Molecular Structure of Bis(difluorophosphino)germylamine in the Gas Phase, determined by Electron Diffraction

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The molecular structure of $N(GeH_3)(PF_2)_2$ in the gas phase has been determined by electron diffraction. The $NGeP_2$ skeleton is planar, and the Ge–N bond is substantially longer than those found in $N(GeH_3)_3$. Principal geometric parameters (r_a) are: r(P–F) 159.2(5), r(P–N) 169.8(8), and r(Ge–N) 188.9(13) pm; angle FPF 96.5(11), FPN 99.6(5), and PNP 114.0(8)°. The conformation adopted by the PF_2 groups is one in which the axes of the nitrogen and phosphorus lone pairs are almost orthogonal, while those of the two phosphorus atoms lie approximately *cis* to each other in the skeletal plane.

A COMPREHENSIVE study has recently been completed on amines containing difluorophosphino- and/or silyl groups bound to nitrogen.[1-9] However, of the five amines with germyl groups bound to nitrogen so far reported[10,11] only one, the very unstable trigermylamine, has been the subject of a gas-phase structure investigation.[12] We have therefore undertaken an electron-diffraction structural study of the molecule $N(GeH_3)(PF_2)_2$, the stability of which relative to trigermylamine appears to be increased by the presence of the two difluorophosphino-groups.

Certain geometrical features likely to be exhibited by this molecule could be predicted from previously determined structures of other amines. First, in all NR_3 compounds ($R = PF_2$, SiH_3, or GeH_3) so far studied the skeletal group was found to be planar, arguably due to delocalisation of the lone pair from the p orbital on nitrogen, and the short M–N bonds found in these compounds have been attributed to some increase in bond order due to $p \rightarrow d$ π bonding from the donor p orbital on nitrogen to vacant d orbitals on the ligands. Furthermore, it has recently been shown that, where PF_2 and SiH_3 groups are bound to the same central nitrogen atom, the electronegative PF_2 groups cause the bonds from nitrogen to silicon to lengthen.[9] Thus we would expect the Ge–N bond to be substantially longer here than in trigermylamine.[12]

Predictions of the likely conformation of the difluorophosphine groups have been made on the basis of the very low $^3J(^{31}P^1H)$ coupling constant (2 Hz) found in the initial study of this molecule.[11] It was suggested that a maximum coupling constant would be obtained when the lone pair on phosphorus lay *cis* to a germyl proton. Therefore it was concluded that it is the fluorine atoms which must lie *cis* to the germyl group. The value for $^2J(^{31}P^{31}P)$ of 405 Hz at room temperature lends further support to this theory, since the two phosphorus lone pairs lying *cis* to each other would generate a large coupling. A similar effect is observed in $NMe(PF_2)_2$[13] and in other bis(difluorophosphino)-compounds.

The conformation suggested by the above evidence would be exactly analogous to that found for $N(PF_2)_2(SiH_3)$,[9] and therefore seems entirely reasonable.

EXPERIMENTAL

A sample of bis(difluorophosphino)germylamine was prepared by the liquid-phase reaction (1) between bis(difluorophosphino)amine and germyl iodide, in the presence of trimethylamine.[11] The product was purified by repeated

$$NH(PF_2)_2 + GeH_3I + NMe_3 \longrightarrow N(GeH_3)(PF_2)_2 + [NMe_3H]I \quad (1)$$

fractional condensation on a vacuum line, and the purity was checked spectroscopically.

Electron-diffraction scattering intensities were recorded using the Cornell/Edinburgh diffraction apparatus,[2,14] with nozzle-to-plate distances of 128 and 288 mm and an accelerating voltage of *ca.* 44 kV. During exposures, samples were maintained at 283 K and the nozzle at room temperature (298 K). Data were recorded on Kodak Electron Image plates, and obtained in digital form using a Jarrell–Ash double-beam microphotometer, with spinning plates.[15] The electron wavelengths were determined from the scattering patterns of gaseous benzene, recorded immediately before or after the sample plates.

Calculations were carried out on ICL 2970 and 2980 computers at the Edinburgh Regional Computing Centre, using established data-reduction and least-squares refinement programs.[16] Weighting points used in setting up the off-diagonal weight matrices are given, together with other experimental data, in Table 1. In all calculations the complex scattering factors of Schäfer *et al.*[17] were used.

