Determination of the Molecular Structure of Difluorophosphine Sulphide by the Combined Analysis of Data from Electron Diffraction, Microwave Spectroscopy, and Liquid Crystal Nuclear Magnetic Resonance Spectroscopy

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Data relating to the molecular structure of difluorophosphine sulphide, PF_2HS, obtained by gas-phase electron diffraction (e.d.), microwave spectroscopy (m.w.), and by n.m.r. spectroscopy for a solution in a liquid crystal solvent (l.c.n.m.r.) have been analysed. Results are presented and compared for refinements using e.d. data only, m.w. only, e.d. plus m.w., e.d. plus l.c.n.m.r., and finally with all the data analysed simultaneously. In this last refinement the parameters ($r_\alpha{}^0$) obtained were: r(P–F) 154.6(2), r(P=S) 187.5(3), r(P–H) 141.9(13) pm; FPF 99.1(1), FPS 117.2(2), and HPS 116.4(6)°.

In studying molecular structures, by any method, one very soon runs up against the problem that the data obtainable may be insufficient for the complete determination of a particular structure. With electron diffraction (e.d.), it is difficult to locate light atoms, particularly hydrogen, in the presence of heavy ones, and it is also often impossible to resolve similar interatomic distances. With microwave spectroscopy (m.w.), there is very limited information obtainable for any one isotopomer and it is often impossible or impracticable to provide sufficient isotopically-substituted species. For liquid crystal nuclear magnetic resonance (l.c.n.m.r.), the only other structural technique widely applicable to molecules in a fluid phase, the information relates only to nuclei with a spin (in practice with spin $\frac{1}{2}$), and the problems are exacerbated by the need to define up to five orientation parameters, which describe the orientation of the molecule with respect to an applied magnetic field.

It is frequently found, therefore, that if only one technique is used, a structure is not determined completely. The chemical properties, however, depend very much on structure, and it is important to measure all structural parameters, and not just to guess some of them. The solution is to analyse simultaneously data obtained in more than one type of experiment, and this has become more or less routine for electron diffraction and rotational spectroscopy.[1–3] It has also been shown that combining electron diffraction and liquid crystal n.m.r. data can be useful.[4] In this paper, we report the results of the first analysis of data obtained by all three methods, and compare parameters obtained in refinements using data from one, two, or all three of the techniques. The compound studied is difluorophosphine sulphide, PF_2HS, chosen because it presents problems for each experiment. The hydrogen atom cannot be located reliably by electron diffraction, fluorine and phosphorus have only one stable isotope each, and so isotopic substitution cannot be used to help define their positions in the microwave work, and there is no suitable isotope of sulphur to be used in the n.m.r. experiments. There is therefore information relevant to each atom in two of the three experiments.

Experimental

Samples of PF_2HS were prepared by reaction between hydrogen sulphide and $PBrF_2$ in the presence of mercury,[5] or as by-products in reactions of $S(PF_2)_2$ with alcohols,[6] and purified by fractional distillation *in vacuo*. Their purity was checked by i.r. and n.m.r. spectroscopy.

Electron Diffraction.—Photographic plates exposed using a Balzers' KD.G2 apparatus and used previously[7] were retraced using a computer-controlled Joyce–Loebl MDM6 densitometer, with automatic centring and circular tracing paths.[8] Data reduction was performed using standard procedures.[8] The electron wavelength was obtained by analysis of the scattering pattern of gaseous benzene. In all diffraction calculations, the scattering factors of Schäfer *et al.*[9] were used.

Microwave Spectroscopy.—The rotational constants of Nave and Sheridan[10] for $PF_2{}^1H^{32}S$, $PF_2{}^2H^{32}S$, and $PF_2{}^1H^{34}S$ were used.

Liquid Crystal N.M.R. Spectroscopy.—Samples containing 0.3 mmol of PF_2HS in 0.4 cm^3 of BDH 'E5' liquid crystal were prepared in 5-mm tubes. These solutions possessed a nematic phase between *ca.* 235 and 295 K. N.m.r. spectra were recorded on a Varian Associates XL100 spectrometer operating in the Fourier-transform mode. Indirect (J) coupling constants were measured in the isotropic phase of the liquid crystal at 313 K. The couplings were also measured in $CDCl_3$ solution at 253 and 298 K. These latter couplings, listed in Table 1, were quite significantly different from those in E5 solution, emphasising the importance of measuring them in the liquid crystal solvent. It was assumed that the temperature coefficients of indirect couplings in $CDCl_3$ and E5 were the same, and so values for these couplings in E5 at 262 K were derived. The relative signs of indirect couplings were determined in a series of double-resonance experiments; the results were in accord with those reported previously.[11] Absolute signs were assigned assuming J(PF) to be negative.

