Electron-diffraction Study and CNDO/2 Calculations of the Molecular Structure of Diaminodifluorophosphorane in the Gas Phase

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The molecular geometry of diaminodifluorophosphorane, $PF_2H(NH_2)_2$, in the gas phase, has been studied by electron diffraction. A trigonal-bipyramidal structure is found, with axial fluorine atoms. Principal parameters are: r_a(P–N) 164.0(5) pm; r_a(P–F) 164.3(5) pm; HPF 89.3(8)°; HPN 118.8(5)°. Assuming these parameters, CNDO/2 calculations suggest that the $P(NH_2)$ groups are planar, and perpendicular to the equatorial plane of the trigonal bipyramid, and that the PNH angles are 124°. The molecule therefore has C_{2v} symmetry.

NUCLEAR magnetic resonance spectra of diaminodifluorophosphorane [1] indicated that the molecule has a trigonal-bipyramidal structure with axial fluorine atoms. At room temperature there is rapid rotation about the P–N bonds, but on cooling to 226 K a fixed conformation is adopted, with the two hydrogen nuclei of each NH_2 group no longer magnetically equivalent with respect to the two fluorine nuclei. Such a conformer would have, at least approximately, C_{2v} symmetry. The vibrational spectra were also interpreted in terms of a C_{2v} model.

In order to ascertain the correctness of these deductions, and to provide further structural information about five-co-ordinate phosphorus compounds, few of which have been studied in the gas phase, this present study of the structure of the molecule was initiated. As electron diffraction alone could not be expected to provide definitive information about the precise positions of hydrogen atoms, CNDO/2 calculations have also been made, as these have been shown to be applicable to problems of conformational analysis and the optimisation of geometries in electronically localised molecular systems.[2]

EXPERIMENTAL

Diaminodifluorophosphorane was prepared by the reaction of ammonia and aminodifluorophosphine,[1] and was purified by fractional condensation *in vacuo*. Its purity was checked spectroscopically.

Electron-diffraction scattering data were recorded photographically (Agfa Gevaert Replica 23 plates) using a Balzers' KD.G2 gas diffraction apparatus. The sample and nozzle were maintained at room temperature (298 K) during experiments. Nozzle-to-plate distances of 250 and 500 mm were used, giving data over a range of 18—300 nm^{-1} in the scattering variable, *s*. Data were obtained in digital form using a Joyce–Loebl automatic microdensitometer. Calculations were made on an ICL 4-75 computer at the Edinburgh Regional Computing Centre, using established data-reduction [3] and least-squares refinement programs.[4] Weighting points (used in setting up the off-diagonal weight matrix), correlation parameters, and scale factors are given in Table 1. In all the calculations, the complex scattering factors of Schäfer *et al.*[5] were used: distances quoted are r_a. The electron wavelength used, 5.660(5) pm, was determined from the diffraction pattern of benzene.

TABLE 1

Weighting functions, correlation parameters, and scale factors

Camera height	Δs	s_{min}	s_1	s_2	s_{max}		
mm			nm^{-1}			p/h	Scale factor
250	4	60	90	260	300	0.437 9	0.741 ± 0.009
500	2	18	45	125	160	0.497 7	0.844 ± 0.013

In refinements of the structure, a simple model was used, assuming C_{2v} symmetry, and planar $P(NH_2)$ groups perpendicular to the equatorial plane. The seven independent parameters defining the structure were taken as the bonded distances H–P, P–F, P–N, and N–H, and the angles HPF, HPN, and PNH. In the light of the CNDO/2 results, further degrees of freedom in the model were considered

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[1] D. E. J. Arnold and D. W. H. Rankin, *J.C.S. Dalton*, 1976, 1130.

[2] M.-C. Bach, F. Crasnier, J.-F. Labarre, and C. Leibovici, *J. Fluorine Chem.*, 1973—1974, **3**, 409.

[3] D. M. Bridges, G. C. Holywell, D. W. H. Rankin, and J. M. Freeman, *J. Organometallic Chem.*, 1971, **32**, 87.

[4] G. C. Holywell, D. W. H. Rankin, B. Beagley, and J. M. Freeman, *J. Chem. Soc.* (*A*), 1971, 786.

