Determination of the Molecular Structure of Tris(difluorophosphino)-amine by Electron Diffraction in the Gas Phase

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The molecular structure of $N(PF_2)_3$ in the gas phase has been determined by electron diffraction. The molecule has a planar skeleton, with overall C_{3h} symmetry, and r_a(P–F) 157.4(2), r_a(P–N) 171.2(4) pm, F–P–F 97.1(5), and F–P–N 99.0(4)°. The root-mean-square amplitude of torsion of the PF_2 groups from their average positions is 17°, corresponding to a harmonic torsional frequency at 30 cm^{-1}.

In recent structural studies of fluorophosphine derivatives two objectives have been of particular importance. One has been the investigation of the extent to which the structures of phosphorus–nitrogen and –oxygen compounds resemble those of their silicon analogues, with wide angles and short bonds. The other has been the determination of the conformations adopted by the fluorophosphine groups, coupled with studies of the torsional vibrations of these groups.

From both points of view, tris(difluorophosphino)-amine is an exceptionally interesting molecule to study: it is the simplest known phosphorus analogue of trisilylamine, the classic ' planar nitrogen ' molecule:[1] it has difluorophosphine groups free to rotate or oscillate without any hydrogen–fluorine interactions, or crowding by other atoms; and it may have a high degree of symmetry, making it an ideal subject for an electron-diffraction investigation. Consequently, having found a way of synthesizing and purifying this compound,[2] we embarked on a study of its structure. The results of that study are reported here.

EXPERIMENTAL

A sample of tris(difluorophosphino)amine was prepared by the gas-phase reaction of chlorodifluorophosphine with ammonia and trimethylamine, and was purified by fractional condensation and further treatment with trimethylamine, repeated several times.[2] The purity of the product was checked spectroscopically.

TABLE 1

Weighting functions, scale factors, correlation parameters, and wavelengths

Camera height mm	Δs nm^{-1}	$s_{min.}$ nm^{-1}	sw_1 nm^{-1}	sw_2 nm^{-1}	$s_{max.}$ nm^{-1}	p/h	Scale factor	Wavelength pm
190	4	32	60	300	324	0.384	0.748(11)	5.852(3)
580	2	20	35	105	134	0.488	0.838(13)	5.847(3)

Scattered electron intensities were recorded photographically on Agfa–Gevaert Replica 23 plates, using a Balzers' KD.G2 diffraction apparatus at the University of Oslo,[3,4] and digitized using an oscillating-table microdensitometer. The sample was maintained at 238 K, and the nozzle at 298 K, during exposures. Two camera heights were used, 190 (3 plates) and 580 mm (5 plates), giving data over a range of 10—324 nm^{-1} in the scattering variable, s.

Apart from data reduction to give uphill curves, all computation was carried out on an ICL 4-75 computer at the Edinburgh Regional Computing Centre, using established data reduction[5] and least-squares refinement[6] programs. The weighting points used in setting up the off-diagonal weight matrix are given in Table 1, together with correlation parameters, scale factors, and electron wavelengths, determined from the diffraction pattern of powdered zinc oxide. In all calculations the complex scattering factors of Schäfer *et al.*[7] were used.

MOLECULAR MODELS AND REFINEMENTS

In all refinements of the structure of $N(PF_2)_3$ it was assumed that the three F_2PN units had identical structures, and that they each had a plane of symmetry. Thus four parameters, chosen to be the P–F and P–N bond lengths and the angles F–P–F and F–P–N, were sufficient to define the geometry of these units. The angles between the three P–N bonds were also assumed to be equal, and early refinements showed that, although this angle parameter was strongly correlated with twist parameters for the PF_2 groups, the optimum value was always 120° within experimental error, which was $\leqslant 0.5°$. Once coplanarity of the P–N bonds had been established, the P–N–P angle was fixed, so that the maximum amount of information about torsional angles could be obtained.

For the study of the conformation of the molecule, a model was constructed giving the greatest possible flexibility in determining the positions of the PF_2 groups. For each group, a dihedral angle, δ, was defined, being the angle between the F–P–F symmetry plane and the P_3N plane. A control parameter was then used to constrain two or more of these angles in a fixed relationship to each other, so that some element of symmetry could be maintained. The relationships used were: (*a*) $\delta_1 = \delta_2 = \delta_3$, giving C_3 symmetry overall, and C_{3h} if $\delta = 0$; (*b*) $\delta_1 = 180 - \delta_2$, $\delta_3 = 90$, giving C_s symmetry; (*c*) $\delta_1 \neq \delta_2 \neq \delta_3$, allowing structures with no symmetry to be investigated. In addition to these, two relationships were used, specifically to consider small deviations from overall C_{3h} symmetry. These were (*d*) $\delta_1 = -\delta_2$, $\delta_3 = 0$, and (*e*) $\delta_1 = \delta_2 = -\delta_3$.