Spectra (^1H, ^{19}F, and ^{31}P) were recorded for the nematic phase at several temperatures around 262 K. Couplings were interpolated so that a fully self-consistent set was obtained, and errors due to changes of orientation parameters with temperature were eliminated, as shown in Table 1; uncertainties are increased to make some allowance for the extrapolation of J values in E5 to 262 K. Relative signs of coupling constants were also obtained from two-dimensional chemical shift correlation spectra. For example, the $^{31}P,^1H$ spectrum had three resonances, as both ^{31}P and ^1H were coupled to two ^{19}F nuclei. The three resonances lay on a line of negative gradient and so the $^{31}P–^{19}F$ and $^{19}F–^1H$ couplings must be of opposite sign. We found that the two-dimensional spectra (run on a Bruker WH300 spectrometer) gave the required information quickly and easily, and that this technique is preferable to performing a time-consuming series of double-resonance experiments.

Table 1. Coupling constants (Hz)

		Nuclei			
Coupling	Temp./K	PF	PH	FH	FF
J in $CDCl_3$	298	−1 157.3(5)	+737.5(1)	+97.8(1)	—
J in $CDCl_3$	253	−1 158.3(4)	+740.9(5)	+97.8(2)	—
J in E5	313	−1 156.8(5)	+758.0(8)	+98.0(5)	—
J in E5[a]	262	−1 157.8(8)	+761.0(8)	+98.0(5)	—
(J + 2D) in E5	262	−1 015.8(5)	+2 025.0(10)	+973.6(5)	+789.4(5)[b]
D in E5	262	+71.0(8)	+632.5(12)	+437.8(7)	+263.1(5)

[a] Extrapolated values. [b] 3D(FF); D = dipolar coupling constant.

Results and Discussion

Structure Analysis.—Normal co-ordinate analysis. A normal co-ordinate analysis using the program GAMP[12] was carried out, to determine amplitudes of vibration, and vibrational corrections needed to relate data obtained by the three techniques to a single structural model. A harmonic force field was developed which fitted the observed vibrational frequencies,[10] which are listed in Table 2, together with their assignments. One of the fundamental modes, the a'' PF_2S deformation, has not been observed. Various frequencies for this mode were tried, and eventually it was set at 230 cm^{-1}, at which value the calculated S•••F amplitude of vibration agreed with the experimental value. The equivalent mode occurs at 250 cm^{-1} in PF_2ClS.[13] Using the force field obtained in this way the terms needed to correct electron-diffraction distances (r_a) to r_α^0, and the rotational constants from B_0 to B_z, were calculated. They are listed in Table 3. Note that we have calculated corrections from r_g to r_α^0 as $\frac{3a}{2}(u_T^2 - u_0^2) + K_T$, which differs from the usual equation, (i); the notation used here is that

$$r_\alpha^0 = r_g - \frac{3a}{2}(u_T^2 - u_0^2) - K_0 \qquad \text{(i)}$$

of ref. 14. Taking $r_\alpha^T = r_e + \langle\Delta z\rangle^T$ equation (ii) applies.

$$r_\alpha^T - r_\alpha^0 = \langle\Delta z\rangle^T - \langle\Delta z\rangle^0 \qquad \text{(ii)}$$

Treating the atom pair concerned as a Morse-oscillator diatomic in the usual way leads to equation (iii). Now r_g is

$$\langle\Delta z\rangle^T - \langle\Delta z\rangle^0 = \frac{3a}{2}(u_T^2 - u_0^2) \qquad \text{(iii)}$$

defined by equation (iv) and combining (ii), (iii), and (iv) leads to (v).

$$r_g = r_e + \langle\Delta z\rangle + K \quad \text{or} \quad r_g^T = r_\alpha^T + K_T \qquad \text{(iv)}$$

$$r_\alpha^0 = r_g^T - \frac{3a}{2}(u_T^2 - u_0^2) - K_T \qquad \text{(v)}$$

This result has been used previously by ourselves[15] and others[16] but in view of the prevalence of the use of equation (i) rather than (v), which is clearly shown to be correct by the results of Hilderbrandt and Kohl,[17] we show its derivation here. Note that no approximations are involved except in equation (iii); replacement of equation (i) by (v) constitutes correction of an error in the derivation of (i), not a different approximation.[16a] The corrections to dipolar couplings, also listed in Table 3, were calculated using the program VIBR.[18] Strictly, the corrected couplings apply to the r_α structure, and not to r_α^0, as no allowance has been made for the temperature-dependence of the couplings on the anharmonic potential terms. However, the difference is extremely small.