[5] L. Schäfer, A. C. Yates, and R. A. Bonham, *J. Chem. Phys.*, 1971, **55**, 3055.

unnecessary. CNDO/2 calculations were made on an IBM 370/168 computer (CIRCE, Orsay, France), according to the method of Pople and his co-workers.[6]

RESULTS

The radial-distribution curve, $P(r)/r$, of $PF_2H(NH_2)_2$ (Figure 1) showed that the principal scattering distances in the molecule, P–F and P–N, came together at *ca.* 164 pm. Attempts to refine these distances and their amplitudes of vibration simultaneously made the latter become unreasonably small, and caused the former to separate under the peak contour. Since the non-bonded F · · · F peak could be clearly seen at *ca.* 328 pm, the P–F distance must have a minimum value of 164 pm. The amplitudes of vibration of the P–N and P–F distances were therefore fixed at reasonable values, allowing refinement of these distances. As the N–H, F · · · N, and F · · · F distances were well resolved, the angles HPN and HPF, the N–H distance, and the amplitudes of vibration of the distances N–H, F · · · F, and F · · · H all refined. The amplitude of vibration of the N · · · N distance was also found to refine satisfactorily, despite the fact that the peak was not prominent in the radial-distribution curve. The remaining geometrical parameters, the P–H distance and PNH angle, were not well defined, nor was there yet any evidence that our initial assumptions, concerning the overall symmetry and planarity of the $P(NH_2)$ groups, were justified.

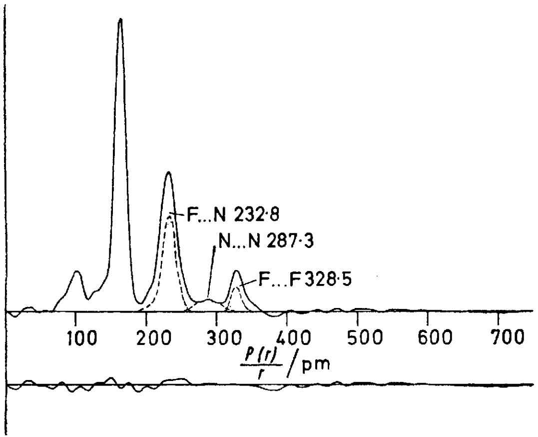

FIGURE 1 Observed and difference radial-distribution curves, $P(r)/r$, for $PF_2H(NH_2)_2$, showing calculated contributions from F · · · N, N · · · N, and F · · · F atom pairs. Before Fourier inversion the data were multiplied by $s\{\exp[(-0.000\,015(s^2)/(z_P - f_P)(z_F - f_F)]\}$

TABLE 2

Least-squares correlation matrix multiplied by 100

*r*2	*r*3	*r*4	<1	<2	*u*4	*u*5	*u*6	*u*7	*k*1	*k*2	
100	−83	8	−48	34	−1	−14	14	14	10	6	*r*2
	100	−13	39	−38	0	15	−14	−18	−9	−3	*r*3
		100	−4	−18	−3	9	−4	2	8	3	*r*4
			100	−90	0	24	−27	15	−16	−17	<1
				100	2	−25	26	−13	13	14	<2
					100	2	2	0	10	3	*u*4
						100	−5	−12	27	19	*u*5
							100	−5	13	10	*u*6
								100	0	−11	*u*7
									100	11	*k*1
										100	2

With the electron-diffraction data as a starting point, and assuming the P–H bond length to be 143 pm, we attempted to calculate the structure of the $P(NH_2)$ groups. In a theoretical study of the $PH_2(NH_2)$ molecule, Barthelat *et al.*[7] showed that, when the restriction PNH = HNH is imposed on the $P(NH_2)$ group, a planar structure results from the application of the CNDO/2 method (as in the case of *ab initio* calculations [8]); if, however, this restriction is lifted, a more stable structure including a pyramidal nitrogen atom is found. We therefore made CNDO/2 calculations for both situations in order to establish the hybridisation state of the nitrogen atoms.

For the case where the restriction was imposed on the $P(NH_2)$ groups, the calculations were made for the following bond angles: HNH = PNH = 109.47 (*sp*^{3}), 115.0, and 120.0° (*sp*^{2}). The effect of rotation of the NH_2 groups about the P–N bonds was investigated, the results suggesting that the most stable conformation possesses a symmetry plane which passes through the phosphorus and both nitrogen atoms.

Without the assumption PNH = HNH, calculations were made for a number of geometries involving an NPN symmetry plane; the angle PNH was varied between 114 and 126° in steps of 2°, and the corresponding values of HNH, which depends on PNP, were taken from the interval 104—132°. Whether the assumption PNH = HNH is imposed or not, planar nitrogen atoms give the most stable conformation, the NH_2 groups being in planes perpendicular to that containing the phosphorus and nitrogen atoms.