TABLE 1

Weighting functions, correlation parameters, and scale factors for $N(GeH_3)(PF_2)_2$

Camera height	Wave-length	Δs	$s_{min.}$	sw_1	sw_2	$s_{max.}$		Scale
mm	pm			nm^{-1}			p/h	factor
128.16	5.811	4	68	100	240	320	0.363	0.750(35)
288.31	5.811	2	34	44	120	140	0.442	0.724(24)

Refinement.—In refinements of the structure of $N(GeH_3)(PF_2)_2$ the $NGeP_2$ skeleton was initially assumed to be planar, although an out-of-plane distortion of the germyl group was subsequently permitted. Local C_s and C_{3v} symmetries were assumed for the NPF_2 and $NGeH_3$ groups respectively. Furthermore, the torsion angles of the two PF_2 groups, defined as zero when the FPF bisectors lay *cis* to the germyl group, were constrained so as to maintain either C_s or C_2 local symmetry for the $N(PF_2)_2$ moiety. The germyl torsion angle was defined as zero when one Ge–H

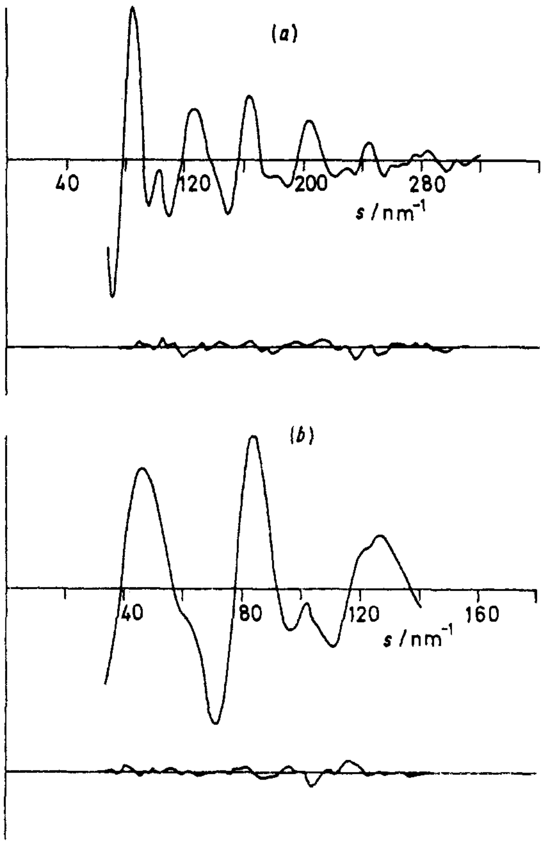

FIGURE 1 Observed and final weighted difference molecular-scattering intensities at nozzle-to-plate distances of (*a*) 128 and (*b*) 288 mm

bond lay in the skeletal plane, and in all cases positive torsion angles corresponded to clockwise rotations about the M–N bonds viewed from M to N. With the adoption of these assumptions, the structure could be defined by 11 geometrical parameters.

The conformation of the germyl group was found by varying the torsion angle and observing the *R* factors obtained. Of the other parameters involving hydrogen, NGeH was fixed at the tetrahedral angle of 110° and r(Ge–H) refined to a reasonable value, albeit with a large estimated standard deviation. All other parameters refined satisfactorily, and it was subsequently found that a somewhat lower *R* factor was obtained when the $N(PF_2)_2$ fragment was constrained to C_s symmetry than when it had C_2 symmetry.

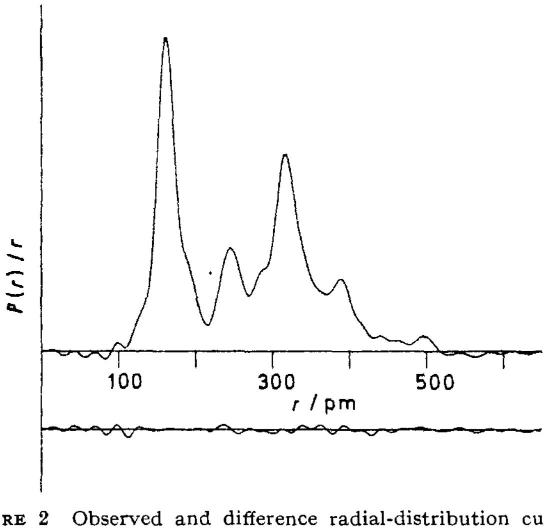

FIGURE 2 Observed and difference radial-distribution curves, $P(r)/r$. Before Fourier inversion the data were multiplied by $s\,.\,\exp[-0.000\,015\,s^2/(Z_{Ge} - f_{Ge})(Z_F - f_F)]$

