Aminodifluorophosphine: Crystal and Molecular Structure at 95 K, and Vibrational Spectra of Condensed Phases *

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The crystal and molecular structure of $PF_2(NH_2)$ has been determined at 95 K. A single crystal was grown *in situ* on a Weissenberg goniometer and transferred to a CAD4 diffractometer for data collection. Crystals of $PF_2(NH_2)$ are monoclinic, space group $P2_1/c$, with a = 5.2125(26), b = 12.830(5), c = 4.896(4) Å, β = 115.07(6)°, and Z = 4. Two quadrants of data were collected and merged to give 1 300 reflections, of which 1 243 were considered to be above background. The final R was 0.0376. The P–N bond length is 1.6384(9) Å, while the P–F(1) [1.6083(11) Å] and P–F(2) [1.5899(6) Å] distances are inequivalent and reflect the involvement of F(1) in intermolecular hydrogen bonding. The N is also hydrogen bonded and the intermolecular bonding gives rise to a corrugated layer of $PF_2(NH_2)$ molecules. Infrared and Raman spectra of $PF_2(NH_2)$ in the liquid, unannealed solid, and crystalline phases have also been recorded and analysed. Spectra of the crystalline solid, formed by a spontaneous annealing process at 110 K, are consistent with the crystal structure, showing shifts in N–H stretching frequencies, and at least one band, absent for non-crystalline phases, assigned to deformations of the hydrogen-bonding network. Stretching frequencies for N–H bonds in NHD species have been used to give accurate N–H bond lengths, and the combined X-ray and spectroscopic data allow the hydrogen-bonding contacts within the crystal, which determine the overall crystal packing, to be fully characterised.

The molecular structure of $PF_2(NH_2)$ has been investigated by both spectroscopic [1] and electron-diffraction [2] methods and the structures deduced are not identical. The microwave study [1] led to a structure with C_s symmetry and planar N, the plane containing P and the NH_2 group bisecting the FPF angle. Whilst the electron-diffraction results [2] were interpreted in terms of a similar torsion about the P–N bond, this study suggested however that the N atom was not planar, so that the molecule was without symmetry. This latter conclusion is consistent with the results of MNDO calculations.[3] The model used in the initial electron-diffraction study was over-simplified (assuming the NH bond lengths and PNH bond angles to be identical) and we have continued our investigations of the structure of this molecule by a variety of techniques.

The present paper reports the crystal and molecular structure of $PF_2(NH_2)$, together with the vibrational spectra of the crystalline and some non-crystalline condensed phases. The results are not directly comparable with those for other phases, as extensive hydrogen bonding occurs in the crystal, so that this work is essentially complete in itself, although the results are of interest in the context of the continuing investigations of the structure of the free molecule.

Experimental

Crystal Structure Determination of $PF_2(NH_2)$.—A sample of aminodifluorophosphine was sealed in a Pyrex capillary (internal diameter 0.4 mm) glued to a metal mount. The mount was secured in a goniometer head and a single crystal grown on an Enraf–Nonius Weissenberg goniometer equipped with a universal low-temperature nitrogen-stream cooling device. Oscillation and zero- and first-layer (equi-inclination) Weissenberg photography at *ca.* 120 K afforded the space group and approximate unit-cell dimensions.

For data collection the same crystal was transferred, without melting, to an Enraf–Nonius CAD4 diffractometer equipped with a similar low-temperature system. As far as we are aware this represents the first such successful transference for a very low melting species [m.p. of $PF_2(NH_2)$ *ca.* 150 K], and we accordingly outline the procedure employed. The sample on the camera was cooled to the lowest temperature attainable, *ca.* 110 K; the layer-line screen gap was widened to the maximum possible and the screw retaining the metal mount was loosened. The mount was carefully separated from the goniometer head, keeping the crystal in the cold gas stream; the entire mount was then rapidly immersed in an adjacent, shallow reservoir of liquid nitrogen for transportation. At the diffractometer the sample tube was carefully raised into the downward flow of cold gas (95 K) and held in it whilst the kappa angle was reduced from 135 to 0°. The mount was then resecured in the head and the sample optically centred.

