

AN ELECTRON-DIFFRACTION DETERMINATION
OF THE MOLECULAR STRUCTURE
OF BIS(DIFLUOROPHOSPHINO)ETHER, F_2POPF_2 , IN THE GAS PHASE

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SUMMARY

Gas-phase electron-diffraction methods have been used to determine the molecular structure of bis(difluorophosphino)ether, F_2POPF_2 . Most of the geometrical parameters are strongly correlated due to overlapping peaks in the radial distribution curve. In the structure that fits the experimental data most closely, the P-F and P-O bond lengths are 159.7 ± 0.4 and 153.3 ± 0.6 pm respectively, and the POP angle is 2.53 ± 0.02 rad (145°). The conformation is such that the molecule has no symmetry elements other than I (point group C_1). In other refinements somewhat longer P-O and shorter P-F distances were obtained.

INTRODUCTION

As part of a study of the bonding in substituted fluorophosphines, we have determined the structures of a number of compounds in which difluorophosphino groups are bound to elements of the first series¹⁻⁴. The similarity of observed structures to those of analogous silyl or germyl compounds⁵⁻⁷ has led us to suppose that phosphorus d-orbital participation in the bonding profoundly influences the shapes of the fluorophosphines.

The compounds studied so far have not included any compounds containing phosphorus-oxygen bonds, but the wide angles at oxygen in disilyl ether⁸ and digermyl ether⁹ led us to expect a similar wide angle in bis(difluorophosphino)-ether. We now report the determination of the molecular structure of this compound in the gas phase.

Also of interest is the conformation of the fluorophosphine groups. Our earlier work on phosphorus-nitrogen derivatives has shown that the preferred orientations of these groups are determined by intramolecular hydrogen-fluorine

contact, where these are possible, and otherwise by lone-pair-lone-pair interactions^{4,10}. The results presented here provide further evidence for the stereochemical importance of lone pairs of electrons in these molecules.

EXPERIMENTAL

Samples of bis(difluorophosphino)ether were prepared by the reaction of bromodifluorophosphine with bis(tributyltin)ether¹¹, and purified by fractional condensation *in vacuo*. The purity of each sample was checked by IR spectroscopy.

Electron-diffraction data were collected photographically on Ilford N60 plates, using a Balzers' KD.G2 gas-diffraction apparatus (with rotating sector)¹², and were converted to digital form using a Joyce-Loebl automatic microdensitometer. Data from two plates, exposed with nozzle-to-plate distances of 250 and 500 mm, were used, giving data over the range $32 < s < 292 \text{ nm}^{-1}$. The nozzle was maintained at 295K and the sample of compound at 195K during the exposures, and the gas temperature may be taken to be near the mean of these. The electron wavelength used was determined from the diffraction pattern of powdered thalious chloride and by direct measurement of the accelerating voltage to be $5.659 \pm 0.003 \text{ pm}$.

All calculations were carried out on an IBM 360/50 computer at the Edinburgh Regional Computing Centre, using established data reduction and least-squares refinement programmes^{1,13}. The scattering factors of Cox and Bonham¹⁴ were used throughout. The weighting points (defined as in Ref. 1) used in setting up the off-diagonal weight matrix are given in Table 1, together with scale factors and correlation parameters¹⁵.

All interatomic distances quoted in this work are r_a values¹⁶.

TABLE 1
WEIGHTING FUNCTIONS, CORRELATION PARAMETERS AND SCALE FACTORS*

Camera height (mm)	Δs	$s_{\text{min.}}$	s_1	s_2	$s_{\text{max.}}$	P/h	Scale factor
250	4	52	80	250	292	0.4719	1.286 ± 0.028
500	2	32	48	128	156	0.4489	1.262 ± 0.022

* s units in nm^{-1} .

MOLECULAR MODEL

As electron diffraction is not a good method for distinguishing between almost identical groups, it was necessary to assume that the two F_2PO^- units within the molecules were identical and, moreover, that these groups had a plane of symmetry. Thus the structures of these groups were defined by the F-P- and

P–O-bonded distances and the FPF and FPO angles. The overall structure depends also on the POP angle and on the conformations of the F₂PO groups. Two dihedral angles were defined, one for each F₂PO group, to describe the rotations about the P–O bonds. In each case, the angle was taken to be zero when the FPF bisector was *trans* with respect to the further P–O bond. The relative directions of the rotations were such that if the dihedral angles were equal, the molecule had overall C₂ symmetry; C_s symmetry was therefore represented by equal and opposite dihedral angles. The parameters that could be included in the refinements were therefore the two bond lengths, five angles, two scale factors and amplitudes of vibration for all the different interatomic distances.

