Preparation and Properties of Bis(difluorophosphino)- and Tris(difluorophosphino)-amine

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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,

$$NH_3 + 3PF_2Cl + 3Me_3N \longrightarrow (F_2P)_3N + 3[Me_3HN]Cl \qquad (1)$$

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).

$$F_2PNH_2 + 2PF_2Cl + 2Me_3N \longrightarrow (F_2P)_3N + 2[Me_3HN]Cl \qquad (2)$$

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

$$F_2PNH_2 + PF_2Cl + Me_3N \longrightarrow (F_2P)_2NH + [Me_3HN]Cl \qquad (3)$$

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

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[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-

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[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 $(F_2P)_3N$

	Raman		
I.r. (gas)	liquid	CCl_3F solution	Assignment
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	ν(PN)
912vs	905w, p	907m	
878w (sh)			
863 vs *P*	874m, p	869s	ν(PF)
858 *Q*			
843 *P*			
838 vs*Q*	837s, p	*	
833 *R*			
816vs	805m, dp	*ca.* 805m	
706w			363 + 345
	558vs, p	557vs	ν(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			ν(NH)
3 333m	2 472w	3 322w	3 313w	
1 248ms	1 066m			δ(NH)
1 210ms	1 044m			
	941vs			
919s	914w	920w	*ca.* 930w	ν_{asym}(PNP)
863s	888s	880vs	885vs	ν(PF) δ(NH)?
830vs	838vs	830m	838s	
823	832vs (sh)			
816 vs	816vs	797s	792s	
810				
747m	741m	743m	775s	ν_{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	δ(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.

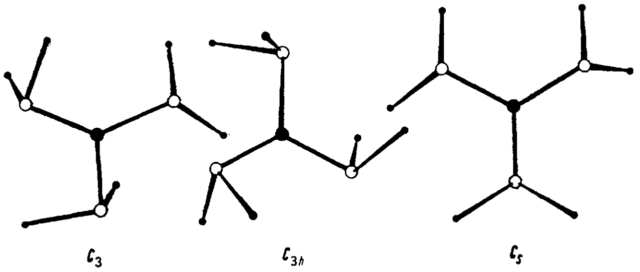

FIGURE 1 Possible structures for $(F_2P)_3N$

The conformation of the PF_2 groups also affects the point group of $(F_2P)_2NH$. Our studies of $H \cdots F$ 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 $H \cdots F$ 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.

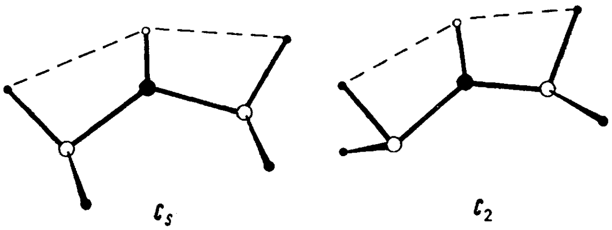

FIGURE 2 Possible structures for $(F_2P)_2NH$. The broken lines represent possible $H \cdots F$ interactions

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. 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 are probably at least three other routes, (9)—(11), by 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]

$$[(F_2P)_3N]^+ \longrightarrow [(F_2P)NPF]^+ + PF_3 \tag{6}$$

$$[(F_2P)NPF]^+ \longrightarrow [PF_3]^+ + PN \tag{7}$$

$$[(F_2P)_2NH]^+ \longrightarrow [(F_2P)NPF]^+ + HF \tag{8}$$

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

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

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

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

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[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.* ^1H, ^{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 ^1H, ^{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

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* 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.

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