

# An Electron-Diffraction Investigation of the Molecular Structure of Gaseous Methylaminobis(difluorophosphine), $\text{CH}_3\text{N}(\text{PF}_2)_2$

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**Abstract:** The molecular structure of  $\text{CH}_3\text{N}(\text{PF}_2)_2$  has been investigated at nozzle-tip temperatures of  $-35$  and  $25^\circ$ . The results indicate that the molecule has heavy-atom symmetry  $C_{2v}$ , with the P-F bonds staggered in respect to the C-N bond. The more important geometrical ( $r$ ,  $\angle$ ) and vibrational-amplitude ( $l$ ) parameter values at  $-35^\circ$  with estimated uncertainties of  $2\sigma$  are  $r(\text{C-H}) = 1.090 \text{ \AA}$  (assumed),  $r(\text{C-N}) = 1.479 (0.017) \text{ \AA}$ ,  $r(\text{P-F}) = 1.583 (0.002) \text{ \AA}$ ,  $r(\text{P-N}) = 1.680 (0.006) \text{ \AA}$ ,  $\angle \text{NCH} = 110.0^\circ$  (assumed),  $\angle \text{PNP} = 116.1 (0.8^\circ)$ ,  $\angle \text{CNP} = 122.0 (0.4^\circ)$ ,  $\angle \text{FPF} = 95.1 (0.3^\circ)$ ,  $\angle \text{NPF} = 99.6 (0.3^\circ)$ ,  $\delta$  (the rms amplitude of torsional motion of the  $-\text{PF}_2$  group) =  $10.4 (2.7^\circ)$ ,  $l(\text{C-H}) = 0.077 \text{ \AA}$  (assumed), and  $l(\text{C-N}) - 0.003 = l(\text{P-F}) = l(\text{P-N}) = 0.045 (0.003) \text{ \AA}$ ; the uncertainties include estimates of systematic error and correlation among the observations. The results at  $25^\circ$  are very similar. The possible presence in the sample of a second conformer differing from that just described by a  $180^\circ$  rotation of one of the  $-\text{PF}_2$  groups around the P-N bond was investigated. Although there is no significant evidence for the presence of such a conformer, small amounts (10–15%) cannot be ruled out. Other results include estimates for the  $-\text{PF}_2$  groups of the torsional frequency ( $260 \pm 50 \text{ cm}^{-1}$ ), and of the torsional force constant in the harmonic approximation  $V = V^*\phi^2/4$  ( $V^* = 28.9 \pm 10.7 \text{ kcal/mol}$ ); the uncertainties are  $1\sigma$ .

Bonds between phosphorus and nitrogen atoms have been suggested to have multiple-bond character involving delocalization of the nitrogen electron pair and utilization of d orbitals from the phosphorus atom. Recent microwave studies of dimethylaminodifluorophosphine ( $(\text{CH}_3)_2\text{NPF}_2$ )<sup>1</sup> and aminodifluorophosphine ( $\text{H}_2\text{NPF}_2$ )<sup>2</sup> as well as an X-ray crystallographic study of the former,<sup>3</sup> support this view; the nitrogen atom and its three ligands were found to be coplanar and the P-N bond to be considerably shorter than the sum of the covalent single-bond radii. An electron-diffraction investigation<sup>4</sup> of both  $(\text{CH}_3)_2\text{NPF}_2$  and  $\text{H}_2\text{NPF}_2$  also gave a short P-N bond, but it was concluded that the  $\text{X}_2\text{NP}$  groupings were noncoplanar.

The structure of methylaminobis(difluorophosphine),  $\text{CH}_3\text{N}(\text{PF}_2)_2$ , is of interest for comparison with those mentioned above and we report here the results of our electron-diffraction investigation of the gaseous compound.

## Experimental Section

**Materials.** A sample of  $\text{CH}_3\text{N}(\text{PF}_2)_2$  was supplied by Drs. R. Wolfe and J. Golen, of Erindale College, Ontario, Canada. It was used without further purification, but the sample was pumped briefly before exposure of the diffraction photographs.