Table 2. Vibrational frequencies and assignments

Species	Frequency/cm^{-1}	Approximate description
a'	2 458	P–H stretch
	1 019	P–H deformation (in plane)
	923	PF_2 stretch (symmetric)
	710	P=S stretch
	419	PF_2S deformation (symmetric)
	344	PF_2 symmetric deformation (scissors)
a''	963	P–H deformation (out of plane)
	901	PF_2 stretch (asymmetric)
	230*	PF_2S deformation (asymmetric)

* Estimated from amplitude of vibration determined by electron diffraction.

Structure refinements. In all refinements, it was assumed that the PF_2HS molecule possessed C_s symmetry. The structure was defined in terms of the three bond distances and the angles FPF, FPS, and HPS. The angle HPF was therefore a dependent parameter. A standard least-squares refinement program[4] was used. This program allows structure-related data from any source to be analysed at the same time as the electron-diffraction data. Indeed, the diffraction data are not essential. For each diffraction data set, the majority of the data points are given unit weights, but points towards the ends of the data sets have reduced weights. The overall weighting functions are trapezoidal; details of the ranges and weighting points *etc.* are given in Table 4. Off-diagonal terms are also included in the weight matrix, to take account of the effects of the correlations between observations. For additional observations, such as rotational constants and dipolar couplings, weights are assigned which are inversely proportional to the squared uncertainties of each observation, scaled to the standard deviation of the fit of the electron-diffraction data points.

In a refinement based only on electron-diffraction data, the parameters shown in Table 5, refinement A, were obtained. When attempts were made to refine the P–H distance and the HPS angle both parameters dropped to wildly unreasonable values, with huge standard deviations. They were therefore fixed at sensible values. The r_a distances found in this refinement agree well with those found previously,[7] but the R factor (R_G) was 0.06, compared to 0.12 for the original results. As the same plates were used on both occasions, the marked improvement in data quality must mainly reflect the advances made in microdensitometry.[8]

Refinement B in Table 5 is based only on the nine rotational constants listed in Table 3, with vibrational corrections applied to convert them from B_0 to B_z values and with vibrational corrections to bond lengths of isotopic species. These parameters, which were obtained by least-squares analysis, are very close indeed to those obtained earlier,[10] partly by use of

Table 3. Vibrational corrections

(*a*) Electron diffraction

Atom pair	u_T/pm	$\frac{3a}{2}(u_T^2 - u_0^2) + K_T$/pm[a]	$\frac{3a}{2}(u_T^2 - u_0^2) + K_T - \frac{u_T^2}{r}$/pm
PH	8.41	1.300	0.797
PF	4.04	0.264	0.158
PS	3.89	0.192	0.112
FF	7.38	0.200	0.000
SF	7.44	0.040	−0.150
SH	10.90	0.620	0.200
FH	11.84	0.770	0.150

(*b*) Microwave

Rotation constant	B_0/MHz	Correction/MHz	B_z/MHz[b]	$B_{calc.}$/MHz[c]
A, $PF_2{}^1H^{32}S$	8 336.572(6)	−16.980	8 319.59(170)	8 319.37
B, $PF_2{}^1H^{32}S$	3 725.667(3)	−5.485	3 720.18(55)	3 720.32
C, $PF_2{}^1H^{32}S$	2 805.302(2)	−1.260	2 804.04(13)	2 804.23
A, $PF_2{}^2H^{32}S$	7 976.61(3)	−15.151	7 961.46(152)	7 961.89
B, $PF_2{}^2H^{32}S$	3 641.52(3)	−5.063	3 636.46(51)	3 636.29
C, $PF_2{}^2H^{32}S$	2 798.88(3)	−1.328	2 797.55(13)	2 797.84
A, $PF_2{}^1H^{34}S$	8 333.40(3)	−16.843	8 316.56(168)	8 316.32
B, $PF_2{}^1H^{34}S$	3 596.86(3)	−5.211	3 591.65(52)	3 591.59
C, $PF_2{}^1H^{34}S$	2 731.91(3)	−1.212	2 730.70(12)	2 730.80

(*c*) Liquid crystal n.m.r.

Nuclei	$D_{obs.}$/Hz	Correction/Hz	D_α/Hz[b]	$D_{calc.}$/Hz[c]
PF	71.0(8)	0.7	71.7(8)	71.75
PH	632.5(12)	24.2	656.7(25)	656.92
FH	437.8(7)	1.7	439.5(8)	439.54
FF	263.1(5)	0.7	263.7(6)	263.74

[a] Anharmonic constants were taken to be 2.0 Å $^{-1}$ for bonded distances, otherwise zero. [b] An uncertainty of 10% was assumed for vibrational corrections. [c] Calculated from parameters obtained in refinement E.