When the steady state had been achieved, 14 relatively low-angle reflections were located (program SEARCH) and their angular settings used to compute the first unit cell and orientation matrix (INDEX). After rapid data collection within the range θ = 13—15° (graphite-monochromated Mo-K_α X-radiation; $\lambda_{\alpha 1}$ = 0.70926 and $\lambda_{\alpha 2}$ = 0.71354 Å), 25 reflections from this shell were accurately centred (SETANG) to yield, by least-squares refinement, accurate cell dimensions and the orientation matrix used in data collection.

Crystal data. H_2F_2NP, M = 84.99, monoclinic, a = 5.2125(26), b = 12.830(5), c = 4.896(4) Å, β = 115.07(6)° (at 95 K), U = 296.6(4) Å^3, Z = 4, D_c = 1.903 g cm^{-3}, $F(000)$ = 168, μ(Mo-K_α) = 7.07 cm^{-1}, space group $P2_1/c$ (C_{2h}^5, no. 14) from systematic absences; crystal size 0.4 × 0.4 × 0.5 mm.

Two quadrants of diffracted data were measured ($+h$ $+k$ $\pm l$ and $-h$ $-k$ $\pm l$) within the range θ = 1—35° by ω—2θ scans in 96 steps. The ω scan width was 0.8 + 0.35 tanθ. After a prescan only those reflections considered sufficiently intense [$I \geqslant 0.5\sigma(I)$] were remeasured, such that their final net intensity had $I \geqslant 33\sigma(I)$ subject to a maximum measuring time of 90 s. Two orientation and two intensity-control reflections were remonitored once every 200 reflections and

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* *Supplementary data available* (No. SUP 23965, 10 pp.): structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Positional and thermal parameters [a]

(*a*) Positional

Atom	x	y	z
P	0.285 57(5)	0.088 54(2)	0.138 29(5)
F(1)	0.204 31(16)	0.083 89(6)	0.420 39(19)
F(2)	0.052 42(13)	0.174 36(5)	−0.032 74(16)
N	0.568 21(19)	0.162 63(7)	0.267 72(22)
H(1)	0.732(4)	0.133 2(20)	0.350(4)
H(2)	0.572(4)	0.218 9(17)	0.364(4)

(*b*) Thermal [b]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	0.015 5(2)	0.016 3(2)	0.016 5(2)	−0.000 5(1)	0.007 1(1)	0.000 3(1)
F(1)	0.026 3(4)	0.030 6(4)	0.021 8(3)	0.003 0(2)	0.014 2(3)	−0.002 4(2)
F(2)	0.018 0(3)	0.026 3(3)	0.024 5(3)	0.005 0(2)	0.005 8(2)	0.005 1(2)
N	0.015 4(4)	0.024 3(4)	0.024 2(4)	−0.002 8(3)	0.008 3(3)	−0.002 0(3)

[a] Estimated standard deviations in parentheses throughout this paper. [b] The anisotropic thermal parameter is defined as $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{23}b^*c^*kl + 2U_{13}a^*c^*hl + 2U_{12}a^*b^*hk)]$.

3 600 s respectively, but their subsequent analysis implied no substantial crystal decay or movement, or source variation, over the *ca.* 32 h of data collection.

The two quadrants of data (1 296 and 1 300 unique reflections respectively) were corrected for Lorentz and polarisation effects and merged, affording $R_{merge} = 0.068$ and supplying 1 300 unique data. Of these, 1 243 with $F_o \geqslant 2.0\sigma(F_o)$ were retained for structure solution and refinement. The former was achieved *via* automatic centrosymmetric direct methods and Fourier difference syntheses, and for the latter full-matrix least squares was used. Structure factors were weighted according to $w^{-1} = [\sigma^2(F_o) + 0.0010\,18\,F_o^2]$, a scheme which gave no unusual variation of the root-mean-square deviation of a reflection of unit weight *versus* the parity group, $(\sin\theta)/\lambda$, F_o, h, k, or l.