Preliminary refinements using relationship (*c*) indicated that there were only two significant minima in the complete three-dimensional least-squares surface, corresponding to structures with approximately C_s and C_{3h} symmetry. Further exploration of the first of these minima gave a lowest R_G of 0.148 for a structure with exact C_s symmetry, with $\delta_1 = -10°$, $\delta_2 = 190°$, and $\delta_3 = 90°$. This gave shortest F · · · F distances between fluorine atoms in different PF_2 groups of 230 pm, and was rejected as being physically unreasonable. For the C_s structure with the least interaction between the PF_2 groups, which had twist angles of −70, −110, and 90°, the shortest F · · · F distance was still 255 pm, compared with 270 pm for twice the van der Waals radius for fluorine, and R_G was 0.22.

The second possible conformation was then investigated. An R factor of 0.102 was obtained assuming C_{3h} symmetry, with twist angles of 10.1°. Use of relationship (*d*) gave R_G 0.099 for $\delta_1 = 10.1°$, $\delta_2 = -10.1°$, and $\delta_3 = 0°$, and a further improvement was obtained using relationship (*e*), with R_G 0.095 for $\delta_1 = \delta_2 = 10.4°$, $\delta_3 = -10.4°$.

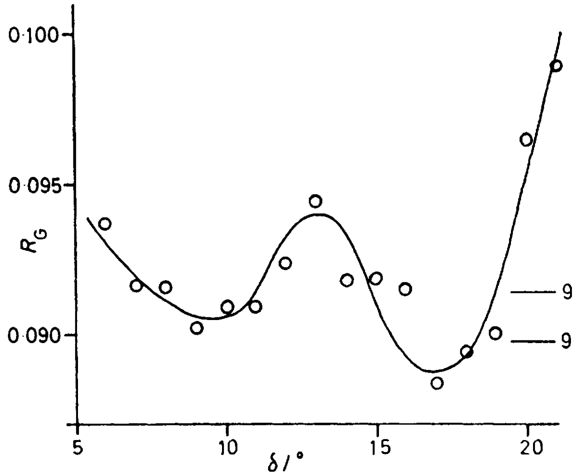

FIGURE 1 Variation of R_G with r.m.s. torsion angle of PF_2 groups, showing 95 and 99.5% confidence limits

It now seemed highly probable that the average structure had C_{3h} symmetry and that the deviations observed were shrinkage effects caused by low-frequency torsional vibrations of the PF_2 groups. Another model was therefore constructed, assuming that the three groups were oscillating independently about their average positions, with root-mean-square (r.m.s.) torsion angles δ. Assuming a harmonic potential function, the probability of a group being twisted by an angle ϕ from the average position is proportional to $\exp(-\phi^2/2\delta^2)$. Using a set of seven fixed positions for each PF_2 group, with $\phi = 0$, $\pm\frac{2}{3}\delta$, $\pm\frac{4}{3}\delta$, and $\pm 2\delta$, as in the study of $NMe(PF_2)_2$,[8] a set of 14 P · · · F distances was calculated. However, for the F · · · F distances, 49 conformations of a pair of PF_2 groups must be considered with a probability distribution proportional to $\exp[-(\phi_1^2 + \phi_2^2)/2\delta^2]$, and 98 different F · · · F distances are involved. In order to save computing time and space, the number of F · · · F distances was reduced to 21 by the following simple approximation. The total F · · · F range, from 300 to 510 pm, was divided into ' pockets ', each 10 pm wide. As each distance was calculated it was assigned to the appropriate pocket, and the probability of that distance occurring was added to the associated multiplicity. When all the distances had been calculated the total multiplicity was evaluated, and the individual distances were then scaled accordingly. The weighted mean distance of the components of each pocket was also calculated, and the set of distances thus obtained was used in determining the theoretical scattering intensities.

