# The Molecular Structures of Difluorophosphino(disilyl)amine and Bis-(difluorophosphino)silylamine in the Gas Phase, determined by Electron Diffraction

By **Graham S. Laurenson** and **David W. H. Rankin,*** Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

The molecular structures of difluorophosphino(disilyl)amine and bis(difluorophosphino)silylamine in the gas phase have been determined by electron diffraction. Both molecules have planar co-ordination at nitrogen, and Si–N bonds that are substantially longer than those in other silylamines. Principal bonds and angles ($r_a$) for $N(PF_2)(SiH_3)_2$ are $r$(P–F) 158.5(3), $r$(P–N) 168.0(4), $r$(Si–N) 175.5(4) pm; FPF 96.9(10), FPN 99.4(7), and SiNSi 119.3(17)°. For $N(PF_2)_2(SiH_3)$ principal parameters are $r$(P–F) 157.0(2), $r$(P–N) 169.1(4), $r$(Si–N) 176.7(7) pm; FPF 96.1(5), FPN 99.3(3), and PNP 117.6(7)°. In each compound the conformation adopted by the difluorophosphino-groups is such that the axes of the nitrogen and phosphorus lone-pair orbitals are approximately orthogonal.

THE molecular geometries of silicon- and phosphorus-substituted amines have been extensively studied. Trisilylamine [1,2] is the most widely known inorganic compound with planar co-ordination at nitrogen, and the wide SiNSi angle in disilylamine [3] suggests that the three bonds to nitrogen are coplanar. Similarly, the tertiary difluorophosphinoamine, $N(PF_2)_3$, has a planar $NP_3$ skeleton,[4] and the secondary amine has a wide PNP angle.[5,6] The planarity of the nitrogen in the primary amine, $NH_2(PF_2)$, is not so definitely established: a microwave study [7] suggests that the $PNH_2$ group is planar, whereas limited information from an electron-diffraction study favours a non-planar arrangement.[8] This apparent anomaly may arise from a low-frequency out-of-phase deformation, which would give a large shrinkage effect,[9] and similar low-frequency modes may account for the apparent non-planarity of the $NC_2Si$ and $NC_2P$ skeletons of $NMe_2(PF_2)$ [8] and $NMe_2(SiH_3)$.[10]

However, of the three amines containing both silyl and difluorophosphino-substituents, only one, $NH(PF_2)(SiH_3)$, has been the subject of a structural study.[11] It was therefore important to study the other two, $N(PF_2)_2(SiH_3)$ and $N(PF_2)(SiH_3)_2$, as these would be expected to have planar arrangements of the bonds to nitrogen. It was also of interest to see whether there was any evidence of competition between phosphorus and silicon for the nitrogen lone pair of electrons, leading to a shortening of one type of bond to nitrogen at the expense of the other type. Finally, the conformations adopted by the difluorophosphino-groups were of interest, as predictions about these had been made on the basis of n.m.r. coupling constants.[12]

## EXPERIMENTAL

Samples of difluorophosphino(disilyl)amine and bis-(difluorophosphino)silylamine were prepared by literature methods [12] and purified by fractional condensation *in vacuo*: purities were checked spectroscopically.

Electron-diffraction scattering intensities were recorded using the Cornell–Edinburgh diffraction apparatus,[5,13] with nozzle-to-plate distances of 128 and 285 mm, and an accelerating voltage of *ca.* 43 kV. During exposure samples were maintained at 250 K, and the nozzle at room temperature, 293 K. Data were recorded on Kodak Electron Image plates, and obtained in digital form using a Jarrell–Ash double-beam microphotometer, with spinning plates.[14] The electron wavelengths were determined from the scattering patterns of gaseous benzene, recorded immediately before or after the sample plates.

All calculations were carried out on an ICL 2970 computer at the Edinburgh Regional Computing Centre, using established data reduction [5] and least-squares refinement programs.[15] Weighting points used in setting up the off-diagonal weight matrices are given, together with other experimental data, in Table 1. In all calculations the complex scattering factors of Schäfer *et al.*[16] were used.