Anisotropic thermal motion was allowed for P, F, and N atoms, whilst H atoms were positionally refined but with fixed ($U = 0.03$ Å^2) * thermal parameters. Refinement converged at $R = 0.0376$, $R' = 0.0620$, at a data : variable ratio better than 28 : 1. A final Fourier difference synthesis had no peak >0.7, nor trough <-0.7 e Å^{-3}.

Table 1 lists the derived atomic parameters (positional and thermal). Structure solution and refinement used programs and inlaid neutral atomic scattering factors of the SHELX 76 package,[4] implemented on the University of Edinburgh ICL 2972 computer. Molecular geometry calculations employed XANADU [5] and *X*-RAY 76,[6] whilst graphics were obtained from ORTEP II.[7]

Vibrational Spectra.—Infrared spectra of solid samples were obtained using a Perkin-Elmer 225 recording spectrophotometer over the range 4 000—200 cm^{-1}; samples were deposited from the gas phase onto a CsI substrate maintained at a controlled low temperature (down to about 10 K) by an Air Products Displex CS202 microrefrigerator, and could be warmed and cooled in a controlled fashion using an electrical heater. Distinct changes were observed when the sample, presumably initially deposited as a glass, warmed to *ca.* 110 K, and were consistent with a transition to a more ordered solid, which we believe can be considered as crystalline. Further annealing led to no further changes in spectra until the onset of melting. Raman spectra were recorded using a Cary 83 spectrometer with Ar$^+$ (488 nm) laser excitation; liquid samples were held in sealed capillaries, and solid samples sprayed onto a copper block cooled by liquid N_2. Annealing of solid samples could be accomplished by removing the coolant and monitoring the spectrum as the temperature of the block and sample rose. Band maxima were measured to ±0.5 cm^{-1} in the i.r., ±2 cm^{-1} in the Raman (using Ar$^+$ plasma lines for calibration). Details of the spectra recorded for liquid, unannealed solid, and annealed solid samples are listed in Table 2.

Results and Discussion

Vibrational Spectra of Condensed Phases.—Table 2 shows that the spectra reported here for unannealed solid (i.r.) and for liquid (Raman) samples are very similar to those reported earlier [8,9] for the gas, except that there are multiple Q branches in the gas phase. In particular, the two clear i.r. bands due to ν(NH) are almost unchanged, although only the lower-frequency component gives rise to a Raman band, and the NH deformation bands at 1 545 and 955 cm^{-1} and the characteristic (scissors) deformation of the PF_2 group at 436 cm^{-1} are also very little affected by the difference of phase. This argues that molecules in the amorphous condensed phases are relatively free from directed hydrogen bonding, which would be expected to affect the ν(NH) bands in particular, and from any other *specific* intermolecular interactions or changes in gross molecular structure compared with the gas. The major differences from the gas-phase spectra are in the regions associated with PF bond stretching and FPN angle deformation modes (900—700 and 400—200 cm^{-1} respectively); the lowest-frequency Raman band, observed at 235 cm^{-1}, may well be due to the lowest-frequency NH deformation mode, which may be viewed as a torsion of the NH_2 group found at 170 cm^{-1} in the i.r. spectrum of the gas.[10] (Other studies, involving ^{15}N substitution and partial deuterium substitution, with i.r. spectroscopy of gaseous and matrix-isolated samples, have confirmed the assignments originally suggested;[8] these will be reported separately in connection with new studies of the structure of the gas-phase molecule.[10])

The spectra (i.r. and Raman) of solid samples which have been annealed by warming to around 110 K are quite different from those of the unannealed or liquid samples. The clearest difference is perhaps in the ν(NH) region, where four peaks appear in the i.r., and two in the Raman. The crystal structure shows that each unit cell contains four molecules, related in pairs by an inversion centre; a very simple factor-group

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* The isotropic thermal parameter is defined as $\exp[-8\pi^2U(\sin^2\theta)/\lambda^2]$.