Table 4. Camera heights, *s* ranges and weighting points, correlation parameters, and scale factors for data sets (refinement E)

Camera height	Δ*s*	$s_{min.}$	sw_1	sw_2	$s_{max.}$	Correlation parameter	Scale factor
mm			nm^{-1}				
999.8	1	10	22	62	75	+0.177	0.722(6)
500.1	2	28	42	138	156	0.496	0.788(5)
250.1	4	72	93	265	300	0.439	0.594(17)

Table 5. Molecular parameters ($r_\alpha{}^0$)

	A e.d.	B m.w.	C e.d. + m.w.	D e.d. + l.c.n.m.r.	E e.d. + m.w. + l.c.n.m.r.
r(P–H)/pm	139.2 (fixed)	139.2(15)	138.6(16)	140.9(20)	141.9(13)
r(P–F)/pm	154.7(2)	155.0(2)	154.7(2)	154.7(2)	154.6(2)
r(P=S)/pm	187.6(3)	187.3(3)	187.5(3)	187.5(3)	187.5(3)
FPF/°	99.3(5)	98.7(2)	99.0(2)	99.4(5)	99.1(1)
FPS/°	116.2(2)	117.1(2)	117.0(2)	116.2(2)	117.2(2)
HPS/°	117.0 (fixed)	119.2(10)	114.3(20)	118.4(8)	116.4(6)
HPF/°	102.7(3)	101.0	103.6	101.8	102.1(2)
δ*r*(PD − PH)/pm	—	0.2 (fixed)	—	—	1.4(7)
δ(DPS − HPS)/°	—	0 (fixed)	—	—	1.4(6)
R_G (e.d. data)	0.06	—	0.056	0.048	0.076
R.m.s. deviation, rotational constants/MHz	—	0.01	0.28	—	0.07
R.m.s. deviation, dipolar couplings/Hz	—	—	—	0.083	0.008

Kraitchman's equations,[19] partly from the inertial defect, and finally by fitting remaining parameters to the observed rotational constants. However, the least-squares procedure probably gives a more realistic estimate of the uncertainties of the parameters, and Table 5 shows that the hydrogen-atom position is poorly determined. Weights were based on uncertainties of 0.10 MHz for *A* and 0.055 MHz for *B* and *C* of the most abundant isotopic species, and 1.0 MHz for the other six data.

It is therefore not surprising that in this case a combined analysis of electron-diffraction data and three rotational constants for the most abundant isotopic species (refinement C in

Table 6. Least-squares correlation matrix (× 100) for refinement E[a]

r(P–F)	FPF	HPS	FPS	S_{xx-yy}	S_{xy}	δr	u(P=S)	k_1	k_2	k_3[b]	
−72	69	−97	88	100	−88	−84					r(P–H)
	−98	64		−65		59					r(P–F)
		58	−81	−57	78						r(P=S)
		−62		63		57					FPF
			−93	−98	89	81				51	HPS
				91	−94	−73				−55	FPS
					−85	−83				−51	S_{xx-yy}
						67				52	S_{xy}
							54	77			u(P–F)
								71			u(P=S)
								56			u(S ··· F)
									60		k_1[b]

[a] Only elements with absolute values > 50 are included. [b] Electron-diffraction scale factors.

Table 7. Final combined structure, refinement E

	Interatomic distance (r_a)/pm	Amplitude/pm	
		E.d.	Spectroscopic
PH	142.69(125)	8.4 (fixed)	8.4
PF	154.76(20)	3.0(5)	4.0
PS	187.65(25)	3.1(5)	3.8
FF	235.23(10)	7.3(10)	7.3
FS	292.35(10)	7.2(4)	7.5
SH	281.26(60)	11.0 (fixed)	11.6
FH	230.87(25)	12.0 (fixed)	11.4
S_{zz}		−3.229(1)	
S_{xx-yy}		14.14(30)	
S_{xy}		1.515(55)	

