Gas-phase Molecular Structures of Bis(difluorophosphino) sulphide, $S(PF_2)_2$, Bis(difluorophosphino) selenide, $Se(PF_2)_2$, and Difluoro(methylthio)phosphine, $PF_2(SMe)$, determined by Electron Diffraction

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The molecular structures of $S(PF_2)_2$ and $Se(PF_2)_2$ in the gas phase have been determined by electron diffraction. Both molecules have average structures with C_{2v} symmetry, but have large-amplitude torsional vibrations, root mean square torsion angles being 22(2) and 20(4)° respectively. Principal parameters (r_a) are: $S(PF_2)_2$, r(P–S) 213.2(4), r(P–F) 157.2(2) pm, FPF 97.4(5), FPS 100.2(4), PSP 91.3(11)°; for $Se(PF_2)_2$, r(P–Se) 227.3(5), r(P–F) 157.3(3) pm, FPF 100.6(11), FPSe 98.7(4), PSeP 94.6(8)°. The structure of $PF_2(SMe)$ has also been determined. Three conformations fit the observed data almost equally well, with the PF_2 group twisted 19(3), 106(9) or 171(5)° away from the position in which the S–C bond lies *anti* to the bisector of the FPF angle. The most favoured structure is the second of these, for which other principal parameters (r_a) are r(P–S) 208.5(3), r(P–F), 158.9(3), r(C–S) 182.2(5) pm, FPF 95.6(6), SPF 101.2(3), PSC 102.0(12)°.

The structure of bis(difluorophosphino) ether, $O(PF_2)_2$, has been the subject of two electron diffraction studies. In one [1] the data were interpreted in terms of a single conformer, with no symmetry, while in the second [2] a mixture of four conformers, with point groups C_{2v}, C_2, C_s, and C_1, was considered. In both studies, the P–O bond lengths were found to be much shorter than the expected distance, based on covalent radii with an electronegativity correction, and the POP angles were found to be wide, *ca.* 140°. Short distances and wide angles are also found in silyl ethers [3,4] and to a lesser extent in digermyl ether,[5] and also in the partially methylated methylsilyl and dimethylsilyl ethers.[6] In contrast, the silyl and germyl derivatives of sulphur [5,7] and selenium [8,9] have normal bond lengths and angles, and in view of the general structural similarities of silyl, germyl, and difluorophosphino compounds, it is of interest to study the structures of difluorophosphino derivatives of sulphur and selenium.

The conformations of these compounds are also important and it is believed that the orientations of the PF_2 groups relate to the couplings between the phosphorus nuclei observed in ^{31}P n.m.r. spectra.[10] In $O(PF_2)_2$, the two-bond ^{31}P–^{31}P coupling constant is only 4 Hz,[11] whereas in $S(PF_2)_2$[12] and $Se(PF_2)_2$[10] the equivalent couplings are very large and highly temperature dependent, in the latter case changing from 232 to 336 Hz as the temperature changes from 293 to 173 K. The large couplings were believed to arise from interactions between the lone pairs of electrons on the phosphorus atoms, and the decreases on raising the temperature can be associated with increasing amplitudes of the torsional vibrations of the PF_2 groups. Similarly, on the evidence of n.m.r. coupling constants, it has been suggested that compounds of the type $PF_2(YMH_3)$ (M = C, Si, or Ge; Y = O, S, or Se) adopt conformations in which there are fairly close contacts between hydrogen and fluorine atoms.[10] We have therefore studied the molecular structures of $S(PF_2)_2$, $Se(PF_2)_2$, and $PF_2(SMe)$, and present our findings here.

Experimental

A sample of $Se(PF_2)_2$ was prepared by the exchange reaction of $PBrF_2$ with $Se(SiH_3)_2$,[13] and $S(PF_2)_2$ was made by the reaction of $PBrF_2$ with $S(SnBu_3)_2$.[14] A sample of $PF_2(SMe)$ was prepared by the reaction of $PClF_2$ and MeSH in the presence of NMe_3.[15] The compounds were purified by fractional condensation *in vacuo*, and purities were checked spectroscopically. It was not possible to remove all traces of $PF_2H(Se)$ from $Se(PF_2)_2$, and allowance for the impurity had to be made in the analysis of the electron diffraction data.