*Refinement.—Difluorophosphino(disilyl)amine.* In refinements of the structure of $N(PF_2)(SiH_3)_2$ it was assumed that the $N(PF_2)$ group had local $C_s$ symmetry, and that the two $N(SiH_3)$ groups had local $C_{3v}$ symmetry. The $N(SiH_3)_2$ group was assumed to have $C_2$ symmetry, with the two $SiH_3$ groups twisted away from the conformation in which one Si–H bond of each group was *trans* to the further N–Si bond. The $PNSi_2$ group was initially assumed to be planar, with $C_{2v}$ symmetry, but distortions of the P–N bond, both in the plane and perpendicular to it, were subsequently permitted: in the final refinements the distortion in the plane was the only one allowed. Finally, the $PF_2$ group was

TABLE 1

Weighting functions, correlation parameters, and scale factors

| Compound | Camera height/mm | Wavelength/pm | $\Delta s$/nm$^{-1}$ | $s_{min.}$/nm$^{-1}$ | $sw_1$/nm$^{-1}$ | $sw_2$/nm$^{-1}$ | $s_{max.}$/nm$^{-1}$ | $p/h$ | Scale factor |
|---|---|---|---|---|---|---|---|---|---|
| $N(PF_2)(SiH_3)_2$ | 128.5 | 5.799 | 4 | 60 | 80 | 230 | 260 | 0.146 | 0.806(14) |
| | 284.3 | 5.799 | 2 | 26 | 40 | 120 | 144 | 0.469 | 0.727(13) |
| $N(PF_2)_2(SiH_3)$ | 128.4 | 5.854 | 4 | 64 | 80 | 240 | 316 | 0.348 | 0.960(18) |
| | 285.6 | 5.854 | 2 | 26 | 30 | 120 | 142 | 0.446 | 0.900(13) |

allowed to twist, about the P–N bond, with zero twist angle defined for the conformation in which the FPF angle bisector lay in the $NSi_2$ plane.

With these assumptions, the structure was defined by 11 geometrical parameters. Although there were strong correlations between parameters (Table 2) caused by overlap of peaks in the radial distribution curve (Figure 1), it was soon clear that the $PNSi_2$ skeleton was planar, and that the three angles at nitrogen were equal, within experimental error. Most of the other heavy-atom parameters refined easily, but the three bonded distances P–F, P–N, and Si–N were strongly correlated, and occasionally the relative positions of the P–F and P–N distances would reverse. On the basis of known bond lengths in other difluorophosphinoamines [4,5,8,11,17] the ratio $r$(P–N) : $r$(P–F) was assumed to be 1.060 ± 0.002 : 1, and this 'predicate observation' [18] was used as an additional experimental datum in subsequent refinements. Similarly, the ratio F–P–N : F–P–F was taken to be 1.035 ± 0.015 : 1, and this mild constraint was sufficient to stabilise the refinements.

The conformation adopted by the $-PF_2$ group was found by fixing the twist angle at various values, and comparing the $R$ factors obtained. By coincidence, the radial distribution curves for twist angles of 10 and 80° are extremely similar but the 10° form gives a significantly lower $R$ factor, and other parameters refine to more reasonable values with the larger twist angle. The silyl twist angle was also found by a similar process, but other parameters associated with hydrogen-atom positions could not be refined, and were fixed at reasonable values.

The results of the final refinement, for which $R_G$ was 0.08 and $R_D$ was 0.06, are given in Table 3. Errors quoted are