TABLE 2

Molecular parameters for $N(GeH_3)(PF_2)_2$ *

	Distance/pm	Amplitude/pm
(*a*) Independent distances		
r_1 (P–F)	159.2(5)	4.9(11)
r_2 (P–N)	169.8(8)	3.4(28)
r_3 (N–Ge)	188.9(13)	6.2(15)
r_4 (Ge–H)	153.6(43)	8.8 (fixed)
(*b*) Dependent distances		
d_5 (N $\cdots$ F)	251.3(6)	7.4(15)
d_6 (P $\cdots$ F)	237.6(16)	7.4 (tied to u_5)
d_7 (F $\cdots$ F)	499.6(11)	10.2(15)
d_8 (F $\cdots$ F)	458.4(23)	10.2 (tied to u_7)
d_9 (F $\cdots$ F)	421.4(28)	10.2 (tied to u_7)
d_{10} (F $\cdots$ Ge)	318.8(11)	17.7(17)
d_{11} (F $\cdots$ Ge)	335.3(12)	17.7 (tied to u_{10})
d_{12} (P $\cdots$ Ge)	315.3(6)	8.4(6)
d_{13} (P $\cdots$ F)	394.8(9)	10.3(13)
d_{14} (P $\cdots$ F)	381.2(12)	10.3 (tied to u_{13})
d_{15} (P $\cdots$ P)	284.7(10)	7.0(12)
d_{16-27} (F $\cdots$ H)	296—467	22.0 (fixed)
d_{28} (H $\cdots$ H)	250(7)	18.0 (fixed)
d_{29-31} (P $\cdots$ H)	343—435	18.0 (fixed)
d_{32} (N $\cdots$ H)	281(4)	15.0 (fixed)
(*c*) Independent angles/°		
1 (FPF)		96.5(11)
2 (FPN)		99.6(5)
3 (PNP)		114.0(8)
4 (Ge–N, out-of-plane def.)		0 (see text)
5 (NGeH)		110 (fixed)
6 (PF_2, twist)		8.2(10)
7 (GeH_3, twist)		28.0 (see text)

* All distances are r_a values.

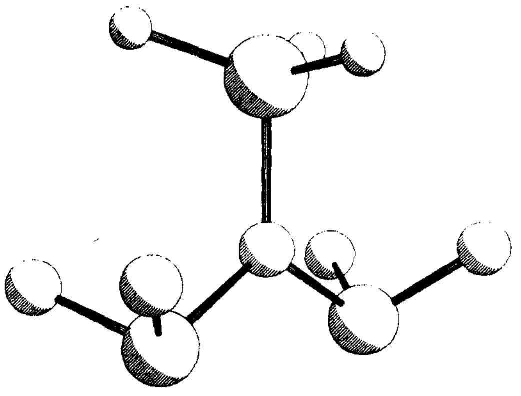

FIGURE 3 Molecular structure of $N(GeH_3)(PF_2)_2$

Results of the final refinement, for which R_G was 0.12 and R_D was 0.08, are given in Table 2. Errors quoted are estimated standard deviations derived from the least-squares analysis, increased to allow for systematic errors of 0.1%. The observed and final weighted difference molecular-scattering intensity curves are shown in Figure 1.

The radial-distribution curve is shown in Figure 2 and the molecule is depicted in Figure 3. Finally, the correlation matrix derived from the final least-squares analysis is given in Table 3.

RESULTS AND DISCUSSION

The $NGeP_2$ skeletal group was found to be entirely planar with no apparent shrinkage, a result also found for $N(PF_2)_2(SiH_3)$.[9] Any deviation from planarity resulted in a large increase in R factor.

TABLE 3

Least-squares correlation matrix (× 100) for $N(GeH_3)(PF_2)_2$

				Angle																
r_1	r_2	r_3	r_4	1	2	3	6	u_1	u_2	u_3	u_6	u_7	u_{10}	u_{12}	u_{13}	u_{15}	k_1	k_2		
100	−60	−64						74	85								51	60	r_1	
	100	−79	−50		−59	−72		−85	−79										r_2	
		100				82		81	78										r_3	
			100			50													r_4	
				100							68								1	Angle
					100														2	
						100		66	61										3	
							100								−70				6	
								100	92								57	61	u_1	
									100	57							50	58	u_2	
										100									u_3	
											100								u_6	
												100							u_7	
													100					54	u_{10}	
														100			59		u_{12}	
															100				u_{13}	
																100			u_{15}	
																	100	71	k_1	
																		100	k_2	

Only elements with absolute values equal to or greater than 50 are included.

