Gas-phase Molecular Structure of Bis(difluorophosphino)amine, determined by Electron Diffraction

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The molecular geometry of bis(difluorophosphino)amine, $NH(PF_2)_2$, in the gas phase has been studied by electron diffraction. Principal parameters are: r_a(P–F) 158.4(3), r_a(P–N) 168.4(8) pm; FPF 95.6(10), FPN 98.3(7), and PNP 122.1(7)°. Two conformers are present in the vapour at room temperature. The predominant form (72%) has almost C_{2v} symmetry, but the PF_2 groups are twisted 5° away from most symmetrical positions. In the less abundant form, one PF_2 group is twisted by 60° from the C_{2v} position but the other only by 5°.

Of the three difluorophosphino-amines, only two have had their gas-phase molecular structures determined. The primary amine, $NH_2(PF_2)$, has been shown by both electron diffraction [1] and microwave spectroscopy [2] to adopt a conformation in which the axes of the phosphorus and nitrogen lone pairs of electrons are orthogonal. The microwave study indicated that the nitrogen atom had planar co-ordination, but in the electron-diffraction results the hydrogen-atom positions were not well defined, although there was some evidence that the PNH_2 group was not planar.

In the case of the tertiary amine, $N(PF_2)_3$, an electron-diffraction study [3] has shown that the NP_3 skeleton is planar, and that each phosphorus lone-pair orbital is orthogonal to the nitrogen lone-pair 2*p* orbital. The conformation of the molecule is such that the overall symmetry is C_{3h}, with the phosphorus lone pairs as far away from each other as possible. This structure contrasts with that of $NMe(PF_2)_2$,[4] which has the lone pairs as close together as possible, with C_{2v} symmetry for the $CN(PF_2)_2$ fragment. The structure of the secondary amine is therefore of particular importance. The vibrational spectra of this compound in the gas phase [5] show two N–H stretching and two in-plane N–H deformation modes, suggesting that two conformers are present. However, a study [6] of the crystalline solid at 160 K indicates that only one conformer is present, the molecules having almost exact C_{2v} symmetry. We have therefore investigated the molecular structure of the secondary amine in the gas phase, to see whether we can identify two distinct conformers.

EXPERIMENTAL

Attempts to prepare bis(difluorophosphino)amine using the published procedure [5] were unsuccessful. Tris(difluorophosphino)amine did not react with HCl, HBr, or H_2S in the gas or liquid phase, over a period of several days at room temperature. Having re-examined the original vibrational spectra, which are perfectly satisfactory, we can only conclude that the acid cleavage of the tertiary amine is catalysed by some material which was not present in recently prepared samples. The secondary amine was therefore prepared by treating a four-fold excess of aminodifluorophosphine with bromodifluorophosphine and trimethylamine, and destroying the excess of primary amine from the mixture of primary and secondary amines with hydrogen bromide. The purity of the sample prepared in this way was checked by i.r. and n.m.r. spectroscopy.

Electron-diffraction scattering intensities were recorded photographically using the Cornell University diffraction apparatus,[7] now installed at the University of Edinburgh. The apparatus was operated in the conventional convergent beam mode, with a sector designed to give uniform scattering intensity from carbon atoms. With an accelerating potential of 44 kV and nozzle-to-plate distances of 128 and 285 mm, data were obtained over a range of the scattering variable *s* of 30—350 mm^{-1}. Data were recorded on Kodak Electron Image plates (three plates at each camera distance were used), with the sample at 228 K and the nozzle at 295 K. The background pressure was 5×10^{-7} Torr,† and was maintained at 3×10^{-6} Torr during exposures. The electron wavelength was determined from the scattering pattern of gaseous benzene, recorded immediately before the amine patterns were recorded.

TABLE 1

Weighting functions, correlation parameters, and scale factors

Camera height mm	Wavelength pm	Scale factor	Δs	$s_{min.}$	s_1	s_2	$s_{max.}$	Correlation parameter
					nm^{-1}			
128.47	5.707	0.847(9)	4	60	80	300	340	0.126
284.76	5.719	0.797(11)	2	34	44	118	146	0.496

The photographic intensities were obtained in digital form using a Jarrell–Ash double-beam microphotometer,[8] with spinning plates. All calculations were carried out using an ICL 2970 computer at the Edinburgh Regional Computing Centre. The data reduction program used was a version of an established program,[9] modified to handle data from the Jarrell–Ash microdensitometer. The least-squares refinement program is a new version of an established program,[1] which uses an off-diagonal weight matrix to allow for correlation between data points. The weighting points used in setting up that matrix are given in Table 1, together with correlation parameters and other experimental details. In all calculations, the complex scattering factors of Schäfer *et al.*[10] were used.