**Apparatus and Procedure.** The photographs were made in the Oregon State apparatus, first at a nozzle temperature of  $25^\circ$  and later, after the preliminary results had been obtained, at  $-35^\circ$ . The experimental conditions were: plates, Kodak projector slide (medium);  $r^3$  sector; beam current, 0.30–0.45  $\mu\text{A}$ ; exposure times, 0.5–8.0 min; ambient apparatus pressure during sample run-in,  $(0.4\text{--}1.5) \times 10^{-5}$  Torr; electron wavelength, 0.05738–0.05743  $\text{\AA}$  as calibrated against  $\text{CO}_2$  ( $r_s(\text{CO}) = 1.1648 \text{ \AA}$ ,  $r_s(\text{O}\cdots\text{O}) = 2.3244 \text{ \AA}$ ); nozzle-to-plate distances, 74.998 and 29.989 cm ( $25^\circ$ ) and 74.977, 29.975, and 12.027 cm ( $-35^\circ$ ); numbers of plates selected for analysis at each of these respective distances, 3, 4, 4, 3, 2. Each

plate yielded a set of data which, for plates made at the long, intermediate, and short distances respectively covered the ranges  $1.00 \leq s \leq 12.25$ ,  $8.00 \leq s \leq 30.25$ , and  $22.00 \leq s \leq 46.50$  at intervals  $\Delta s = 0.25$  ( $s = 4\pi\lambda^{-1} \sin \theta$ , where  $2\theta$  is the scattering angle).

After the usual reduction of each set of data, computer calculated backgrounds were subtracted to yield intensity curves, one corresponding to each plate. The curves from the plates made at a given nozzle temperature and nozzle-to-plate distance were combined to give average curves for that distance and temperature. A preliminary radial distribution curve calculated from a composite of the average curves from the  $25^\circ$  experiments suggested an approximate geometry for the molecule. The theoretical curve corresponding to this geometry was used in recalculation of the backgrounds. A preliminary refinement of this model led to a better theoretical curve which was used in a second stage of background recalculation. The composite experimental intensity curves<sup>5</sup> resulting from this procedure are shown in Figure 1. These curves are in the form

$$sI_M(s) = k \sum_{i>j} n_{ij} A_i A_j r_{ij}^{-1} V_{ij} \cos |\eta_i - \eta_j| \sin r_{ij}s \quad (1)$$

The average curves (in the same form) were used for the refinements of the structure. The sources of the  $A_i$  and  $\eta_i$  have been described previously; the other symbols have their usual significances.<sup>6</sup>

**Trial Structure.** The radial distribution curves were calculated according to

$$D(r) = \frac{2}{\pi} \Delta s \sum_{s_{\min}}^{s_{\max}} I'(s) \exp(-Bs^2) \sin rs \quad (2)$$

from composites of the average curves scaled to the same amplitude in the overlap region and multiplied by  $Z_P Z_F A_P^{-1} A_F^{-1}$  to give  $I_M'$ . Data in the unobserved or uncertain region  $s < 3.00$  were taken from theoretical curves. Figure 2 shows the final radial distribution curves, which do not differ in any important way from the earlier ones. As mentioned in the preceding section, the first analysis was based on the  $25^\circ$  data. This analysis led to identification of a model with heavy-atom symmetry  $C_{2v}$  (Figure 3) which accounted for all peaks of the observed curve. However, preliminary theoretical radial distribution curves calculated for this type of model showed much too prominent a peak for distance  $F_1 \cdots F_3$  when a value for  $l(F_1 \cdots F_3)$  commensurate with little or no torsional motion of the  $-\text{PF}_2$  groups was inserted. We interpreted the discrepancy as a clear indication of the importance of torsional motion which we took eventual account of in our structure refinements.

(1) P. Forti, D. Damiani, and P. G. Favero, *J. Amer. Chem. Soc.*, **95**, 756 (1973).

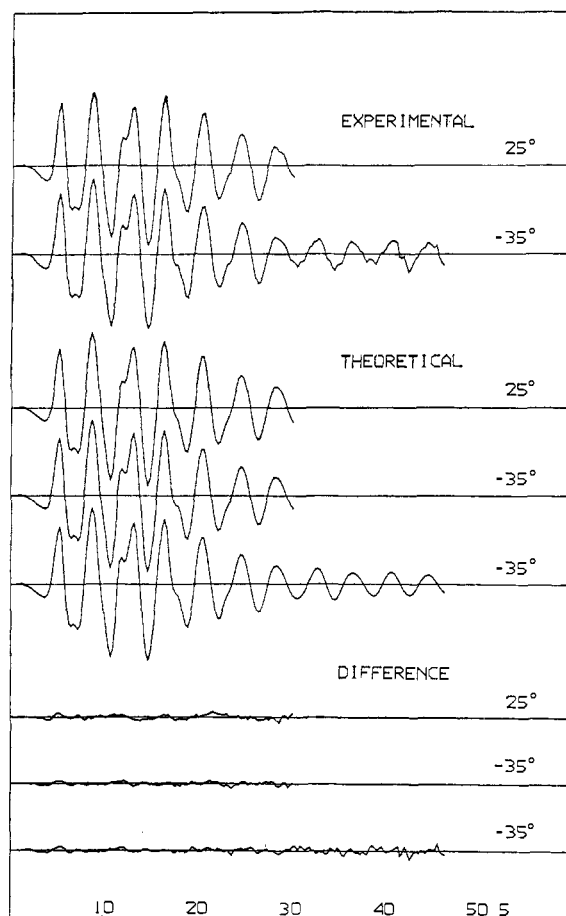
(2) A. H. Brittain, J. E. Smith, P. L. Lee, K. Cohn, and R. H. Schwendeman, *J. Amer. Chem. Soc.*, **93**, 6772 (1971).

