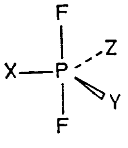
Molecular Structures of Phosphorus Compounds. Part V.[1] Electron Diffraction Study of Tris(dimethylamino)difluorophosphorane

By **Heinz Oberhammer,*** Institut für Physikalische und Theoretische Chemie der Universität Tübingen, Germany
Reinhard Schmutzler, Lehrstuhl B für Anorganische Chemie der Technischen Universität Braunschweig, Germany

The molecular structure of $PF_2(NMe_2)_3$ has been determined by electron diffraction of the gas. A trigonal-bipyramidal structure with the fluorine atoms in axial positions is obtained with the following geometric parameters (r_a values): r(C–H) = 1.120 + 0.006, r(N–C) = 1.460 ± 0.003, r(P–F) = 1.632 ± 0.006, r(P–N) = 1.674 ± 0.005 Å; CNC = 113.0 ± 2.3, PNC = 122.2 ± 0.5, and HCH = 109.3 ± 1.3°. The configuration at the nitrogen atom is nearly planar and the torsional angle of the dimethylamino-groups around the P–N bonds, τ = 70.1 ± 2.7°. SCF–LCAO–MO calculations in the CNDO/2 approximation result in a very similar value for the torsional angle.

CONTINUING interest is attached to the chemistry and stereochemistry of five-co-ordinate phosphorus compounds in general [2] and, particularly, to such compounds containing electronegative fluorine, the fluorophosphoranes.[3] The characteristic feature of many of these compounds is their stereochemical non-rigidity which often manifests itself in the observation of temperature-dependent n.m.r. spectra,[4] which suggest fast intramolecular exchange of ligands at five-co-ordinate phosphorus. In connection with the n.m.r. studies, a knowledge of the ground-state geometry of the fluorophosphoranes was also desirable and both X-ray [1] and electron-diffraction techniques [5] have been employed. A number of studies have confirmed trigonal-bipyramidal stereochemistry for fluorophosphoranes in which the axial positions are invariably occupied by fluorine as the most electronegative substituent at phosphorus, *i.e.*



(I)

as in (I) where X, Y, Z = fluorine or other substituent groups.

Fluorophosphoranes in which one or more of the groups X, Y, and Z contain nitrogen [6] are of further stereochemical interest because of the possibility of π bonding between phosphorus and nitrogen.[7] The only known gas-phase molecular structure of a nitrogen-containing fluorophosphorane is that of the cyclic diazadiphosphetidine $[NMe(PF_3)]_2$,[5b] and it was of interest to have structural information on further compounds, especially those of acyclic structure. The compound $PF_2(NMe_2)_3$ was chosen for its expected simple structure; also, the n.m.r. spectra of this compound indicate it to be stereochemically rigid, relative to the n.m.r. time scale, and no positional exchange between axial and equatorial substituents is evident.

EXPERIMENTAL

A sample of tris(dimethylamino)difluorophosphorane [8] was provided by Dr. H. Bestian, Hoechst A.G., Hoechst, Germany. The product (b.p. 40 °C, 6 mmHg) was checked by n.m.r. spectroscopy, and no impurities were detected.† The following parameters were observed: (^{19}F) δ_F +53.3 p.p.m. (internal CCl_3F), $^1J_{PF}$ 696 Hz; (^{31}P) δ_P +65.5 p.p.m. (external H_3PO_4); (^1H) δ_H −2.76 p.p.m. (internal $SiMe_4$); $^3J_{HP}$ 10.8, $^4J_{HF}$ 2.8 Hz.

The usual techniques were used for obtaining the diffraction photographs with the KDG2 apparatus.[9] An accelerating voltage of 60 kV was chosen and the electron wavelength was determined by ZnO powder diffraction. Details are given in Table 1.‡ The small difference in the nozzle temperatures for the two camera distances will have a negligible effect on the mean-square amplitudes. The procedure for data reduction, background refinement, and calculation of the radial distribution function is described elsewhere.[10a] In the range s = 0—1.4 Å^{-1} the theoretical molecular intensity function was used in the Fourier transform with the damping factor γ = 0.002 Å^{-2}. The modified molecular intensities $sM^{\text{expt.}}(s)$ and the theoretical intensity function $sM^{\text{theor.}}(s)$ as calculated for the final model (Tables 2 and 3) are shown in Figure 1 together with

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† 1 mmHg ≈ 13.6 × 9.8 Pa.