TABLE 2

Least-squares correlation matrix (× 100) for $N(PF_2)(SiH_3)_2$ *

| | | | Angle | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $r_1$ | $r_2$ | $r_3$ | 1 | 2 | 4 | 5 | 7 | $u_2$ | $u_5$ | $u_6$ | $u_{11}$ | $u_{14}$ | $u_{26}$ | $k_1$ | $k_2$ | |
| 100 | 42 | | | | | | | 56 | | | | | | | | $r_1$ |
| | 100 | | | | | | | 69 | | | | | | | | $r_2$ |
| | | 100 | | | | | −53 | | | | | | | 51 | | $r_3$ |
| | | | 100 | −45 | −40 | | | | 67 | | | | | | | 1 |
| | | | | 100 | | | | | −62 | | −55 | | | | | 2 |
| | | | | | 100 | −57 | | | | | −79 | | −45 | | | 4 |
| | | | | | | 100 | | | | | | | | | | 5 |
| | | | | | | | 100 | | | 43 | | | 46 | −42 | −43 | 7 |
| | | | | | | | | 100 | | | | | | | | $u_2$ |
| | | | | | | | | | 100 | | | | | | | $u_5$ |
| | | | | | | | | | | 100 | | | 46 | | | $u_6$ |
| | | | | | | | | | | | 100 | −44 | | | | $u_{11}$ |
| | | | | | | | | | | | | 100 | | | | $u_{14}$ |
| | | | | | | | | | | | | | 100 | | | $u_{26}$ |
| | | | | | | | | | | | | | | 100 | | $k_1$ |
| | | | | | | | | | | | | | | | 100 | $k_2$ |

Angle

* Only elements with absolute values ⩾40 are included.

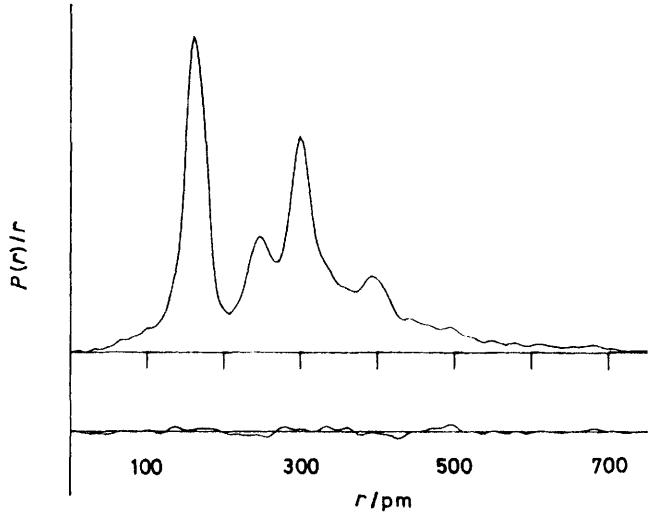


FIGURE 1 Observed and difference radial distribution curves, $P(r)/r$, for $N(PF_2)(SiH_3)_2$. Before Fourier inversion the data were multiplied by $s \cdot \exp[-0.000\,015\ s^2/(Z_P - f_P)(Z_F - f_F)]$

TABLE 3

Molecular parameters for $N(PF_2)(SiH_3)_2$ *

| | Distance/pm | Amplitude/pm |
|---|---|---|
| (*a*) Independent distances | | |
| $r_1$ (P–F) | 158.5(3) | 4.7 (fixed) |
| $r_2$ (P–N) | 168.0(4) | 5.3(5) |
| $r_3$ (Si–N) | 175.5(4) | 5.3 (tied to $u_3$) |
| $r_4$ (Si–H) | 149.0 (fixed) | 8.8 (fixed) |
| (*b*) Dependent distances | | |
| $d_5$ (F · · · N) | 249.1(12) | 10.8(11) |
| $d_6$ (F · · · Si) | 407.3(15) | 11.3(12) |
| $d_7$ (F · · · Si) | 385.4(21) | 11.3 (tied to $u_6$) |
| $d_8$ (F · · · Si) | 295.7(22) | 11.3 (tied to $u_6$) |
| $d_9$ (F · · · Si) | 324.0(19) | 11.3 (tied to $u_6$) |
| $d_{10}$ (F · · · F) | 237.3(18) | 10.8 (tied to $u_5$) |
| $d_{11}$ (Si · · · Si) | 304.0(25) | 10.1(6) |
| $d_{12}$ (Si · · · P) | 296.7(13) | 10.1 (tied to $u_{11}$) |
| $d_{13}$ (Si · · · P) | 298.1(23) | 10.1 (tied to $u_{11}$) |
| $d_{14-25}$ (F · · · H) | 255.5—514.7 | 11.1(39) |
| $d_{26-28}$ (P · · · H) | 309.9—402.2 | 11.9(39) |
| $d_{29}$ (N · · · H) | 266.2(15) | 12.0 (fixed) |
| $d_{30-32}$ (Si · · · H) | 339.5—428.4 | 11.9 (tied to $u_{26}$) |
| $d_{33}$ (H · · · H) | 242.5 (fixed) | 12.0 (fixed) |
| $d_{34-39}$ (H · · · H) | 296.7—530.8 | 20.0 (fixed) |