REFINEMENT AND RESULTS

Refinement of the structure of bis(difluorophosphino)ether proved to be unusually difficult. The difficulties arose from the similarities of the phosphorus–fluorine and phosphorus–oxygen bond lengths and of the FPF and FPO angles: these made it necessary for some of the amplitudes of vibration for the closest atom pairs to be fixed. In addition, there has been some uncertainty about the relative lengths of the phosphorus–fluorine and phosphorus–oxygen bonds: in some refinements, one type was the longer, and in others, the reverse was true. We therefore quote (in Table 2) the results of three separate refinements, obtained under very different conditions.

In refinement A, most of the different interatomic distances in the molecule were allowed to refine independently, without any overall structural constraints. In this case, the lowest *R* factor (0.137) was obtained when the P–F distance was less than that for P–O.

Refinements B and C are the best with P–F < P–O and with P–F > P–O respectively. Some of the parameters of refinement C are rather different from those in other fluorophosphines or phosphorus–oxygen compounds, although not impossible. However, the *R* factors for the refinements are 0.150 and 0.119. Using the *R* factor ratio test¹⁷, refinement B can be rejected at the 99.5% confidence level.

Because of strong correlations between angles FPF, FPO, POP and the dihedral angles, it was not possible to refine more than two or three of these at any one time. They were therefore refined in turn, until a self-consistent solution was obtained. Such a procedure must lead to unrealistically low estimated standard deviations, and so the errors quoted in Table 2 have been increased to allow for the correlation. The least-squares correlation matrix (Table 3) corresponds to refinement C of Table 2.

Final molecular scattering intensity and difference curves are shown in Figure 1. The intensity data or uphill curves may be obtained from the authors on request.

TABLE 2
MOLECULAR PARAMETERS*

	Refinement A		Refinement B		Refinement C	
	Distance	Amplitude	Distance	Amplitude	Distance	Amplitude
r 1 (P-F)	156.2 (5)	4.5 (fixed)	157.0 (5)	4.5 (fixed)	159.7 (4)	4.5 (fixed)
r 2 (P-O)	161.6 (9)	4.7 (fixed)	159.7 (9)	4.7 (fixed)	153.3 (6)	4.7 (fixed)
r 3 (F...F)	238.5 (11)	7.4 (6)	239.0 (12)	6.9 (6)	242.0 (5)	7.2 (6)
r 4 (F...O)	240.4 (fixed)	8.7 (tied to μ 3)	240.1 (7)	8.1 (tied to μ 3)	237.8 (5)	8.5 (tied to μ 3)
r 5 (P...F)	336.5 (14)	4.9 (14)	341.9 (15)	7.0 (fixed)	389.7 (10)	4.9 (18)
r 6 (P...F)	390.6 (16)	5.6 (14)	399.6 (17)	7.0 (fixed)	338.7 (10)	4.9 (18)
r 7 (P...F)	308.6 (16)	7.0 (fixed)	305.4 (14)	7.0 (fixed)	311.9 (9)	5.0 (fixed)
r 8 (P...F)	363.9 (17)	6.4 (15)	370.0 (16)	7.0 (fixed)	364.2 (10)	5.0 (18)
r 9 (P...P)	294.4 (15)	10.0 (fixed)	297.8 (16)	23.0 (50)	292.5 (13)	9.8 (14)
r10 (F...F)	301.2 (fixed)	28.0 (fixed)	316.0 (15)	28.0 (fixed)	453.3 (9)	22.8 (35)
r11 (F...F)	459.1 (fixed)	28.0 (fixed)	461.7 (18)	28.0 (fixed)	429.9 (8)	24.0 (fixed)
r12 (F...F)	447.2 (fixed)	22.5 (40)	448.2 (15)	18.5 (fixed)	318.5 (8)	18.5 (fixed)
r13 (F...F)	443.9 (fixed)	22.5 (tied to μ 12)	446.5 (19)	18.5 (fixed)	459.5 (10)	22.8 (tied to μ 10)
1 (F-P-F)			1.73 (2)	[99.2]	1.719 (fixed)**	[98.5]
2 (F-P-O)			1.72 (fixed)**	[98.6]	1.725 (5)	[98.8]
3 (P-O-P)			2.40 (2)	[137.5]	2.533 (fixed)**	[145.1]
4 (dihedral)			0.98 (fixed)**	[56.2]	-1.07 (fixed)**	[-61.3]
5 (dihedral)			2.13 (fixed)**	[122.0]	2.16 (fixed)**	[123.5]

* All distances and amplitudes are in pm. Angles are given in radians and (in square brackets) in degrees.
** Refined earlier.

