A Determination by Electron Diffraction of the Molecular Structure of Difluoro(phenyl)phosphine in the Gas Phase

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The molecular structure of $PPhF_2$ in the gas phase has been determined by electron diffraction. Principal bond lengths (r_a) and angles are: P–F 158.0(3), P–C 180.9(7), C–C (mean) 139.2(3), and C–H 110.6(8) pm; F–P–F 102.3(12) and F–P–C 98.8(11)°. The dihedral angle between the ring and FPF bisector is 31(2)°. The structure is compared with those of difluoro(phenyl)phosphine ligands in transition-metal complexes.

ALTHOUGH very many transition-metal complexes of different fluorophosphines have been prepared and characterised, few of their structures have been determined, often because the complexes have low melting points or are volatile, making them difficult subjects for crystallographic study. For those that have been studied, it is found that, in general, the three bonds to phosphorus are shorter, and the angles between them are slightly wider, in the complexes compared to the free ligand. Thus the bond length and interbond angle change from 157.0 pm and 97.9° in PF_3 [1] to 156.1 pm and 99.3° in $[Ni(PF_3)_4]$.[2] Similar changes occur when the phosphorus is made four-co-ordinate in other ways. Thus in $PF_3{\cdot}BH_3$ the P–F bond length and F–P–F angle are 153.8 pm and 99.8° respectively,[3] and in PF_3O they are 152.4 pm and 101.3°.[4]

With other fluorophosphine ligands there are very few cases where the structures of both the complexes and the free ligand are known. As the structures of two transition-metal complexes of difluoro(phenyl)phosphine have been determined,[5,6] we have investigated the gas-phase structure of the free phosphine to gain information about the changes in the bonding at the phosphorus atom on co-ordination, and also to find out about the conformation of the phenyl ring relative to the PF_2 group, in a situation free from possible crystal-packing constraints.

EXPERIMENTAL

Difluoro(phenyl)phosphine was prepared by fluorination of dichloro(phenyl)phosphine with sodium fluoride in tetrahydrothiophen 1,1-dioxide.[7] It was purified by distillation and its purity was checked spectroscopically immediately before use. Electron-diffraction scattering intensities were recorded photographically on Kodak electron image plates using a Balzers' KD.G2 gas-diffraction apparatus, with the sample maintained at 297 K and the nozzle at 311 K. The electron wavelength used, 5.660 ± 0.005 pm, was determined from the diffraction pattern of gaseous benzene.

The intensity data were obtained in digital form using a Joyce–Loebl automatic microdensitometer, and calculations were made with an ICL 4–75 computer at the Edinburgh Regional Computing Centre, using established programs for data reduction [8] and least-squares refinement.[9] The complex scattering factors of Schäfer *et al.*[10] were used. Details of the plates used, taken with nozzle-to-plate distances of 250, 500, and 1 000 mm, weighting points used in setting up the off-diagonal weight matrix,[9] correlation parameters, and refined scale factors are given in Table 1. The molecular-scattering intensity curves are shown in Figure 1: these curves are the averages for three plates taken at each of the 250- and 500-mm camera heights, and two taken at 1 000 mm.

TABLE 1

Weighting functions, correlation parameters, and scale factors

Camera height mm	Δs	$s_{min.}$	sw_1	sw_2	$s_{max.}$	p/h	Scale factor
	nm^{-1}						
250	4	60	100	250	300	0.072 7	0.767 ± 0.022
500	2	32	66	140	154	0.482 3	0.654 ± 0.015
1 000	1	10	22.5	62.5	75	0.483 9	0.724 ± 0.014

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MOLECULAR MODEL

For the first refinements it was assumed that in the phenyl group all the C–C bond lengths were equal, all the C–H bond lengths were equal, and all the angles were 120° The CPF_2 group was assumed to have a plane of symmetry. The structure was then defined in terms of four bonded distances (P–F, P–C, C–C, and C–H) and three angles (F–P–F, F–P–C, and dihedral). The dihedral angle was defined as zero when the bisector of the F–P–F angle lay in the same plane as the ring.