† Throughout this paper: 1 Torr = (101 325/760) Pa.

Refinement.—In the early stages of refinement the molecular model used allowed for the presence of only a single conformer. The basic structure had C_{2v} symmetry and was defined in terms of P–F, P–N, and N–H distances, and FPF, FPN, and PNP angles. The hydrogen atom was assumed to lie in the PNP plane. Distortion from C_{2v} symmetry (with the FPF angle bisectors eclipsing the N–H bond) was possible by twisting the PF_2 groups around the P–N bonds. These two twists could be constrained to be equal, or equal and opposite, giving structures of C_2 or C_s symmetry. Using this model, the principal bond lengths and angles refined readily, and the best fit ($R_G = 0.067$) was obtained for a C_2 structure, with PF_2 groups twisted 5° from the C_{2v} positions.

The model was then modified so that a variable amount of a second conformer, differing from the first only in the PF_2 twist angles, could be included. As it was not feasible to investigate all combinations of the four twist angles defining two conformations and the relative proportions of the two, some constraints on the twist angles were applied. All possible mixtures of conformations that could be described by two twist angles and a proportionality factor were explored. There was no significant reduction of the R factor for any amount of a second conformer with C_2 or C_s symmetry including those forms (of C_s and C_{2v} symmetry respectively) in which one or more of the phosphorus lone pairs eclipse the N–H bond. However, a considerable improvement was obtained when it was assumed that the second conformer had one angle which was the same as those in the major form, and the second angle was treated as a variable. In Figure 1 the variations of the R factor with this angle and with the percentage of the second conformer are shown. The lowest R factor (0.057) was obtained for 27.5% of a form with twist angles of 5 and 58°.

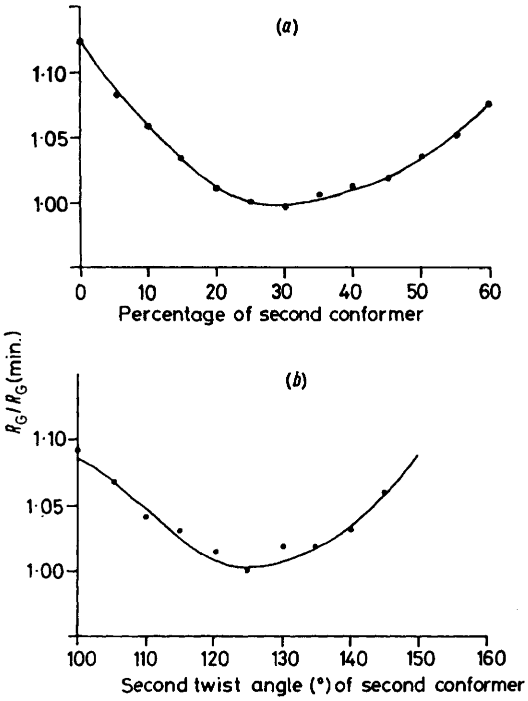

FIGURE 1 Variations of the R factor with (*a*) percentage of second conformer present and (*b*) second twist angle in the second conformer

RESULTS AND DISCUSSION

The results of the final refinement are given in Table 2. All distances quoted are r_a, and errors are estimated standard deviations obtained in the least-squares analysis, increased to allow for systematic errors. The final least-squares correlation matrix (Table 3) shows several strong correlations between parameters caused by overlap of the P–F and P–N and F $\cdots$ F and F $\cdots$ N peaks in the radial distribution curve (Figure 2). The intensity data and final weighted difference curves are shown in Figure 3.

TABLE 2

Molecular parameters for $NH(PF_2)_2$

	Distance/pm	Amplitude/pm
(*a*) Independent geometrical parameters		
r_1(P–F)	158.4(3)	5.6(4)
r_2(P–N)	168.4(8)	6.8 (tied to u_1)
r_3(N–H)	97.3(23)	5.7(24)
	Angle/°	
Angle 1 (F–P–F)	95.6(10)	
Angle 2 (F–P–N)	98.3(7)	
Angle 3 (P–N–P)	122.1(7)	
Angle 4 (twist 1) [a]	5.3(13)	
Angle 5 (twist 2) [b]	58 [c]	
% of conformer 2	27.5 [c]	
(*b*) Dependent distances		
d_4(F $\cdots$ F)	234.8(9)	7.4(7)
d_5(F $\cdots$ N)	247.3(11)	9.2 (tied to u_4)
d_6(P $\cdots$ P)	294.8(14)	10.0(7)
d_7(P $\cdots$ F) [d]	387.6(27)	12.4(6)
d_8(P $\cdots$ F) [d]	395.5(30)	
d_9(P $\cdots$ F) [e]	333.0(25)	
d_{10}(P $\cdots$ F) [e]	409.7(24)	
d_{11}(F $\cdots$ F) [f]	436(4)	15.7(20)
d_{12}(F $\cdots$ F) [f]	494(2)	13.4(20)
d_{13}(F $\cdots$ F) [e]	379(3)	15.7 (tied to u_{11})
d_{14}(F $\cdots$ F) [e]	469(3)	13.4 (tied to u_{12})
d_{15}(F $\cdots$ F) [e]	470(3)	13.4 (tied to u_{12})
d_{16}(F $\cdots$ F) [e]	485(4)	15.7 (tied to u_{11})
d_{17}(P $\cdots$ H)	231.7(22)	11.0 (fixed)
d_{18}(F $\cdots$ H) [d]	250—310	18.4(80)