| (*c*) Independent angles/° | |
|---|---|
| Angle 1 (F–P–F) | 96.9(10) |
| Angle 2 (F–P–N) | 99.4(7) |
| Angle 3 (N–Si–H) | 110 (fixed) |
| Angle 4 (Si–N–Si) | 120.0(15) |
| Angle 5 (P–N in plane def.) | 0.5(9) |
| Angle 6 ($SiH_3$ twist) | 8 (fixed) |
| Angle 7 ($PF_2$ twist) | 14.0 (12) |

* All distances are $r_a$.

estimated standard deviations obtained in the least-squares analysis, increased to allow for systematic errors. The observed and final weighted difference molecular scattering intensities are shown in Figure 2. The structure of the molecule is shown in Figure 3(*a*).

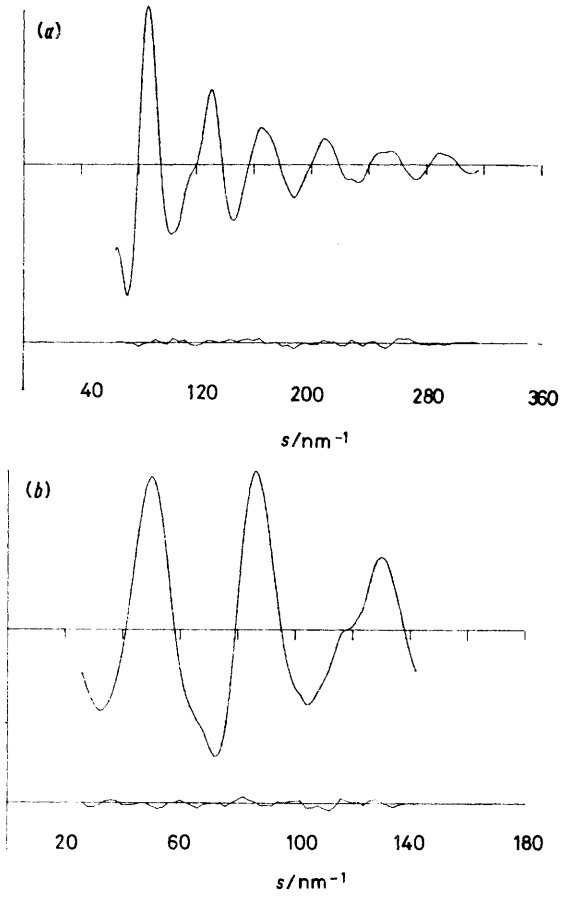


FIGURE 2 Observed and final weighted difference molecular scattering intensities for $N(PF_2)(SiH_3)_2$ at nozzle-to-plate distances of (*a*) 128 and (*b*) 284 nm

*Bis(difluorophosphino)silylamine.*—In the molecular model used for the refinements of this structure, it was assumed that the two $N(PF_2)$ groups were identical, and had $C_s$ symmetry, that the $N(SiH_3)$ group had $C_{3v}$ local