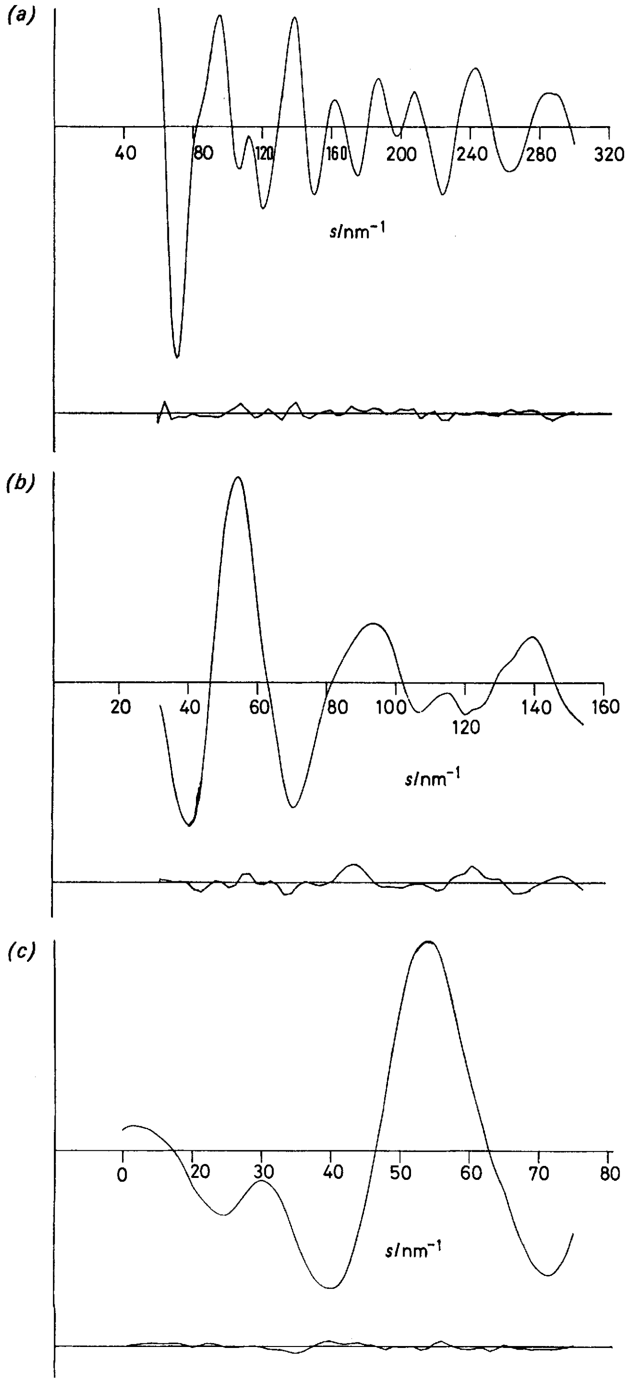

FIGURE 1 Observed (upper) and final weighted-difference (lower) molecular-scattering intensity curves for difluoro(phenyl)phosphine at nozzle-to-plate distances of (*a*) 250, (*b*) 500, and (*c*) 1 000 mm

In some later refinements, restrictions on the regularity of the ring structure were relaxed, but without any significant improvement in the fit of calculated to experimental data. In the final refinements, therefore, the original model was used.

REFINEMENTS

The radial-distribution curve (Figure 2) shows three distinct peaks corresponding to the C–H, C–C, and P–F bond distances, and a shoulder at *ca.* 180 pm, corresponding to the P–C bond. These four distances and their associated amplitudes of vibration all refined to reasonable values, with fairly large uncertainties for the P–C parameters. The angles F–P–F and F–P–C are dependent on the F · · · F and F · · · C distances of *ca.* 240—260 pm, but in this region there are also cross-ring C · · · C distances, and the two-bond P · · · C distance is also similar. With the ring constrained to regular hexagonal geometry, the F–P–C angle refined to 98.8(11)°, much as would be expected, but the F–P–F angle consistently refined to *ca.* 102°, some 3—4° larger than is usual in phosphines of this type. This suggested that the assumed regularity of the ring was not justified, and several more complex models were used. It was found that addition of one extra parameter to describe the ring (for example, varying the angle C^2–C^1–C^6 or allowing the bonds C^2–C^3 and C^5–C^6 to differ in length from the others) led to stable refinements, but no significant improvement in the structure. The large correlations between parameters in these refinements indicated that further relaxation of restrictions on the ring structure would not be possible. But it is possible that the ring is distorted, perhaps by interaction of the asymmetric PF_2 group with one side of the ring, and that failure to allow for this ring asymmetry may account for the unusual apparent F–P–F angle.