‡ Throughout this paper 1 Å = 100 pm, 1 Torr = (101.325/760) kPa, and 1 cal = 4.1868 J.

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the difference curve. Scattering factors and phase shifts of Haase[10b] were used for calculating the theoretical intensity function.

Structure Determination.—The radial distribution function $f^{\text{expt.}}(r)$ (Figure 2) was used to obtain a preliminary model of the molecule (Figure 3). This analysis showed that equatorial positions for the dimethylamino-groups have to be assumed. Any other grouping of the ligands resulted in large discrepancies between experiment and model.

TABLE 1

Experimental conditions

Camera distance	θ_c/°C		Pressure of camera	Exposure time	Electron wavelength	s Range *
mm	Sample	Nozzle	10^{-6} Torr	min	Å	Å^{-1}
500	20	30	5	1.0—1.5	0.049 24 (1)	1.4—17.0
250	35	45	15	2.5—3.5	0.049 27 (1)	7.0—34.0

* $s = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$, where θ is the scattering angle.

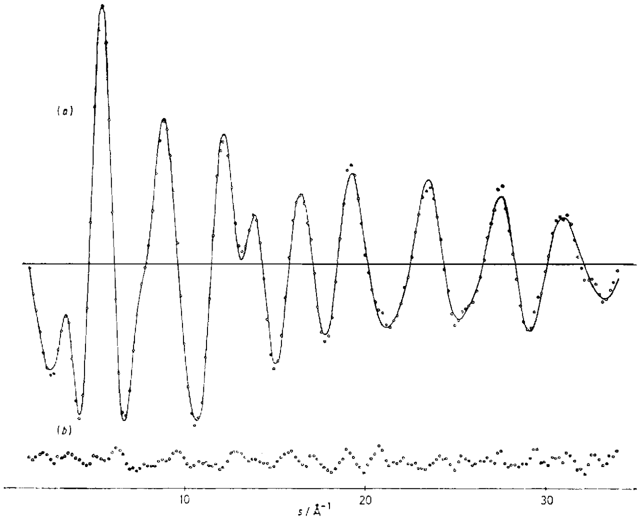

FIGURE 1 Experimental (...) and theoretical (——) molecular intensities (*a*) and difference curve $sM^{\text{expt.}}(s) - sM^{\text{theor.}}(s)$ (*b*)

TABLE 2

Geometric parameters (r_a values)

Distance/Å		Angle/°	
C–H	1.120 ± 0.006	CNC	113.0 ± 2.3
N–C	1.460 ± 0.003	PCN	122.2 ± 0.5
P–F	1.632 ± 0.006	HCH	109.3 ± 1.3
P–N	1.674 ± 0.005	τ *	70.1 ± 2.7

Scale factors: $R_{500} = 0.91 \pm 0.03$; $R_{250} = 0.93 \pm 0.06$

* Torsional angle of the NMe$_2$ groups around the P–N bonds (see text).

Furthermore, it was found that the configuration at the nitrogen atoms is planar or nearly planar and that the CNC planes of the dimethylamino-groups deviate slightly from the directions perpendicular to the equatorial plane. The positions of the NMe$_2$ groups are characterized by the torsional angle τ (Figure 3); $\tau = 0$ corresponds to the position of all the carbon atoms in a plane parallel to the equator.

This preliminary model was then refined by a least-squares procedure based on the molecular intensities. A diagonal weight matrix was used which increases exponentially from $s_{\text{min.}}$ to $s = 4$ Å^{-1}, remains unity in the range $4 \leqslant s \leqslant 30$ Å^{-1}, and decreases exponentially from $s = 30$ Å^{-1} to $s_{\text{max.}}$. A constant interval of $\Delta s = 0.2$ Å^{-1} was used. The following assumptions were made in the least-squares refinement. (*i*) C_{3v} Symmetry for the methyl groups. (*ii*) C_3 Symmetry for the molecule. Model calculations with different torsional angles, τ, for the dimethylamino-groups resulted in poorer agreement between experimental and theoretical radial distribution functions. (*iii*) In the final least-squares analysis the mean-square

TABLE 3

Mean-square amplitudes (Å)

