Fig. 4. Stereoviews of the molecular packing in (a) BEMB1 and (b) BEMB2 with all molecules in orientation (I). Shaded circles represent Br atoms.

in favour of Br—methyl contacts. Such an observation is in general agreement with the notion of localized dipoles and a detailed analysis along these lines is in progress. Since previous studies were only carried out with 'average' or 'idealized' Br and methyl positions it was not possible to correlate the degree of order with the precise details of each intermolecular contact. In the present study, the use of constrained refinements has allowed determination of positions for both the Br and the methyl at each disordered site. It is therefore hoped that a more quantitative description of the causes of the short-range ordering can be made.

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Structure of Difluoro(methylamino)phosphine, CH₄F₂NP, at 97 K

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Abstract. $M_r = 99.02$, triclinic, $P\bar{1}$, $a = 4.9969$ (18), $b = 5.4618$ (18), $c = 8.2231$ (25) Å, $\alpha = 106.435$ (26), $\beta = 108.088$ (29), $\gamma = 76.780$ (29)°, $U = 202.2$ (4) Å³, $Z = 2$, $D_x = 1.641$ Mg m⁻³, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 0.531$ mm⁻¹, $F(000) = 100$. Final $R = 0.0397$ for 1055 observed reflections. Molecules are linked by hydrogen bonding into chains which run alternately parallel and antiparallel to the crystallographic b axis.

Individual molecules have pyramidal and planar geometries at P and N respectively and a short P—N distance of 1·6174 (12) Å. The P—F bond lengths are inequivalent, reflecting the involvement of F(1) in hydrogen bonding. The lone pair on P and the N p_z orbital are approximately orthogonal.

Introduction. As part of continuing work in this Department on simple PF_2 derivatives (Barrow, Ebsworth, Harding & Henderson, 1979; Blake, Cradock, Ebsworth, Rankin & Welch, 1984) we have determined the crystal structure of difluoro-(methylamino)phosphine, PF_2NHMe. This compound is of particular interest since it is intermediate between PF_2NH_2, which in the crystal exhibits extensive hydrogen bonding and a pyramidal environment at N (Blake *et al.*, 1984), and PF_2NMe_2, which has no such intermolecular contacts and is planar at N (Morris & Nordman, 1969). The N environment in solid $(PF_2)_2NH$ also appears to be planar, although the poorly located H atom leaves some doubt in this case (Barrow *et al.*, 1979). Gas-phase electron diffraction (ED) data for PF_2NHMe can be interpreted in terms of a single conformer in which the N—C bond lies *trans* to the lone pair on P, although the presence of up to 20% of a second conformer could not be ruled out (Laurenson & Rankin, 1979). However, both conformers appeared to have planar groupings around N.

Experimental. Colourless, block-like crystal, 0·3 × 0·3 × 0·4 mm grown *in situ* on low-temperature-equipped Weissenberg goniometer from sample sealed in Pyrex capillary. Crystal transferred without melting as described previously (Blake *et al.*, 1984) to similarly equipped CAD-4 diffractometer, 22 reflections (17 < θ < 18°) centred, graphite-monochromated Mo $K\alpha$ radiation. For data collection $\theta_{max} = 30°$, ω–2θ scan in 96 steps, ω-scan width 0·8° +0·35°tanθ, rapid prescan after which reflections with $I > 0·5\sigma(I)$ remeasured such that final net intensity had $I > 33\sigma(I)$ subject to maximum measuring time of 90 s. Two hemispheres measured over 45 X-ray hours with no significant crystal decay or movement. Data not corrected for absorption, observed structure factors determined (range of h,k,l: h −7→7, k −7→7, l −11→11) and merged to give 1175 unique reflections, $R_{int} = 0·0623$. Space group identified by E statistics and successful refinement. For structure solution and refinement 1055 amplitudes [$F > 2·0(F)$], automatic centrosymmetric direct methods (Sheldrick, 1976), full-matrix least squares (F), $w^{-1} = [\sigma^2(F) + 0·00375(F)^2]$, anisotropic thermal parameters for P,F,N and C, isotropic for H (located from difference map), R 0·0397, wR 0·0528, data: variable ratio 17:1, max. shift:error in final cycle <0·05, max. peak and min. trough in final ΔF synthesis 0·70 and −0·78 e Å^{-3} respectively; neutral scattering factors for P,F,N and C (Cromer & Liberman, 1970)

and H (Stewart, Davidson & Simpson, 1965); computer programs *SHELX*76 (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1976), *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), *ORTEP*II (Johnson, 1976) and *PLUTO* (Motherwell, 1976).