Table 2. Vibrational bands (cm^{-1}) and assignments *

Gas	Liquid Raman	Solid i.r.	Crystal i.r.	Crystal Raman	
3 520	—	3 510	3 435	—	ν(NH)
			3 428		
3 405	3 390p	3 390	3 298	3 320	
			3 271	3 285	
1 545	1 555?	1 543	1 552	1 553	$\delta_{sym}(NH_2)$
955	958p	959	972	970	$\delta(NH_2)$ *a′*
			890		
875	890p	892	904	890	ν(PN)
806	780p	782	785	780	ν(PF)
	760dp?	767	774		
		748			
	708p		714	720	
weak	665vw	weak	670		$\delta(NH_2)$ *a″*
peaks	585vw	peaks	527	550br	
only	500w	only			
				472	
436	436	436	440 (sh)		$\delta_{sym}(PF_2)$
			436	436	
		365			
315	355	358	357	348	δ_{asym}(FPN)
280	252	—	311	308	δ_{sym}(FPN)
			275	265	
170	235	—	—	220	$\tau[\delta(NH_2)$ *a″*]

* p = Polarised, dp = depolarised.

analysis leads us to expect four components from each internal motion of the molecule, two active in the i.r. and two in the Raman. If we accept that the higher of the two ν(NH) modes is very weak in the Raman, as in the liquid phase, we have the expected pattern arising from the *two* ν(NH) modes. The 'large splitting' of *ca.* 100 cm^{-1} is clearly still related to a difference in the two normal modes of each molecule, but the small splittings (5—35 cm^{-1}) and the difference between i.r. and Raman band frequencies (*ca.* 20 cm^{-1}) are due to coupling between molecules through the hydrogen-bond network. As we shall see below, it is possible to derive NH bond distances from the observed ν(NH) frequencies, and hence obtain additional information about the molecular structure in the crystal. It may be noted at this stage that both ν(NH) frequencies have fallen some 100 cm^{-1} compared with the values found for gaseous *or* non-crystalline condensed samples, which is consistent with the observed crystal structure in which both hydrogen atoms are involved in hydrogen bonding, one to a fluorine and the other to a nitrogen in (different) neighbouring molecules.

The molecule in the crystal has no symmetry and it is not strictly permissible to treat the NH_2 groups and PF_2 groups as possessing even a mirror plane of symmetry. Nevertheless, each still shows its characteristic 'scissors' deformation, near 1 550 cm^{-1} and at 436 cm^{-1}, each practically unaltered from the non-crystalline phases. Any factor-group splittings are small in these instances. This constancy of the scissors mode is perhaps more surprising for the PF_2 group, where one (only) of the F atoms is involved in a hydrogen bond in the crystal. In the lower-frequency region there are three clear sharp bands probably assignable to skeletal bends, but the absence of molecular symmetry and the possibility of factor-group splittings leave us reluctant to make definite assignments.

The observation that one PF band is longer than the other in the crystal, presumably because it is involved in a P–F ··· H′–N′ hydrogen bond,* leads us to look for a lower-frequency PF bond stretch. The spectra of the crystalline solid shows a clear band at 714 (i.r.) or 720 cm^{-1} (Raman), which is much lower than the ν(PF) band at 806 cm^{-1} for the gaseous sample, but the liquid and unannealed solid also show low-frequency shifts compared with the gas phase, and we are not convinced that hydrogen bonding is responsible in this instance. The two bands between 1 000 and 800 cm^{-1} remain remarkably constant over the wide range of phases; they are assigned to a NH deformation and ν(PN), probably somewhat mixed with ν(PF).

