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(Si–N) = 1·720 ± 0·008; r(N–P) = 1·657 ± 0·007; r(P–F) = 1·574 ± 0·003 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 been interested in the geometries and electronic structures of silicon–nitrogen compounds and have investigated the reaction between silyl halides and PF_2NH_2.

$$3RNH_2 + 2SiH_3X \longrightarrow 2RNH_3X + RN(SiH_3)_2 \quad (1)$$

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	$s_{min.}$	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

$r1$	$r2$	$r4$	∠1	∠3	∠5	$u6$	$u11$	$u19$	$k1$	$k2$	$k3$	
1000	−690	508	−15	107	−97	−202	−27	0	−204	3	40	$r1$
	1000	−543	−94	−144	131	329	34	−37	223	34	−18	$r2$
		1000	292	111	−169	57	65	119	333	458	102	$r4$
			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	$u6$
							1000	90	158	116	7	$u11$
								1000	182	161	6	$u19$
									1000	376	38	$k1$
										1000	49	$k2$
											1000	$k3$

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.

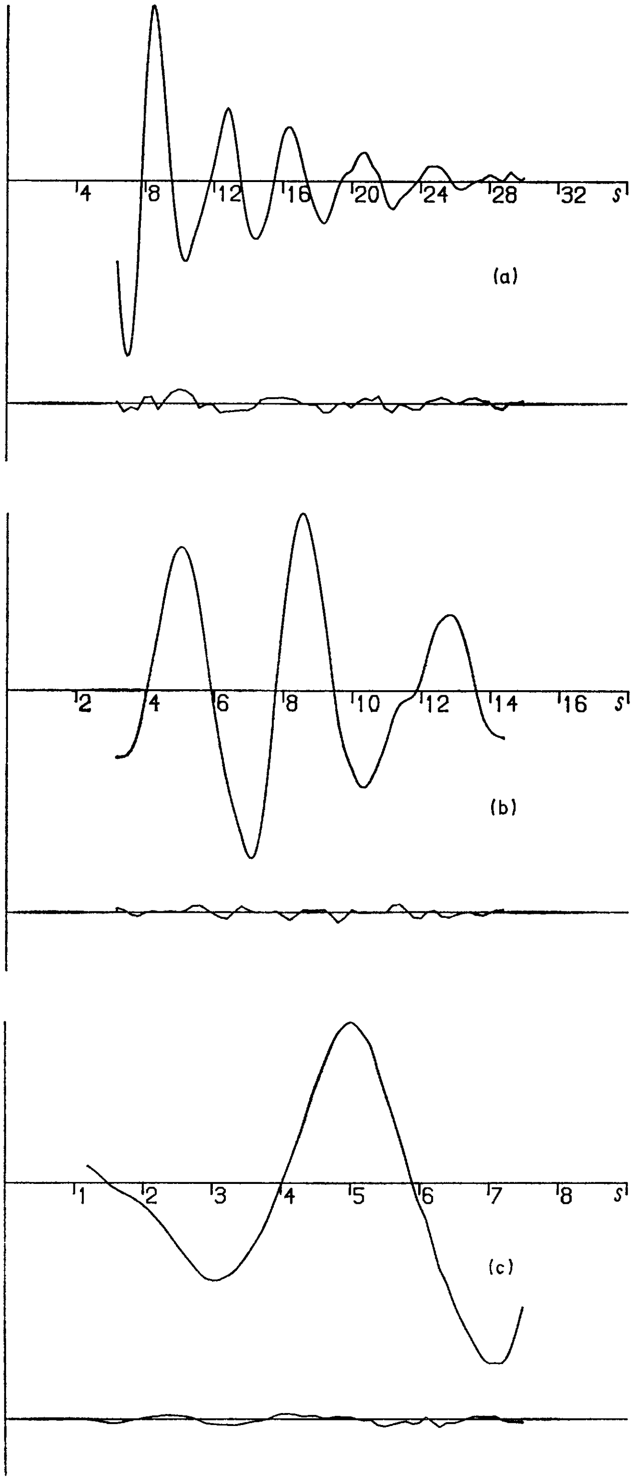

FIGURE 1 Observed and final weighted difference molecular scattering intensities for silylaminodifluorophosphine; nozzle-to-plate distances (a) 250, (b) 500 and (c) 1000 mm

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 $\mathrm{SiH_3{\cdot}NH{\cdot}PF_2}$ and related species