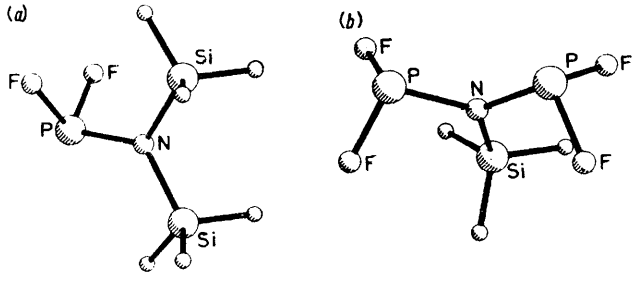


FIGURE 3 Molecular structures of (*a*) $N(PF_2)(SiH_3)_2$ and (*b*) $N(PF_2)_2(SiH_3)$

symmetry, and that the $P_2NSi$ skeleton had $C_s$ symmetry. It was soon apparent that the bonds to nitrogen were co-planar, and in the later refinements this was assumed, with a single angle (PNP) describing the co-ordination at nitrogen.

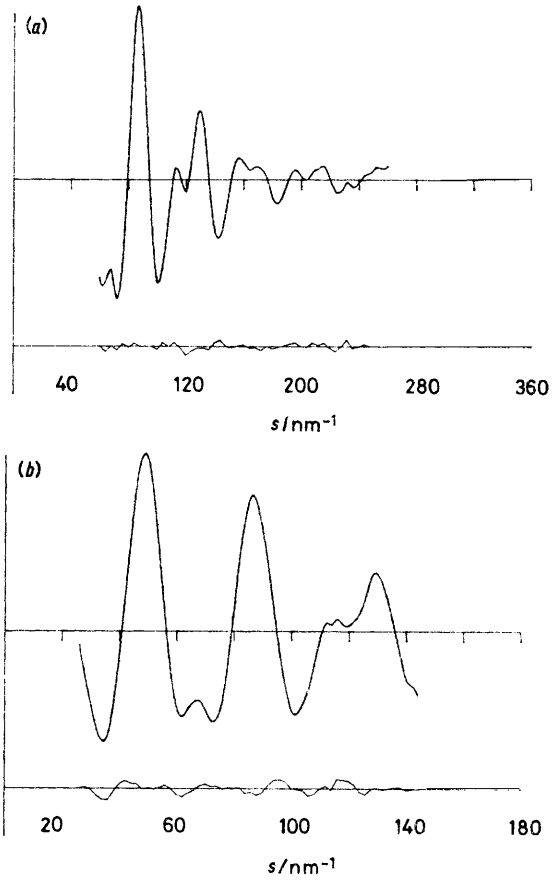


FIGURE 4 Observed and final weighted difference molecular scattering intensities for $N(PF_2)_2(SiH_3)$ at nozzle-to-plate distances of (*a*) 128 and (*b*) 285 nm

The conformation was described by three angles. The $SiH_3$ twist angle was taken to be zero when one Si–H bond lay in the skeletal plane. The two $PF_2$ twist angles were defined to be zero when the FPF angle bisectors lay *cis*

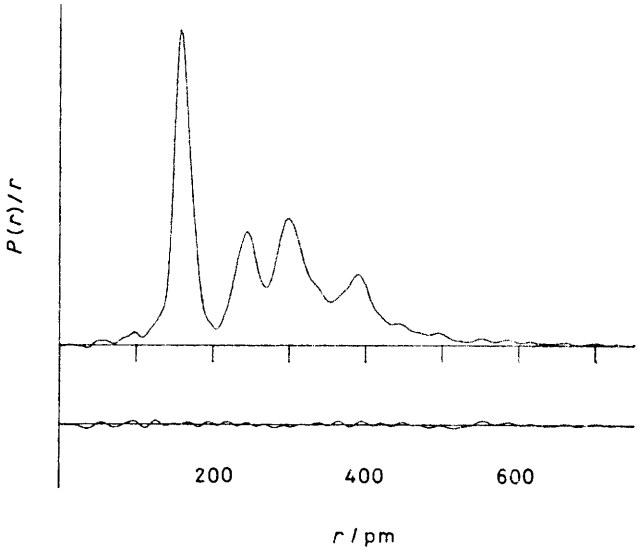


FIGURE 5 Observed and difference radial distribution curves, $P(r)/r$, for $N(PF_2)_2(SiH_3)$. Before Fourier inversion the data were multiplied by $s \cdot \exp[-0.000\,015\ s^2/(Z_P - f_P)(Z_F - f_F)]$

to the N–Si bond. These two angles could be constrained to be equal, or equal and opposite, giving $C_2$ or $C_s$ symmetry to the $N(PF_2)_2Si$ unit, or they could be varied independently.