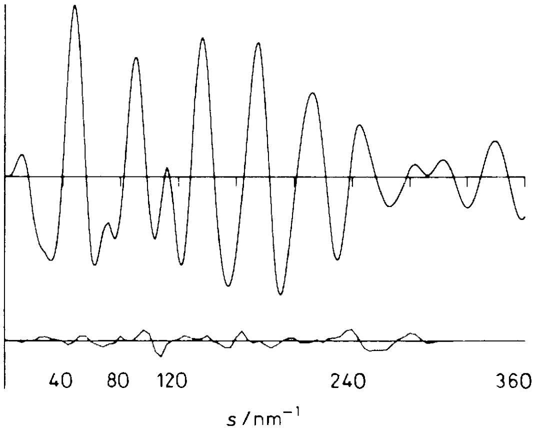

Figure 1. Observed and weighted difference molecular scattering intensities for PF_2HS; combined curves for all distances

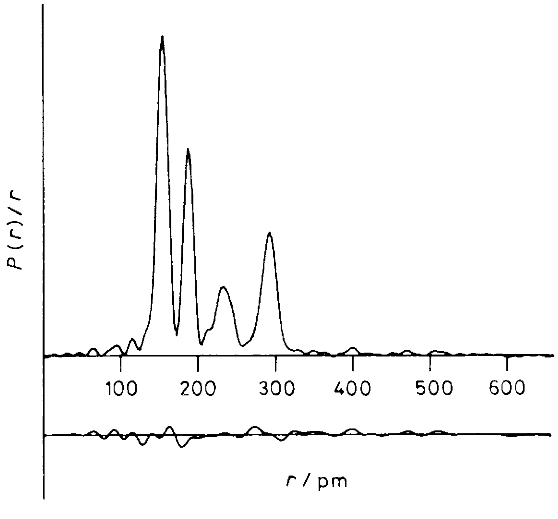

Figure 2. Observed and difference radial-distribution curves for PF_2HS

Table 5) is not a great success. The effect of including the diffraction data is mainly to force the HPS angle down, from 119.2 to 114.3°, but with an estimated standard deviation of 2.0°. It should be noted that, even with the large change in structure, the r.m.s. deviation in the fit to three rotation constants was only 0.010 MHz, compared with <0.001 MHz in refinement B for the same three rotation constants.

On the other hand, the liquid crystal n.m.r. data do give information about the hydrogen-atom position. However, only four dipolar couplings can be measured, and there are three orientation parameters required to define the average orientation of the molecules in the solvent with respect to the magnetic field. The n.m.r. experiments therefore provide just a single structural datum, which is nevertheless invaluable.

Refinement D in Table 5 shows results based on diffraction and n.m.r. data. The three orientation parameters were included as independent variables in the refinement, in which all the geometrical parameters were released. Thus the addition of the n.m.r. data to the diffraction data has allowed us to determine the whole structure, including the hydrogen-atom position, and to obtain results which are clearly compatible with those based on microwave data (refinement B). It was therefore possible to proceed with the final refinement (E) using all the available information (including ^{2}D isotopic rotation constants). For this refinement two extra geometrical parameters were introduced, to represent the changes in atomic position when hydrogen is replaced by deuterium. These changes are small, but it is necessary to allow for them in order to fit the rotational constants properly. Another refinement, using electron diffraction and n.m.r. data, with rotational constants for $PF_2{}^1H^{32}S$ and $PF_2{}^1H^{34}S$ gave parameters almost identical to those of refinement E. At first sight, some of the parameters obtained in this refinement are surprisingly different from those found earlier. However, it must be remembered that the spectroscopic data can be fitted quite well by widely varying structures. Refinements B and C illustrate this well for the rotational constants. The n.m.r. data do not provide direct information about the HPS and FPS angles, but do relate to the HPF angles. Consequently there is a strong correlation between the HPS and FPS angles, as shown in the final least-squares correlation matrix, Table 6. Refinement E therefore simply represents the best structure that can be obtained at present, and it is consistent with all the observations. Full details of the r_a distances and amplitudes of vibration obtained in this refinement are given in Table 7, and molecular scattering intensity and radial-distribution curves are shown in Figures 1 and 2.

Discussion of Structure.—The structure of PF_2HS is unremarkable, although somewhat different from that reported earlier.[10] It closely resembles that of the analogous selenium compound, PF_2HSe, studied by electron diffraction and liquid crystal n.m.r.[4] In particular, the P–H distances in these compounds are 141.9(13) and 142.2(7) pm respectively, compared with 139.2(15) pm in PF_2HS in the first microwave study, 138.7(10) pm in PF_2HO[20] and 141.2(6) pm in PF_2H.[21] Typical distances are 142—144 pm in phosphines, and 140—142 pm in compounds with four-co-ordinate phosphorus.

Similarly, the parameters for the PF_2S group are very similar to those of related compounds.[7] Angles between sulphur and the other ligands in compounds of type PX_3S are usually between 116 and 118°, with the other angles at phosphorus being close to 100°.

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