers, Chemical Abstracts, (1965), 63, 2981.

212. N.P. Grechkin, R.R. Shagidullan, and L.N. Grishina, Dokl. Akad. Nauk., (1965), 161, 115.

213. R. Burgada, D. Houalla, and R. Wolf, C.R. Acad. Sci., Paris, (1967), C, 264, 356.

214. D. Houalla, J.-F. Brazier, M. Sanchez, and R. Wolf, Tet. Letters, (1972), 2969.

APPENDIX I

Published Research Papers.

Preparation and Molecular Structure of Silylaminodifluorophosphine

By **D. E. J. Arnold, E. A. V. Ebsworth,* H. F. Jessep,** and **D. W. H. Rankin,** Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Reprinted from

JOURNAL
OF
THE CHEMICAL SOCIETY

DALTON TRANSACTIONS

1972

Preparation and Molecular Structure of Silylaminodifluorophosphine

By **D. E. J. Arnold, E. A. V. Ebsworth,* H. F. Jessep,** and **D. W. H. Rankin,** Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Silylaminodifluorophosphine has been prepared in high yield from the reaction between silyl bromide and aminodifluorophosphine; the compound decomposes slowly at room temperature. Its i.r. spectrum indicates that there are two conformers in the vapour at room temperature, but that in the solid at 77 K one conformer is much the more stable; the electron diffraction pattern of the vapour can also be interpreted in terms of the presence of two conformers, in each of which there are short H · · · F non-bonded distances. In each conformer the main structural parameters are taken to be the same, and are found to be: $r(\text{Si–N}) = 1{\cdot}720 \pm 0{\cdot}008$; $r(\text{N–P}) = 1{\cdot}657 \pm 0{\cdot}007$; $r(\text{P–F}) = 1{\cdot}574 \pm 0{\cdot}003$ Å; ∠SiNP = 127·9 ± 0·7°; ∠FPF = 100·8 ± 1·2°; ∠FPN = 95·6°. The n.m.r. spectra (^{1}H,^{19}F) of $SiH_3{}^{14}NHPF_2$ and $SiH_3{}^{15}NHPF_2$ at room temperature show that the SiH protons behave as equivalent, as do the F nuclei, and that any NH exchange is slow on the n.m.r. timescale.

REACTIONS (1) of excess of silyl (SiH_3) chloride, bromide, or iodide with ammonia, primary amines, or secondary amines or related compounds are rapid at room temperature and almost always lead [1] to complete replacement of hydrogen bound to nitrogen by SiH_3. We have

$$3RNH_2 + 2SiH_3X \longrightarrow 2RNH_3X + RN(SiH_3)_2 \quad (1)$$

been interested in the geometries and electronic structures of silicon–nitrogen compounds and have investigated the reaction between silyl halides and PF_2NH_2.

EXPERIMENTAL

Silyl bromide,[2] [$^2H_3$]silyl bromide,[3] silyl chloride,[4] and PF_2NH_2 [5] were prepared by established methods; $^{15}NH_3$ (95% enriched) was purchased as ammonium chloride and ND_3 was made from ammonium chloride that had been dissolved twice in a large excess of D_2O (99% enriched) and then treated with CaO and D_2O. I.r. spectra were obtained by means of a Perkin-Elmer 225 spectrometer (4000—200 cm^{-1}), mass spectra with a double-focusing AEI MS902 instrument, and n.m.r. spectra with a Varian Associates HA100 spectrometer operating at 100 MHz (for ^{1}H) or 94·1 MHz (for ^{19}F).

TABLE 1

Weighting functions, correlation parameters, and scale factors

Camera height/mm	Δs	$s_{\text{min.}}$	s_1	s_2	s_{max}	p/h	Scale factor
250	0·4	6·40	8·60	25·00	30·00	0·4368	1·062 ± 0·019
500	0·2	3·20	5·00	12·00	14·40	0·4123	0·997 ± 0·012
1000	0·1	1·20	2·25	6·25	7·50	0·4934	0·770 ± 0·031

Sectored electron diffraction data were recorded on Ilford N60 photographic plates by use of a Balzers KDG2 gas diffraction apparatus.[6] Plates obtained with nozzle-to-plate distances of 250, 500, and 1000 mm were used, giving a range of 1·2—30·0 Å^{-1} in the scattering variable *s*. During the experiments the sample of compound was maintained at 273 K and the nozzle at 333 K. The electron wavelength (0·05659 ± 0·00003 Å) was determined both by direct measurement of the accelerating voltage and from the diffraction pattern of powdered thallous chloride. A Joyce–Loebl automatic microdensitometer was used to convert the data into digital form and data reduction and least-squares refinements were carried out on the IBM 360/50 computer at the Edinburgh Regional Computing Centre, with established procedures and programmes.[7,8] The complex scattering factors of Cox and Bonham [9] were used throughout. Values of weighting functions (defined as in ref. 7) used in setting up the off-diagonal weight matrix, together with scale factors and correlation parameters,[10] are listed in Table 1. The observed and final weighted difference molecular scattering intensities are shown in Figure 1; the uphill curves are available from the authors and the final least-squares correlation matrix is given in Table 2.

TABLE 2

Least-squares correlation matrix multiplied by 1000

*r*1	*r*2	*r*4	∠1	∠3	∠5	*u*6	*u*11	*u*19	*k*1	*k*2	*k*3	
1000	−690	508	−15	107	−97	−202	−27	0	−204	3	40	*r*1
	1000	−543	−94	−144	131	329	34	−37	223	34	−18	*r*2
		1000	292	111	−169	57	65	119	333	458	102	*r*4
			1000	663	−757	−48	102	308	243	249	−7	∠1
				1000	−989	7	61	333	−10	130	42	∠3
					1000	−12	−75	−349	−49	−176	−41	∠5
						1000	44	−100	375	309	49	*u*6
							1000	90	158	116	7	*u*11
								1000	182	161	6	*u*19
									1000	376	38	*k*1
										1000	49	*k*2
											1000	*k*3

Reaction of PF_2NH_2 *with* SiH_3Br.—When SiH_3Br (1·33

---

[1] U. Wannagat, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 225.

[2] G. Fritz and D. Kummer, *Z. anorg. Chem.*, 1961, **308**, 105.

[3] A. Stock and C. Somieski, *Ber.*, 1917, **50**, 1739.

[4] A. G. MacDiarmid, Ph.D. Thesis, Cambridge, 1955.

[5] D. W. H. Rankin, *J. Chem. Soc.* (*A*), 1971, 783.

[6] B. Beagley, A. H. Clark, and T. G. Hewitt, *J. Chem. Soc.* (*A*), 1968, 658.

[7] D. M. Bridges, G. C. Holywell, D. W. H. Rankin, and J. M. Freeman, *J. Organometallic Chem.*, 1971, **32**, 87.

[8] G. C. Holywell, D. W. H. Rankin, B. Beagley, and J. M. Freeman, *J. Chem. Soc.* (*A*), 1971, 785.

[9] H. L. Cox and R. A. Bonham, *J. Chem. Phys.*, 1967, **47**, 2599.

[10] Y. Murata and Y. Morino, *Acta Cryst.*, 1966, **20**, 605.

mmol) was allowed to react with PF_2NH_2 (2·00 mmol) at room temperature in the vapour phase, a faint white cloud of solid (presumably NH_4Br) was produced, but this cannot have represented more than 1% reaction; there was no sign of further reaction during 1 h. When the reactants were condensed together at 250 K (40 min), however, much solid was formed. Fractional distillation of the volatile products gave a fraction volatile at 177 K that was shown spectroscopically to consist of SiH_4, PF_3, PF_2Br, and SiH_3Br; the fraction volatile at 210 K consisted of ***silylaminodifluorophosphine*** (1·2 mmol) [Found: *M* (vap. density), 115; Si*H*, 2·47; N, 12·2%. H_4F_2NPSi requires *M*, 115; Si*H*, 2·60; N, 12·2%], m.p. 167—169 K. Vapour pressures were measured between 200 and 273 K; within this range they were given by the equation $\log_{10} p/\text{mmHg} = (1792/T) + 8{\cdot}327$; the latent heat of vaporization calculated from this equation is 34·3 kJ mol^{-1}, and the extrapolated b.p. is 329 K. After *ca.* 20 min at temperatures above 250 K in the liquid phase some traces of white solid were formed, and the vapour pressure at 218 K was found to have risen from *ca.* 1 mmHg to *ca.* 3 mm. In clean i.r. cells the compound was stable as vapour at 330 K for at least 1 h, but in contaminated cells the spectra showed the formation of SiH_3F after a few minutes.

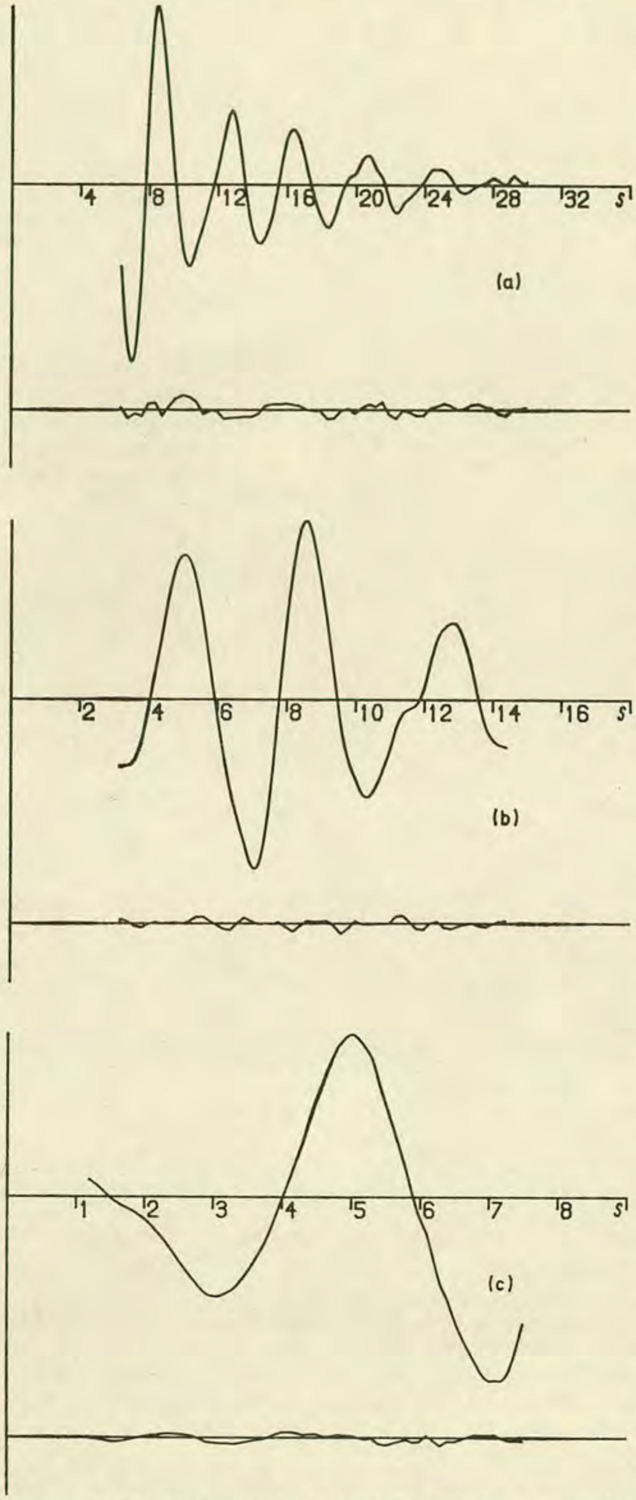


FIGURE 1 Observed and final weighted difference molecular scattering intensities for silylaminodifluorophosphine; nozzle-to-plate distances (a) 250, (b) 500 and (c) 1000 mm

Reaction of PF_2NH_2 *with* SiH_3Cl.—When equimolar proportions of SiH_3Cl and PF_2NH_2 were allowed to mix in the vapour phase at room temperature, traces of white solid were formed; there was no further sign of reaction. The reactants were condensed together and held first at 250 K and then at 230 K (40 min); a little more solid was formed, but the i.r. spectrum of the products showed that little reaction had occurred.

RESULTS

Mass Spectrum.—In the mass spectrum, groups of peaks were observed at *m/e* values associated with the molecular ion (115) and with species that had lost up to 4 H atoms; strong groups of peaks associated with the fragments $PFNH{\cdot}SiH_3$ (96), PF_2NH (84), $PNHSiH_3$ (77), and smaller fragments were observed, as well as peaks due to impurities including $(PF_2)_3N$ (221), $PF_2N(SiH_3)_2$ (145), and $PF(NHSiH_3)_2$ (142).

I.r. Spectra.—I.r. spectra of $SiH_3{\cdot}NH{\cdot}PF_2$, $SiD_3{\cdot}NH{\cdot}PF_2$, $SiH_3{\cdot}ND{\cdot}PF_2$, and $SiD_3{\cdot}ND{\cdot}PF_2$ as vapours, and of $SiH_3{\cdot}NH{\cdot}PF_2$ and $SiH_3{\cdot}ND{\cdot}PF_2$ as solids, were recorded; the isotopically labelled compounds were prepared by use of labelled starting materials (isotopic purity estimated from i.r. spectra: SiD_3Br, 98 atom-%; ND_3, 95 atom-%), though exchange while handling reduced the ND-enrichment of the products to an estimated 80%. The presence of the enriched species was confirmed in each case by mass spectroscopy. The observed frequencies are set out in Table 3.