The PNH angle in the plane conformation was optimised, the lowest energy being obtained when PNH = 124° and hence HNH = 112°. The calculated optimum P–H bond length was found to be 152 pm, which seems to be too long,[9] but it must be noted that the conformation described above remains the most stable solution for any P–H bond length between 133 and 152 pm. The rotation barrier for an NH_2 group about the PN bond was calculated to be 64.6 kJ mol^{-1} for the optimised structure with P–H = 152 pm, and 64.5 kJ mol^{-1} with P–H 143 pm. Attempts to refine the PNH angle and PH bond length using the electron-diffraction data were unsuccessful, but series of refinements were carried out with these parameters fixed at various values. Lowest *R* factors were obtained using values of 122° and 143 pm respectively, and these were used in subsequent refinements. Under these conditions refinements converged, giving a final R_G 0.096.

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[6] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, 1965, **43**, 5129; J. A. Pople and G. A. Segal, *ibid.*, p. 5136; 1966, **44**, 3289.

[7] M. Barthelat, R. Mathis, J.-F. Labarre, and F. Mathis, *Compt. rend.*, 1975, **C280**, 645.

[8] I. G. Csizmadia, A. H. Cowley, M. W. Taylor, L. M. Tel, and S. Wolfe, *J.C.S. Chem. Comm.*, 1974, 433.

[9] S. B. Pierce and C. D. Cornwell, *J. Chem. Phys.*, 1968, **48**, 2118.

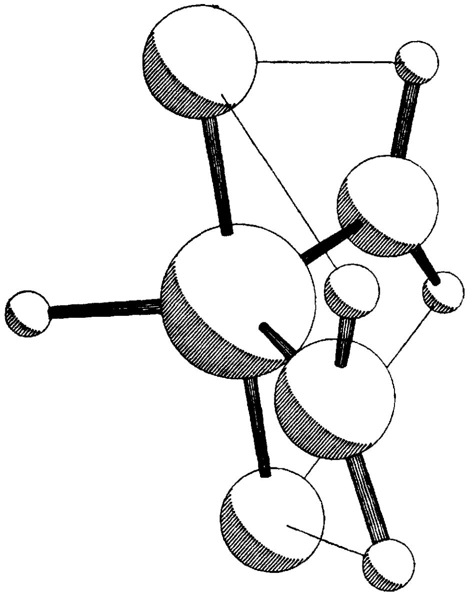

FIGURE 2 Perspective view of the $PF_2H(NH_2)_2$ molecule, showing short F · · · H interatomic distances

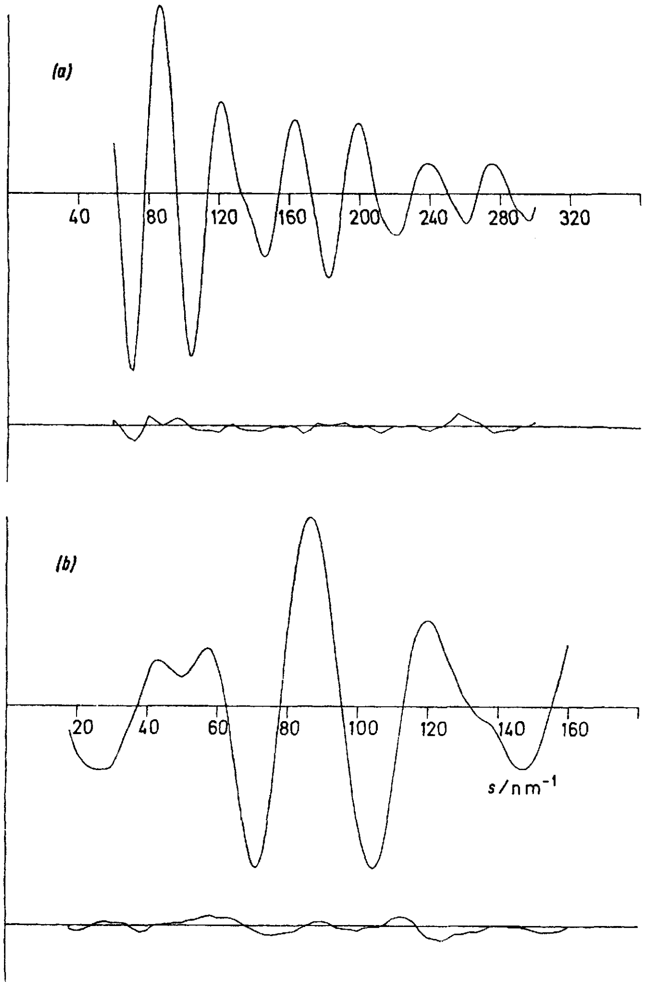

FIGURE 3 Experimental and final difference molecular-scattering intensities for camera heights of (*a*) 250 and (*b*) 500 nm

The parameters found for $PF_2H(NH_2)_2$ are presented in Table 2, and Figure 2 depicts the structure. The final least-squares correlation matrix is given in Table 3, and the molecular-scattering intensity curves are shown in Figure 3.