(3) E. D. Morris and C. E. Nordman, *Inorg. Chem.*, **8**, 1673 (1969).

(4) G. C. Holywell, D. W. H. Rankin, B. Beagley, and J. M. Freeman, *J. Chem. Soc. A*, 785 (1971).

(5) See paragraph at end of paper regarding supplementary material.

(6) K. Hagen and K. Hedberg, *J. Amer. Chem. Soc.*, **95**, 1003 (1973).

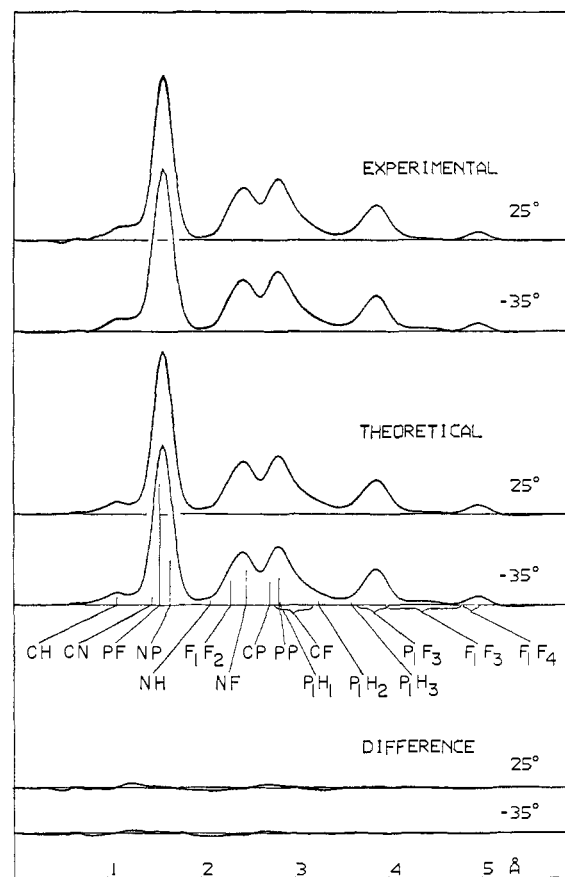


**Figure 1.** Intensity curves. The experimental curves at 25 and  $-35^\circ$  are composites of data from experiments at two and three nozzle-to-plate distances, respectively. The shorter theoretical curves correspond to models with the average structures given in Table I and the longer theoretical curve to a very similar model. The difference curves are the experimental minus theoretical.

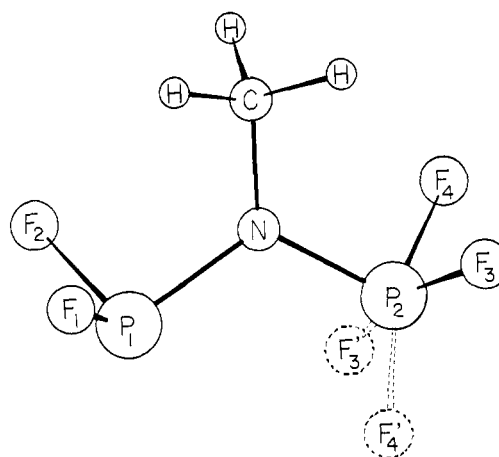
The evidence for torsional motion in our room-temperature data led us to the experiments at the lower temperature; it was hoped that such experiments would reveal further details of the motion. The results were a bit disappointing in that the radial distribution curve calculated from the  $-35^\circ$  data did not show a substantially stronger  $F_1 \cdots F_3$  peak. However, careful comparison of the curves in Figures 1 and 2 reveals small differences consistent with the temperature difference of the two experiments.