TABLE 3
LEAST-SQUARES CORRELATION MATRIX ($\times 1000$)

<i>r</i> 1	<i>r</i> 2	< 2	<i>u</i> 3	<i>u</i> 5	<i>u</i> 6	<i>u</i> 8	<i>u</i> 9	<i>u</i> 10	<i>k</i> 1	<i>k</i> 2	
1000	-574	121	63	111	53	28	40	17	443	300	<i>r</i> 1
	1000	-688	-95	-129	-83	-29	-33	-31	-557	-334	<i>r</i> 2
		1000	76	2	103	1	-126	28	345	166	<2
			1000	35	15	20	-156	18	307	205	<i>u</i> 3
				1000	-141	-34	19	-82	136	69	<i>u</i> 5
					1000	-41	-107	35	85	24	<i>u</i> 6
						1000	45	-1	62	7	<i>u</i> 8
							1000	-6	16	45	<i>u</i> 9
								1000	41	45	<i>u</i> 10
									1000	248	<i>k</i> 1
										1000	<i>k</i> 2

DISCUSSION

The difficulties encountered in the present study illustrate well the limitations of electron diffraction as a method of structural determination for molecules that have low symmetry, or several sets of interatomic distances that are so similar as to be unresolvable. The number of peaks above 250 pm in the radial distribution curve for bis(difluorophosphino)ether (Fig. 2) indicates that a C_s or C_2 structure is impossible. In addition, the P-F and P-O distances appear as a single peak at about 155 pm, as do the F...F and F...O distances, at 240 pm. But if the molecule has no symmetry at all, then there are no grounds for assuming that the two F₂PO- groups are equivalent and have planes of symmetry. Thus the structure of each such group depends on six parameters (three bond lengths and three angles), giving 12 in all, compared with four in our idealised model. It may be, therefore, that although refinement C fits the experimental data much better than refinement B, the latter could be improved by applying one or more of the eight possible distortions to the F₂PO- groups, while keeping the mean values of the P-F, P-O, F...F and F...O distances unchanged.

However, despite the uncertainties outlined above, certain features of the structure are quite clear. In particular, the phosphorus-oxygen bond length is short compared with the value of 171 pm predicted by the Schomaker-Stevenson rule¹⁸, and with most experimental values^{19,20}. This shortness, and the wide POP angle (2.53 rad, 145°) suggest that, as in disilyl ether, which has an SiOSi angle of 2.51 rad (144°), the bonds to oxygen are not simple single bonds. It thus seems probable that in both molecules, the bonds are strengthened by delocalisation of lone-pair electrons from oxygen into low-lying vacant phosphorus or silicon orbitals.

The conformation of the F₂P- groups is interesting. The very small amplitudes of vibration found for three of the P...F atom pairs suggest that the amplitudes of

the torsional vibrations are not very great and the distinct peaks in the radial distribution curve show clearly that one conformation is preferred. These amplitudes may also reflect to some extent the quality of the intensity data in the region of