$\mathrm{SiH_3{\cdot}NH{\cdot}PF_2}$		$\mathrm{SiH_3{\cdot}ND{\cdot}PF_2}$		$\mathrm{SiD_3{\cdot}NH{\cdot}PF_2}$	$\mathrm{SiD_3{\cdot}ND{\cdot}PF_2}$	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	$\delta\mathrm{SiH_3}$, 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	$\rho\mathrm{SiH_3}$, $\delta\mathrm{SiD_3}$
			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	$\delta\mathrm{PF_2}$
320m		320m		317m	316m	
315m	311m	314m	312s	311m	311m	$\delta\mathrm{PF_2}$
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 $\mathrm{SiD_3{\cdot}NH{\cdot}PF_2}$ vapour; moreover, there are two bands of almost equal intensity near 2500 $\mathrm{cm^{-1}}$ in the spectra of both $\mathrm{SiH_3{\cdot}ND{\cdot}PF_2}$ and $\mathrm{SiD_3{\cdot}ND{\cdot}PF_2}$, 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 $\mathrm{SiH_3{\cdot}NH{\cdot}PF_2}$ and of $\mathrm{SiD_3{\cdot}NH{\cdot}PF_2}$ near 1250 and 1200 $\mathrm{cm^{-1}}$; 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 [$R_G = (\mathbf{U'WU/I'WI})^{1/2}$ where **I** and **U** are the vectors of observed intensities and residuals and **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 $\cdots$ Si distance that was approximately three times greater than those found for the F $\cdots$ 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), $\angle$FPN, $\angle$NSiH, $\angle$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 $\cdots$ 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.

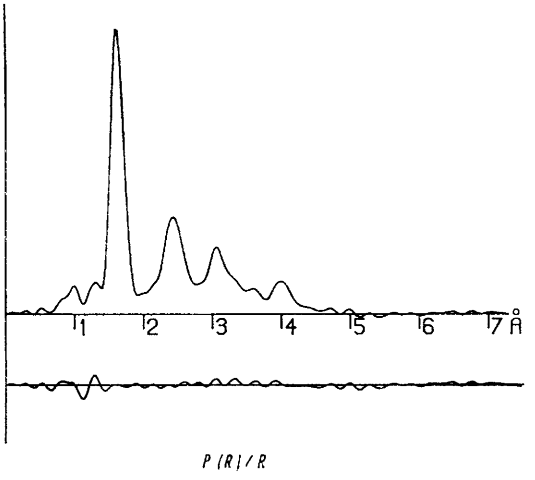

FIGURE 2 Observed and difference radial distribution curves, $P(r)/r$, for silylaminodifluorophosphine. Before Fourier inversion the data were multiplied by $s\exp(-0\cdot0015\, s^2)/(z_P - f_P)(z_F - f_F)$

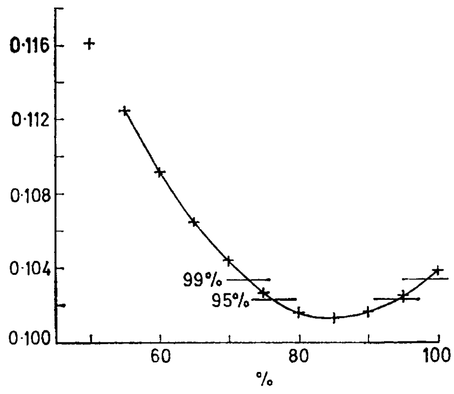

FIGURE 3 Variation in *R* factor with percentage of conformer with PF_2 twist angle of 90°, showing 95 and 99·5% confidence limits

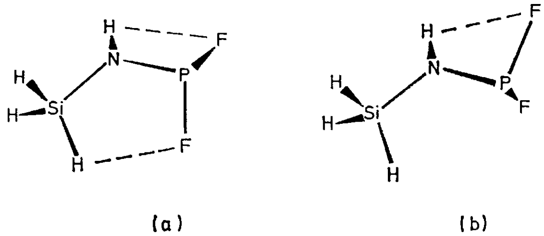

FIGURE 4 The two configurations of silylaminodifluorophosphine. Conformer (A) has a PF_2 twist angle of 90° and conformer (B) has a twist of 26°

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.

$$2SiH_3X + 3PF_2NH_2 \longrightarrow PF_2X + NH_4X + 2SiH_3\cdot NH\cdot PF_2 \qquad (2)$$

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, 21st February,* 1972]