Since the molecule is shown by electron diffraction to have no symmetry element other than *I* (point-group C_1), the 21 vibrational modes can only be classified in a very general way in terms of group frequencies as νNH, νSiH (3 modes), δNH (2 modes), δSiH_3 (3 modes), skeletal stretches (2 modes), νPF (2 modes), SiH_3 rocking (2 modes), δPF_2 (3 modes), skeletal bending, and torsional modes (2). Some of these are easily identified in the observed spectra, but others are obviously strongly coupled, and even the isotopic labelling does not simplify the assignments much. For a molecule with only one NH bond, only one NH stretching fundamental would be expected in the vapour phase. The appearance of two bands of roughly equal intensity near 3400 cm^{-1} in the spectrum of the vapour of $SiH_3{\cdot}NH{\cdot}PF_2$ is therefore surprising. The first explanation to come to mind is that one of the bands should be assigned to an overtone or combination tone intensified by Fermi

TABLE 3

I.r. frequencies of $SiH_3{\cdot}NH{\cdot}PF_2$ and related species

$SiH_3{\cdot}NH{\cdot}PF_2$		$SiH_3{\cdot}ND{\cdot}PF_2$		$SiD_3{\cdot}NH{\cdot}PF_2$	$SiD_3{\cdot}ND{\cdot}PF_2$	Assignment
Vapour	Solid	Vapour	Solid	Vapour	Vapour	
3427m	3380w	(3424w)	n.o.	3426m	(3425m)	νNH
3363m		(3370w)	n.o.	3364m	(3370w)	
3150vw						
3120vw						
		2540m	2480m		2540m	νND
		2500m	2468m		2500m	
2460vw						
2400vw						
2240vs,sh						νSiH
2194vs						
2189vs	2175vs	2195vs	2170vs	2190w	2190w	
2184vs						
2145vs,sh						
1850vw						
1634vw						
				~1645vs,sh	~1630vs,sh	νSiD
				1601vs	1600vs	
				1577vs	1575vs	
				1558vs	1570vs	
					~1558vs,sh	
1490vw,vbr						
1450vw						
1388vw						
1365vw						
1253s				1248s		δNH
1247s	1247s	(1244mw)	n.o.	1241s	(1240mw)	
1241s				1235s		
1210s	1212s	(1208mw)	n.o.	1203s	(1200mw)	
		1070vvs	1070vvs		1064vvs	
970s,sh	990m	968vs	968vs	970s,sh	970m,sh	δSiH$_3$, ν skeleton, ?δNH
936vs	952vs		955vs	942vs	942m	
926vs		925s	940vs	936vs	933m	
921vs	918vs		920vs		924m	
		858s,sh	860s		858s,sh	
829vs		830s,sh		830vs,sh	834s,sh	
806vs	810vs	804vs	800vs	820vs	806vs	νPF
	800vs	800vs	790vs	802vs	801vs	
794vs	791vs	792vs	768vs	794vs	793vs	
	779vs	780s,sh				
729m	730m	730m	732vs	728vs	745vs	ρSiH$_3$, δSiD$_3$
			720vs	700vvs	725vs	
				690vs	685vs	
650w						
			610m			
	561m			560sh		
550w		550vw	540m	550m	550m	
			506w	507sh	510sh	
496m						
488m	475m	484m		450vw	480vw	
478m						
			451s			
466sh	455m					
					441w	
					433w	
	428m	424m,br	429m		412m,br	
390w						
362m	355m	360m,br	352w	365m,br	360m,br	δPF$_2$
320m		320m		317m	316m	
315m	311m	314m	312s	311m	311m	δPF$_2$
310m		308m		302m	304m	
287m,sh	290w	263m	260m	~280sh	255m,br	?δSiNP

s = Strong, m = medium, w = weak, v = very, br = broad. n.o. = Not observed

resonance with the single fundamental. There are, however, two bands at almost exactly the same frequencies in the spectrum of $SiD_3{\cdot}NH{\cdot}PF_2$ vapour; moreover, there are two bands of almost equal intensity near 2500 cm^{-1} in the spectra of both $SiH_3{\cdot}ND{\cdot}PF_2$ and $SiD_3{\cdot}ND{\cdot}PF_2$, shifted by almost 1/1·41 from the frequencies in the NH-compounds. It is extremely unlikely that suitable combinations in all four molecules should give rise to such similar Fermi resonance, and so that explanation for the origin of the additional band must be rejected. Further, there are two bands in the spectra of $SiH_3{\cdot}NH{\cdot}PF_2$ and of $SiD_3{\cdot}NH{\cdot}PF_2$ near 1250 and 1200 cm^{-1}; in each case both bands are of moderate intensity, and are so much weakened on *N*-deuteriation that they must both be primarily associated with NH-modes. We assign them both to in-plane NH deformation modes.

The only explanation we can offer for this doubling of NH stretching and bending modes is that in the vapour phase there are molecules in two different conformations at room temperature. Such a suggestion would affect the interpretation of the electron diffraction patterns and the n.m.r. spectra (see below). The i.r. spectrum of a freshly-sprayed film of solid $SiH_3{\cdot}NH{\cdot}PF_2$ at temperatures near 77 K showed two bands near 3400 cm^{-1} and two in the region 1200—1250 cm^{-1} (as in the spectrum of the vapour), but in each region the band at the higher frequency was much the weaker, and disappeared completely after a few minutes' standing at the low temperature. We conclude that interchange between the two conformers is possible even in solid films at 77 K, and that under these conditions the conformer giving the lower-frequency NH bands is the more stable.

It is not possible to make detailed assignments for the remaining modes. There are strong bands in regions associated with SiH or SiD stretching; symmetrical but weak satellites associated with ν(SiH) may be due to sums and differences involving the SiH_3-torsion, which would then be expected at *ca.* 50 cm^{-1}. The moderately strong bands in the spectra of both NH compounds near 1240 and 1200 cm^{-1} both shift on deuteriation, but their analogues in the spectra of the ND-species cannot be identified: a new and very strong band appears near 1070 cm^{-1} in the spectra of $SiD_3{\cdot}ND{\cdot}PF_2$ and of $SiH_3{\cdot}ND{\cdot}PF_2$, but the shift (1240—1070 cm^{-1}) is far too small to arise simply from the mass effect of substituting D for H. The band at 1070 cm^{-1} is much more likely to represent a skeletal stretching mode that in the NH compounds is near 950 cm^{-1} but which is raised in frequency by coupling with δ(ND) in the *N*-deuteriated species. There is a similar pattern of frequencies in the spectra of $(Me_3Si)_2NH$ and $(Me_3Si)_2ND$, save that in the NH-species the band assigned to δ(NH) is not double.[11] We have assigned the bands near 1240 and 1200 cm^{-1} in the spectra of $SiH_3{\cdot}NH{\cdot}PF_2$ and of $SiD_3{\cdot}NH{\cdot}PF_2$ to the in-plane NH deformation modes of two conformers rather than to the in-plane and out-of-plane NH deformation modes of a single species because the spectra of $(SiH_3)_2NH$ and of $(Me_3Si)_2NH$ each show only one band in this region.[11,12]

The spectra between 1000 and 400 cm^{-1} are very complicated. There are strong bands in the spectra of the SiH_3-derivatives near 930 cm^{-1} that can be assigned to $\delta(SiH_3)$, and these shift on Si-deuteriation to *ca.* 700 cm^{-1}; bands near 730 cm^{-1} (SiH species) are assigned to SiH_3 rocking modes. The very strong bands near 800 cm^{-1} that are not affected by deuteriation are assigned to PF stretching modes.[13] It is clear that at least one and possibly two bands near 950 cm^{-1} are not substantially shifted by deuteriation; one skeletal stretching mode and perhaps the out-of-plane NH deformation [11] would be expected in this region. However, the marked redistribution of intensity that occurs on *N*-deuteriation shows that there is extensive coupling and assignments to localized modes would be meaningless. Even the PF_2 deformation mode that is expected [13] between 400 and 500 cm^{-1} is involved in this coupling. Only the bands at 300 and 310 cm^{-1} (PF deformation modes) [13] and 265—290 cm^{-1} (tentatively assigned to the PNSi deformation mode) are relatively unaffected by deuteriation at either N or Si.

N.m.r. Spectra.—At 300 K the observed ^1H n.m.r. spectrum of this compound can be analysed in terms of the structure given, on the assumption of equivalence of the two F atoms and of the SiH protons; the same is true of the ^1H and ^{19}F n.m.r. spectra of $SiH_3{\cdot}{}^{15}NH{\cdot}PF_2$, which also show that NH exchange, if it occurs, must be slow on the n.m.r. time-scale. At room temperature the spectra all appear to be of the first order. There is no feature suggesting either non-equivalence of the F atoms or the presence of more than one conformer, so that if two conformers are present they must interchange rapidly on the n.m.r. time-scale with one another. At 200 K further splitting is observed in the ^1H spectrum; the number of additional lines is too great to be accounted for merely by postulating non-equivalence of the two fluorine atoms in a single conformer.

The magnitudes of most of the coupling constants (Table 4) were obtained directly from the observed spectra.

TABLE 4

N.m.r. parameters [a] for $SiH_3{\cdot}NH{\cdot}PF_2$

τ (Si*H*)	5·56(2) p.p.m.	$^2J(F^{15}N)$	4·2(2) Hz
τ (N*H*)	7·11(2) p.p.m.	$^2J(^{15}NH)$	4·1(1) Hz
ϕ_F	55·2(3) p.p.m.	^3J(PH)	8·0(2) Hz
^1J(PF)	1215(5) Hz	^3J(FH)	14·0(2) Hz
$^1J(^{29}SiH)$	224(1) Hz	^3J(NH)	3·1(1) Hz
$^1J(^{15}NH)$	73·1(3) Hz	^4J(FH)	2·1(1) Hz
^2J(PH)	18·8(2) Hz		

[a] Measured for 10% solution in CCl_3F–C_6H_{12}.

The relative signs of these and the magnitudes and relative signs of other coupling constants, determined by studying the effects of weak spin decoupling on the n.m.r. spectra, are reported elsewhere.[14]

Molecular Structure.—(a) *Molecular model.* Silylaminodifluorophosphine has little symmetry and is therefore a fairly difficult subject for an electron diffraction study. It was necessary to make a number of assumptions in order to reduce the large number of geometrical parameters necessary to define the structure. These assumptions were (i) that the $NSiH_3$ group possesses local C_{3v} symmetry, (ii) that the NPF_2 group has local C_s symmetry, and (iii) that the hydrogen atom bound to nitrogen lies in the PNSi plane. The wide angle PNSi found subsequently probably justifies the third of these assumptions. Distortions from the idealised symmetry defined by (i) and (ii) probably show as unexpectedly large experimental amplitudes of vibration involving the fluorine or hydrogen atoms. With the assumptions, the structure is defined by 12 parameters, chosen to be the five bonded distances, the angles PNSi, FPF, FPN, NSiH, and PNH, and the angles of rotation of the PF_2 and SiH_3 groups about the P–N and Si–N bonds. Zero PF_2 twist is taken to be when the FPF bisector is eclipsed with respect to the N–H bond. The SiH_3 twist is taken as zero when one SiH bond is *trans* with respect to the P–N bond. If a positive twist rotates the PF_2 group clockwise when viewed along the P–N bond towards the nitrogen atom, then a positive SiH_3 twist involves rotation of the group in a clockwise direction when viewed along the Si–N bond towards the nitrogen atom.

(b) *Refinement.* Early refinements showed that it was easily possible to refine the bonded distances and valence angles that did not involve hydrogen atoms, with the exception that the angles FPF, FPN, and PNSi and the PF_2 twist were all strongly correlated. However, two independent structures were obtained, giving overall *R* factors $[R_G = (\mathbf{U'WU}/\mathbf{I'WI})^{1/2}$ where $\mathbf{I}$ and $\mathbf{U}$ are the vectors of observed intensities and residuals and $\mathbf{W}$ is the weight matrix] of 0·130 and 0·129. The first of these had a

---

[11] H. Burger, Habilitationsschrift, Braunschweig, 1966.

[12] B. J. Aylett and M. J. Hakim, *J. Chem. Soc. (A)*, 1969, 639.

[13] D. E. C. Corbridge, 'Topics in Phosphorous Chemistry,' Interscience, New York, 1971, vol. 6, p. 235.

[14] J. E. Bentham, E. A. V. Ebsworth, and D. W. H. Rankin, to be published.

PNSi angle of 121° and a twist angle of 83°, whereas these angles in the second structure were 127 and 90° respectively. The other geometrical parameters were similar in the two cases, but the first one involved an amplitude of vibration for the non-bonded P · · · Si distance that was approximately three times greater than those found for the F · · · Si distances (0·28 Å compared with 0·10 Å). As this situation is virtually physically impossible, further work was limited to refining the second structure, the *R* factor for which eventually reached 0·098.

Refinement of further geometrical parameters was difficult, owing to the strong correlations between the parameters and the weak contributions to the total scattering by atom pairs involving hydrogen. The problem was partly overcome by making a series of refinements in which one parameter was varied stepwise, and comparing *R* factors for the various refinements. The parameters obtained by this method have not all been refined simultaneously and so may be slightly in error. However, after the parameters concerned [*r*(NH), *r*(SiH), ∠FPN, ∠NSiH, ∠PNH, and SiH_3 twist angle] had been estimated once, the whole procedure was repeated with the new values inserted for non-refining parameters. None of the new *R* factor minima was at a parameter value that differed significantly from the original one. The parameter set is therefore self-consistent.

After completion of the work on the assumption that only one conformer was present (the results are in Table 5), the possible presence of a proportion of a second conformer was investigated. It was necessary to assume that the two forms are identical in all except the PF_2 twist angle. A small peak at *ca.* 3·6 Å in the radial distribution curve (Figure 2), and the absence of further unassigned peaks, suggested that a proportion of the molecules might have a twist angle of *ca.* 30°, with the longer F · · · Si distance being about the same as when the twist angle is 90°. This angle refined to *ca.* 26° when the proportion of the original conformer was fixed at 0·65. This proportion was evaluated more precisely by making several refinements while fixing it at various values. Figure 3 shows the variation of *R* factor with percentage of the predominant conformer, with 95 and 99·5% confidence limits [15] marked. Thus it seems that at 303 K the gas contains about 84% of a conformer with a PF_2 twist angle of 90° and 16% of a conformer with a twist angle of 26°. The parameters for the two forms are listed in Table 5 and the two conformations are shown in Figure 4.

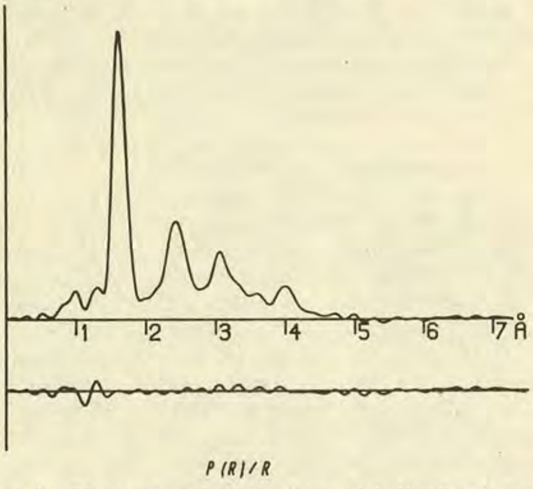


FIGURE 2 Observed and difference radial distribution curves, $P(r)/r$, for silylaminodifluorophosphine. Before Fourier inversion the data were multiplied by $s \exp(-0{\cdot}0015\, s^2)/(z_P - f_P)(z_F - f_F)$

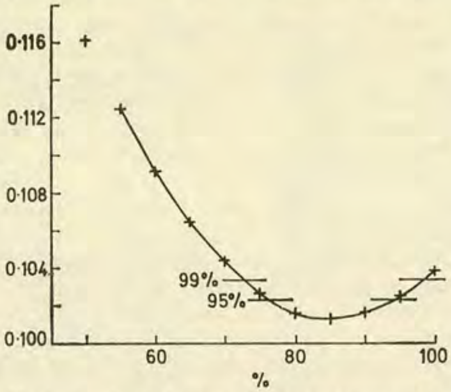


FIGURE 3 Variation in *R* factor with percentage of conformer with PF_2 twist angle of 90°, showing 95 and 99·5% confidence limits

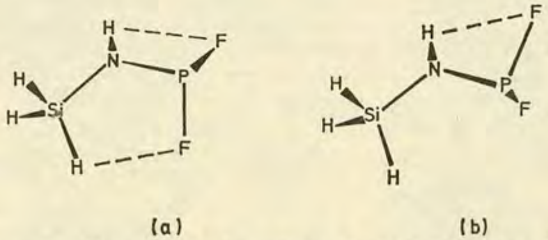


FIGURE 4 The two configurations of silylaminodifluorophosphine. Conformer (A) has a PF_2 twist angle of 90° and conformer (B) has a twist of 26°

DISCUSSION

The formation of a secondary amine as the sole volatile product of the reaction of PF_2NH_2 with silyl bromide is in contrast to reactions of silyl bromide with other primary amines. We have found no evidence for the formation of the tertiary amine $(SiH_3)_2NPF_2$, nor was SiH_4 found as a by-product; both of these observations probably reflect the weakly basic character of PF_2NH_2. It is usually supposed that reactions of silyl halides with amines involve nucleophilic attack by N at Si; if so, $SiH_3{\cdot}NH{\cdot}PF_2$ may well be too weakly basic to react further with excess of silyl bromide. The poor yields from the reactions between SiH_3Cl and PF_2NH_2 can be understood in terms of bond energies; the reaction (2) produces one mole-proportion of difluorohalogenophosphine.

$$2SiH_3X + 3PF_2NH_2 \longrightarrow PF_2X + NH_4X + 2SiH_3{\cdot}NH{\cdot}PF_2 \quad (2)$$

The bond-energy difference ΔE(PCl–SiCl) is much smaller [16] than is ΔE(PBr–SiBr),

---

[15] W. C. Hamilton, ‘Statistics in Physical Science,’ Ronald Press, New York, 1964.