Using this model, two minima were found when R_G was plotted against δ (Figure 1). The parameters obtained in refinements with δ fixed at the value giving the first minimum, 9°, are listed as refinement A in Table 2. The other minimum, with $R_G = 0.088$ and $\delta = 17°$, gave a set of parameters (refinement B of Table 2) almost identical to the first set, with the exception of the framework vibrational amplitudes of the F · · · F and P · · · F distances. These could not be refined at the same time as other amplitudes, for any value of δ. Two groups of amplitudes were therefore allowed to refine in alternate refinements, until a self-consistent set of values was obtained. Not surprisingly, the refinements with larger values of δ gave smaller framework amplitudes of vibration: the values obtained with δ = 9° seem to be unreasonably large, and it is probable that some of the effects of the torsions are being reflected in the other parameters.

Refinements using a quartic torsion-potential function did not lead to any significant improvement of the fit of experimental and theoretical intensities.

TABLE 2

Molecular parameters for $N(PF_2)_3$

	Refinement A		Refinement B	
(*a*) Independent distances and amplitudes (pm)				
r_1(P–N)	171.1(4)	4.0(7)	171.2(4)	4.1(7)
r_2(P–F)	157.4(2)	3.5(3)	157.4(2)	3.6(3)
(*b*) Dependent distances and amplitudes (pm)				
d_3(P · · · P)	296.4(6)	10.4(5)	296.5(6)	10.8(6)
d_4(N · · · F)	250.4(6)	7.2(8)	250.1(6)	7.5(8)
d_5(F · · · F)	235.6(9)	5.8(10)	236.0(10)	6.3(10)
cis-(P · · · F)	293—328	21.1(14) [a]	284—348	15.2(18) [a]
trans-(P · · · F)	378—406	18.2(9) [a]	360—412	13.7(10) [a]
(F · · · F) [b]	300—510	22.4(18) [a]	300—510	18.7(28) [a]
(*c*) Angles (°)				
1 N–P–F	99.2(3)		99.0(4)	
2 F–P–F	96.9(3)		97.1(5)	
3 δ [c]	9.0 (see text)		17.6 (see text)	
4 P–N–P	120 (fixed, see text)		120 (fixed, see text)	

[a] Not included in final refinements. The values and estimated standard deviations quoted were obtained in earlier refinements, in which other amplitudes of vibration were fixed. [b] All F · · · F distances were within the range quoted, but did not necessarily extend to the limits of the range. [c] Root-mean-square torsional angle of PF_2 groups from average positions.

TABLE 3

Least-squares correlation matrix for $N(PF_2)_3$, refinement B, multiplied by 100

r_1	r_2	<1	<2	u_1	u_2	u_3	u_4	u_5	k_1	k_2	
100	41	−39	10	12	12	15	8	24	34	17	r_1
	100	−16	−2	19	10	7	1	6	8	4	r_2
		100	−91	−3	−4	−9	−52	−58	−13	−9	<1
			100	−2	0	−6	64	54	4	4	<2
				100	75	13	8	8	42	25	u_1
					100	17	15	16	62	28	u_2
						100	−12	2	25	15	u_3
							100	63	24	14	u_4
								100	29	19	u_5
									100	25	k_1
										100	k_2

The final least-squares correlation matrix for refinement B is given in Table 3. Estimated standard deviations in Table 2 include random errors, determined in the least-squares analysis, and allowances for systematic errors and constraints applied during refinement. Observed and final weighted difference scattering intensities are shown in Figure 2, and the experimental and difference radial-distribution curves are illustrated in Figure 3.

DISCUSSION

The planarity of the P_3N skeleton of tris(difluorophosphino)amine illustrates again the similarity of the structures of fluorophosphine derivatives to those of their silyl analogues. It is interesting that the P–N bonds are longer in this tris(phosphino)amine [171.2(4) pm] than in other difluorophosphinoamines [165.4—168.4 pm] [5,8,9] just as the Si–N bonds are longer in trisilylamine [173.4(2) pm] [1] than in other silylamines (171.5—172.6 pm).[10-12]

The conformation adopted by the difluorophosphine groups is the one that would be expected on steric grounds, although twists of up to *ca.* 40° from the equilibrium positions are possible without giving unduly short non-bonded P • • • F contacts. The small coupling constant $^2J(PP)$ [2] is consistent with the proposed structure, since it seems that this coupling is largest when there is strong interaction between the lone pairs of electrons on the phosphorus atoms, as in $NMe(PF_2)_2$,[8] $S(PF_2)_2$, and $Se(PF_2)_2$.[13] In the present system, this lone-pair–lone-pair interaction is minimized in the C_{3h} conformation.