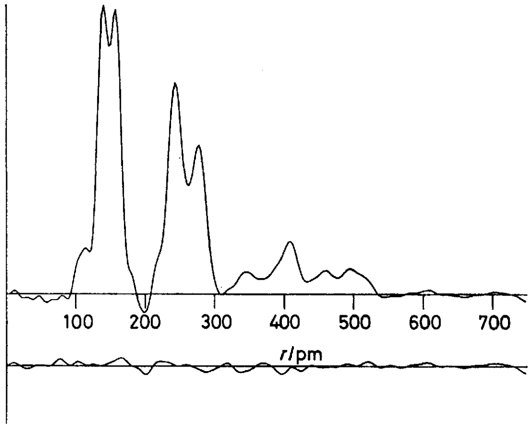

FIGURE 2 Observed and difference radial distribution curves, $P(r)/r$, for difluoro(phenyl)phosphine. Before Fourier inversion the data were multiplied by $s.\exp[(-0.000\,02s^2)/(z_P - f_P)(z_C - f_C)]$

Refinements were carried out with the dihedral angle set at many different values, but the F–P–F angle refined to $\geqslant 102°$, even for dihedral angles of 0 or 90°. When the F–P–F angle was fixed at 99° the dihedral angle giving the lowest R factor was *ca.* 20°. After locating the angles giving the lowest overall R factor, the C $\cdots$ F amplitudes of vibration were refined in groups and the dihedral angle was then refined. It was not possible to refine the angle and the amplitudes simultaneously. It should be noted that the dihedral angle correlates strongly with the F–P–F angle. The full least-squares correlation matrix is given in Table 2.

TABLE 2

Least-squares correlation matrix multiplied by 100

r_1	r_2	r_3	r_4	<1	<2	<3	u_1	u_2	u_3	u_4	u_5	u_6	u_7	u_{22}	u_{24}	k_1	k_2	k_3	
100	72	55	8	42	−50	−28	36	−47	52	10	23	14	1	10	−21	46	38	44	r_1
	100	35	15	64	−73	−36	44	−28	51	−2	15	14	−1	−4	−38	41	41	48	r_2
		100	26	12	−18	−20	−23	−30	−6	42	−8	0	2	−11	−8	−14	−3	11	r_3
			100	29	−10	−29	−9	6	−9	14	−18	15	6	−24	−3	2	−17	−25	r_4
				100	−43	−85	39	−21	42	−10	34	15	4	−23	−22	46	29	26	<1
					100	−8	−32	16	−36	3	−2	−9	7	−4	43	−26	−24	−31	<2
						100	−22	20	−26	3	−34	−11	−9	27	2	−33	−19	−14	<3
							100	−4	81	−34	36	19	2	30	−16	75	43	36	u_1
								100	−20	−5	−19	−7	−2	−10	6	−29	−22	−24	u_2
									100	−26	38	20	2	30	−15	78	45	41	u_3
										100	−16	−7	0	−11	2	−31	−19	−9	u_4
											100	10	1	41	0	47	31	30	u_5
												100	−17	8	−4	26	16	6	u_6
													100	−1	4	5	0	−2	u_7
														100	24	40	19	16	u_{22}
															100	−8	−18	−23	u_{24}
																100	42	33	k_1
																	100	33	k_2
																		100	k_3

At convergence, the generalised R factor, R_G,[9] was 0.11, and the factor calculated using a diagonal weight matrix, R_D, was 0.06. The final parameters are listed in Table 3. Errors quoted are estimated standard deviations, increased to allow for systematic errors. No extra allowance was made for the effect of the constraints described in this section: if this were done, the errors, particularly of the dihedral and F–P–F angles, would need to be increased.

DISCUSSION

In general the parameters found in this structural analysis are close to values that would be expected in the light of other known structures. Thus the P–F bond length [158.0(3) pm] is similar to those in difluoro(methyl)phosphine [158.2(5) pm] [11] and difluoro(t-butyl)phosphine [159.0(3) pm].[12] The P–C bond length [180.9(7) pm] approximates that for an sp^2-hybridised carbon atom, being shorter than bonds to sp^3- [$PMeF_2$,[11] 182.5(2) pm; PBu^tF_2,[12] 182.3(12) pm] but longer than those to sp-hybridised atoms [$P(CN)F_2$,[13] 179.7(9) pm]. Both P–F and P–C bonds in $PPhF_2$ are significantly longer than those in transition-metal complexes of the ligand, [$CoBr_2(PPhF_2)_3$] [5] and [$FeCl(PPhF_2)_5$][$FeCl_4$],[6] in which the mean P–F distances are 155.3(15) and 155.8(5) pm respectively, and the mean P–C distances are 180.1(16) and 179.4(4) pm. Thus the changes on co-ordination are similar to those observed for other fluorophosphine ligands.[1,2,8]

Similarly, the mean F–P–C angle in the two metal complexes [101.0(9)°] is slightly wider than that found in the free ligand [98.8(11)°], but the F–P–F angles in the complexes [mean 98.3(12)°] are apparently narrower than that in uncomplexed $PPhF_2$. As described above, the latter trend may not be significant, but a reflection of the constraints of the model used.