[16] E. A. V. Ebsworth, ‘Organometallic Compounds of the Group IV Elements,’ ed. A. G. MacDiarmid, Marcel Dekker Inc., New York, 1968, vol. 1, p. 46; T. L. Cottrell, ‘Strengths of Chemical Bonds,’ Butterworths, London, 2nd edn., 1958, pp. 157—158.

so that reaction (2) would be expected to be less exothermic when X = Cl than when X = Br. The difference in lattice energy $\Delta U(NH_4Cl-NH_4Br)$ is quite small.[17] Although the compound is more stable[12] than is $(SiH_3)_2NH$, it is not stable enough at room temperature to allow an extensive study of its chemistry. The only decomposition product we have identified is silyl fluoride; the other appears to be a P–N polymer.

TABLE 5

Molecular parameters

	Assuming 1 conformer present		Assuming 2 conformers present, ratio 84 : 16			
			Conformer A		Conformer B	Both conformers
	Distance/Å	Amplitude/Å	Distance/Å		Distance/Å	Amplitude/Å
(*a*) Independent distances						
*r*1 (P–F)	1·575 (3)	0·045 (fixed)		1·574 (3)		0·045 (fixed)
*r*2 (P–N)	1·654 (6)	0·048 (fixed)		1·657 (7)		0·048 (fixed)
*r*3 (N–H)	0·998 [a]	0·055 (fixed)		0·998 [a]		0·055 (fixed)
*r*4 (Si–N)	1·724 (7)	0·048 (fixed)		1·720 (8)		0·048 (fixed)
*r*5 (Si–H)	1·470 [a]	0·075 (fixed)		1·470 [a]		0·075 (fixed)
(*b*) Dependent distances						
*d*6 (F · · · F)	2·442 (22)	0·090 (6)		2·436 (21)		0·092 (7)
*d*7 (F · · · N)	2·386 (10)	0·112 (tied to u6)		2·395 (10)		0·115 (tied to *u*6)
*d*8 (F · · ·(N)H)	3·25 (2)	0·150 (fixed)	3·26 (2)		3·33 (3)	0·150 (fixed)
*d*9 (F · · ·(N)H)	2·50 (4)	0·150 (fixed)	2·52 (6)		2·40 (5)	0·150 (fixed)
*d*10 (F · · · Si)	3·025 (30)	0·287 [a]	3·039 (50)		3·669 (40)	0·260 [a]
*d*11 (F · · · Si)	3·972 (13)	0·098 (13)	3·976 (13)		4·049 (18)	0·095 (10)
*d*12 (F · · · (Si)H)	4·29 (3)	0·200 (fixed)	4·31 (4)		4·59 (5)	0·200 (fixed)
*d*13 (F · · · (Si)H)	4·79 (4)	0·200 (fixed)	4·79 (6)		4·93 (6)	0·200 (fixed)
*d*14 (F · · · (Si)H)	2·66 (2)	0·200 (fixed)	2·67 (3)		3·64 (2)	0·200 (fixed)
*d*15 (F · · · (Si)H)	4·29 (4)	0·200 (fixed)	4·28 (7)		4·77 (7)	0·200 (fixed)
*d*16 (F · · · (Si)H)	3·73 (3)	0·200 (fixed)	3·74 (3)		4·65 (5)	0·200 (fixed)
*d*17 (F · · · (Si)H)	4·86 (2)	0·200 (fixed)	4·87 (2)		4·50 (4)	0·200 (fixed)
*d*18 (P · · · (N)H)	2·31 (2)	0·100 (fixed)		2·31 (2)		0·100 (fixed)
*d*19 (Si · · · P)	3·033 (12)	0·122 (7)		3·034 (12)		0·122 (7)
*d*20 (P · · · (Si)H)	4·19 (2)	0·180 (fixed)		4·19 (2)		0·180 (fixed)
*d*21 (P · · · (Si)H)	3·40 (3)	0·180 (fixed)		3·41 (3)		0·180 (fixed)
*d*22 (P · · · (Si)H)	3·59 (3)	0·180 (fixed)		3·59 (3)		0·180 (fixed)
*d*23 (N · · · (Si)H)	2·61 (2)	0·105 (fixed)		2·61 (2)		0·105 (fixed)
*d*24 (Si · · · (N)H)	2·31 (2)	0·100 (fixed)		2·31 (2)		0·100 (fixed)
*d*25 (H(Si)H)	2·40 (2)	0·100 (fixed)		2·40 (2)		0·100 (fixed)
*d*26 (H(Si) · · · (N)H)	2·66 (2)	0·160 (fixed)		2·65 (2)		0·160 (fixed)
*d*27 (H(Si) · · · (N)H)	3·36 (2)	0·160 (fixed)		3·35 (2)		0·160 (fixed)
*d*28 (H(Si) · · · (N)H)	3·22 (2)	0·160 (fixed)		3·21 (2)		0·160 (fixed)
(*c*) Angles/°						
∠1 F–P–F	101·6 (12)			100·8 (12)		
∠2 F–P–N	95·2 [a]			95·6 [a]		
∠3 P–N–Si	127·4 (8)			127·9 (7)		
∠4 N–Si–H	109·3 [a]			109·3 [a]		
∠5 PF_2 twist	89·9 (15)		90(3)		26 (3)	
∠6 P–N–H	118·8 [a]			118·8 [a]		
∠7 SiH_3 twist	12·0 [a]			12·0 [a]		

[a] These parameters were not included in the final least-squares refinements. The values quoted were obtained as described in the text. Many of the independent parameters involving H atoms were not included in the least-squares refinements. The quoted errors for non-bonded distances involving H have been increased to allow for this, but some uncertainty as to the errors in these measurements must remain.

There is little question about the gross features of the molecular structure. The PNSi skeleton has the bond lengths and angles that would have been expected in the light of previous work. The Si–N bond length is close to those in disilylamine, *N*-methyldisilylamine, and tetrasilylhydrazine, molecules in which there are two SiH_3 groups bound to each nitrogen atom,[18] but is longer than in *N*-dimethylsilylamine;[19] the P–N bond length is close to those[20] in PF_2NH_2 and PF_2NMe_2, and the PNSi angle is much the same as the SiNSi angles in the disilylamino-compounds. These results emphasize the similarity in structure between analogous SiH_3- and PF_2-compounds. It should be noted that the PF, PN, and SiN bond lengths are so similar that it was impossible to refine their amplitudes of vibration. However, the amplitudes found for these bonds in other molecules vary over very narrow ranges, so that the refined distances should not have been affected significantly by fixing the amplitudes.

The conformations adopted by the molecule are of particular interest. The i.r. spectra leave little doubt that in the vapour at room temperature there are two

---

[17] T. C. Waddington, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 158.

[18] D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, W. S. Sheldrick, B. J. Aylett, I. A. Ellis, and J. J. Monaghan, *J. Chem. Soc.* (*A*), 1969, 1224.

[19] C. Glidewell, D. W. H. Rankin, A. G. Robiette, and G. M. Sheldrick, *J. Mol. Struct.*, 1969, **4**, 215.

[20] J. S. Harman and D. W. A. Sharp, *Inorg. Chem.*, 1971, **10**, 1538.

conformers in comparable concentrations and that the lower value for ν(NH) is associated with the lower δ(NH); the n.m.r. spectra confirm that interconversion of these conformers is rapid in the liquid phase at room temperature but may well be slow at 200 K. The electron diffraction data indicate that in the predominant conformer the PF_2 and SiH_3 groups are rotated so that one fluorine atom is 2·52 Å from the amino-hydrogen atom and the other fluorine atom is 2·67 Å from one of the silyl hydrogen atoms. The sum of the van der Waals radii for F and H is 2·55 Å, so that some form of intramolecular hydrogen bonding may well be responsible for the stability of this conformation, as well as for those of aminodifluorophosphine and dimethylaminodifluorophosphine.[8] Similar hydrogen bonding has been postulated [20] to account for the non-equivalence of the axial fluorine atoms of methylaminotetrafluorophosphorane at 193 K. The widely different amplitudes of vibration for the two F · · · Si distances reflect the relative changes in the distances on twisting the PF_2 group by a small angle about the P–N bond. One amplitude is very large, suggesting that even within one conformation there is considerable rotational motion about the P–N bond. The large uncertainty of only one of the F · · · Si distances when the estimated standard deviation in the twist angle is also large is consistent with this explanation of the vibrational amplitudes.

Unfortunately it was not possible to determine structural parameters other than the PF_2 twist angle for the other isomer, so we had to assume that the two conformers were otherwise identical. If this is so, the second conformer has F · · · (N)H distances of 2·39 and 3·33 Å; the shortest F · · · (Si)H distance is 3·64 Å with a twist angle of 12° for the SiH_3 group and effectively the same for the twist angle that minimises this distance. This conformer appears to have one strong and one much weaker hydrogen bond, both involving the amino-hydrogen atom. Such hydrogen bonding almost certainly means that the molecules do not have the localised symmetries (C_s and C_{3v}) for the NPF_2 and SiH_3N groups that have been assumed, although such deviations, if fairly small, cannot be detected on the basis of data from electron diffraction. Hydrogen bonding may also account for the unusually small FPN angles. Correlation between these angles and the FPF angle could mean that the one should be smaller and the others larger, but refinements in which the FPN angle was fixed at higher values all led to significantly higher *R*-factors.

If there is significant hydrogen bonding in $PF_2{\cdot}NH{\cdot}SiH_3$ it is of an unusual kind. Few examples of hydrogen bonding involving hydrogen bound to silicon have previously been described. Further, the bands due to vibration of the amino-hydrogen show no broadening. It is interesting that the lower NH stretching frequency appears to be associated with the conformer giving the lower NH deformation frequency; hydrogen bonding is normally supposed to lower NH stretching and to raise NH deformation frequencies, but the kind of hydrogen bonding suggested here is so unusual that its effect on the vibrational spectrum cannot be assumed to be the same as commonly observed. The large vibrational amplitudes are consistent with the easy interconversion between conformers that is implied by the n.m.r. spectra. The energy difference between the conformers, calculated from the estimated relative populations, is *ca.* 4 kJ mol^{-1}.

We thank Professor D. W. J. Cruickshank and Dr. B. Beagley for experimental facilities, Imperial Chemical Industries Limited for a Fellowship (to D. W. H. R.), and the S.R.C. for a maintenance grant (to H. F. J.).

[2/375 *Received*, 21*st February*, 1972]

Exchange Reactions of Bromodifluorophosphine with Silyl and Germyl Derivatives of the Group VI Elements

By **D. E. J. Arnold, J. S. Dryburgh, E. A. V. Ebsworth,** and **D. W. H. Rankin,*** Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Reprinted from

JOURNAL
OF
THE CHEMICAL SOCIETY

DALTON TRANSACTIONS

1972

Exchange Reactions of Bromodifluorophosphine with Silyl and Germyl Derivatives of the Group VI Elements

By **D. E. J. Arnold, J. S. Dryburgh, E. A. V. Ebsworth,** and **D. W. H. Rankin,*** Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

The reactions of PF_2X (X = Cl or Br) with $(MH_3)_2Y$ (M = Si or Ge; Y = O, S, Se, or Te) have been studied by n.m.r. spectroscopy. When X = Br and Y = S, Se, or Te, reaction occurs at room temperature to give the species MH_3YPF_2, $(PF_2)_2Y$, and MH_3Br. ^{19}F and ^{1}H N.m.r. and double-resonance techniques have been used to determine the chemical shifts (^{1}H, ^{19}F, ^{31}P, and ^{77}Se) and coupling constants (including relative signs) of the products. The PF_2Se– and PF_2Te– compounds have exceptionally low ^{31}P chemical shifts. The ^{19}F spectrum of $(PF_2)_2Se$ has been studied over a wide range of temperatures, and $^{2}J(PP)$ and both $^{4}J(FF)$ values are found to be strongly temperature-dependent. The ^{1}H spectrum of SiH_3TePF_2 is also temperature-dependent.

THERE have been a number of studies of exchange reactions involving substituted silyl and germyl compounds.[1-3] In general these have shown that in the equilibrium state the more electronegative groups are preferentially bound to silicon, but that kinetic factors may make some exchanges extremely slow.[3] It is possible that this preference is associated with the tendency of atoms with lone pairs of electrons to indulge in π-bonding to a greater extent with silicon than with germanium. Our structural studies of fluorophosphine derivatives have suggested that bonds from phosphorus to nitrogen or oxygen have properties similar to those of bonds from silicon or germanium to nitrogen or oxygen.[4-6] We have, therefore, made a study of the reactions of a series of silyl and germyl Group VI derivatives with chloro- and bromo-difluorophosphine, to see whether chemical evidence would confirm or contradict our conclusions based on structural evidence.

EXPERIMENTAL

All manipulations of volatile materials were carried out in a conventional Pyrex vacuum system, with Apiezon L and N greases on taps and ground-glass joints. Tellurium compounds were handled in a grease-free section, with polytetrafluoroethylene taps. Bromo- and chloro-difluorophosphine were prepared from hydrogen bromide or chloride and dimethylaminodifluorophosphine.[7] Silyl and germyl compounds of elements of Group VI were obtained by use of reactions (1)—(5). Purities were checked by i.r. spectroscopy.

$$(SiH_3)_2Y + H_2O \longrightarrow (SiH_3)_2O + H_2Y \qquad (Y = S \text{ and } Se) \quad (1)$$

$$(SiH_3)_3N + 2H_2Y \longrightarrow NH_4^+YSiH_3^- + (SiH_3)_2Y \qquad (Y = S, Se, \text{ and } Te) \text{ (ref. 8)} \quad (2)$$

$$2SiH_3Br + K_2Y \longrightarrow (SiH_3)_2Y + 2KBr \qquad (Y = S, Se, \text{ and } Te) \text{ (refs. 9 and 10)} \quad (3)$$

$$2GeH_3Br + Pb(OH)_2 \longrightarrow (GeH_3)_2O + H_2O + PbBr_2 \qquad \text{(ref. 11)} \quad (4)$$

$$2GeH_3Br + (SiH_3)_2Y \longrightarrow (GeH_3)_2Y + 2SiH_3Br \qquad (Y = S, Se, \text{ and } Te) \text{ (refs. 3 and 9)} \quad (5)$$

Reactions were studied in a 1 : 1 mixture of cyclohexane and CCl_3F as solvent. Usually 0·2 mmol of the Group VI compound in *ca.* 0·7 ml of solvent was treated at room temperature with 0·2—0·7 mmol of the fluorophosphine (the amount of the latter used depending on which products were to be studied) for periods of from a few minutes up to several weeks.