Table 3. Interatomic separations (Å) and bond angles (°)

P–F(1)	1.608 3(11)
P–F(2)	1.589 9(6)
P–N	1.639 4(9)
N–H(1)	0.862(19), 0.998(10) *
N–H(2)	0.860(22), 1.008(10) *
F(1)–P–F(2)	93.29(4)
F(1)–P–N	102.13(5)
F(2)–P–N	99.41(4)
P–N–H(1)	118.7(16)
P–N–H(2)	120.7(14)
H(1)–N–H(2)	109.1(18)

* From i.r. evidence, see text.

Table 4. Stereochemistry of $PF_2(NH_2)$

Technique (phase)	θ/°	φ/°	Ref.
Electron diffraction (gas)	35	89	2
Microwave (gas)	0	90	1
MNDO (–)	20	82	3
X-Ray (solid)	31	74	This work

The most distinctive feature of the spectra of crystalline solid samples is a broad strong band between 460 and 600 cm^{-1} in both the i.r. and Raman spectra. This region of the spectra of gas, liquid, and unannealed solid samples contains only weak peaks, probably due to a mode related to the 'umbrella' inversion of NH_3, which here couples strongly with the torsion of the NH_2 group. These two motions, both of *a″* symmetry in the most symmetric, planar-N model suggested by the microwave spectra,[1] may also be regarded as separate deformations of a 'tightly held' and a 'loosely held' NH bond respectively. In the solid, the strong hydrogen bonds will clearly affect these motions to a greater extent, and we suggest that the broad band around 550 cm^{-1} is due to a deformation of the hydrogen-bond network. The band at 220 cm^{-1} in the Raman spectrum of the crystal is probably due to another mode of this type, and it is possible that one of the bands between 260 and 360 cm^{-1} is another. (Deuterium substitution leads to shifts to lower frequency of *all* i.r. bands below 700 cm^{-1} except, perhaps, that at 275 cm^{-1}.)

Solid-state Molecular Structure of $PF_2(NH_2)$.—A perspective view of a single molecule is given in Figure 1, and Table 3 lists derived molecular parameters. There is extensive intermolecular hydrogen bonding in the crystalline phase of $PF_2(NH_2)$ (see below), involving all atoms except P and F(2), and thus the molecular geometry determined may well differ markedly from that of the 'free' molecule.

The stereochemistry of a molecule of $PF_2(NH_2)$ may be described by two key parameters: (*i*) the extent of deviation from planarity at N, defined by an angle θ between the NH_2 plane and the extension of the PN bond; and (*ii*) the torsion angle about the PN bond, φ, defined here as the angle between

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* Primed superscripts indicate atoms in a neighbouring molecule.

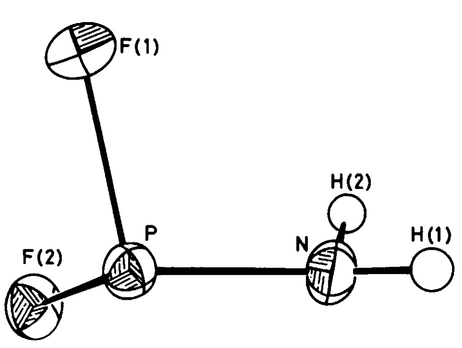

Figure 1. Perspective view of a single molecule of $PF_2(NH_2)$. Thermal ellipsoids are drawn at the 50% probability level, except for H atoms which have an artificial radius of 0.1 Å for clarity