TABLE 4

Molecular parameters for $N(PF_2)_2(SiH_3)$ *

| | | Distance/pm | Amplitude/pm |
|---|---|---|---|
| (*a*) | Independent distances | | |
| | $r_1$ (P–F) | 157.0(2) | 4.7(3) |
| | $r_2$ (P–N) | 169.1(4) | 5.2 (tied to $u_1$) |
| | $r_3$ (Si–N) | 176.7(7) | 5.2 (tied to $u_1$) |
| | $r_4$ (Si–H) | 145.8(30) | 8.8 (fixed) |
| (*b*) | Dependent distances | | |
| | $d_5$ (N · · · F) | 248.7(5) | 8.1(8) |
| | $d_6$ (F · · · F) | 233.5(8) | 8.1 (tied to $u_5$) |
| | $d_7$ (F · · · F) | 496.5(8) | 21.2(25) |
| | $d_8$ (F · · · F) | 431.2(7) | 21.2 (tied to $u_7$) |
| | $d_9$ (F · · · F) | 445.2(7) | 21.2( tied to $u_7$) |
| | $d_{10}$ (F · · · Si) | 316.2(31) | 25.6(25) |
| | $d_{11}$ (F · · · Si) | 309.6(30) | 25.6 (tied to $u_{10}$) |
| | $d_{12}$ (P · · · Si) | 301.2(6) | 11.5(7) |
| | $d_{13}$ (P · · · F) | 386.5(24) | 14.0(7) |
| | $d_{14}$ (P · · · F) | 391.8(21) | 14.0 (tied to $u_{13}$) |
| | $d_{15}$ (P · · · P) | 289.3(11) | 11.5 (tied to $u_{12}$) |
| | $d_{16-27}$ (F · · · H) | 260.5—455.8 | 22 (fixed) |
| | $d_{28}$ (H · · · H) | 237.3(50) | 18 (fixed) |
| | $d_{29-31}$ (P · · · H) | 328.6—419.0 | 18 (fixed) |
| | $d_{32}$ (N · · · H) | 264.7(21) | 15 (fixed) |
| (*c*) | Independent angles/° | | |
| | Angle 1 (F–P–F) | | 96.1(5) |
| | Angle 2 (F–P–N) | | 99.3(3) |
| | Angle 3 (P–N–P) | | 117.6(7) |
| | Angle 4 (N–Si–H) | | 110 (fixed) |
| | Angle 5 ($PF_2$ twist) | | −3.3(27) |
| | Angle 6 ($SiH_3$ twist) | | 50 (fixed) |

* All distances are $r_a$.

Of the 11 geometrical parameters, only the NSiH and the $SiH_3$ twist angles could not be refined. The latter was fixed at 50°, the value giving the lowest $R$ factor in a series of test refinements. The $PF_2$ twist angles were varied over a wide range, but the lowest $R$ factors were obtained when both angles were close to zero; a small $C_s$ distortion was preferred to a $C_2$ distortion.

The results of the final refinement, for which $R_G$ was 0.06 and $R_D$ was 0.04, are listed in Table 4, and the least-squares correlation matrix is given in Table 5. The intensity data are shown in Figure 4, and the radial distribution curve in Figure 5. The molecular structure is shown in Figure 3(*b*).