N.m.r. spectra were recorded on a Varian Associates HA100 spectrometer operating at 100 MHz (^{1}H) or 94·075 MHz (^{19}F), the probes of which were double-tuned to accept a second radiofrequency provided by a Schlumberger frequency synthesizer.[12] Although the circuits were designed for ^{1}H–{^{19}F} and ^{19}F–{^{1}H} double resonance, satisfactory results have been obtained with irradiating frequencies of *ca.* 40·5 MHz, and 19·1 MHz in ^{1}H–{^{31}P}, ^{19}F–{^{31}P}, and ^{19}F–{^{77}Se} spin-tickling experiments.

Although the spectrometer and irradiation frequencies are derived from independent crystal sources, we find the relative frequencies to be stable to within a few parts in 10^8 during several months. Consequently, by comparing irradiation frequencies for the same nucleus in different compounds, we have been able to determine chemical shifts for ^{31}P and ^{77}Se, without the need for continuous monitoring of the spectrometer operating frequency.

Estimated standard deviations of quoted chemical shifts are 0·01(^{1}H), 0·1(^{19}F), or 0·5(^{31}P,^{77}Se) p.p.m. Errors in coupling constants are of the order of 2% of the value quoted.

RESULTS AND DISCUSSION

During the early stages of this work, a number of observations were made which influenced the choice of starting materials and conditions for subsequent reactions. The most important of these was that chlorodifluorophosphine exchanged with the germyl Group VI derivatives only slowly, with the result that mixed products, most of which are unstable during long periods at room temperature, could only be obtained in low con-

---

[1] K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, 1966, **5**, 547.

[2] J. R. Van Wazer, K. Moedritzer, and L. C. D. Groenweghe, *J. Organometallic Chem.*, 1966, **6**, 242.

[3] S. Cradock and E. A. V. Ebsworth, *J. Chem. Soc.* (*A*), 1967, 1226.

[4] G. C. Holywell, D. W. H. Rankin, B. Beagley, and J. M. Freeman, *J. Chem. Soc.* (*A*), 1971, 785.

[5] D. E. J. Arnold, E. A. V. Ebsworth, H. F. Jessep, and D. W. H. Rankin, *J.C.S. Dalton*, 1972, 1681.

[6] D. E. J. Arnold and D. W. H. Rankin, *J. Fluorine Chem.*, in the press.

[7] J. G. Morse, K. Cohn, R. W. Rudolph, and R. W. Parry, *Inorg. Synth.*, 1967, **10**, 147.

[8] S. Cradock, E. A. V. Ebsworth, and H. F. Jessep, *J.C.S. Dalton*, 1972, 359.

[9] S. Cradock, E. A. V. Ebsworth, D. W. H. Rankin, *J. Chem. Soc.* (*A*), 1969, 1628.

[10] H. Burger and U. Goetze, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 549.

[11] S. Cradock, personal communication.

[12] A. Charles and W. McFarlane, *Mol. Phys.*, 1968, **14**, 299.

centrations. With the silyl compounds, reactions were fast, but expected products, other than silyl chloride, were not observed. Consequently, the results reported here all concern exchange reactions of bromodifluorophosphine.

Secondly, it was observed that with sulphur, selenium, and tellurium derivatives, relative exchange rates were Si > Ge and Te > Se > S. Moreover, the equilibria were such that, if sufficient bromodifluorophosphine was present, all the silyl starting materials were apparently consumed, whereas some germyl compounds remained. At no time could high concentrations of the mixed MH_3YPF_2 species be obtained.

Thirdly, the disilyl ether exchange reaction was found to be slow, even with bromodifluorophosphine, only small amounts of silyl bromide being formed in 24 h, whereas digermyl ether reacted too quickly for the spectra of the starting materials to be observed. Neither oxygen system gave peaks which could be assigned to mixed MH_3OPF_2 species, and although MH_3Br was formed, yields of bis(difluorophosphino) ether were much lower than expected; trifluorophosphine appeared instead.

TABLE 1

Reactions of $(MH_3)_2Y$ and PF_2Br

Reagents	Molar ratio	Reaction	$(MH_3)_2Y$	Observed products			
PF_2Br+	$PF_2Br : (MH_3)_2Y$	time/s	remaining/%	MH_3Br	MH_3YPF_2	$(PF_2)_2Y$	Others
$(SiH_3)_2O$	2·5 : 1	80,000	65	✓		✓	
	3·5 : 1	80,000	55	✓		✓	
$(GeH_3)_2O$	2 : 1	600	0	✓		✓	OPF_2H
	1 : 1	600	0	✓			PF_3
$(SiH_3)_2S$	1·8 : 1	2000	60	✓	✓	✓	
	1·8 : 1	50,000	30	✓	✓	✓	SiH_3F
$(GeH_3)_2S$	2·5 : 1	7000	100				
	2·5 : 1	180,000	80	✓	✓	✓	
$(SiH_3)_2Se$	2·5 : 1	25,000	15	✓	✓	✓	
	3 : 1	4000	30	✓	✓	✓	
	3 : 1	8000	0	✓	✓	✓	
$(GeH_3)_2Se$	2·5 : 1	8000	90	✓			
	2·5 : 1	200,000	60	✓	✓	✓	
$(SiH_3)_2Te$	1 : 1	2000	65	✓	✓	✓	Te
$(GeH_3)_2Te$	2 : 1	5000	70	✓			Te

Finally, the reactions gave unstable products. The sulphur and selenium systems precipitated small amounts of yellow solids on standing, and the tellurium systems precipitated much metallic tellurium very rapidly. These solid products did not appear to interfere with the recording of n.m.r. spectra.

These observations, although only qualitative, do include some important results. Most important, they show that the tendency is, in fluorophosphine–silyl exchanges, for the more electronegative atoms to be bound to silicon, whereas in fluorophosphine–germyl systems the electronegative atoms tend to be bound to phosphorus. This is consistent with the idea that in these and other fluorophosphine derivatives, the PF_2 group is a π-electron acceptor intermediate in strength between the silyl and germyl groups.[4] If this also explains why some reactions go rapidly and to completion while others do not, then one would expect chlorodifluorophosphine to react to a greater extent than bromodifluorophosphine with the silyl derivatives, but to a lesser extent with the germyl ones. This is to a certain extent substantiated experimentally. With the germyl compounds reactions were slow, as shown by the rate of formation of germyl chloride, and the products, most of which are unstable, decomposed as rapidly as they were formed, and so were not observed in the n.m.r. spectra. With the silyl compounds, silyl chloride was formed in a few minutes, and the reactions apparently went to completion. However further reactions occurred giving insoluble products.

Some of the details of the more important experiments with bromodifluorophosphine are in Table 1. In addition to the products listed there, small amounts of $(PF_2)_2O$ and YPF_2H (Y = S or Se) were also formed if traces of water were present.

Reactions involving germyl and silyl ethers gave only bis(difluorophosphino) ether and the appropriate halide, and no mixed species. GeH_3TePF_2 was not observed. As the germyl exchanges were slow, and decomposition of fluorophosphine–tellurium compounds was rapid, the products of this reaction, other than germyl bromide, were not observable in the n.m.r. spectra.

Chemical Shifts.—Chemical shifts for all the Group VI species studied are in Table 2. The interpretation of chemical shifts is difficult and may be misleading. Nevertheless, a number of noteworthy trends are apparent in the shifts listed.

There is a downfield shift in the proton resonances when one $-MH_3$ group in $(MH_3)_2Y$ is replaced by a $-PF_2$ group. This shift, for a given element Y, is roughly the same when M is Ge as when it is Si, but it varies with Y in the order Te > Se > S. The downfield shifts probably reflect the electron-withdrawing character of the $-PF_2$ groups. The variations in the shift could be due to changes in the geometry of the molecules, as the extent of intramolecular hydrogen bonding, in a five-membered ring (I) would be very dependent on the precise bond lengths and valence angles in the compound.

^{19}F Chemical shifts increase in the order O < S < Se < Te, and it is also noticeable that for any one element Y, $\delta(SiH_3YPF_2) \sim \delta(GeH_3YPF_2) < \delta(PF_2YPF_2)$.

The first of the trends is very similar to that found for the difluorohalogenophosphines,[13,14] and may be attributed simply to electronegativity differences. Such differences do not account for the second observed relationship, for which there is no obvious rationalisation.

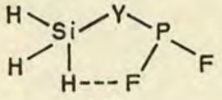
TABLE 2

Chemical shifts

Compound	$\tau(^1H)$	$\delta(^{19}F)$ [a]	$\delta(^{31}P)$ [b]	$\delta(^{77}Se)$ [c]
$(SiH_3)_2O$	+5·44			
$(GeH_3)_2O$	+4·72			
$(PF_2)_2O$		+36·7	−111 [d]	
$(SiH_3)_2S$	+5·71			
SiH_3SPF_2	+5·65	+57·3	−229·5	
$(GeH_3)_2S$	+5·40			
GeH_3SPF_2	+5·32	+57·1	−232·0	
$(PF_2)_2S$		+64·3	−219·4	
$(SiH_3)_2Se$	+5·98			+666·0
SiH_3SePF_2	+5·83	+59·6	−255·4	n.o.
$(GeH_3)_2Se$	+5·82			+611·5
GeH_3SePF_2	+5·70	+59·5	−258·9	n.o.
$(PF_2)_2Se$ [e]		+66·4	−246·9	−700·8
$(SiH_3)_2Te$	+6·41			
SiH_3TePF_2	+6·06	+68·5	−297·0	
$(GeH_3)_2Te$	+6·48			
$(PF_2)_2Te$		+72·6	−295·8	

N.o., Not observed.

[a] P.p.m. to high field of CCl_3F. [b] P.p.m. to high field of 85% H_3PO_4. [c] P.p.m. to high field of Me_2Se. [d] R. W. Rudolf, R. C. Taylor, and R. W. Parry, *J. Amer. Chem. Soc.*, 1966, **88**, 3729. [e] Measured at 193 K. All other spectra recorded at 300 K.



(I)

Phosphorus chemical shifts are useful in that they confirm that the compounds studied are derivatives of trico-ordinate phosphorus.[15] Variations are much as would be expected, with the shifts decreasing as the associated ^{19}F shifts increase.[16] All the shifts are lower than those in the corresponding simple difluorohalogenophosphines, with the consequence that those in the tellurium compounds are lower than any reported previously. Clearly, the phosphorus atoms are in some extreme environment: the multiplicity of explanations of phosphorus chemical shifts [17] makes it impossible for us at this stage to explain fully the nature of the bonding in these compounds.

The selenium shifts are also difficult to interpret, this time because of the lack of comparable data in the literature. However, it seems probable that simple electronegativity effects can account for the observed shifts. We are now studying the effects of substitution on the chemical shifts (^{77}Se and ^{125}Te) of a variety of selenium and tellurium compounds, and hope to be able to rationalise the present results more fully.

Coupling Constants.—The observed coupling constants for the mixed Group VI derivatives MH_3YPF_2 are in Table 3. The magnitudes of the directly bonded phosphorus–fluorine coupling constants increase with increasing electronegativity of the third atom bonded to phosphorus, in the usual manner.[18] The three-bond coupling, J(PYMH), is found to be positive [it being assumed that ^1J(PF) is negative [19,20]] in each compound studied, and to be larger in compounds with lighter elements Y and M. The positive sign is as expected for a three-bond coupling, and the trend in magnitude is also consistent with trends observed in other silyl and germyl derivatives of the Group VI elements.[21] However, on the basis that reduced coupling constants are usually negative over even, but positive over odd, numbers of bonds, the fluorine–hydrogen coupling in each of these molecules should be negative. In each case it is positive. This may be accounted for, at least in part, by the possibility of direct interaction between hydrogen atoms on silicon or germanium, and the fluorine atoms bonded to phosphorus, as described above. Such direct interaction might well provide a positive contribution to the four-bond coupling.

TABLE 3

Coupling constants for MH_3YPF_2

Compound	T/K	^1J(PF)/Hz	^3J(PH)/Hz	^4J(FH)/Hz
SiH_3SPF_2	300	−1298	+13·3	+2·7
GeH_3SPF_2	300	−1285	+11·8	+3·4
SiH_3SePF_2	300	−1286	+11·6	+2·9
GeH_3SePF_2	300	−1287	+11·2	+3·3
SiH_3TePF_2	203		11·4	3·0
	233		10·1	2·9
	273		9·6	2·7
	300	−1253	+9·3	+2·8

TABLE 4

Coupling constants for $(PF_2)_2Y$

Compd.	T/K	^1J(PF)/Hz	^3J(PF)/Hz	$|^2J(PP)|$/Hz	$|^4J(FF)|$/Hz	$|^2J(FY)|$/Hz
$(PF_2)_2O$	300	−1365	+14	5	0	
$(PF_2)_2S$	300	−1303	+28	274	8·5, 2·5	
$(PF_2)_2Se$	293	−1305	+21	232	8·8, 2·8	39
	273	−1300	+25	249	9·3, 1·8	36
	253	−1301	+24	264	10·0, 1·5	36
	233	−1297	+25	281	10·5, 1·5	35
	213	−1293	+26	300	11·4, 0·9	35
	193	−1299	+35	316	12·0, 0·0	36
	173	−1297	+28	336	12·5, 0·0	36
$(PF_2)_2Te$	300	(1244) [a]	n.o.	n.o.	n.o.	n.o.

n.o., not observed.

[a] $|^1J(PF) + {}^3J(PF)|$

Coupling constants for the bis(difluorophosphino)-Group VI derivatives are in Table 4. The ^{19}F spectrum of $(PF_2)_2S$ and its temperature-dependence have been described.[22] We have studied the temperature-variation

---

[13] A. Muller, E. Niecke, and O. Glemser, *Z. anorg. Chem.*, 1967, **350**, 256.

[14] R. W. Rudolph, J. G. Morse, and R. W. Parry, *Inorg. Chem.*, 1966, **5**, 1464.

[15] J. F. Nixon and R. Schmutzler, *Spectrochim. Acta*, 1964, **20**, 1835.

[16] J. F. Nixon, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 363.

[17] M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Topics in Phosphorus Chem.*, 1967, **5**, 19.

[18] G. Mavel, *J. Chim. phys.*, 1968, **65**, 1692.

[19] J. A. Pople and D. P. Santry, *Mol. Phys.*, 1964, **8**, 1.

[20] A. V. Cunliffe, E. G. Finer, R. K. Harris, and W. McFarlane, *Mol. Phys.*, 1967, **12**, 497.

[21] C. Glidewell, D. W. H. Rankin, and G. M. Sheldrick, *Trans. Faraday Soc.*, 1967, **65**, 1409.