**Formulation of Refinements, Objectives and Models.** Considerations based on the preliminary interpretation of the radial distribution curves suggested that in addition to the determination of bond distance and bond angle values our refinements be directed toward answering questions about (1) the possible noncoplanarity of the nitrogen atom and its ligands, (2) the orientation of the  $-CH_3$  group, (3) the effect of the short-camera data, which were gathered only in the low-temperature experiments, on the results, (4) the possible presence of a second conformer of symmetry  $C_s$  as shown in Figure 3, and (5) the  $-PF_2$  group torsional barrier. It seemed quite likely that the first three of these items could be adequately explored with a simple model (hereafter called model A) of the  $CH_3N(PF_2)_2$  geometry, namely one of  $C_{2v}$  equilibrium symmetry for the  $-N(PF_2)_2$  group. (Computing costs made highly desirable the use of the simple model instead of the more complicated model described below.) Item 1, for example, depends almost entirely on the relative lengths of the C,P-N bonds and the P,C $\cdots$ P distances; the contributions from distances between the  $-CH_3$  group and the fluorine atoms, which in a more rigid molecule would have to be taken into account, are nearly completely damped out. Similarly, in respect to item 2 it is essentially only the P $\cdots$ H distances which play a role. Item 3 is a matter of the consistency of the different sets of data rather than a matter of the model.

The last two items seemed to demand a more complicated model (hereafter called model B) which took specific account of torsional



**Figure 2.** Radial distribution curves. The experimental at  $25^\circ$  and the theoretical curves were calculated from the shorter intensity curves of Figure 1. The  $-35^\circ$  experimental curve was obtained from an intensity curve corresponding to that of Figure 1 from which the short nozzle-to-plate distance data were removed.  $B = 0.0025$ . The difference curves are experimental minus theoretical.



**Figure 3.** Diagram of the model.

motion. Model A, since it channels the consequences of large-amplitude torsions into frame vibrations, leads to misleading values for amplitudes related to torsion-affected distances. The effect of torsional motion may be approximated by a superposition of appropriately weighted instantaneous molecular conformations. A reasonable and adequate assumption about the  $-PF_2$  group torsions is that each is independent of the other and that the probability distribution of each is proportional to  $\exp(-\phi^2/2\delta^2)$ . The joint distribution for the two  $-PF_2$  groups is then

$$p'(\phi_1, \phi_2) = Q^{-1} \exp[-(\phi_1^2 + \phi_2^2)/2\delta^2] \quad (3)$$

Table I. Final Structural Results for  $\text{CH}_3\text{N}(\text{PF}_2)_2^a$ 

Parameter	-35°		-25°	
	$r_a, \theta$	$l^b$	$r_a, \theta$	$l^b$
C-H	1.090	0.077	1.090	0.077
C-N	1.479 (0.017)	0.048	1.480 (0.022)	0.044
P-F	1.583 (0.002)	0.045	1.584 (0.002)	0.041
P-N	1.680 (0.006)	0.045	1.681 (0.007)	0.041
$\angle \text{NCH}$	110.0		110.0	
$\tau(\text{CH}_3)^c$	0		0	
$\angle \text{PNP}$	116.1 (0.8)		115.9 (1.0)	
$\alpha^c$	0		0	
$\angle \text{FPF}$	95.1 (0.3)		95.2 (0.5)	
$\angle \text{NPF}$	99.6 (0.3)		99.8 (0.4)	
$\delta^c$	10.4 (2.7)		11.6 (4.3)	
$\text{F}_1 \cdots \text{F}_2$	2.334 (0.006)	0.066	2.340 (0.009)	0.068
$\text{N} \cdots \text{F}$	2.492 (0.005)	0.066	2.497 (0.007)	0.068
$\text{C} \cdots \text{P}$	2.764 (0.010)	0.067	2.767 (0.014)	0.066
$\text{P} \cdots \text{P}$	2.851 (0.008)	0.067	2.851 (0.011)	0.066
$\text{N} \cdots \text{H}$	2.116 (0.015)	0.110	2.117 (0.019)	0.110
$\text{P}_1 \cdots \text{H}_1$	2.840 (0.012)	0.117	2.843 (0.017)	0.127
$\text{P}_1 \cdots \text{H}_2$	3.255 (0.010)	0.117	3.257 (0.014)	0.127
$\text{P}_1 \cdots \text{H}_3$	3.623 (0.009)	0.117	3.625 (0.012)	0.127
$\text{P}_1 \cdots \text{F}_3$	3.877 (0.006)	0.064 (0.019)	3.880 (0.008)	0.071 (0.029)
$\text{C} \cdots \text{F}$	2.973 (0.009)	0.103 (0.028)	2.982 (0.014)	0.104 (0.042)
$\text{F}_1 \cdots \text{F}_3$	4.393 (0.008)	0.192 (0.107)	4.401 (0.011)	0.332 (0.348)
$\text{F}_1 \cdots \text{F}_4$	4.975 (0.008)	0.085 (0.014)	4.985 (0.012)	0.092 (0.021)
$\angle \text{CNP}$	122.0 (0.4)		122.0 (0.5)	
$\beta^d$	104.2 (0.4)		104.6 (0.6)	
$R^e$	0.040		0.054	