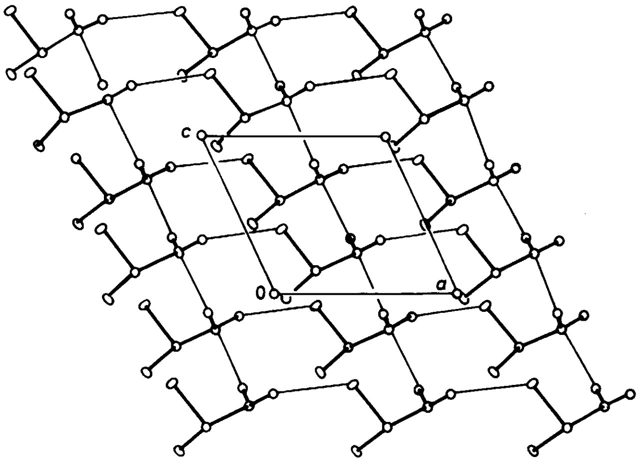

Figure 2. One layer of the crystal structure of $PF_2(NH_2)$ in *b*-axis projection

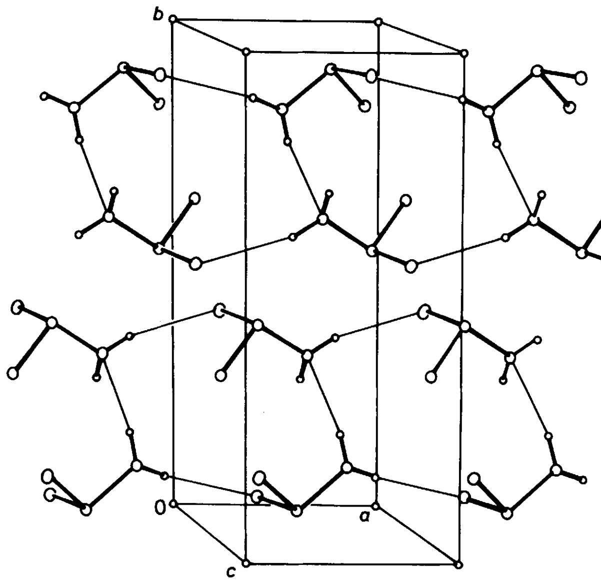

Figure 3. Perspective view of the crystal structure of $PF_2(NH_2)$

the plane containing the PN bond and the bisector of the FPF angle, and the plane perpendicular to the NH_2 plane through the bisector of the HNH angle. (This is equivalent to the angle between the planes containing the P and N lone pairs.) The values found for θ and φ by various techniques are listed in Table 4. There is clearly a general agreement about the torsion angle, but the conclusion drawn from the microwave spectrum that the molecule is planar at N is not supported by either experimental (electron diffraction) [2,10] or theoretical (MNDO) [3] evidence. It is clear from the MNDO calculations, however, that the potential surface for pyramidal deformation at N is rather flat, and this is supported by recent electron-diffraction work,[10] which suggests that an 'inversion' at N involving motion mainly of the H atom *trans* to the PF_2 group is very easy.

The molecular parameters of a number of aminodifluorophosphines have recently been tabulated.[11] The P–F distances [which are significantly different and reflect hydrogen-bonding to F(1) only] and the P–N lengths in solid $PF_2(NH_2)$ all fall within the appropriate ranges but lie towards the upper and lower extremes respectively. The possibility that *intra*-molecular H · · · F interactions play a significant role in determining the preferred conformation in aminodifluorophosphines needs to be considered, but for solid $PF_2(NH_2)$ we find little experimental evidence for this view since, even though H(2) is roughly equidistant from F(1) [2.686(22) Å] and F(2) [2.642(16) Å], and hence is as near as possible to both simultaneously, these lengths are slightly greater than the sum of van der Waals radii [12] for H and F (2.55 Å). The fact that the PNH(2) angle is if anything larger than the PNH(1) angle also argues against any strong attractive F · · · H interactions within the molecule, which would tend to narrow the angle to H(2).

The crystal packing. Table 5 documents the significant intermolecular contacts. Molecules in one conformation, say φ positive, are linked *via* F(1) · · · H(1′) interactions into infinite chains running parallel to the *a* axis. Cross-linking of these with adjacent, parallel chains of molecules of the other (φ negative) conformation *via* N · · · H(2′) bonds affords a corrugated sheet (Figure 2) whose waves run parallel to *c* and whose channels are parallel to *a*. A second layer, antiparallel to the first, is displaced from it by *b*/2 to yield the full crystal structure (Figure 3). There are no close contacts between adjacent sheets.