[22] R. W. Rudolph and R. A. Newmark, *J. Amer. Chem. Soc.*, 1970, **92**, 1195.

of the ^{19}F spectrum of $(PF_2)_2Se$ in detail, and Table 4 includes the parameters determined at each of seven temperatures. Absolute temperatures quoted may be up to 5 K in error, but relative values should be correct to within 1 K. The spectra (Figure 1) are of the second order, and have been analysed, on the assumption that $|^1J(PF) - ^3J(PF)| \gg |^2J(PP)| \gg |^4J(FF)|, |^4J(FF)'|$, by the method of Harris *et al.*[23] The parameters in the oxygen compound are remarkable in that all couplings across the oxygen atom are small compared with similar couplings in the sulphur, selenium, and tellurium compounds. In particular, $^2J(PP)$ is only 5 Hz compared with over 200 Hz in the other compounds and *ca.* 400 Hz in some $(PF_2)_2NR$ compounds. Also, no four-bond fluorine–fluorine coupling is evident, whereas all other $(PF_2)_2X$ compounds studied show two different couplings, averaging *ca.* 6 Hz.

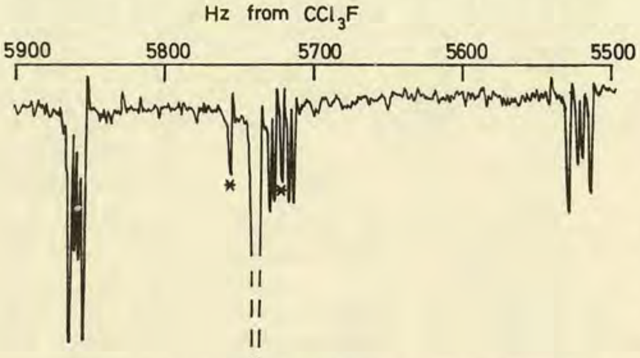


FIGURE 1 Low-field half of the ^{19}F n.m.r. spectrum of $(PF_2)_2Se$ at 173 K; *^{77}Se satellites

These parameters distinguishing $(PF_2)_2O$ most dramatically from the other bis(difluorophosphino)-compounds are also those that change most significantly with temperature in $(PF_2)_2Se$. The parameters for this compound listed in Table 4 have been expressed (by least-squares fitting) as simple polynomial functions of temperature. The results (Table 5) have been used in obtaining Figure 2, which shows how the various line positions in one half of the spectrum change with temperature. These positions have been extrapolated outside the temperature range studied experimentally.

TABLE 5

Temperature-dependence of n.m.r. parameters of $(PF_2)_2Se$

$$\phi(F) = 69{\cdot}05(8) - 0{\cdot}009(1)T \text{ p.p.m.}$$
$$^1J(PF) = -1284{\cdot}7(74) - 0{\cdot}061(31)T \text{ Hz}$$
$$^3J(PF) = 44{\cdot}2(78) - 0{\cdot}077(33)T \text{ Hz}$$
$$|^2J(PP)| = 525{\cdot}2(152) - 1{\cdot}238(133)T + 0{\cdot}00081(29)T^2 \text{ Hz}$$
$$|^4J(FF)| = 4{\cdot}0(7) - 0{\cdot}022(3)T \text{ Hz}$$
$$|^4J(FF)'| = 18{\cdot}1(3) - 0{\cdot}032(1)T \text{ Hz}$$
$$|^2J(SeF)| = 36(1) \text{ Hz}$$

Estimated standard deviations are given in parentheses; T refers to absolute temperature.

Although changes could be caused by movements of the positions of equilibria, it seems probable that the variations in these parameters, and in those for SiH_3-$TePF_2$ (Table 3), are caused by conformational changes within the molecules, with the long-range couplings between various atoms being affected by the interactions between the lone pairs of electrons, which are present on every atom in the molecules. The wide POP angle (over 140° in the gas phase) and staggered conformation of the PF_2 groups in bis(difluorophosphino) ether[6] result in fairly small interactions between the lone pairs on the phosphorus atoms, and between the remote pairs of fluorine atoms. However in the sulphur, selenium, and tellurium compounds and in the amines, the PF_2 groups can be much closer together, with consequent greater direct interaction. In addition to this, conformational changes with temperature will be possible in the Group VI compounds, where such changes might well be hindered by the presence of an alkyl or aryl group in the amines. Such an interpretation must be speculative. Since further structural work will be invaluable in understanding the behaviour of these compounds we are investigating ways of preparing them pure: the present reaction method is unsuitable as it gives several products of similar volatility.

Thus the extents to which these reactions proceed, and the various n.m.r. parameters of the products, give much information about the nature of the bonding in these compounds. One important question remains: why are these compounds apparently stable as phosphorus(III) derivatives, whereas other, similar, compounds revert to the phosphorus(V) forms? Thus species such as F_2PSH[24] and Me_2PSMe[25] are more stable in their phosphorus(V) forms, whereas F_2PSSiH_3 and $(CF_3)_2PSH$[26] exist exclusively with phosphorus(III). One possibility is that the stability of a particular form may be increased by intramolecular hydrogen bonding,

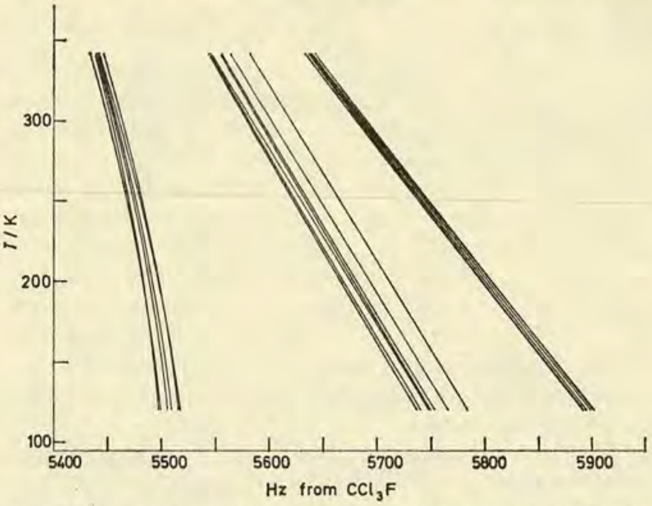


FIGURE 2 Variation of the positions of lines in the low-field half of the ^{19}F n.m.r. spectrum of $(PF_2)_2Se$ with temperature

---

[23] R. K. Harris, J. R. Woplin, R. E. Dunmur, M. Murray, and R. Schmutzler, *Ber. Bunsenges. phys. Chem.*, 1972, **76**, 44.

[24] T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, 1967, **6**, 2204.

[25] F. Seel and K.-D. Velleman, *Chem. Ber.*, 1972, **105**, 406.

[26] R. C. Dobbie and B. P. Straughan, *Spectrochim. Acta*, 1971, **27**, *A*, 255.

readily possible in the last two cases, where four bonds separate the fluorine and hydrogen atoms. An alternative explanation, for the silyl and germyl derivatives, is that these groups, when attached to phosphorus, reduce the electron density there by delocalisation of the lone pair of electrons, if present, into their vacant *d* orbitals. This mechanism has been suggested to account for the low base strength of trisilylphosphine,[27] and would certainly decrease the probability of forming phosphorus(V) silyl (or germyl) derivatives. In addition there is the possibility of some additional stabilisation of the phosphorus(III) forms by $(p \longrightarrow d)\pi$-interactions in the silicon–sulphur bonds. Further information is required to enable the structure-determining factors to be identified.

[2/1205 *Received, 26th May,* 1972]

---

[27] C. Glidewell and E. A. V. Ebsworth, *J. Chem. Soc.* (*A*), 1969, 352.

Preparation and Properties of Bis(difluorophosphino)- and Tris(difluorophosphino)-amine

By David E. J. Arnold and David W. H. Rankin,* Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Reprinted from

JOURNAL
OF
THE CHEMICAL SOCIETY

DALTON TRANSACTIONS

1975

Preparation and Properties of Bis(difluorophosphino)- and Tris(difluorophosphino)-amine

By **David E. J. Arnold** and **David W. H. Rankin**,* Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Bis(difluorophosphino)amine, $(F_2P)_2NH$, and tris(difluorophosphino)amine, $(F_2P)_3N$, have been prepared by the gas-phase reaction of ammonia, trimethylamine, and chlorodifluorophosphine. The compounds have been characterised by i.r., Raman, n.m.r., mass, and photoelectron spectroscopy. The tertiary amine reacts with hydrides HX (X = Cl, Br, or I) and H_2Y (Y = O, S, Se, or Te) to give the secondary amine and PF_2X or $Y{=}PF_2H$; $O{=}PF_2H$, $S{=}PF_2H$, and $Te{=}PF_2H$ decompose further.

AMMONIA and difluorohalogenophosphines have been shown to react in the gas phase to give the primary amine, aminodifluorophosphine, F_2PNH_2.[1,2] Further reaction to give secondary and tertiary amines is slow and incomplete, probably reflecting the electronegative character of the difluorophosphino-group, rather than any delocalisation of the nitrogen lone-pair electrons into phosphorus 3*d* orbitals. Chlorobis(trifluoromethyl)phosphine and ammonia also give only a primary amine, but on addition of a base (trimethylamine) the secondary amine is formed. The tertiary amine, $[(F_3C)_2P]_3N$, is formed only by way of the anion $[\{(F_3C)_2P\}_2N]^-$.[3] We have now studied the reactions of chloro- and bromodifluorophosphine with ammonia in the presence of trimethylamine, and find that by controlling the conditions carefully it is possible to prepare secondary and tertiary difluorophosphino-amines.

RESULTS AND DISCUSSION

Preparation.—The preparation of the secondary and tertiary difluorophosphino-amines is exceedingly difficult and time-consuming, and the volatilities of all three amines and of trimethylamine are so similar that separation by trap-to-trap distillation is impossible. The techniques described here represent the best methods that we found of preparing and isolating the compounds, having tried 57 varieties of physical and chemical conditions.

Secondary and tertiary difluorophosphino-amines were both prepared starting with ammonia or with aminodifluorophosphine. For the preparations of the tertiary amine that used ammonia it is possible to describe the gas-phase reaction in terms of equation (1). However,

$$NH_3 + 3PF_2Cl + 3Me_3N \longrightarrow (F_2P)_3N + 3[Me_3HN]Cl \quad (1)$$

it is expected that ammonium chloride will also be formed to some extent, and therefore if ammonia, chlorodifluorophosphine, and trimethylamine are used in the ratio 1 : 3 : 3 complete conversion of the ammonia to $(F_2P)_3N$ or NH_4Cl will take place and some trimethylamine and chlorodifluorophosphine will remain unchanged. In practice no trimethylamine was recovered, and some of the secondary and primary amines remained. Additional trimethylamine and chlorodifluorophosphine are expected to increase the proportion of tertiary amine in the products, but it was found that as the initial trimethylamine : ammonia ratio was increased beyond 3 : 1 so the total yield of difluorophosphinoamines decreased. So it was necessary to prepare a mixture of amines and to estimate the extent to which reaction had occurred (usually by i.r. spectroscopy), and then to add more chlorodifluorophosphine (*ca.* 1·5 mol per remaining N–H bond) followed by more trimethylamine (*ca.* 1 mol per N–H bond). The whole procedure was repeated until the reaction was essentially complete. If there was any trimethylamine left in the product after completion of this process it was removed by adding a small excess of boron trifluoride which gave a solid involatile adduct with trimethylamine but did not appear to give a stable adduct with the tertiary difluorophosphinoamine.

An alternative method, which gave less complicated mixtures of products and was therefore somewhat easier to regulate, started with aminodifluorophosphine and initially used reagents in the proportions in equation (2).

$$F_2PNH_2 + 2PF_2Cl + 2Me_3N \longrightarrow (F_2P)_3N + 2[Me_3HN]Cl \quad (2)$$

The subsequent stages were exactly as in the former method, except that it was usually possible to gauge quantities so that use of boron trifluoride to remove excess of trimethylamine was unnecessary.

A study of the reactions of $(F_2P)_3N$ with various hydrides showed that the secondary amine could be prepared in a pure form by removal of one of the PF_2 groups with a hydrogen halide. This seems to be the best method of obtaining small amounts of really pure amine and was the one adopted for the preparation of $(F_2P)_2ND$. A more direct route starts with aminodifluorophosphine, chlorodifluorophosphine, and trimethylamine in the ratio 1 : 2 (excess) : 1. These yielded a

$$F_2PNH_2 + PF_2Cl + Me_3N \longrightarrow (F_2P)_2NH + [Me_3HN]Cl \quad (3)$$

mixture of primary, secondary, and tertiary amines in a ratio of *ca.* 30 : 65 : 5. When boron trifluoride was added to this mixture the primary amine decomposed,[4] leaving a mixture of secondary and tertiary amines, inseparable by distillation. Alternatively, a hydrogen halide could be added, destroying the primary amine and converting the tertiary to secondary amine.

Reactions of $(F_2P)_3N$.—Reactions of tertiary difluorophosphinoamine were undertaken to determine its usefulness as a preparative intermediate and eventually led to

---

[1] D. W. H. Rankin, *J. Chem. Soc.* (*A*), 1971, 783.

[2] J. E. Smith and K. Cohn, *J. Amer. Chem. Soc.*, 1970, **92**, 6185.

[3] A. B. Burg and J. Heners, *J. Amer. Chem. Soc.*, 1965, **87**, 3092.

[4] D. E. J. Arnold and D. W. H. Rankin, unpublished work.

the best preparative route to the secondary amine. Reaction with hydrogen halides was rapid for chloride and bromide, but rather slower for iodide, and resulted in cleavage of just one P–N bond per molecule, even when excess of hydrogen halide was used. A small amount of

$$(F_2P)_3N + HX \longrightarrow (F_2P)_2NH + PF_2X \quad (4)$$
$$(X = Cl, Br, or I)$$

white solid was formed, indicating that further reaction does occur to a limited extent. However, as reaction of the primary amine with halogen acids is fast, no other volatile products were observed. This rather surprising behaviour, with primary and tertiary amines being reactive and secondary amine unreactive, is similar to that observed for the analogous series of bis(trifluoromethyl)phosphino-compounds.[3]

Group 6 hydrides reacted in a similar manner, but the presumed intermediates PF_2–Y–H rearrange rapidly to the phosphorus(V) forms, Y=PF_2H. The remaining hydrogen is no longer acidic and further reaction did not occur. For selenium, the reaction was clean and gave

$$(F_2P)_3N + H_2Y \longrightarrow (F_2P)_2NH + Y{=}PF_2H \quad (5)$$
$$(Y = O, S, Se, or Te)$$

just the two expected products. For sulphur, the secondary amine was obtained in high yield, but S=PF_2H decomposed. For oxygen, both products decomposed and trifluorophosphine was the main volatile product. For tellurium, the secondary difluorophosphinoamine remained intact, but the other observed products were phosphine, trifluorophosphine, and elemental tellurium. We were unable to observe Te=PF_2H.

Spectroscopic Properties.—In compounds such as the difluorophosphinoamines there is the possibility that the nitrogen atoms have a planar arrangement of ligands. The spectroscopic studies were therefore intended to give some indication of whether this is in fact so, as well as to assist in the routine characterisation of the new compounds. N.m.r. parameters are listed in Table 1, together with those for F_2PNH_2. These were mainly obtained by direct observation of ^1H, ^{19}F, and ^{31}P spectra; information about the ^{15}N spectra and signs of coupling constants were obtained by heteronuclear double-resonance experiments.