<sup>a</sup> Distances in ångströms, angles in degrees. Parenthesized numbers are  $2\sigma$  and include estimates of systematic error calculated by formulas given previously: V. Plato, W. Hartford, and K. Hedberg, *J. Chem. Phys.*, **53**, 3488 (1970). <sup>b</sup> Bracketed values were refined as a group. <sup>c</sup> See text. <sup>d</sup> Angle between FPF plane and P-N bond. <sup>e</sup>  $R = \sum w_i \Delta_i^2 / \sum w_i I_i^2(\text{obsd})$ ;  $\Delta_i = I_i(\text{obsd}) - I_i(\text{calcd})$ .

Accordingly, one may calculate  $sI_{31}(s)$  curves representative of a  $\text{CH}_3\text{N}(\text{PF}_2)_2$  molecule undergoing torsion from eq 1 by first calculating distances  $r_{ij} = r_{ij}(\phi_1, \phi_2)$  at suitably selected angles  $\phi$ , assigning appropriate frame vibrational amplitudes  $l_{ij}$  to them, and weighting each term by  $p'(\phi_1, \phi_2)$ .

The geometry of model A may be conveniently described by the ten parameters  $r(\text{C-H})$ ,  $r(\text{C-N})$ ,  $r(\text{P-N})$ ,  $r(\text{P-F})$ ,  $\angle \text{NCH}$ ,  $\tau$  (the  $-\text{CH}_3$  group torsion angle, taken equal to zero when one of the group mirror planes is perpendicular to the PNP plane),  $\angle \text{PNP}$ ,  $\alpha$  (the angle between the C-N bond and the PNP plane),  $\angle \text{FPF}$ , and  $\angle \text{NPF}$ . For arbitrary  $\tau$  19 different distances exclusive of the low-weight, strongly damped  $\text{H} \cdots \text{H}$  and  $\text{H} \cdots \text{F}$  distances are obtained.

The geometry of model B may be described by the set used for model A augmented by the parameter  $\delta$  which from eq 3 is seen to be the rms amplitude of the  $-\text{PF}_2$  group torsions. It has the dimension of angle. Tests showed that a satisfactory representation of the continuous distribution of distances  $r_{ij}(\phi_1, \phi_2)$  was given by values of  $\phi_1$  and  $\phi_2$  equal to 0,  $\pm 2/3\delta$ ,  $\pm 4/3\delta$ , and  $\pm 2\delta$ , where the zero values correspond to  $C_{2v}$  symmetry for the  $-\text{N}(\text{PF}_2)_2$  group. The individual instantaneous conformations thus numbered 49 as derived from all combinations of  $\phi_1$  and  $\phi_2$ . The number of different distances comprising model B is large; for example, with a coplanar  $\text{CNP}_2$  grouping the total exclusive of  $\text{H} \cdots \text{H}$  and  $\text{H} \cdots \text{F}$  distances is 82, among which are 56  $\text{F} \cdots \text{F}$ , 7  $\text{P} \cdots \text{F}$ , and 7  $\text{C} \cdots \text{F}$ .

**Refinement Conditions.** A unit weight matrix was used in all refinements. The first refinements were done using model A, from which it was discovered that  $r(\text{C-H})$  and  $\angle \text{NCH}$  among the geometrical parameters and  $l(\text{C-H})$  and  $l(\text{N} \cdots \text{H})$  among the amplitude parameters could not be refined. They were assigned reasonable values and at the same time some of the remaining amplitudes were assembled into groups and refined as such. Refinements based on model B drew on the results from model A; the parameters  $\tau$  and  $\alpha$ , having been found to have values insignificantly different from zero, were given zero values. The parameters  $r(\text{C-H})$ ,  $\angle \text{NCH}$ ,  $l(\text{C-H})$ , and  $l(\text{N-H})$  were assigned the same values as in the case of model A, and similar groupings of refinable amplitudes were formed. The frame vibrational amplitudes for all conformational components of a given torsion-sensitive distance were assigned the same value. The quantitative aspects of these assumptions for model B and except for  $\tau$  and  $\alpha$  for model A are seen in Table I.