Discussion. Table 1 lists derived fractional coordinates and isotropic thermal parameters and Fig. 1 shows a perspective view of the molecule.* Table 2 lists interatomic distances and interbond angles while torsion angles have been deposited as Table 3. Molecules of PF_2NHMe form chains *via* F(1)$\cdots$H(1)'† interactions as detailed in Table 4. As shown in Fig. 2, these chains run alternately parallel and antiparallel to the crystallographic *b* axis, but in contrast to PF_2NH_2 (Blake *et al.*, 1984) are not cross-linked *via* N$\cdots$H' contacts. The intramolecular geometry in the crystal is essentially that of the major (*trans*) gas-phase conformer, except for the conformation of the methyl H atoms which are staggered with respect to the N—H bond rather than eclipsed as assumed in the ED study (Laurenson & Rankin, 1979). Planarity at N is evidenced by the sum (359·2°) of the P—N—C, P—N—H(1) and C—N—H(1) angles. The lone pair on P and the N p_z orbital are approximately orthogonal as indicated by the value of 93° for the torsion angle bis(FPF)—P—N—bis(CNH), where bis(FPF) and bis-(CNH) are the bisectors of the FPF and CNH(1) angles; it is a consequence of the centrosymmetric space group that equal numbers of molecules with values of +93 and −93° are found.

As in PF_2NH_2, the P—F distances are inequivalent, P—F(1) − P—F(2) = 0·0127 (16) Å, as a result of the involvement of only F(1) in intermolecular hydrogen bonding. The P—N bond in PF_2NHMe [1·6174 (12) Å] is significantly shorter than that in PF_2NH_2 [1·6384 (9) Å] and we associate both this and the planarity at N with the non-involvement of N in hydrogen bonding in the present compound, and thus in enhanced $p_\pi(N) \rightarrow d_\pi(P)$ overlap.

The structural parameters for some aminodifluorophosphines have been tabulated (Laurenson & Rankin, 1979) and thus a wider comparison of P—N distances can be made. Another striking illustration of the effect that changing the coordination at N has on this parameter is furnished by PF_2NMe_2: in the gas phase the N is clearly pyramidal and the P—N distance is 1·684 (8) Å (ED) while in the solid the environment at

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* Lists of structure factors, anisotropic temperature factors and Table 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39339 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Primed atoms are located in a neighbouring molecule at *x*, 1 + *y, z*.

Table 1. *Positional parameters (fractional coordinates) with e.s.d.'s in parentheses and isotropic thermal parameters (Å²)*

	x	y	z	U_{eq}* or U†
P	0.29099 (7)	0.74071 (6)	0.84324 (4)	0.0215
F(1)	0.06587 (23)	0.58417 (18)	0.85492 (14)	0.0363
F(2)	0.30806 (24)	0.57024 (20)	0.65427 (13)	0.0368
N	0.08926 (24)	1.00204 (21)	0.79598 (15)	0.0211
C	−0.1864 (3)	1.0234 (3)	0.66618 (19)	0.0279
H(1)	0.133 (7)	1.155 (5)	0.868 (4)	0.0517
H(2)	−0.200 (7)	0.861 (5)	0.583 (4)	0.0507
H(3)	−0.194 (6)	1.151 (5)	0.599 (3)	0.0395
H(4)	−0.342 (7)	1.092 (5)	0.729 (3)	0.0499

* $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

† The isotropic temperature factor is defined as $\exp[8\pi^2 U(\sin^2\theta)/\lambda^2]$.

Fig. 1. The difluoro(methylamino)phosphine molecule, with thermal ellipsoids at the 50% electron probability level, except for H atoms which have an artificial radius of 0·1 Å for clarity.

Table 2. *Interatomic distances (Å) and interbond angles (°)*

P—F(1)	1.5997 (11)	N—H(1)	0.90 (3)
P—F(2)	1.5870 (12)	C—H(2)	0.96 (3)
P—N	1.6174 (12)	C—H(3)	0.99 (3)
N—C	1.4610 (20)	C—H(4)	1.01 (3)
F(1)—P—F(2)	92.74 (6)	N—C—H(2)	108.1 (19)
F(1)—P—N	101.86 (6)	N—C—H(3)	109.3 (16)
F(2)—P—N	101.71 (6)	N—C—H(4)	109.1 (17)
P—N—C	127.41 (10)	H(2)—C—H(3)	106.3 (25)
P—N—H(1)	118.0 (20)	H(2)—C—H(4)	116.7 (26)
C—N—H(1)	113.8 (20)	H(3)—C—H(4)	107.1 (24)

Table 4. *Intermolecular geometry*

	H(1)···F(1)′	N—H(1)···F(1)′	H(1)···F(1)′—P′
N—H(1)···F(1)′—P′	2.32 (3) Å	138.8 (24)°	128.2 (9)

Primed atoms are generated by the symmetry operation $x, y + 1, z$.

Fig. 2. Crystal-packing diagram for difluoro(methylamino)-phosphine.

N is planar (presumably for packing reasons) with a P—N bond of 1·628 (5) Å (X-ray). However, significant changes in P—N distance can occur with change of phase and no apparent change in geometry at N. Thus, for example, in PF_2NHMe the N is planar in the crystal and apparently so in the vapour yet the respective P—N values of 1·6174 (12) and 1·648 (7) Å are significantly different.

For planar N, the P—N distance increases with the number of PF_2— (or other π-acceptor) groups attached to N (which compete for its p_z electron density). Thus the lengths of P—N bonds in compounds with one, two and three such groups fall into the reasonably well defined ranges 1·61–1·65, 1·65–1·68 and >1·70 Å, respectively.

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