[a] Twist angle for both PF_2 groups of major conformer, and for one group of second conformer. [b] Twist angle for one PF_2 group of second conformer. [c] See text. [d] Both conformers. [e] Minor conformer only. [f] Major conformer only.

Some structural parameters for some aminodifluorophosphines are compared in Table 4. It is clear that there is very little variation of P–F distances and FPF and FPN angles in the series of compounds, but that the P–N bond lengths increase from around 165 pm in amines with one PF_2 group to 168 pm in amines with two PF_2 groups to 171 pm in $N(PF_2)_3$. This may be interpreted in terms of $(p \rightarrow d)\pi$ bonding, with competition between phosphorus atoms for the nitrogen lone pair of electrons, or in terms of non-bonded contacts between phosphorus atoms. The P $\cdots$ P distance in $NH(PF_2)_2$ is 295 pm, with a PNP angle of 122°, but in $N(PF_2)_3$ the maximum possible PNP angle is 120° and as the P $\cdots$ P distance of 296 pm is essentially the same the long P–N bond length may be explained. The short P $\cdots$ P distance (285 pm) in $NMe(PF_2)_2$,[4] associated with a PNP angle of 116°, is an enigma.

The very close agreement of X-ray[6] and electron-diffraction results for the main geometrical parameters indicates that, although the conformation may change between gaseous and crystalline phases, there is very little distortion of bond lengths and inter-bond angles. This is to be expected, as the *X*-ray study showed that there were no strong intermolecular contacts.

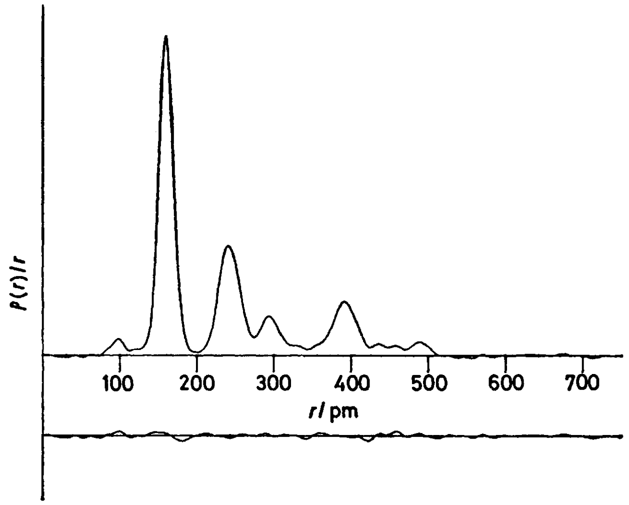

FIGURE 2 Observed and final difference radial distribution curves, $P(r)/r$, for $NH(PF_2)_2$, calculated with a damping factor of 0.000 015 nm^{-2}

The conformations adopted by bis(difluorophosphino)-amine are of particular interest. The predominant gas-phase form is very similar to that found in the crystalline solid. It seems highly likely that the gas-phase form has C_{2v} symmetry, and that the apparent 5° twist angles observed are shrinkage effects caused by torsional vibrations of the PF_2 groups. In this form there are four intramolecular F · · · H contacts of 263—270 pm, and these may provide the weak attractive forces that stabilise this arrangement. In the solid there are additional intermolecular F · · · H contacts: these do not appear to affect the structure of individual molecules, but only the packing arrangement.

TABLE 3

Least-squares correlation matrix, multiplied by 100

r_1	r_2	r_3	Angle 1	2	3	4	u_1	u_3	u_4	u_6	u_7	u_{11}	u_{12}	u_{17}	k_1	k_2		
100		−27			41		54										r_1	
	100		−23	54	−21	−47			−34	33	25			56			r_2	
		100															r_3	
			100	−47		−66	−24			−28		33	27	−35			1	Angle
				100	−37				48	42				81	28		2	
					100		49							−23	−27		3	
						100			22			−49		−22			4	
							100								43		u_1	
								100									u_3	
									100					39	36	26	u_4	
										100				58			u_6	
											100	26			21		u_7	
												100					u_{11}	
													100				u_{12}	
														100			u_{17}	
															100	32	k_1	
																100	k_2	

Only correlations with absolute values greater than 0.2 are included.