C–H	0.070 ± 0.007	$C^1 \cdots C^3$	0.451 ± 0.195
N–C	0.049 ± 0.003 [a]	$C^2 \cdots C^4$	
P–F	0.049 ± 0.003 [a]	$C^1 \cdots C^4$	
P–N	0.049 ± 0.003 [a]	$C^1 \cdots C^6$	0.583 ± 0.480
$P \cdots C$	0.071 ± 0.004	$C^1 \cdots C^2$	0.070 [c]
$F \cdots N$	0.070 ± 0.004	$F \cdots F$	0.055 [c]
$N \cdots N$	0.107 ± 0.036	$F \cdots H$	0.250 [c]
$F^1 \cdots C^1$	0.103 ± 0.022	$(N \cdots H)$ (short)	0.150 [c]
$F^1 \cdots C^2$	0.098 ± 0.013	$(N \cdots H)$ (long)	0.250 [c]
$N \cdots C$	0.262 ± 0.063 [b]	$(C \cdots H)$	0.300 [c]
$P \cdots H$	0.105 ± 0.080	$(H \cdots H)$	0.250 [c]

[a] Assumed to be equal (see text). [b] All non-bonded $N \cdots C$ amplitudes were assumed to be equal. [c] Assumed.

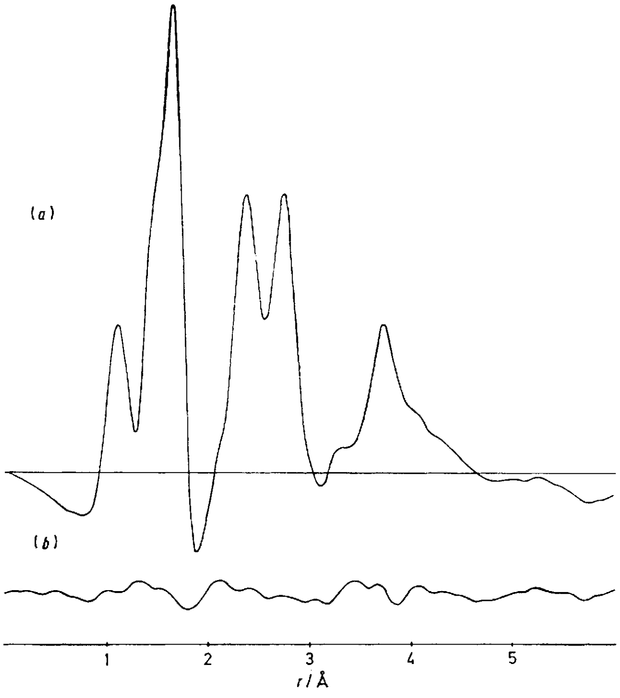

FIGURE 2 Experimental radial distribution function (*a*) and difference curve $\Delta(r)$ (*b*)

amplitudes of the C–N, P–F, and P–N bond distances were assumed to be equal. In the first calculations only l(C–N) and l(P–F) were taken to be equal, since preceding structure determinations resulted in very similar values for these amplitudes in other molecules. For methylamine [11] and trimethylamine [12] values of 0.046 ± 0.002 and 0.045 ± 0.003 Å respectively were determined for the C–N amplitude. For the two extremely different axial P–F bonds in PF_5 and PMe_3F_2 the experimental amplitudes are 0.043 ± 0.002 [13] and 0.048 ± 0.001 Å respectively.[14] Since the value for the P–N amplitude, which was varied separately in the first calculations, was always very close (±0.002 Å) to the value for the C–N or P–F amplitude, this assumption seems to be justified. (*iv*) The mean-square amplitudes for some non-bonded distances were assumed to be equal and some amplitudes were not refined in the least-squares procedure (see Table 3).

With these assumptions eight basic independent geometric parameters, eleven mean-square amplitudes, and the scale factors R_{500} and R_{250} for the two camera distances were refined simultaneously. Five elements of the correlation matrix $\{c_{ij}\}$ had absolute values >0.6, *i.e.* c [r(P–F), r(P–N)] = −0.88, c (CNC, PNC) = −0.66, c [CNC, l(F$^1\cdots$C^1)] = 0.80, c [r(P–F), l(P–F)] = 0.84, and c [r(P–N), l(P–N)] = −0.80.* The results of the least-squares analysis are given in Tables 2 and 3. The error limits are three times the standard deviations. The error limits for the bond distances include possible uncertainties due to assumption (*iii*), since for the P–N and P–F distances variations are smaller than ±0.003 Å when differences of ±0.005 Å are permitted for the respective mean-square amplitudes. The corresponding uncertainty in the C–N bond length is smaller than ±0.002 Å. Values for the non-bonded distances without hydrogen atoms are given in Table 4.