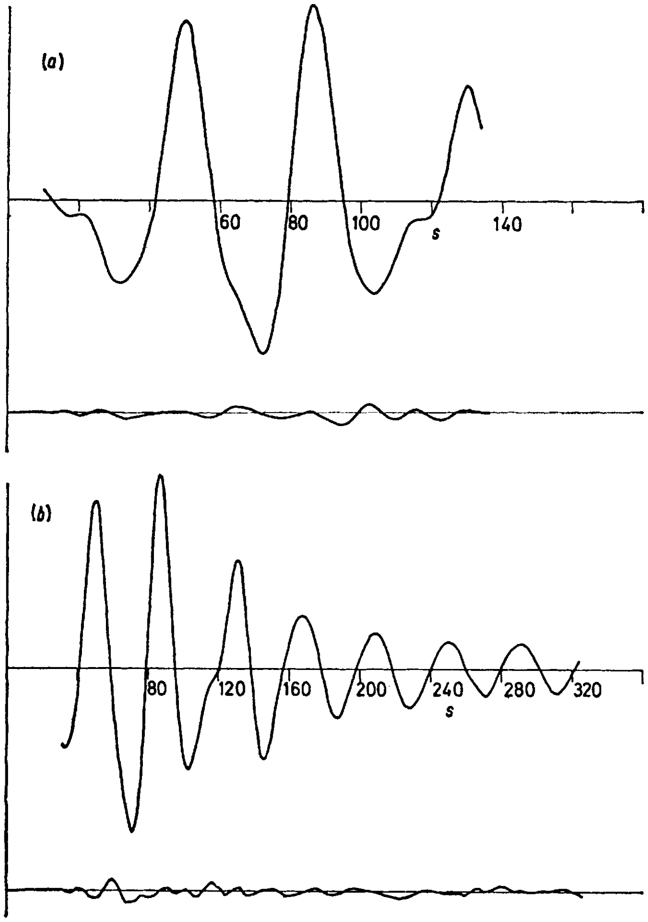

FIGURE 2 Observed and final weighted difference molecular scattering intensities for nozzle-to-plate distances of (*a*) 580 and (*b*) 190 mm

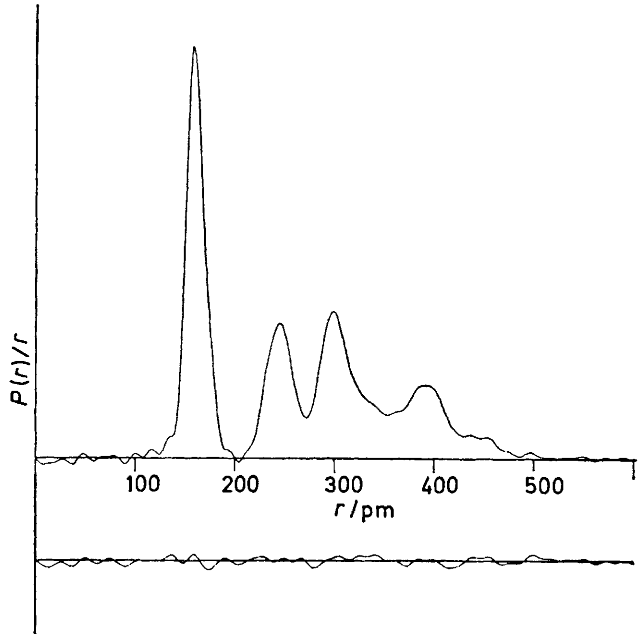

FIGURE 3 Observed and final difference radial-distribution curves, $P(r)/r$ against r, for $N(PF_2)_3$. Before Fourier inversion the data were multiplied by $s.\ \exp\{-0.000\,015s^2/[(Z_P - f_P) - (Z_F - f_F)]\}$

The possibility of the presence of a small amount of a second conformer cannot be excluded, but is difficult to envisage what form such a conformer could take, since the C_s structure involves unreasonably short non-bonded contacts. The complexity of the observed gas-phase i.r. spectrum [2] remains unexplained.

If the torsional vibrations are assumed to be harmonic, frequencies at 30 and 57 cm^{-1} may be calculated, corresponding to r.m.s. amplitudes of torsion of 17 and 9° respectively. We have not yet observed vibrational bands near these frequencies, although analogous torsional modes in fluorophosphine pseudohalides have been observed near 50 cm^{-1}.[14] The much higher frequencies calculated for $NMe(PF_2)_2$[8] seem to be derived from incorrect reduced moments of inertia. Using the published geometrical parameters, we calculate I_{red} = 64.6 a.m.u. Å^2* and a harmonic frequency at 55 cm^{-1}.

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* Throughout this paper: 1 a.m.u. Å^2 = 1.66 × 10^{-47} kg m^2.

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