The ^1H spectrum of $(F_2P)_2{}^{15}NH$ appeared to be of the first order, the resonance being split by ^{15}N, ^{31}P, and ^{19}F into a doublet of triplets of quintets; the ^{15}N spectrum similarly seemed to be of the first order. The ^{19}F and ^{31}P spectra, however, were of the second order and showed long-range PF and FF couplings. The spectra were analysed in terms of an $[A[X]_2]_2MQ$ spin system,[5] assuming that M and Q caused only first-order splittings of the A and X spectra. On cooling, the ^{19}F spectrum became more complex, mainly due to changes in the long range FF couplings which were no longer equal. No other coupling constants appeared to change significantly. The ^{19}F and ^{31}P spectra of $(F_2P)_3{}^{15}N$ were complex, and full analysis for the $[A[X]_2]_3M$ spin system was impossible. However, it would appear that $^2J(PP)$ in this molecule is less than 80 Hz and may be considerably smaller than this, and that the long range (four-bond) FF couplings are significant (probably of the same order of magnitude as in the secondary amine).

TABLE 1

N.m.r. parameters of difluorophosphino-amines [a]

	$F_2P^{15}NH_2$	$(F_2P)_2{}^{15}NH$	$(F_2P)_3{}^{15}N$
$\tau(^1H)$	+6·77 (2)	+5·62 (2)	
$\delta(^{19}F)$ [b]	−58·1 (2)	−62·0 (1)	−63·2 (3)
$\delta(^{31}P)$ [c]	+147·5 (1)	+144·4 (1)	+150·3 (1)
$\delta(^{15}N)$ [d]	+21·4 (2)	+86·3 (3)	+139·0 (1)
$^1J(PF)$	−1200 (1)	−1253 (1)	(−)1224 (1) [e]
$^1J(PN)$	+72·5 (3)	+78·9 (3)	+87·0 (3)
$^1J(NH)$	−80·4 (4)	−74·7 (2)	
$^2J(PH)$	+18·8 (2)	+13·6 (2)	
$^2J(NF)$	−6·4 (4)	−3·6 (2)	±2·5 (4)
$^2J(PP')$		±154 (1)	[f]
$^3J(FH)$	+12·8 (4)	+11·2 (2)	
$^3J(PF')$		+21·0 (5)	[f]
$^4J(FF')$		±5·4 (5)	[f]
$^4J(FF'')$		±5·4 (5)	[f]

Values of *J* are given in Hz, δ in p.p.m.; estimated standard deviations are quoted in parentheses.

[a] Solutions in $C_6D_6 : Me_4Si$ ratio 1 : 1, at 308 K. [b] To high frequency of external CCl_3F. [c] To high frequency of external 85% H_3PO_4. [d] To high frequency of external $[Me_4N]I$. [e] $|^1J(PF) + 2\ ^3J(PF')|$. [f] Not determined due to complexity of spectra (see text).

Most of the observed parameters are as expected, an exception being ^{31}P chemical shifts which differ by small but significant amounts, the order being $(F_2P)_2NH < F_2PNH_2 < (F_2P)_3N$. The ^{15}N resonance was shifted to high frequency on replacement of hydrogen atoms by PF_2 groups. This probably reflects the electronegative character of the groups, rather than any π-bonding involving the nitrogen lone-pair electrons, as replacement of hydrogen atoms by SiH_3 groups results in a small low-frequency shift.[6]

The smaller absolute value of $^1J(^{15}N^1H)$ in $(F_2P)_2NH$ than in F_2PNH_2 is surprising as this is normally associated with a smaller *s*-orbital contribution to the nitrogen–hydrogen bond.[7] Increasing the number of PF_2 groups should, if anything, increase the *s* contribution to the remaining N–H bonds. However, *J*(NH) may also be affected by other factors such as the presence nearby of electronegative atoms. The magnitudes and signs of the $^1J(^{31}P^{15}N)$ couplings are consistent with the few that have been determined previously.[6,8] The small value of $^2J(PP)$ in $(F_2P)_2NH$, and the probably smaller value in $(F_2P)_3N$, are perhaps the most unexpected parameters. A number of alkyl- and aryl-bis(difluorophosphino)amines have been studied and the values of $^2J(PP)$ in these all lie between 370 and 450 Hz.[9] It seems possible that this coupling constant is very sensitive to the conformation adopted by the PF_2 groups, per-

---

[5] R. K. Harris, J. R. Woplin, R. E. Dunmur, M. Murray, and R. Schmutzler, *Ber. Bunsengesellschaft Phys. Chem.*, 1972, **76**, 44.

[6] D. W. W. Anderson, J. E. Bentham, and D. W. H. Rankin, *J.C.S. Dalton*, 1973, 1215.

[7] G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1964, **86**, 5564.

[8] A. H. Cowley, J. R. Schweiger, and S. L. Manatt, *Chem. Comm.*, 1970, 1491.

[9] J. F. Nixon, *J. Chem. Soc. (A)*, 1969, 1087.

haps being related to the extent to which the phosphorus lone pairs interact. The small value found for $(F_2P)_2O$[10] could therefore be related to the very wide angle at oxygen in this molecule,[11] while the much smaller angles likely in $(F_2P)_2S$ and $(F_2P)_2Se$ would account for the large and temperature-dependent $^2J(PP)$ values in these compounds.[12,13]

TABLE 2

Vibrational spectra (cm^{-1}) of $(F_2P)_3N$

I.r. (gas)	Raman		Assignment
	liquid	CCl_3F solution	
1 880vw			2 × 939
1 750vw			939 + 816, 912 + 838
1 167w			816 + 363
1 075w			2 × 542
1 045w			816 + 234
1 004mw			542 + 468
939vs	936w, dp	937m	$\nu(PN)$
912vs	905w, p	907m	
878w (sh)			
863 vs *P*	874m, p	869s	$\nu(PF)$
858 vs *Q*			
843 *P*			
838 vs *Q*	837s, p	*	
833 *R*			
816vs	805m, dp	*ca.* 805m	
706w			363 + 345
	558vs, p	557vs	$\nu(PN)$
542m	537vs, p	*	
509vw			363 + 142
503vw			
468m	467m, p	466m	$\delta(PF_2)$ and $\delta(P_3N)$
450m	447m, dp	442m	
	421ms, p	422ms	
	404ms, p		
366 *P*			$\omega(PF_2)$
363 ms *Q*	389vw, p	*	
359 *R*			
345s	347vs, ?	*	
295m	295vw, p	293w	$\rho(PF_2)$
	251s, p	*	$\delta(P_3N)$
	234vs, p	231s	
	142m, ?	145s	$\tau(PF_2)$

s = Strong, m = medium, w = weak, v = very, sh = shoulder, p = polarised, and dp = depolarised.

* Obscured by CCl_3F.

TABLE 3

Vibrational spectra (cm^{-1}) of $(F_2P)_2NH$ and $(F_2P)_2ND$

I.r. (gas)		Raman		
H	D	H (liquid)	H (solid)	Assignment
3 373m	2 502w			$\nu(NH)$
3 333m	2 472w	3 322w	3 313w	
1 248ms	1 066m			$\delta(NH)$
1 210ms	1 044m			
	941vs			
919s	914w	920w	*ca.* 930w	$\nu_{asym}(PNP)$
863s	888s	880vs	885vs	$\nu(PF)$ $\delta(NH)$?
830vs	838vs	830m	838s	
823	832vs (sh)			
816 vs	816vs	797s	792s	
810				
747m	741m	743m	775s	$\nu_{sym}(PNP)$
		669m		
566m	571vw	593w		
	542w			
508vw	508w	510m		2 × 264 ?
	470vw			
444m	449w	430s	430w	$\delta(PF_2)$
427w (sh)				
361m	360m (sh)			$\omega(PF_2)$
323w	350m		325m	
291w	296w	295w	380w	$\rho(PF_2)$
		264vs	265m	$\delta(PNP)$
		240vw		
		150m	170w	$\tau(PF_2)$

I.r. and Raman data for $(F_2P)_3N$ and $(F_2P)_2NH$ are presented in Tables 2 and 3. Possible point groups for $(F_2P)_3N$ are C_{3h}, C_{3v}, C_3, C_s, or C_1. Any of these could be consistent with a planar P_3N skeleton, and in the case of C_{3h} this is essential. The C_{3h} structure would give rise to 12 Raman-active fundamentals, four of which would be polarised, and nine i.r.-active fundamentals: it is immediately obvious from Table 2 that this is not consistent with the observed spectra. Similarly, on the basis of the number of polarised Raman bands, the C_{3v} and C_3 structures can be eliminated. This only leaves C_s and C_1, or possibly a mixture of conformers. Any conclusion about which of these possibilities is correct depends on assignment of the skeletal vibrations. These may, of course, be mixed with the vibrations of the PF_2 groups, but as bands occur in the regions normally expected for difluorophosphines it is likely that the concept of skeletal vibrations is a useful one.

After assignment of PF_2 group vibrations three sets of bands remain unassigned, in the regions 1 000—900, *ca.* 550, and *ca.* 250 cm^{-1}. A planar P_3N skeleton could well have stretching vibrations in the two higher-frequency regions, and a deformation in the lowest region, by analogy with trisilylamine.[14] The effect of the PF_2 groups would be to lower the skeletal symmetry from D_{3h}. An overall C_s structure would allow the asymmetric skeletal stretch to be split into a' and a'' components, both Raman active, one polarised and one depolarised. The symmetric stretch would remain as a single fundamental, but would become i.r.-allowed. The Raman spectrum of the liquid phase, however, showed bands at both 558 and 537 cm^{-1}. These wavenumbers are rather too high for PF_2 deformations, the only other reasonable assignment. Neither band can be accounted for in terms of Fermi resonance, as there was just one corresponding band in the i.r. spectrum (admittedly of the gas phase) and also the two Raman bands had distinctly different widths and degrees of polarisation. We therefore tentatively suggest that these vibrations, and those at 251 and 234 cm^{-1}, are skeletal vibrations of different conformers of $(F_2P)_3N$, one probably of C_s symmetry, and one of another symmetry, possibly C_3. The bands at 905 and 936 cm^{-1} are also assigned as skeletal modes, but these could both arise from a single conformer. Use of models of the molecule shows that the structures likely to minimise fluorine–fluorine interactions are those with C_s and C_3 or C_{3h} symmetry (Figure 1).

---

[10] R. W. Rudolph, R. C. Taylot, and R. W. Parry, *J. Amer. Chem. Soc.*, 1966, **88**, 3729.

[11] D. E. J. Arnold and D. W. H. Rankin, *J. Fluorine Chem.*, 1973, **2**, 405.

[12] R. W. Rudolph and R. A. Newmark, *J. Amer. Chem. Soc.*, 1970, **92**, 1195.

[13] D. E. J. Arnold, J. S. Dryburgh, E. A. V. Ebsworth, and D. W. H. Rankin, *J.C.S. Dalton*, 1972, 2518.

[14] E. A. V. Ebsworth, J. R. Hall, M. J. Mackillop, D. C. McKean, N. Sheppard, and L. A. Woodward, *Spectrochim. Acta*, 1958, **13**, 202.

We therefore assigned the spectra in terms of these structures. We would emphasise that conclusions about conformations are of necessity only tentative, and represent our opinion as to the most probable arrangement: an investigation of the molecular structure by electron diffraction is currently being undertaken with a view to settling the matter with more certainty.

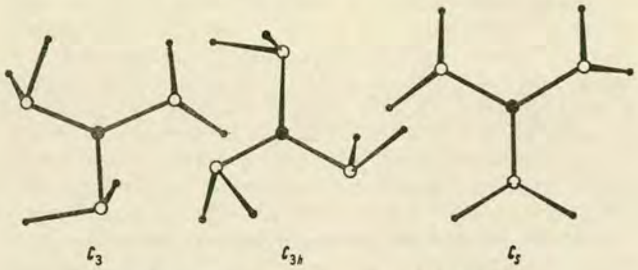


FIGURE 1 Possible structures for $(F_2P)_3N$

The conformation of the PF_2 groups also affects the point group of $(F_2P)_2NH$. Our studies of H · · · F interactions of this type of molecule [15] leads us to anticipate the most stable conformations to have C_s and C_2 symmetry, with two H · · · F interactions in each case (Figure 2). Observation of two N–H deformation frequencies near 1 200 cm^{-1} in the gas-phase i.r. spectrum suggests strongly that two conformers are indeed present in the gas phase. As with $(F_2P)_3N$, a number of bands can readily be assigned to vibrations of the PF_2 groups. The three bands between 790 and 890 cm^{-1} will include P–F stretching modes, but the remaining NH deformations (presumably two bands, one for each conformer) may also lie in this region. Bands at *ca.* 920, 745, and 265 cm^{-1} have been assigned to skeletal modes, although these may be strongly coupled with PF_2 vibrations. Frequencies observed for $(F_2P)_2ND$ are generally consistent with this assignment, although a strong band rather surprisingly appeared at 941 cm^{-1}. This may be a P–F or P–N stretching mode raised in frequency by coupling with an ND deformation.

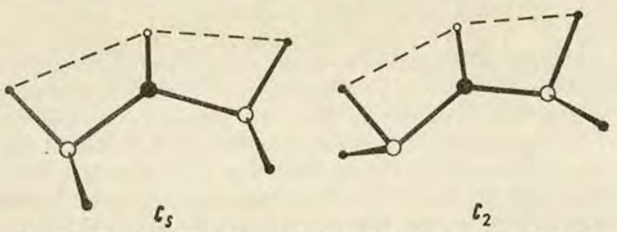


FIGURE 2 Possible structures for $(F_2P)_2NH$. The broken lines represent possible H · · · F interactions

Details of the mass spectra of $(F_2P)_3N$ and $(F_2P)_2NH$ are presented in Tables 4 and 5. It seems that the most important breakdown path for the tertiary amine involves the following reactions (6) and (7). Other reactions involve loss of PF_2 or F, and in one case a rearrangement must occur giving rise to the ion $[(F_2P)_2NF]^+$, which must contain either an N–F bond or a four-co-ordinate phosphorus atom.

$$[(F_2P)_3N]^+ \longrightarrow [(F_2P)NPF]^+ + PF_3 \qquad (6)$$

$$[(F_2P)NPF]^+ \longrightarrow [PF_3]^+ + PN \qquad (7)$$

The ion $[(F_2P)NPF]^+$ was also formed by loss of HF from the parent ion of $(F_2P)_2NH$ [equation (8)]. However, in this case there

$$[(F_2P)_2NH]^+ \longrightarrow [(F_2P)NPF]^+ + HF \qquad (8)$$

are probably at least three other routes, (9)—(11), by

$$[(F_2P)_2NH]^+ \longrightarrow [(F_2P)_2N]^+ + H \qquad (9)$$

$$[(F_2P)_2NH]^+ \longrightarrow [(F_2P)NH(PF)]^+ + F \qquad (10)$$

$$[(F_2P)_2NH]^+ \longrightarrow [(FP)NH]^+ + PF_3 \qquad (11)$$

which the parent ion can dissociate. The last of these routes yields the ion $[(FP)NH]^+$, one which has been observed previously to be particularly readily formed.[1]

TABLE 4

Mass spectrum of $(F_2P)_3N$

m/e	Intensity	Assignment
221	32	$[(F_2P)_3N]^+$
202	1·2	$[(F_2P)_2N(PF)]^+$
171	0·3	$[(F_2P)_2NF]^+$
152	4	$[(F_2P)_2N]^+$
133	53	$[(F_2P)N(PF)]^+$
114	27	$[(FP)N(PF)]^+$
107	6	$[PF_4]^+$ and $[P_3N]^+$
95	0·5	$[(FP)NP]^+$
88	46	$[PF_3]^+$
69	100	$[PF_2]^+$
66·5	<0·1	$[(F_2P)N(PF)]^{2+}$
50	9	$[PF]^+$
47·5	<0·1	$[(FP)NP]^{2+}$
45	1·0	$[PN]^+$
34·5	0·5	$[PF_2]^{2+}$
31	1·3	P^+
Metastable		
58·1	Weak	$[(F_2P)N(PF)]^+ \longrightarrow [PF_3]^+ + PN$
80·0	Strong	$[(F_2P)_3N]^+ \longrightarrow [(F_2P)N(PF)]^+ + PF_3$

TABLE 5

Mass spectrum of $(F_2P)_2NH$

m/e	Intensity	Assignment
153	90	$[(F_2P)_2NH]^+$
152	53	$[(F_2P)_2N]^+$
134	7	$[(F_2P)NH(PF)]^+$
133	21	$[(F_2P)N(PF)]^+$
114	2	$[(F_2P)NP]^+$
88	10	$[PF_3]^+$
81	5	$[P_2F]^+$
69	100	$[PF_2]^+$
65	70	$[(FP)NH]^+$
50	6	$[PF]^+$
47·5	0·1	$[(FP)NP]^{2+}$
46	48	$[PNH]^+$
34·5	<0·1	$[PF_2]^{2+}$
32·5	<0·1	$[(FP)NH]^{2+}$
31	1	P^+
20	2	$[HF]^+$
Metastable		
115·4	Weak	$[(F_2P)_2NH]^+ \longrightarrow [(F_2P)N(PF)]^+ + HF$
151·0	Medium	$[(F_2P)_2NH]^+ \longrightarrow [(F_2P)_2N]^+ + H$

Some details of the He(I) photoelectron spectra of the

---

[15] D. E. J. Arnold, E. A. V. Ebsworth, H. F. Jessep, and D. W. H. Rankin, *J.C.S. Dalton*, 1972, 1681.

three difluorophosphinoamines are given in Table 6. There is a general increase in binding energies with increasing replacement of hydrogen atoms by PF_2 groups.