In order that the refinements for the low- and high-temperature experiments be as similar as possible, the short nozzle-to-plate dis-

tance average curve for the former was not included except in those runs meant specifically to test its effect.

## Results

**Refinement Results.** Table I summarizes the results obtained for model B; these results differ by not more than a small fraction of one standard deviation from those obtained with model A. The values given for the torsion-sensitive distances correspond to the equilibrium  $C_{2v}$  heavy-atom positions and the amplitudes associated with these distances are frame amplitudes. The effect of torsion on the distances is contained in the values of  $\delta$ . Theoretical intensity and radial distribution curves for the models of Table I are shown in Figures 1 and 2 and the correlation matrix for the  $-35^\circ$  model is given in Table II; the correlation matrix for the  $25^\circ$  model is very similar.<sup>5</sup>

**Noncoplanarity of the  $\text{CNP}_2$  Grouping.** There is no evidence for noncoplanarity of the  $\text{CNP}_2$  grouping; the values  $\alpha = 9^\circ$  with  $2\sigma = 9^\circ$  and  $\alpha = 6^\circ$  with  $2\sigma = 10^\circ$  were obtained for the 25 and  $-35^\circ$  experiments even without shrinkage<sup>7</sup> corrections, the inclusion of which would tend to reduce each.

**Orientation of the  $-\text{CH}_3$  Group.** Because the  $\text{H} \cdots \text{X}$  distances sensitive to methyl group torsion angle give rise to such relatively weak scattering (*cf.* the  $\text{P} \cdots \text{H}$  distance weights in Figure 2), it was judged not worthwhile to investigate the hindered rotation properties of the group. Refinement of the methyl-group torsion angle parameter  $\tau$  showed that slightly, but perhaps not significantly, better agreement is provided by orientation of the group corresponding to  $\tau$  in the range  $\pm 15^\circ$  than with the C-H and P-N bonds eclipsed ( $\tau = 0$ ).

(7) O. Bastiansen and M. Traetteberg, *Acta Crystallogr.*, **13**, 1108 (1960).

Table II. Correlation Matrix for Parameters of CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub> at -35°<sup>a</sup>

	r(C-N)	r(P-N)	r(P-F)	∠PNP	∠FPF	∠NPF	δ	l(C-N)	l(F <sub>1</sub> F <sub>2</sub> )	l(CP)	l(PH)	l(PF <sub>2</sub> )	l(CF)	l(F <sub>1</sub> F <sub>3</sub> )	l(F <sub>1</sub> F <sub>4</sub> )
σ <sup>b</sup>	0.0059	0.0018	0.0003	0.2679	0.1158	0.0954	0.9673	0.0010	0.0015	0.0025	0.0232	0.0068	0.0097	0.0379	0.0138
	1.000	-0.772	0.589	0.616	-0.305	0.262	0.030	0.733	-0.080	0.403	0.139	-0.031	0.390	-0.010	-0.052
		1.000	-0.303	-0.783	0.127	-0.589	-0.031	-0.839	0.059	-0.066	-0.054	0.037	-0.079	-0.021	0.046
			1.000	0.203	-0.311	-0.042	0.009	0.389	0.038	0.357	0.089	-0.005	0.283	-0.020	-0.023
				1.000	-0.110	0.335	-0.099	0.659	-0.159	-0.242	0.231	0.128	0.359	-0.127	-0.005
					1.000	0.363	-0.024	-0.177	0.189	-0.269	-0.223	-0.007	-0.265	0.049	0.001
						1.000	-0.029	0.466	0.108	-0.097	-0.269	-0.004	-0.283	0.097	0.048
							1.000	0.041	0.013	0.060	0.298	-0.927	-0.463	-0.252	0.115
								1.000	-0.017	0.185	0.087	-0.011	0.168	-0.011	0.023
									1.000	-0.105	-0.056	-0.011	-0.259	0.063	0.012
										1.000	0.311	-0.101	0.218	0.111	-0.035
											1.000	-0.160	0.180	-0.262	-0.018
												1.000	0.497	0.175	0.105
													1.000	-0.056	0.060
														1.000	-0.087
															1.000

<sup>a</sup> Distances (r) and amplitudes (l) in ångströms; angles in degrees. <sup>b</sup> Standard deviations from least squares.

**Effect of Short Nozzle-to-Plate Distance Data.** Identical refinements with and without the short-distance data gave values differing by less than one standard deviation for all refined geometrical and vibrational parameters. Figure 1 shows the two theoretical curves for the resulting models; comparison of the corresponding difference curves reveals them to be about equally good.