The unreliability of H-atom positions determined by *X*-ray methods makes it unrealistic to attempt to assess the lengths (and hence strengths) of the H · · · F′ and H · · · N′ contacts referred to above from purely *X*-ray data. We have therefore used the suggested [13] correlation between NH bond-stretching frequencies and NH bond lengths (as determined for solids by neutron diffraction) to deduce more accurate H-atom positions in the solid state as follows.

The 'large splitting' of the ν(NH) bands in the i.r. spectrum of the crystal of $PF_2(NH_2)$ reflects, in principle, both the intrinsic difference between the *cis*- and *trans*-NH bond stretches (defined relative to the PF_2 group) *and* the coupling (mixing) between these modes. To remove any effect of coupling we have studied partially deuterium-substituted samples, whose i.r. spectra after annealing of the solid give two sharp peaks, at 3 416 and 3 301 cm^{-1}. The published correlation shows that these correspond to NH bond lengths of 0.998 and 1.008 Å respectively, whereas the *X*-ray data suggest that both NH bond lengths are 0.86(2) Å. Using the (accurately determined) distances N · · · F(1′) and N · · · N′ from the *X*-ray results, and the NH bond distances derived from i.r. frequencies, and assuming the directions of the NH vectors determined from the *X*-ray data to be correct, we find (Table 5) hydrogen-bond distances H(1) · · · F(1′) of 2.29 Å and H(2) · · · N′ of 2.36 Å with an estimated uncertainty

Table 5. Significant intermolecular contacts (Å and °), A−H ··· B−C

Atom A	H	Atom B	Atom C	Symmetry B, C	A ··· B	H ··· B	A−H ··· B	H ··· B−C
N	H(1)	F(1)	P	$x + 1, y, z$	3.236 3(13)	2.292(10)	158.7(20)	120.3(4)
N	H(2)	N	P	$x, \frac{1}{2} - y, \frac{1}{2} + z$	3.319 5(15)	2.361(10)	159.7(20)	110.2(4)
			H(1)					109.1(16)
			H(2)					86.3(15)

Heavy-atom positions are from *X*-ray data; hydrogen-atom positions were derived from spectroscopic data as described in the text.

of ±0.01 Å in each case. These are comfortably shorter (*ca.* 0.3 Å) than the sums of the van der Waals radii for H and F or H and N, confirming that fairly strong hydrogen bonding does indeed occur. The shortening is greater for the H(2) ··· N′ contact, suggesting that this is a slightly stronger hydrogen bond, which is why H(2) has been assigned to the longer N−H bond.

Finally, it should be noted that one hydrogen atom (the one closer to the fluorine atoms) lies more or less equidistant from the two fluorine atoms, and in this respect the solid-state structure is in close agreement with those determined for the gas phase by electron diffraction [2,10] and microwave spectroscopy.[1] However, the second hydrogen atom is displaced well to one side of the approximate F_2PNH mirror plane, in agreement with the electron-diffraction results, but not with the conclusion based on microwave data. It is possible that the average gas-phase structure does have C_s symmetry, but that one hydrogen atom is very easily distorted from the mirror plane. In the gas phase, this would cause apparent non-planarity of the nitrogen atom (a shrinkage effect), and in the solid phase this atom would move to maximise hydrogen bonding. A fuller theoretical study of the structure of this molecule, and investigation of the potential function relating to NH bond deformations, would be most illuminating.*

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* *Note added at proof*: *Ab initio* calculations for $PF_2(NH_2)$ show that the PNH_2 group is non-planar. The angles depend on the basis set used, but at the 4–21-N**P* level (with two sets of *d* functions on nitrogen and one on phosphorus) the angle θ was 44.5° (J. E. Boggs and Z. Hiu, personal communication).

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