TABLE 3

Molecular parameters

(*a*) Independent distances (r_a) and amplitudes (pm)		
r_1(P–F)	158.0(3)	4.6(3)
r_2(P–C)	180.9(7)	8.1(8)
r_3(C–C)	139.2(3)	4.6(3)
r_4(C–H)	110.6(8)	8.4(11)
(*b*) Dependent distances and amplitudes (pm)		
d_5(P $\cdots$ C^2)	278.0(12)	8.8(9)
d_6(P $\cdots$ C^3)	408.0(16)	10.4(8)
d_7(P $\cdots$ C^4)	459.4(18)	10.3(16)
d_8(F $\cdots$ F)	246.0(18)	8.5 [a]
d_9(P $\cdots$ H^2)	291.4(12)	8.5 [a]
d_{10}(P $\cdots$ H^3)	494.8(19)	9.0 [a]
d_{11}(P $\cdots$ H^4)	569.9(23)	7.5 [a]
d_{12}(C^1 $\cdots$ F)	257.4(8)	8.8 (tied to u_5)
d_{13}(C^2 $\cdots$ F)	277.1(10)	13.0 [a]
d_{14}(C^2 $\cdots$ F)	317.0(13)	20.0 [b]
d_{15}(C^6 $\cdots$ F)	357.5(11)	13.7 [b]
d_{16}(C^6 $\cdots$ F)	389.2(12)	13.7 [b]
d_{17}(C^3 $\cdots$ F)	415.4(16)	13.7 [b]
d_{18}(C^5 $\cdots$ F)	443.0(17)	13.7 [b]
d_{19}(C^3 $\cdots$ F)	472.8(15)	20.5 [b]
d_{20}(C^5 $\cdots$ F)	497.3(19)	20.5 [b]
d_{21}(C^4 $\cdots$ F)	507.7(19)	20.5 [b]
d_{22}(C $\cdots$ C)	241.2(8)	5.9(5)
d_{23}(C $\cdots$ C)	278.5(8)	6.5 [a]
d_{24}(C $\cdots$ H)	216.8(10)	9.7(12)
d_{25}(C $\cdots$ H)	341.4(14)	10.0 [a]
d_{26}(C $\cdots$ H)	389.1(15)	9.0 [a]
Shortest (F $\cdots$ H)	228.3(11)	15.0 [a]
Shortest (F $\cdots$ H)	307.7(12)	15.0 [a]
(*c*) Angles (°)		
<1 (F–P–F)	102.3(12) [b]	
<2 (F–P–C)	98.8(11)	
<3 (dihedral)	31(2)	

[a] Fixed. [b] See text.

The other important parameter is the dihedral angle. We find that in $PPhF_2$, as in $PPhCl_2$,[14] the ring plane

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lies between the two phosphorus–halogen bonds. Whether the average structure has the ring bisecting the F–P–F angle, with the apparent asymmetry being the result of low-frequency torsional vibration, we are unable to say. What is certain is that the conformation adopted involves at least one F · · · H distance being shorter than the sum of the van der Waals radii for fluorine and hydrogen. This type of interaction probably determines the most stable conformations of a number of fluorophosphine derivatives.[15] In contrast to this, in all the five phosphine ligands of $[FeCl(PPhF_2)_5][FeCl_4]$,[6] and in one of the three in $[CoBr_2(PPhF_2)_3]$,[5] the ring planes lie outside the projections of the P–F bonds, with dihedral angles between 70 and 90°, the remaining two ligands in $[CoBr_2(PPhF_2)_3]$ having dihedral angles close to 0°. This does not rule out the possibility of direct F · · · H interactions, but it does illustrate the fact that it is difficult to predict the conformation of a complexed ligand, even when the structure of the free species is known. Neither transition-metal complex displays evidence of steric crowding, inter- or intra-molecular, but nevertheless it seems more likely that packing criteria, rather than electronic factors, are responsible for the conformations adopted by the ligands.

We thank the Deutsche Forschungsgemeinschaft and the S.R.C. for support (to O. S. and D. W. H. R. respectively), Professor D. W. J. Cruickshank and Dr. B. Beagley for the provision of experimental facilities, Mrs. V. Ulbrecht for technical assistance, and Professors R. Schmutzler and E. A. V. Ebsworth for their interest.

[6/2018 *Received, 29th October,* 1976]

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