TABLE 6

Photoelectron spectra

F_2PNH_2	$(F_2P)_2NH$	$(F_2P)_3N$	Assignment
10·9	11·3	11·2	N $2p_z$
11·5	11·9	12·2	P $3p_z$
	12·3	12·5	
15·4	15·6	15·8 *	PN σ, NH σ
	16·0		
16·7	16·8		F $2p_\pi$
	17·4	17·4	
17·9	18·5	18·7	PF σ

Vertical ionisation potentials in eV ± 0·1 eV.

* Intense broad band.

The fact that the nitrogen $2p_z$ level in the tertiary amine is slightly lower than that in the secondary amine probably reflects a change in the amount of interaction of this level with the phosphorus lone-pair levels. This interaction in turn depends on the orientations of the phosphorus groups:[16] these are unknown at the present time. However, the C_{3h} structure for $(F_2P)_3N$ would probably have the smallest such interactions, and so what evidence there is is against this structure.

EXPERIMENTAL

Volatile compounds were handled in Pyrex-glass vacuum systems, fitted with 'Sovirel' polytetrafluoroethylene taps and joints greased with Apiezon N. Chlorodifluorophosphine was prepared from hydrogen chloride and dimethylaminodifluorophosphine,[17] and aminodifluorophosphine by reaction of chlorodifluorophosphine and ammonia.[1] Purities were checked by i.r. spectroscopy.

I.r spectra were recorded on a Perkin-Elmer 225 grating spectrometer, using cells equipped with caesium iodide or potassium bromide windows. Raman spectra were obtained using a Cary 83 spectrophotometer with argon-ion 488 nm laser excitation, mass spectra using an A.E.I. MS902 spectrometer operating at 70 eV ionising voltage, and u.v. photoelectron spectra using a Perkin-Elmer PS16 spectrometer with He(I) (21·22 eV) excitation.* ^{1}H, ^{19}F, and ^{31}P N.m.r. spectra were recorded on Varian Associates HA100 and XL100 spectrometers, operating at 100, 94·1, and 40·5 MHz respectively. Irradiation of ^{1}H, ^{19}F, ^{31}P, or ^{15}N nuclei for heteronuclear double-resonance experiments was carried out using either a Schlumberger FS30 frequency synthesiser (for the HA100) or the standard double-resonance equipment of the XL100 spectrometer.

Preparation of Tris(difluorophosphino)amine.—The compound was prepared in an apparatus consisting of two bulbs, of *ca.* 2 l and 100 cm^3 capacity, linked by a 'Sovirel' greaseless tap. The reaction took place in three stages, the apparatus being cleaned and dried between the stages with final drying being achieved by allowing silyl chloride or bromide to stand in the bulbs for a few minutes. In the first stage, the small bulb was filled with trimethylamine (4·5 mmol) and the large one with a mixture of aminodifluorophosphine (2·0 mmol) and chlorodifluorophosphine (5·0 mmol). The connecting tap was opened to allow the pressures to equalise (admitting *ca.* 4 mmol of Me_3N) and closed again. Clouds of white solid trimethylammonium chloride were formed. After 40 min the volatile products were removed and fractionated. The fraction retained at 195 K but passing 209 K consisted of 1·6 mmol [80% based on $PF_2(NH_2)$ used] of a mixture of F_2PNH_2, $(F_2P)_2NH$, and $(F_2P)_3N$. Secondly, trimethylamine (1·05 mmol) was added from the small bulb to chlorodifluorophosphine (3·2 mmol) and the mixed amines (1·6 mmol) in the large bulb. After 45 min the volatile products were collected and fractionated, yielding *ca.* 1·4 mmol of tertiary amine containing some secondary amine (*ca.* 90% based on the amines used). Finally, the second step was repeated so that the ratios of phosphorus amines : chlorodifluorophosphine : trimethylamine was again 1·0 : 2·0 : 0·5. This time the fraction retained at 195 K but passing 209 K was essentially pure tertiary difluorophosphinoamine. The overall yield (over the three stages) was 65% based on F_2PNH_2 used.

The molecular weight of the product was found to be 221 ± 3 (calc. 221), and the vapour pressure is given by the equation, $\log p(\text{mm}) = -(1\,625/T) + 7{\cdot}911$; $\Delta H_{\text{vap.}} = 31{\cdot}20$ kJ mol^{-1}, $\Delta S_{\text{vap.}} = 99{\cdot}4$ J K^{-1} mol, and the extrapolated b.p. was 314 K.

Preparation of Bis(difluorophosphino)amine.—Hydrogen bromide (0·2 mmol) was added from a 200 cm^3 bulb to $(F_2P)_3N$ (0·2 mmol) in a 2 l bulb. A small amount of white solid was formed. Volatile products, separated by fractional condensation, were $(F_2P)_2NH$ (0·1 mmol, 50%, retained at 195 K) and PF_2Br (0·16 mmol, 80%, retained at 143 K). The secondary amine decomposed readily, and could only be handled in apparatus that had been first dried by allowing silyl chloride or bromide to stand in it for a time. Determinations of vapour pressures were not possible, but the molecular weight was found to be 158 ± 5 (calc. 153).

Reactions.—$(F_2P)_3N$ *with* HX (X = Cl, Br, *or* I). Reactions were carried out in the liquid phase, by condensing reagents together and allowing them to warm slowly to room temperature, or in the gas phase, using a two-bulb apparatus as described above. In a typical reaction, $(F_2P)_3N$ (0·2 mmol) and hydrogen iodide (0·4 mmol) were condensed together and allowed to warm to room temperature. A small amount of white solid was formed. The volatile products, separated by fractional condensation, were $(F_2P)_2NH$ (0·15 mmol, 75%), PF_2I (0·11 mmol, 55%), and excess of HI. In general, yields of $(F_2P)_2NH$ were higher for gas-phase reactions than for liquid-phase ones, and use of excess of hydrogen halide reduced the yield of secondary amine. The compound F_2PNH_2 was not observed in any of these reactions.

$(F_2P)_2NH$ *with* HCl. When $(F_2P)_2NH$ and HCl were condensed together (ratio 1 : 1 or 1 : 2) and allowed to warm to room temperature no white solid was formed and the reagents were recovered unchanged.

$(F_2P)_3N$ *with* H_2O. The amine and water (0·2 mmol of each) were mixed in the gas phase and allowed to stand for 10 min. No solid material was formed. The volatile products were removed and on condensation and warming again decomposed, giving a white solid, $(F_2P)_2NH$ (0·07 mmol, 35%), and PF_3 (0·11 mmol).

$(F_2P)_3N$ *with* H_2S. The amine and hydrogen sulphide reacted slowly (10 min or longer) in the gas phase giving $(F_2P)_2NH$ in high yield (*ca.* 85%) and a trace of PF_3 as the

---

* 1 eV ≈ 1·60 × 10^{-19} J.

[16] S. Cradock and D. W. H. Rankin, *J.C.S. Faraday II*, 1972, 940.

[17] J. G. Morse, K. Cohn, R. W. Rudolph, and R. W. Parry, *Inorg. Synth.*, 1967, **10**, 147.

only volatile products. The involatile residue was a colourless liquid or film of solid.

$(F_2P)_3N$ *with* H_2Se. The amine (0·2 mmol) and H_2Se (0·6 mmol) were condensed together and allowed to warm to room temperature. The volatile products were $(F_2P)_2NH$ (0·12 mmol, 60%), $Se{=}PF_2H$ (0·06 mmol), PF_3 (0·05 mmol), and unchanged H_2Se.

$(F_2P)_3N$ *with* H_2Te. The amine (0·2 mmol) and H_2Te (0·25 mmol) were allowed to react together in an n.m.r. tube with benzene–tetramethylsilane solvent at *ca.* 200 K. The products observed were $(F_2P)_2NH$, PH_3, PF_3, and elemental tellurium.

We thank Dr. S. Cradock for his assistance in running and interpreting the photoelectron spectra.

[4/2111 *Received, 14th October,* 1974]

Journal of Fluorine Chemistry
Elsevier Sequoia S.A., Lausanne — Printed in Switzerland

AN ELECTRON-DIFFRACTION DETERMINATION OF THE MOLECULAR STRUCTURE OF BIS(DIFLUOROPHOSPHINO)ETHER, F_2POPF_2, IN THE GAS PHASE

D. E. J. ARNOLD AND D. W. H. RANKIN

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ (Great Britain)

(Received June 26, 1972)

SUMMARY

Gas-phase electron-diffraction methods have been used to determine the molecular structure of bis(difluorophosphino)ether, F_2POPF_2. Most of the geometrical parameters are strongly correlated due to overlapping peaks in the radial distribution curve. In the structure that fits the experimental data most closely, the P–F and P–O bond lengths are 159.7 ± 0.4 and 153.3 ± 0.6 pm respectively, and the POP angle is 2.53 ± 0.02 rad (145°). The conformation is such that the molecule has no symmetry elements other than I (point group C_1). In other refinements somewhat longer P–O and shorter P–F distances were obtained.

INTRODUCTION

As part of a study of the bonding in substituted fluorophosphines, we have determined the structures of a number of compounds in which difluorophosphino groups are bound to elements of the first series[1–4]. The similarity of observed structures to those of analogous silyl or germyl compounds[5–7] has led us to suppose that phosphorus d-orbital participation in the bonding profoundly influences the shapes of the fluorophosphines.

The compounds studied so far have not included any compounds containing phosphorus–oxygen bonds, but the wide angles at oxygen in disilyl ether[8] and digermyl ether[9] led us to expect a similar wide angle in bis(difluorophosphino)ether. We now report the determination of the molecular structure of this compound in the gas phase.

Also of interest is the conformation of the fluorophosphine groups. Our earlier work on phosphorus–nitrogen derivatives has shown that the preferred orientations of these groups are determined by intramolecular hydrogen–fluorine contact, where these are possible, and otherwise by lone-pair–lone-pair interactions[4,10]. The results presented here provide further evidence for the stereochemical importance of lone pairs of electrons in these molecules.

EXPERIMENTAL

Samples of bis(difluorophosphino)ether were prepared by the reaction of bromodifluorophosphine with bis(tributyltin)ether[11], and purified by fractional condensation *in vacuo*. The purity of each sample was checked by IR spectroscopy.

Electron-diffraction data were collected photographically on Ilford N60 plates, using a Balzers' KD.G2 gas-diffraction apparatus (with rotating sector)[12], and were converted to digital form using a Joyce–Loebl automatic microdensitometer. Data from two plates, exposed with nozzle-to-plate distances of 250 and 500 mm, were used, giving data over the range $32 < s < 292$ nm^{-1}. The nozzle was maintained at 295K and the sample of compound at 195K during the exposures, and the gas temperature may be taken to be near the mean of these. The electron wavelength used was determined from the diffraction pattern of powdered thallous chloride and by direct measurement of the accelerating voltage to be 5.659 ± 0.003 pm.

All calculations were carried out on an IBM 360/50 computer at the Edinburgh Regional Computing Centre, using established data reduction and least-squares refinement programmes[1,13]. The scattering factors of Cox and Bonham[14] were used throughout. The weighting points (defined as in Ref. 1) used in setting up the off-diagonal weight matrix are given in Table 1, together with scale factors and correlation parameters[15].

All interatomic distances quoted in this work are r_a values[16].

TABLE 1

WEIGHTING FUNCTIONS, CORRELATION PARAMETERS AND SCALE FACTORS*

Camera height (mm)	Δs	$s_{min.}$	s_1	s_2	$s_{max.}$	P/h	Scale factor
250	4	52	80	250	292	0.4719	1.286 ± 0.028
500	2	32	48	128	156	0.4489	1.262 ± 0.022

* s units in nm^{-1}.

MOLECULAR MODEL

As electron diffraction is not a good method for distinguishing between almost identical groups, it was necessary to assume that the two F_2PO– units within the molecules were identical and, moreover, that these groups had a plane of symmetry. Thus the structures of these groups were defined by the F–P- and

P–O-bonded distances and the FPF and FPO angles. The overall structure depends also on the POP angle and on the conformations of the F_2PO groups. Two dihedral angles were defined, one for each F_2PO group, to describe the rotations about the P–O bonds. In each case, the angle was taken to be zero when the FPF bisector was *trans* with respect to the further P–O bond. The relative directions of the rotations were such that if the dihedral angles were equal, the molecule had overall C_2 symmetry; C_s symmetry was therefore represented by equal and opposite dihedral angles. The parameters that could be included in the refinements were therefore the two bond lengths, five angles, two scale factors and amplitudes of vibration for all the different interatomic distances.

REFINEMENT AND RESULTS

Refinement of the structure of bis(difluorophosphino)ether proved to be unusually difficult. The difficulties arose from the similarities of the phosphorus–fluorine and phosphorus–oxygen bond lengths and of the FPF and FPO angles: these made it necessary for some of the amplitudes of vibration for the closest atom pairs to be fixed. In addition, there has been some uncertainty about the relative lengths of the phosphorus–fluorine and phosphorus–oxygen bonds: in some refinements, one type was the longer, and in others, the reverse was true. We therefore quote (in Table 2) the results of three separate refinements, obtained under very different conditions.