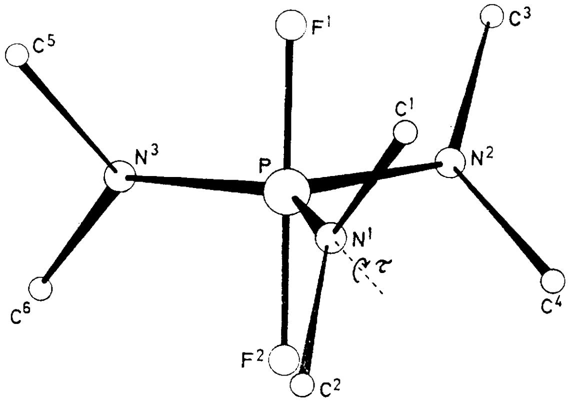

FIGURE 3 Molecular model for $PF_2(NMe_2)_3$

Since the contributions of the P–F and the P–N distances to the molecular intensities are very similar there is the possibility that the values for these two distances could be interchanged, *i.e.* r(P–N) < r(P–F). Comparison with the respective bond distances in molecules like PMe_3F_2 [$r(\text{P–F})_{ax}$ 1.685 ± 0.001 Å] [14] or $[NMe(PF_3)]_2$ [$r(\text{P–N})_{eq}$ 1.595 Å] [15] seems to support such a possibility. Several calculations with different starting values for r(P–N) and r(P–F) were made in order to confirm that the values in Tables 2 and 3 represent the correct minimum of the least-squares analysis. When interchanging the starting values, the least-squares procedure converged to the values in Tables 2 and 3 after 12 iterations. Although the peak in the radial distribution function corresponding to the bonded distances could be fitted almost equally well with interchanged P–N and P–F bond distances, $f^{\text{expt.}}(r)$ could not be reproduced consistently in the range $r > 2$ Å when r(P–F) > r(P–N). In this case the sum of the errors squared is more than twice as large as for the results given in Tables 2 and 3.

TABLE 4

Non-bonded distances (Å) without hydrogen atoms (r_a values)

$P\cdots C$	2.745	$F^1\cdots C^1$	2.496
$N\cdots N$	2.899	$F^1\cdots C^2$	3.702
$C^1\cdots C^2$	2.435	$F^2\cdots C^1$	3.765
$F\cdots F$	3.264	$F^2\cdots C^2$	2.589
$F\cdots N$	2.338	$C^1\cdots C^3$	4.263
$N^1\cdots C^3$	3.882	$C^1\cdots C^4$	4.477
$N^1\cdots C^4$	3.559	$C^2\cdots C^4$	4.378
$N^1\cdots C^5$	3.718	$C^1\cdots C^6$	5.204
$N^1\cdots C^6$	4.028		

The positions of the methyl groups were not refined in the least-squares procedure. The agreement between experimental and theoretical intensities was better for the staggered than for the eclipsed position.

DISCUSSION

The equatorial P–N bond lengths in $PF_2(NMe_2)_3$ are considerably longer than those in the cyclic compounds $[NMe(PPhF_2)]_2$,[16] $[NMe(PCl_3)]_2$,[17] and $[NMe(PF_3)]_2$,[15] where values for $r(\text{P–N})_{eq}$ of 1.64, 1.635 ± 0.007, and 1.595 Å respectively were determined. They are very similar to P–N bonds in compounds of three-co-ordinate phosphorus, where for most molecules the bond lengths are between 1.65 and 1.70 Å. A detailed review of the stereochemistry of compounds containing P–N bonds was published recently.[18] The axial P–F bond lengths in phosphoranes depend very strongly on the electronegativity of the equatorial ligands. The value obtained for $PF_2(NMe_2)_3$ is between those determined for PF_5 [$r(\text{P–F})_{ax}$ 1.577 ± 0.005 Å] [13] and PMe_3F_2 [$r(\text{P–F})_{ax}$ 1.685 ± 0.001 Å] [14] corresponding to the intermediate electronegativity of the dimethylamino-groups [$\chi(NMe)_2$ 3.0].[19]

The sum of the bond angles at the nitrogen atoms is 357.4 ± 2.4°, *i.e.* the configuration of the bonds to nitrogen is almost planar. The planar or near-planar

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* The correlation matrix has been deposited as Supplementary Publication No. SUP 21768 (2 pp.). For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue (items less than 10 pp. are supplied as full-size copies).