TABLE 5

Least-squares correlation matrix (× 100) for $N(PF_2)_2(SiH_3)$ *

| $r_1$ | $r_2$ | $r_3$ | $r_4$ | Angle 1 | Angle 2 | Angle 3 | Angle 5 | $u_1$ | $u_5$ | $u_7$ | $u_{10}$ | $u_{12}$ | $u_{13}$ | $k_1$ | $k_2$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 100 | | 51 | | | | | | 40 | | | | | | | | $r_1$ |
| | 100 | −43 | | | −57 | | | | | | | | | | | $r_2$ |
| | | 100 | | | | 46 | | 40 | | | 46 | | | | | $r_3$ |
| | | | 100 | | | | | | | | | | | −49 | −47 | $r_4$ |
| | | | | 100 | | | | | 66 | | | | | | | 1 |
| | | | | | 100 | | | | −35 | | −43 | | | | | 2 |
| | | | | | | 100 | | | | | | 65 | | | | 3 |
| | | | | | | | 100 | | | 48 | 48 | | 69 | | | 5 |
| | | | | | | | | 100 | | | | | | 47 | | $u_1$ |
| | | | | | | | | | 100 | | | | | | | $u_5$ |
| | | | | | | | | | | 100 | | | 48 | | | $u_7$ |
| | | | | | | | | | | | 100 | | | 48 | 48 | $u_{10}$ |
| | | | | | | | | | | | | 100 | | | | $u_{12}$ |
| | | | | | | | | | | | | | 100 | | | $u_{13}$ |
| | | | | | | | | | | | | | | 100 | 64 | $k_1$ |
| | | | | | | | | | | | | | | | 100 | $k_2$ |

Angle

* Only elements with absolute values ≥ 40 are included.

## DISCUSSION

The gas-phase structures of $N(PF_2)(SiH_3)_2$ and $N(PF_2)_2(SiH_3)$ in both cases reveal an entirely planar arrangement of ligands around nitrogen. The absence of any apparent shrinkage due to out-of-plane deformations of the $NR_3$ group may be attributed to the fact that the atoms bound to nitrogen in all cases contact each other at distances approximating to the sums of their Bartell hard-sphere radii,[19] precluding closer approach.

The angles at nitrogen are 120° within experimental error in the case of $N(PF_2)(SiH_3)_2$. A slight narrowing of the PNP angle in $N(PF_2)_2(SiH_3)$ from 120° [118.2(10)°] may be due to the absence of steric crowding between neighbouring $PF_2$ groups, since the fluorines tend to point away from each other in the preferred conformation.

In both molecules $r$(Si–H) was fixed at a reasonable value and $r$(P–F) refined to a value consistent with those expected for the $F_2PN$ moiety, as shown in Table 6. Since some π character can be assigned to the R–N bonds, which are in all cases shorter than those expected for a corresponding single bond, some interest lay in investigating the effect of $PF_2$ and silyl groups competing for the lone pair on nitrogen. It was found that while the P–N bond lengths for the mono and bis $PF_2$ species, being 168.0(4) pm and 169.1(4) pm respectively, were substantially shorter than those found in $N(PF_2)_3$ [171.1(4) pm],[4] the Si–N bond lengths in both cases were some 2—3 pm longer than that measured in trisilylamine (Table 6). This clearly demonstrates that the $PF_2$ group has a greater propensity for accepting electron density from the $p$ orbital on nitrogen than the silyl group, and this is almost certainly due to the electron-withdrawing effect of the fluorines bonded to phosphorus. It has been shown that replacing hydrogens with fluorines on silyl groups bound to nitrogen shortens the Si–N bond,

from 171.5 pm in $NMe_2(SiH_3)$ [10] to 165 pm in $NMe_2(SiF_3)$.[20] We hope soon to undertake a gas-phase study of the molecular $NH(PMe_2)_2$ which may therefore be expected to have P–N bonds substantially longer than those found for $NH(PF_2)_2$.

The angles at phosphorus require no special comment: analysis of the last molecule. In $N(PF_2)(SiH_3)_2$ the FPF bisector was found to lie 14° away from the skeletal plane, corresponding to a substantially larger torsional vibration than that found for $N(PF_2)_2(SiH_3)$.