TABLE 4

Important geometrical parameters [a]

(*a*) For some bis(difluorophosphino)amines $NR(PF_2)_2$

			Angle				Shortest	
R	r(P–F)	r(P–N)	FPF	FPN	PNP	$d(P \cdots P)$	$d(F \cdots H)$	Ref.
H	158.4(3)	168.4(8)	95.6(10)	98.3(7)	122.1(7)	294.8(14)	250	2
CH_3	158.4(2)	168.1(7)	95.2(5)	99.8(4)	115.9(10)	285.1(11)	(not given)	*b*
SiH_3	157.0(2)	169.1(4)	96.1(5)	99.3(3)	117.6(7)	289.3(11)	260(4)	9
GeH_3	159.2(5)	169.8(8)	96.5(11)	99.6(5)	114.0(8)	284.7(10)	297(3)	*c*
PF_2	157.4(2)	171.1(4)	96.9(3)	99.2(3)	120 (fixed)	296.4(6)		1

(*b*) For some germyl- and silyl-amines (M = Si or Ge)

Compound	r(M–N)	Ref.
$N(GeH_3)_3$	183.6(5)	12
$N(SiH_3)_3$	173.4(2)	4, 5
$N(GeH_3)(PF_2)_2$	188.9(13)	*c*
$N(SiH_3)(PF_2)_2$	176.7(7)	9

[a] All distances in pm, all angles in degrees. [b] E. Hedberg, L. Hedberg, and K. Hedberg, *J. Am. Chem. Soc.*, 1974, **96**, 4417. This work.

The geometrical parameters of the NPF_2 groups [r(P–N), r(P–F), angles FPN and FPF] all refined to expected values, commensurate with those found in other bis(difluorophosphino)amines [Table 4(*a*)]. The value found for r(P–N) of 169.8(8) pm is close to that found in $N(PF_2)_2(SiH_3)$ [169.1(4) pm], indicating that steric crowding due to the bulkier germyl group is not severe.

The Ge–N bond length in this study deserves special comment: compared to trigermylamine this parameter is over 5 pm longer. A similar difference has been observed for the analogous silylamines [Table 4(*b*)]. This has been attributed to the electronegative PF_2 group having greater π-acceptor capability than the silyl group.[9] Since the difference is greater in the germyl than the silyl case, it could be argued that the former is a weaker π acceptor than the latter.

The PNP angle of 114.0(8)° is somewhat small, and the $P \cdots P$ non-bonded contact (285 pm) is at the small end of a range of values found for other bis(difluorophosphino)amines [Table 4(*a*)]. Using the formula $a(P \cdots Ge) = \frac{1}{2}[d(Ge \cdots Ge) + d(P \cdots P)]$, and assuming values for $d(Ge \cdots Ge)$ [12,18] and $d(P \cdots P)$ of 316 and 290 pm respectively, the expected value for the germanium–phosphorus distance would be 303 pm. The observed value of 315 pm suggests that the narrow PNP angle found is not a result of steric crowding due to the germyl group. By comparing the results tabulated for all bis(difluorophosphino)amines it can be seen that $d(P \cdots P)$ here is similar to that found in the methyl case, and less than 5 pm smaller than that found for $N(PF_2)_2(SiH_3)$. In the silyl case, it may be that the PNP angle is marginally wider because the fluorine atoms are attracted to the silyl protons, whereas in $N(CH_3)(PF_2)_2$ optimum H · · · F contact would be possible with a narrower PNP angle. In the germyl case the shortest H · · · F distance is too long (297 pm) for any strong interaction to take place, as the optimum distance for this lies in the region 250—265 pm,[2,3,8,9,19] and it appears here that the PNP angle relaxes back to a smaller value.

The conformation of the PF_2 groups can be deduced directly from the form of the radial-distribution curve, since only a configuration in which the FPF angle bisectors lay *trans* to each other would give rise to F · · · F distances up to 500 pm. The apparent distortion of *ca.* 8° away from C_{2v} symmetry for the $N(PF_2)_2$ moiety probably represents torsional shrinkage away from the higher symmetry. The result is in accordance with the expectations discussed above.

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