TABLE 3

Molecular parameters for $PF_2H(NH_2)_2$

	Distance/pm	Amplitude/pm
(*a*) Independent distances		
*r*1(P–H)	143.0 [a]	8.5 [a]
*r*2(P–F)	164.3(5)	4.3 [a]
*r*3(P–N)	164.0(5)	4.3 [a]
*r*4(N–H)	99.3(11)	5.5(19)
(*b*) Dependent distances		
*d*5(F · · · N)	232.8(10)	7.3(5)
*d*6(F · · · F)	328.5(12)	3.7(12)
*d*7(N · · · N)	287.3(16)	11.1(27)
*d*8(F · · · H)	216.5(12)	8.0 [a]
*d*9(F · · · H)	228.4(12)	15.0 [a]
*d*10(F · · · H)	329.6(20)	15.0 [a]
*d*11(N · · · H)	264.5(10)	9.0 [a]
*d*12(N · · · H)	342.6(19)	17.0 [a]
*d*13(P · · · H)	230.3(11)	10.0 [a]
*d*14(H · · · H)	320.9(13)	20.0 [a]
*d*15(H · · · H)	374.3(21)	20.0 [a]
*d*16(H · · · H)	411.9(26)	20.0 [a]
*d*17(H · · · H)	172.0(19)	10.0 [a]
(*c*) Angles (°)		
<1(H–P–F)	89.3(8)	
<2(H–P–N)	118.8(5)	
<3(P–N–H)	122.0 [b]	

[a] Fixed. [b] See text.

DISCUSSION

Bond lengths and angles in some fluorophosphoranes are given in Table 4. The P–F_{ax} bond lengths vary over a wide range, and seem to correlate well with the electronegativities of the equatorial substituents. Diaminodifluorophosphorane fits well into the series, with the same P–F_{ax} distance as in trifluorodimethylphosphorane.[10] The P–N bond length is also much as would be expected, being *ca.* 2 pm shorter than that in aminodifluorophosphine:[4] a similar difference in P–C bond lengths is found for difluoromethylphosphine[11] and difluorotrimethylphosphorane.[12]

TABLE 4

Bond lengths and angles in some fluorophosphoranes, PF_2XY_2

			r(P–F_{ax})	Angle/°		
Compound	X	Y	pm	$F_{ax}PX_{eq}$	$X_{eq}PY_{eq}$	Ref.
PF_5	F	F	157.7	90	120	*a*
PF_4H [b]	H	F	159.4	90	124	9
$PMeF_4$	Me	F	161.2	91.8	122.2	10
PMe_2F_3	F	Me	164.3	89.9	118.0	10
PMe_3F_2	Me	Me	168.5	90	120	12
$PF_2H(NH_2)_2$	H	NH_2	164.3	89.3	118.8	*c*

[a] K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, 1965, **4**, 1775. [b] Microwave determination. All the others were by electron diffraction. [c] This work.

The small distortions from regular trigonal-bipyramidal geometry seem steric in origin, and not attributable to electronegativity effects. This can be seen in the displacement of axial and equatorial groups away

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[10] L. S. Bartell and K. W. Hansen, *Inorg. Chem.*, 1965, **4**, 1777.

[11] E. G. Codding, R. A. Creswell, and R. H. Schwendeman, *Inorg. Chem.*, 1974, **13**, 856.

[12] H. Yow and L. S. Bartell, *J. Mol. Structure*, 1973, **15**, 209.

from the least electronegative group, CH_3, in $PMeF_4$ and PMe_2F_3,[10] whereas in $PF_2H(NH_2)_2$ displacement is towards the least electronegative group and away from the NH_2 groups.

The conformation of the amino-groups suggested by the CNDO/2 calculations, and consistent with the diffraction data, is entirely as expected from earlier spectroscopic results, and analysis of the vibrational spectra in terms of C_{2v} symmetry has been justified. The short F · · · H distances, between the axial fluorine and amino-group hydrogen atoms (228 pm), imply considerable interaction between these atoms, and account for the observation (in n.m.r. spectra) that rotation about the P–N bonds is restricted. There can be little doubt that similar effects observed for aminotetrafluorophosphorane[13] and diaminotrifluorophosphorane[14] arise in the same way, and that the fluxional behaviour of these compounds is also greatly reduced by these interactions.

We thank Professor D. W. J. Cruickshank, Dr. B. Beagley, and Mrs. V. Ulbrecht for the provision of experimental facilities and for assistance with their use.

[6/1589 *Received*, 13*th August*, 1976]

[13] A. H. Cowley and J. R. Schweiger, *J.C.S. Chem. Comm.*, 1972, 560.

[14] M. Lustig and H. W. Roesky, *Inorg. Chem.*, 1970, **9**, 1289.