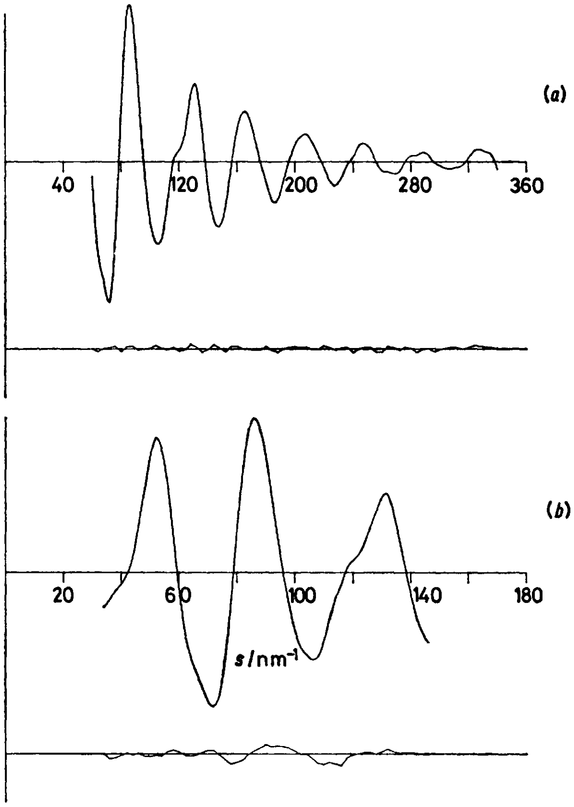

FIGURE 3 Observed and final weighted difference molecular-intensity curves, for nozzle-to-plate distances of (*a*) 128 and (*b*) 285 mm

The existence of two N–H stretching and two N–H in-plane deformation bands in the gas-phase i.r. spectrum of $NH(PF_2)_2$ [5] indicated that two conformers probably existed in the gas phase. This has now been confirmed by the structural study. In the less abundant form, one PF_2 group is twisted about 60° from the C_{2v} position. Why this particular structure should be favoured is not clear, but it should be noted that one F · · · H contact is

TABLE 4

Structural parameters of some aminodifluorophosphines

Compound	Technique	Bond distance/pm r(P–F)	r(P–N)	Angle/° FPF	FPN	PNP	Ref.
$NH_2(PF_2)$	ED	158.1(3)	166.1(7)	95.3(11)	101.1(11)		1
	MW	158.7(4)	165.0(4)	94.6(2)	100.6(2)		2
$NMeH(PF_2)$	ED	159.3(4)	164.8(7)	94.1(8)	100.6(4)		11
$NH(PF_2)_2$	ED	158.4(3)	168.4(8)	95.6(10)	98.3(7)	122.1(7)	This work
$NH(PF_2)_2$	X	157.8(5)	166.7(10)	95.7(4)	99.4(4)	120.7(4)	6
$NMe(PF_2)_2$	ED	158.3(2)	168.0(6)	95.1(3)	99.6(3)	116.1(8)	4
$N(PF_2)_3$	ED	157.4(2)	171.2(4)	97.1(5)	99.0(4)	120.0	3

ED = Electron diffraction, gas phase; MW = microwave spectroscopy, gas phase; X = *X*-ray diffraction, crystalline phase.

now at 250 pm, which is slightly less than the sum of the van der Waals radii of fluorine and hydrogen.

It is not possible to draw conclusions about the conformation in solution of bis(difluorophosphino)amine from the present work, but it is interesting to note that the coupling constant $^2J(PP')$ is much smaller for this compound [5] than for substituted bis(difluorophosphino)-amines [12,13] and that large couplings have been associated with strong interactions between lone pairs of electrons on phosphorus atoms.[14] The existence of a conformer in which this interaction is reduced by the twisting of one PF_2 group away from the position giving maximum lone-pair interaction may provide a rationalisation of the observed n.m.r. coupling constants. We have studied the Raman spectrum of liquid $NH(PF_2)_2$ and have observed two N–H stretching bands at 3 315 and 3 355 cm^{-1}, with an intensity ratio of *ca.* 5 : 1. Thus it seems likely that in condensed fluid phases the conformational properties relate more closely to those in the vapour than to those in the crystal.

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