In both molecules studied here, attractive H · · · F interactions almost certainly play the major part in

TABLE 6

Geometric parameters for some difluorophosphino- and silyl-amines

| Compound | Distances/pm | | | Angles/° | |
|---|---|---|---|---|---|
| | r(P–F) | r(P–N) | r(Si–N) | FPF | FPN |
| $N(PF_2)_3$ [a] | 157.4(2) | 171.1(4) | | 96.9(3) | 99.2(3) |
| $N(PF_2)_2(SiH_3)$ [b] | 157.0(2) | 169.1(4) | 176.7(7) | 96.1(5) | 99.3(3) |
| $N(PF_2)(SiH_3)_2$ [b] | 158.7(3) | 168.0(4) | 175.5(4) | 96.9(10) | 99.4(7) |
| $N(SiH_3)_3$ [c] | | | 173.4(2) | | |
| $NH(PF_2)_2$ [d] | 158.4(3) | 168.4(8) | | 95.6(10) | 98.3(7) |
| $NH(PF_2)(SiH_3)$ [e] | 157.5(3) | 165.4(6) | 172.4(7) | 101.6(12) [f] | 95.2 [f] |
| $NH(SiH_3)_2$ [g] | | | 172.5(3) | | |

[a] Ref. 4. [b] This work, [c] Ref. 2. [d] Ref. 5. [e] Ref. 11. [f] See text. [g] Ref. 3.

FPF and FPN in both cases give expected values for the $F_2PN$ group (Table 6). Typical values for these parameters range from 95—97° and 98—100° respectively. In the case of $NH(PF_2)(SiH_3)$ it may be that these strongly correlated angles have been reversed in the refinements.

The conformation of the $PF_2$ groups in $PF_2$ amines is generally of some interest, since they can be directed by two factors: lone-pair repulsions between P and P or P and N; and attractive interactions between F and H, the latter being important for all $NR_3$ compounds (R = $PF_2$, $SiH_3$, $CH_3$, or H) containing $PF_2$ groups, except $N(PF_2)_3$. In general fluorine–hydrogen interactions predominate over lone-pair repulsions, as is evident in the cases of $NMe(PF_2)_2$ [21] and $NH(PF_2)_2$ [5] where attractive H · · · F interactions force the phosphorus lone pairs, although orthogonal to that on nitrogen, to lie *cis* to each other in the major conformer for each molecule. For $N(PF_2)_2(SiH_3)$ and $N(PF_2)_2(SiH_3)$ n.m.r. studies had already been used to predict the likely orientations of the $PF_2$ groups.[12] It has been suggested [22,23] that some two- or three-bond couplings to three-co-ordinate phosphorus are sensitive to conformation, with large couplings resulting from atoms lying *cis* to the lone pair on phosphorus. In $N(PF_2)_2(SiH_3)$ both $^3J(^{31}P^1H)$ and $^2J(^{31}P^{29}Si)$ are small (3.5 and 7 Hz respectively), indicating that the FPF bisectors lie *cis* to the silyl group. In $N(PF_2)(SiH_3)_2$ n.m.r. couplings have been explained in terms of the average of one *cis* and one *trans* $J$(PX) (X = $^{29}$Si or $^1$H), indicating fast rotation of the $PF_2$ group on the n.m.r. time scale. These predictions have been verified by the present study.

In $N(PF_2)_2(SiH_3)$ the $PF_2$ torsions refined as a single parameter, with the best fit being for a conformation where the $N(PF_2)_2$ group adopts a local $C_s$ symmetry with the FPF angle bisectors lying 3° away from being *cis* to the Si–N bond. This result is identical in principle to those found for $NH(PF_2)_2$ and $NMe(PF_2)_2$, and a similar situation has been predicted for $N(GeH_3)(PF_2)_2$.[22] We are at present undertaking a gas-phase structural determining the conformations of the $PF_2$ groups. $N(PF_2)(SiH_3)_2$ contains H · · · F contacts from 255.5 pm and $N(PF_2)_2(SiH_3)$ similar contacts from 260.5 pm. The lower values in both cases correspond to the sum of the van der Waals radii for fluorine and hydrogen, and represent the optimum distance for maximum H · · · F interaction.

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