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configuration of the bonds to nitrogen is characteristic of most dimethylamino-groups bonded to phosphorus.[18] The NMe_2 groups are rotated around the P–N bonds by an angle of $\tau = 70.1 \pm 2.7°$. The position of these groups relative to the equatorial plane was also the main subject of a SCF–MO investigation using the CNDO/2 approximation (see Appendix). The minimum total energy was obtained for a torsional angle $\tau = 67°$ (Figure 4), very similar to the experimental result. The shallow minimum in the potential energy and the low potential barrier of *ca.* 3.4 kcal mol^{-1} at $\tau = 90°$ allow large-amplitude torsional motions of the NMe_2 groups. The frequency of the torsional vibration cannot be determined from the electron-diffraction experiment and we know of no spectroscopic investigation of this molecule. The very large experimental values for the $N \cdots C$, $C^1 \cdots C^3$, and $C^1 \cdots C^4$ mean-square amplitudes (Table 3) indicate that the potential barrier at $\tau = 90°$ may be even lower than the value obtained from the CNDO/2 calculations. Furthermore, inversion of the slightly non-planar $P–NMe_2$ groups may also contribute to these large amplitudes.

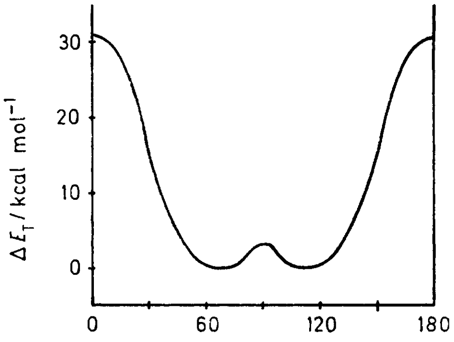

FIGURE 4 Total energy as a function of torsional angle τ

APPENDIX

CNDO/2 Calculations.—The CNDO/2 approximation with the original parameterization was used.[20] Only the torsional angle τ was investigated. The position of the CH_3 groups was optimized for each value of the dihedral angle. The total energy as a function of τ is shown in Figure 4, indicating that a torsional angle of $\tau = 67°$ is the optimum compromise between steric repulsion of the atom cores and the electronic energy. The optimized position of the methyl groups for this dihedral angle is almost staggered. The breakdown of the total energy into electronic and Coulomb-repulsion energy of the cores is shown in Figure 5. The electronic energy would have a minimum for vertical ($\tau = 90°$) positions of the NMe_2 groups and the Coulomb repulsion would be a minimum at $\tau = 45°$. The electronic energy for horizontal positions ($\tau = 0°$) is *ca.* 40 kcal mol^{-1} higher than for vertical positions, indicating that the vertical positions would also be preferred in the absence of steric interactions. The following net charges (in atomic units) were obtained: P +0.64; F −0.32; N −0.18; and Me +0.09.

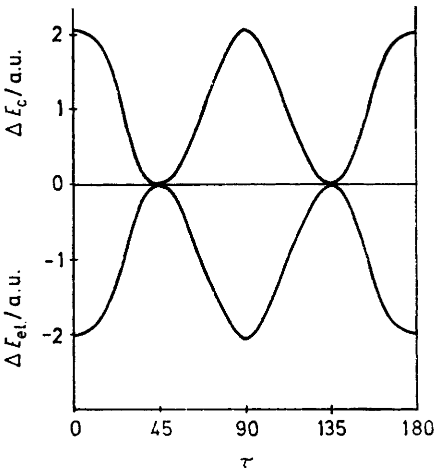

FIGURE 5 Electronic energy ΔE_{el}, and Coulomb-repulsion energy of the cores, ΔE_c, as a function of torsional angle τ (1 a.u. ≈ 627 kcal mol^{-1})

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