**Possible Presence of a Second Conformer.** In addition to the form of the CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub> molecule discussed in the preceding sections, two other rotational conformers differing from it by rotation of one or both of the -PF<sub>2</sub> groups by 180° may be visualized. The one obtained by rotation of both groups (C<sub>2v</sub> heavy-atom symmetry) has a distribution of rotation-sensitive distances quite different from that observed and for this and steric reasons may be ignored. However, the conformer obtained by rotation of only one of the -PF<sub>2</sub> groups (C<sub>s</sub> heavy-atom symmetry, see Figure 1) is not implausible on steric grounds and has a distance distribution which, except for the absence of a long F<sub>1</sub>...F<sub>4</sub> type, is similar to that of the principal conformer. For example, if these two conformers are assumed to differ only in the torsion angle of the one -PF<sub>2</sub> group, the C...F<sub>3</sub> and P<sub>1</sub>...F<sub>3</sub>' distances are both 2.97-2.98 Å, the P<sub>1</sub>...F<sub>3</sub> at 3.88 Å and the C...F<sub>3</sub>' and F<sub>1</sub>...F<sub>4</sub>' at 3.74-3.75 Å are similar, and the F<sub>1</sub>...F<sub>3</sub> and F<sub>1</sub>...F<sub>3</sub>' are both 4.40-4.41 Å. Moreover, the weights of the P<sub>1</sub>...F<sub>3</sub> and the C...F<sub>3</sub>' plus F<sub>1</sub>...F<sub>4</sub>' terms are practically identical (weight is proportional to  $n_{ij}Z_iZ_jr_{ij}^{-1}$  where  $n$  is the number of distances and  $Z_i$  is the atomic number) as are those of the F<sub>1</sub>...F<sub>3</sub> and F<sub>1</sub>...F<sub>3</sub>' terms.

The similarities between the assumed two conformers led to results which in respect to the presence of the second conformer are inconclusive; the compositions were found to be 7.6% C<sub>s</sub> form (2σ = 21.0) at -35° and 6.4% C<sub>s</sub> (2σ = 21.2) at 25° with R factors nearly identical with those gotten when this conformer was excluded. Thus, although there is no significant evidence for the presence of any of the C<sub>s</sub> conformer, neither can small amounts of it be ruled out.

**Torsional Force Constant and Torsional Frequency of the -PF<sub>2</sub> Group.** Our measurements of the torsional amplitude of the -PF<sub>2</sub> group permits a rough prediction of the values of these torsional parameters. If the hindering potential is assumed to be of the form

$$2V_\phi = \sum_{n=1}^{\infty} V_n(1 - \cos n\phi) \quad (4)$$

the quadratic approximation (an approximation which seems justified by the results to follow) leads to

$$2V_\phi = \frac{1}{2}V^*\phi^2 = k_\phi\phi^2 \quad (5)$$

where  $V^* = V_1 + 4V_2 + 9V_3$ . In this approximation the relationship between the rms torsional amplitude δ and the potential constant is given by<sup>6</sup>

$$k_\phi = kT/\delta^2 = V^*/2 \quad (6)$$

Values of V\* equal to 28.9 (σ = 10.7) kcal/mol and 28.7 (σ = 7.5) kcal/mol are obtained from the 25° and -35° data, respectively, and from the relationship  $\nu = (k_\phi/\mu_I)^{1/2}/2\pi$  the values 260 cm<sup>-1</sup> (σ = 50) and 280 cm<sup>-1</sup> (σ = 40) are predicted for the torsional frequency.

## Discussion

Table III summarizes the important geometrical

**Table III.** Bond Distances and Bond Angles in Some Aminodifluorophosphines<sup>a,b</sup>

Parameter	CH <sub>3</sub> N(PF <sub>2</sub> ) <sub>2</sub> (this work)	(CH <sub>3</sub> ) <sub>2</sub> NPF <sub>2</sub>		H <sub>2</sub> NPF <sub>2</sub>		
		X-ray diff <sup>3</sup>	Electron diff <sup>4</sup>	Microwave <sup>1</sup>	Electron diff <sup>4</sup>	Microwave <sup>2</sup>
r(P-N)	1.680 (0.006)	1.628 (0.005)	1.684 <sup>c</sup> (0.008)	1.66	1.661 (0.007)	1.650 (0.004)
r(P-F)	1.583 (0.002)	1.610 (0.004)	1.589 (0.003)	1.57	1.581 (0.003)	1.587 (0.004)
r(C-N)	1.479 (0.017)	1.460 (0.009)	1.448 (0.006)	1.48 (assumed)		
r(C,N-H)	1.090 (assumed)		1.15 (0.01)	1.09 (assumed)	1.031 (0.018)	{1.002 (0.005) (cis) 0.981 (0.005) (trans)}
∠FPF	95.1 (0.3)	91.5 (3.0)	99 (3)	95.3	95.3 (1.1)	94.6 (0.2)
∠NPF	99.6 (0.3)	101.6 (2.0)	97 (4)	99.8	101.0 (1.1)	100.6 (0.2)
∠CNP	122.0 (0.4)	{123.7 (0.5) (cis) 120.4 (0.5) (trans)}	118.3 (0.6)	{124.5 (cis) 121.3 (trans)}		
α <sup>d</sup>	0	0	32	0	35	0