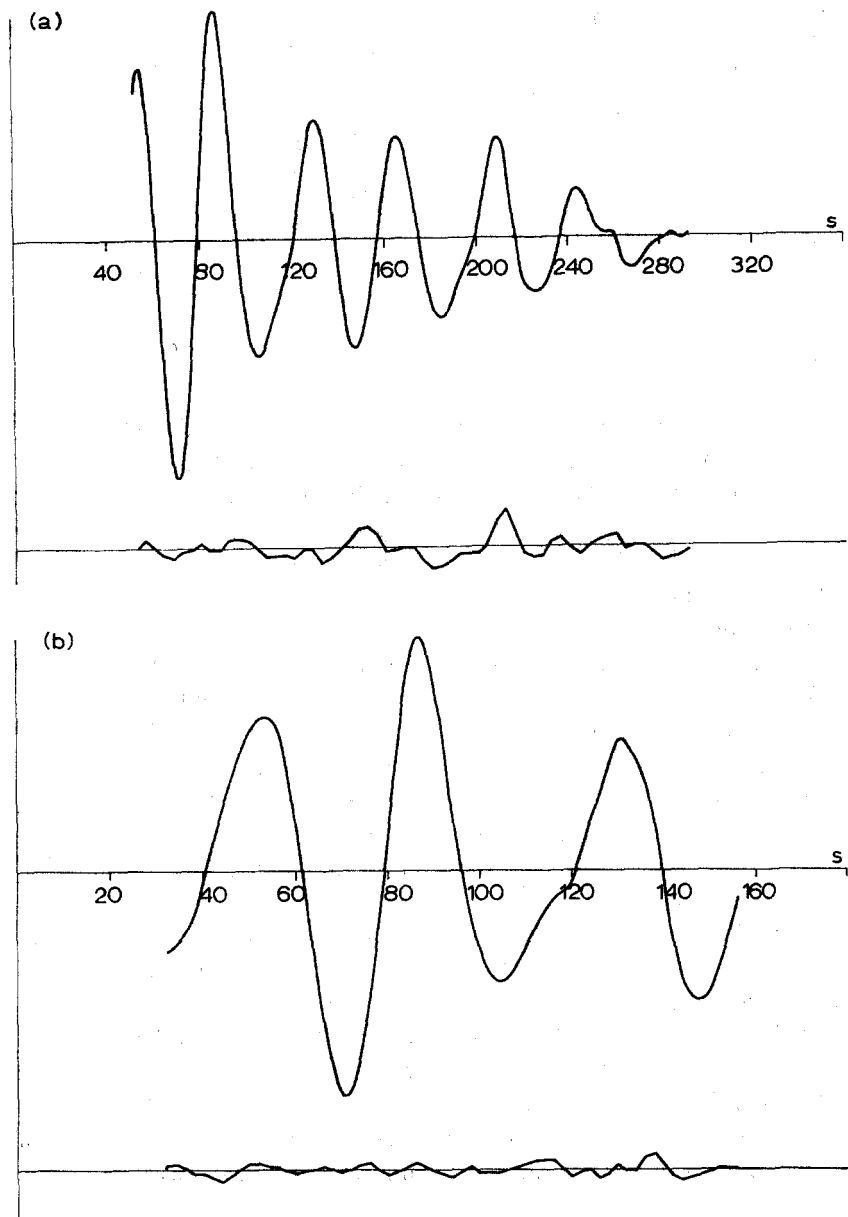


Fig. 1. Observed and final weighted difference molecular scattering intensities for bis(difluorophosphino)ether for nozzle-to-plate distances of (a) 250 mm and (b) 500 mm.

$s = 200 \text{ nm}^{-1}$, and too much significance should not be attached to the values given. But the conformation adopted cannot be attributed solely to fluorine-fluorine interactions, for the shortest such distance observed is over 310 pm, compared with 270 pm for twice the van der Waal's radius of fluorine. Thus the structure must be determined by the interactions of the lone pairs of electrons on the phosphorus and oxygen atoms, both with each other and with the fluorine atoms.

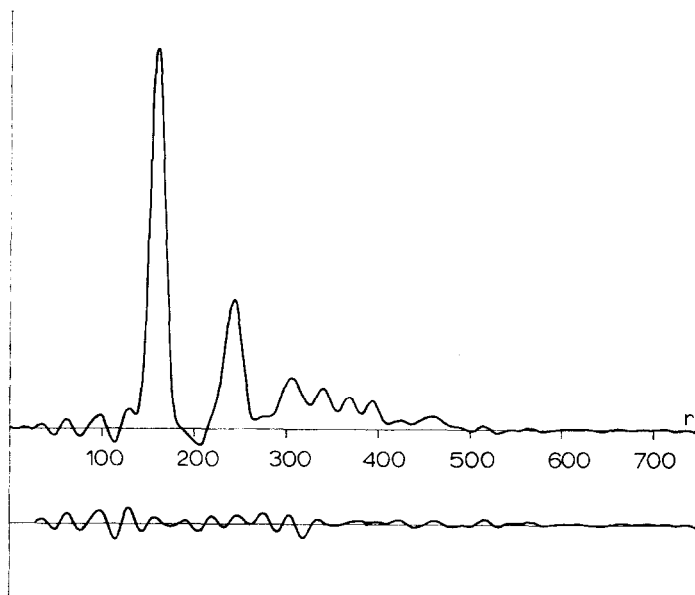


Fig. 2. Observed and difference radial distribution curves, $P(r)/r$, for bis(difluorophosphino)ether. Before Fourier inversion, the data were multiplied by $s \exp(-0.0015s^2)/(z_P - f_P)(z_F - f_F)$.

Our understanding of the conformation-determining forces in this type of molecule may well be helped by a study of the structure of bis(difluorophosphino)sulphide. An NMR study of this molecule²¹ has indicated that there must be considerable interaction between the two F₂P- groups. With a probable PSP angle of about 1.7 to 1.8 rad, the P...F and F...F distances should on average be much shorter than in the ether, and the freedom of rotation or torsion should be even more restricted than in the present case.

It should be pointed out that, in the absence of a full vibrational analysis for bis(difluorophosphino)ether, no shrinkage corrections have been applied in the refinements. As a consequence, the observed POP angle will probably be somewhat smaller than the true average angle, and the dihedral angles may also differ from those in the average structure. However, the observed amplitudes of vibration suggest that the torsional vibrations have small amplitudes, and so the corresponding shrinkage corrections will be small.

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