In refinement A, most of the different interatomic distances in the molecule were allowed to refine independently, without any overall structural constraints. In this case, the lowest R factor (0.137) was obtained when the P–F distance was less than that for P–O.

Refinements B and C are the best with P–F $<$ P–O and with P–F $>$ P–O respectively. Some of the parameters of refinement C are rather different from those in other fluorophosphines or phosphorus–oxygen compounds, although not impossible. However, the R factors for the refinements are 0.150 and 0.119. Using the R factor ratio test[17], refinement B can be rejected at the 99.5% confidence level.

Because of strong correlations between angles FPF, FPO, POP and the dihedral angles, it was not possible to refine more than two or three of these at any one time. They were therefore refined in turn, until a self-consistent solution was obtained. Such a procedure must lead to unrealistically low estimated standard deviations, and so the errors quoted in Table 2 have been increased to allow for the correlation. The least-squares correlation matrix (Table 3) corresponds to refinement C of Table 2.

Final molecular scattering intensity and difference curves are shown in Figure 1. The intensity data or uphill curves may be obtained from the authors on request.

TABLE 2

MOLECULAR PARAMETERS *

	Refinement A		Refinement B		Refinement C	
	Distance	Amplitude	Distance	Amplitude	Distance	Amplitude
r 1 (P–F)	156.2 (5)	4.5 (fixed)	157.0 (5)	4.5 (fixed)	159.7 (4)	4.5 (fixed)
r 2 (P–O)	161.6 (9)	4.7 (fixed)	159.7 (9)	4.7 (fixed)	153.3 (6)	4.7 (fixed)
r 3 (F...F)	238.5 (11)	7.4 (6)	239.0 (12)	6.9 (6)	242.0 (5)	7.2 (6)
r 4 (F...O)	240.4 (fixed)	8.7 (tied to *u* 3)	240.1 (7)	8.1 (tied to *u* 3)	237.8 (5)	8.5 (tied to *u* 3)
r 5 (P...F)	336.5 (14)	4.9 (14)	341.9 (15)	7.0 (fixed)	389.7 (10)	4.9 (18)
r 6 (P...F)	390.6 (16)	5.6 (14)	399.6 (17)	7.0 (fixed)	338.7 (10)	4.9 (18)
r 7 (P...F)	308.6 (16)	7.0 (fixed)	305.4 (14)	7.0 (fixed)	311.9 (9)	5.0 (fixed)
r 8 (P...F)	363.9 (17)	6.4 (15)	370.0 (16)	7.0 (fixed)	364.2 (10)	5.0 (18)
r 9 (P...P)	294.4 (15)	10.0 (fixed)	297.8 (16)	23.0 (50)	292.5 (13)	9.8 (14)
*r*10 (F...F)	301.2 (fixed)	28.0 (fixed)	316.0 (15)	28.0 (fixed)	453.3 (9)	22.8 (35)
*r*11 (F...F)	459.1 (fixed)	28.0 (fixed)	461.7 (18)	28.0 (fixed)	429.9 (8)	24.0 (fixed)
*r*12 (F...F)	447.2 (fixed)	22.5 (40)	448.2 (15)	18.5 (fixed)	318.5 (8)	18.5 (fixed)
*r*13 (F...F)	443.9 (fixed)	22.5 (tied to *u*12)	446.5 (19)	18.5 (fixed)	459.5 (10)	22.8 (tied to *u*10)
1 (F–P–F)			1.73 (2) [99.2]		1.719 (fixed) ** [98.5]	
2 (F–P–O)			1.72 (fixed) ** [98.6]		1.725 (5) [98.8]	
3 (P–O–P)			2.40 (2) [137.5]		2.533 (fixed) ** [145.1]	
4 (dihedral)			0.98 (fixed) ** [56.2]		—1.07 (fixed) ** [–61.3]	
5 (dihedral)			2.13 (fixed) ** [122.0]		2.16 (fixed) ** [123.5]	

---

* All distances and amplitudes are in pm. Angles are given in radians and (in square brackets) in degrees.

** Refined earlier.

TABLE 3

LEAST-SQUARES CORRELATION MATRIX (×1000)

r 1	r 2	< 2	u 3	u 5	u 6	u 8	u 9	u 10	k 1	k 2	
1000	−574	121	63	111	53	28	40	17	443	300	r 1
	1000	−688	−95	−129	−83	−29	−33	−31	−557	−334	r 2
		1000	76	2	103	1	−126	28	345	166	<2
			1000	35	15	20	−156	18	307	205	u 3
				1000	−141	−34	19	−82	136	69	u 5
					1000	−41	−107	35	85	24	u 6
						1000	45	−1	62	7	u 8
							1000	−6	16	45	u 9
								1000	41	45	u10
									1000	248	k 1
										1000	k 2

DISCUSSION

The difficulties encountered in the present study illustrate well the limitations of electron diffraction as a method of structural determination for molecules that have low symmetry, or several sets of interatomic distances that are so similar as to be unresolvable. The number of peaks above 250 pm in the radial distribution curve for bis(difluorophosphino)ether (Fig. 2) indicates that a C_s or C_2 structure is impossible. In addition, the P–F and P–O distances appear as a single peak at about 155 pm, as do the F...F and F...O distances, at 240 pm. But if the molecule has no symmetry at all, then there are no grounds for assuming that the two F_2PO– groups are equivalent and have planes of symmetry. Thus the structure of each such group depends on six parameters (three bond lengths and three angles), giving 12 in all, compared with four in our idealised model. It may be, therefore, that although refinement C fits the experimental data much better than refinement B, the latter could be improved by applying one or more of the eight possible distortions to the F_2PO– groups, while keeping the mean values of the P–F, P–O, F...F and F...O distances unchanged.

However, despite the uncertainties outlined above, certain features of the structure are quite clear. In particular, the phosphorus–oxygen bond length is short compared with the value of 171 pm predicted by the Schomaker–Stevenson rule[18], and with most experimental values[19, 20]. This shortness, and the wide POP angle (2.53 rad, 145°) suggest that, as in disilyl ether, which has an SiOSi angle of 2.51 rad (144°), the bonds to oxygen are not simple single bonds. It thus seems probable that in both molecules, the bonds are strengthened by delocalisation of lone-pair electrons from oxygen into low-lying vacant phosphorus or silicon orbitals.

The conformation of the F_2P– groups is interesting. The very small amplitudes of vibration found for three of the P...F atom pairs suggest that the amplitudes of the torsional vibrations are not very great and the distinct peaks in the radial distribution curve show clearly that one conformation is preferred. These amplitudes may also reflect to some extent the quality of the intensity data in the region of

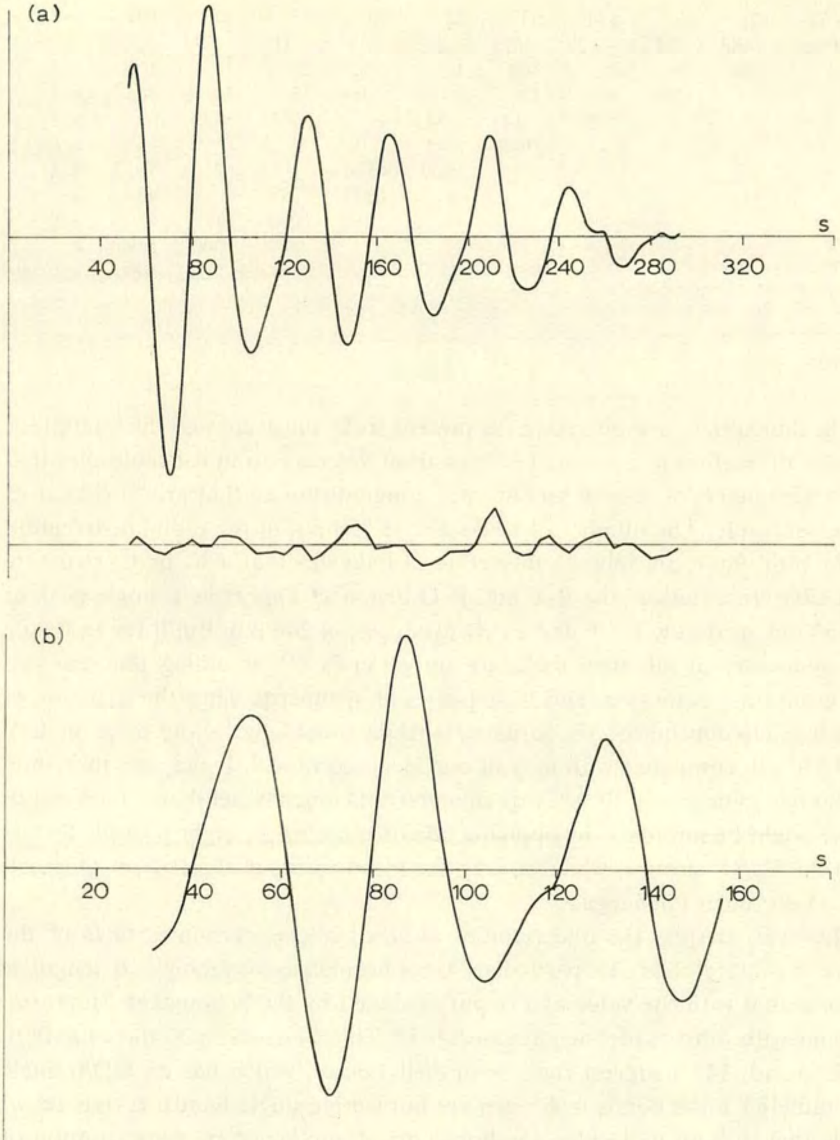


Fig. 1. Observed and final weighted difference molecular scattering intensities for bis(difluorophosphino)ether for nozzle-to-plate distances of (a) 250 mm and (b) 500 mm.

$s = 200\ \mathrm{nm}^{-1}$, and too much significance should not be attached to the values given. But the conformation adopted cannot be attributed solely to fluorine–fluorine interactions, for the shortest such distance observed is over 310 pm, compared with 270 pm for twice the van der Waal's radius of fluorine. Thus the structure must be determined by the interactions of the lone pairs of electrons on the phosphorus and oxygen atoms, both with each other and with the fluorine atoms.

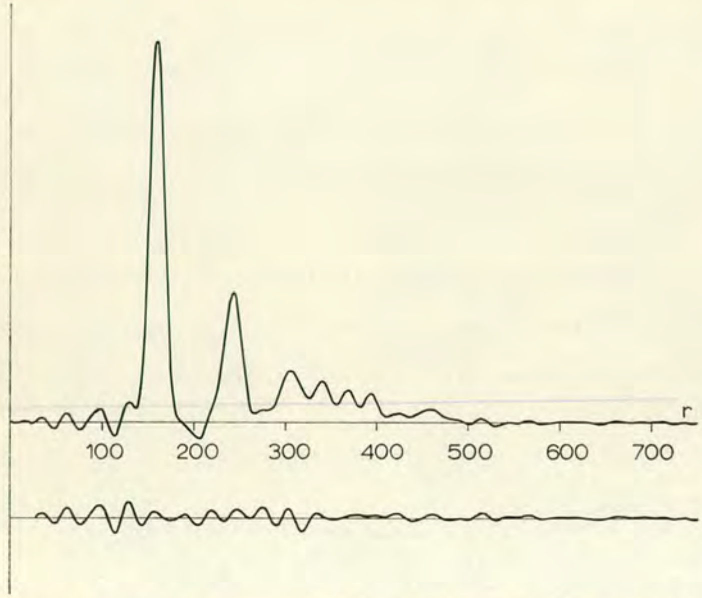


Fig. 2. Observed and difference radial distribution curves, $P(r)/r$, for bis(difluorophosphino)ether. Before Fourier inversion, the data were multiplied by $s \exp(-0.0015s^2)/(z_P - f_P)\ (z_F - f_F)$.

Our understanding of the conformation-determining forces in this type of molecule may well be helped by a study of the structure of bis(difluorophosphino)-sulphide. An NMR study of this molecule[21] has indicated that there must be considerable interaction between the two F_2P– groups. With a probable PSP angle of about 1.7 to 1.8 rad, the P...F and F...F distances should on average be much shorter than in the ether, and the freedom of rotation or torsion should be even more restricted than in the present case.

It should be pointed out that, in the absence of a full vibrational analysis for bis(difluorophosphino)ether, no shrinkage corrections have been applied in the refinements. As a consequence, the observed POP angle will probably be somewhat smaller than the true average angle, and the dihedral angles may also differ from those in the average structure. However, the observed amplitudes of vibration suggest that the torsional vibrations have small amplitudes, and so the corresponding shrinkage corrections will be small.

ACKNOWLEDGEMENTS

We thank Professor D. W. J. Cruickshank, Dr. B. Beagley and Dr. M. J. Smyth for the provision of experimental facilities.

REFERENCES

1 G. C. Holywell, D. W. H. Rankin, B. Beagley and J. M. Freeman, *J. Chem. Soc. (A)*, (1971) 785.
2 G. C. Holywell and D. W. H. Rankin, *J. Mol. Structure, 9* (1971) 11.
3 D. W. H. Rankin and S. J. Cyvin, *J. Chem. Soc. Dalton Trans.*, (1972) 1277.
4 D. E. J. Arnold, E. A. V. Ebsworth, H. F. Jessep and D. W. H. Rankin, *J. Chem. Soc. Dalton Trans.*, (1972) 1681.
5 C. Glidewell, D. W. H. Rankin, A. G. Robiette and G. M. Sheldrick, *J. Mol. Structure, 6* (1970) 231.
6 J. Sheridan and A. C. Turner, *Proc. Chem. Soc.*, (1960) 21.
7 S. J. Cyvin, J. Brunvoll and A. G. Robiette, *Chem. Phys. Letters, 11* (1971) 263.
8 A. Almenningen, O. Bastiansen, V. Ewing, K. Hedberg and M. Traetteberg, *Acta Chem. Scand., 17* (1963) 2455.
9 C. Glidewell, D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, B. Beagley and S. Cradock, *J. Chem. Soc. (A)*, (1970) 315.
10 S. Cradock and D. W. H. Rankin, *J. Chem. Soc. Faraday Trans. II, 68* (1972) 940.
11 L. Centofanti and R. W. Rudolph, *Inorg. Synth., 12* (1970) 281.
12 B. Beagley, A. H. Clark and T. G. Hewitt, *J. Chem. Soc. (A)*, (1968) 658.
13 D. M. Bridges, G. C. Holywell, D. W. H. Rankin and J. M. Freeman, *J. Organometallic Chem., 32* (1971) 87.
14 H. L. Cox and R. A. Bonham, *J. Chem. Phys., 47* (1967) 2599.
15 Y. Murata and Y. Morino, *Acta Cryst., 20* (1967) 605.
16 L. S. Bartell, *J. Chem. Phys., 23* (1955) 1219.
17 W. C. Hamilton, *Statistics in Physical Science,* Ronald Press, New York, 1964.
18 V. Schomaker and D. P. Stevenson, *J. Amer. Chem. Soc., 63* (1941) 37.
19 I. A. Karle and K. Britts, *Acta Cryst., 20* (1967) 118.
20 N. L. Paddock, J. Trotter and S. H. Whitlow, *J. Chem. Soc. (A)*, (1968) 2227.
21 R. W. Rudolph and R. A. Newmark, *J. Amer. Chem. Soc., 92* (1970) 1195.