<sup>a</sup> Distances in ångströms, angles in degrees. <sup>b</sup> The parenthesized uncertainties from the different investigations do not necessarily have the same meaning. <sup>c</sup> The value 1.648 Å given in the original article is a typographical error. <sup>d</sup> The angle between the CNC (or HNH) plane and the P-N bond in the cases of (CH<sub>3</sub>)<sub>2</sub>NPF<sub>2</sub> and H<sub>2</sub>NPF<sub>2</sub> and between the PNP plane and the C-N bond in the case of CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub>.

parameter values for several aminodifluorophosphines. The P-N bond in CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub>, as in (CH<sub>3</sub>)<sub>2</sub>NPF<sub>2</sub> and H<sub>2</sub>NPF<sub>2</sub>, is considerably shorter than the sum of the single-bond covalent radii corrected for electronegativity difference<sup>8</sup> (1.76 Å). Both this short distance, which corresponds to about 30% double-bond character, and the coplanar CNP<sub>2</sub> grouping are consistent with the view that the P-N links in the aminodifluorophosphines involve (p-d)π bonding.

The P-N bond in CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub> is significantly longer than in (CH<sub>3</sub>)<sub>2</sub>NPF<sub>2</sub> and H<sub>2</sub>NPF<sub>2</sub>, presumably because the electron pair from the nitrogen atom is involved in two bonds in CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub> and only one in the others. The C-N bond in the monomethyl compound is longer than in the dimethyl, a circumstance which may also exist in the case of CH<sub>3</sub>NH<sub>2</sub><sup>9</sup> and (CH<sub>3</sub>)<sub>2</sub>NH.<sup>10</sup> The FPF and NPF angles do not change much from molecule to molecule, at least in the gas phase; however, the CNP angle in (CH<sub>3</sub>)<sub>2</sub>NPF<sub>2</sub> measured by electron diffraction is not only different from that in CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub> but also from those measured by the other methods. It seems quite likely that the electron-diffraction value for ∠CNP in (CH<sub>3</sub>)<sub>2</sub>NPF<sub>2</sub> is too small; a larger value is compatible with a coplanar arrangement of the nitrogen atom and its ligands which doubtless exists in all the aminodifluorophosphines.

(8) V. Schomaker and D. P. Stevenson, *J. Amer. Chem. Soc.*, **63**, 37 (1941).

(9) (a) H. K. Higgenbotham and L. S. Bartell, *J. Chem. Phys.*, **42**, 1131 (1965); (b) D. R. Lide, Jr., *ibid.*, **27**, 343 (1957); (c) T. Nishikawa, T. Itoh, and K. Shimoda, *ibid.*, **23**, 1735 (1955).

(10) (a) J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, **48**, 5058 (1968); (b) B. Beagley and T. G. Hewitt, *Trans. Faraday Soc.*, **64**, 2561 (1968).

After completion of this work we became aware of an independent, concurrent electron-diffraction study of methylaminobis(difluorophosphine) by Drs. Anne Foord and B. Beagley of the University of Manchester Institute of Science and Technology. Their results concerning the geometry of the molecule are as follows: r(C-N) = 1.470 Å (assumed), r(P-F) = 1.590 Å (0.002), r(P-N) = 1.652 Å (0.006), ∠PNP = 119.3° (2.0°), ∠FPF = 94.5° (0.4°), and ∠NPF = 100.1° (0.2°). These are in fair agreement with ours except for r(P-N) and ∠PNP, parameters which are strongly correlated in both investigations. Although we are not cognizant of the details of Drs. Foord and Beagley's investigation, we understand that it is based on substantially fewer diffraction photographs and that the data reflect a smaller range of scattering angle. Accordingly, we believe it likely that our results are the more accurate.

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**Supplementary Material Available.** The data for these curves and the correlation matrix for the lower temperature results will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-4417.