Electron diffraction data were recorded photographically on Kodak Electron Image plates, using the Cornell/Edinburgh diffraction apparatus [16,17] [for $S(PF_2)_2$ and $PF_2(SMe)$] or a Balzers' KD.G2 apparatus [18] [for $Se(PF_2)_2$]. Data were obtained in digital form using automatic Joyce-Loebl MDM6 [19] or MDM3 microdensitometers. During the diffraction experiments samples were maintained at 273 K [$S(PF_2)_2$ and $PF_2(SMe)$] or 228 K [$Se(PF_2)_2$], and in each case the nozzle was kept at room temperature, 295 K. Calculations were done on ICL 4-75 and 2972 computers using established data reduction [19,20] and least-squares refinement programs.[21,22] Weighting points, used in setting up the off-diagonal weight matrices for the refinements, are given in Table 1, together with correlation parameters and scale factors. Electron wavelengths are also listed in Table 1: these were determined from the diffraction patterns of gaseous benzene. The scattering factors of Schäfer *et al.*[23] were used in all calculations. We have observed that with the tracing procedure used on the Joyce-Loebl MDM6 [19] correlations between observations have been greatly reduced, and for short distance data sets the correlation parameters are effectively zero. Of course, this parameter is experimentally determined, and subject to random errors which are large when the parameter is close to zero; in practice it normally falls within the range ±0.2. With such values the effect on standard deviations of geometrical parameters is extremely small, and we are therefore effectively using a diagonal weight matrix. A small negative correlation parameter is of no particular significance.

Refinement of the $S(PF_2)_2$ *Structure.*—In the early stages of the refinements, the structure of $S(PF_2)_2$ was described by a model in which the conformations of the two PF_2 groups were each defined by a single torsion angle, taken to be zero when the bisector of the FPF angle was *anti* with respect to the further P–S bond. The two PF_2 groups were identical, and had C_s local symmetry, and so the whole structure was defined by the P–S and P–F distances, the angles FPF, FPS, and PSP, and the two twist angles, which could be constrained to be equal (giving overall C_2 symmetry), or equal and opposite (giving overall C_s symmetry).

With this model it was possible to refine the five major

Table 1. Weighting functions, correlation parameters, scale factors, and wavelengths

Compound	Camera height (mm)	Δs	$s_{min.}$	sw_1	sw_2	$s_{max.}$	Correlation parameter	Scale factor	Wavelength (pm)
				nm^{-1}					
$S(PF_2)_2$	128	4	60	80	300	344	−0.194	0.517(11)	5.680
	286	2	20	40	120	146	0.423	0.576(15)	5.679
$Se(PF_2)_2$	250	4	60	80	250	292	0.199	0.635(20)	5.660
	500	2	30	55	125	158	0.495	0.612(27)	5.660
$PF_2(SMe)$	128	4	60	70	300	324	0.192	0.639(24)	5.618
	286	2	20	50	120	140	0.475	0.752(25)	5.858

Table 2. Molecular parameters [a] for $S(PF_2)_2$ and $Se(PF_2)_2$

	$S(PF_2)_2$		$Se(PF_2)_2$	
	Distance (pm)	Amplitude (pm)	Distance (pm)	Amplitude (pm)
(*a*) Independent distances				
r_1(P–F)	157.2(2)	3.8(3)	157.3(3)	4.7(5)
r_2(P–S/Se)	213.2(4)	5.3(4)	227.3(5)	5.7(5)
(*b*) Dependent distances				
d_3(F ··· F)	236.2(8)	6.0(7)	242.1(25)	7.8 (tied to u_2)
d_4(F ··· S/Se)	286.3(8)	8.7(5)	295.3(27)	13.0(9)
d_5(P ··· P)	304.8(21)	18.1(48)	334.1(37)	11.2(27)
d_6(P ··· F) [b]	376—442	16.9(28) [c]	404—466	15.0 [c] (fixed)
d_7(F ··· F) [b]	328—561	8.6(50) [c]	330—580	20.0 [c] (fixed)
(*c*) Independent angles (°)				
Angle 1 (F–P–F)	97.4(5)		100.6(11)	
Angle 2 (F–P–S/Se)	100.2(4)		98.7(4)	
Angle 3 (P–S/Se–P)	91.3(11)		94.6(8)	
R.m.s. torsion [b]	22.3(24)		20.0(40)	

[a] Errors quoted in parentheses are estimated standard deviations obtained in least-squares analyses, increased to allow for systematic errors. [b] See text for definition of torsion-dependent parameters. [c] ' Framework ' amplitude (see text).

parameters, and the associated one- or two-bond amplitudes of vibration. The torsion angles were varied widely, but the best refinements were those in which both angles were in the ranges ±(15—20°). In the refinement giving the lowest *R* factor ($R_G = 0.089$) the angles were 16 and −16° (overall C_s symmetry), but the equivalent structure with C_2 symmetry was only a marginally poorer fit. In these refinements three amplitudes of vibration for long-range P ··· F and F ··· F groups of distances were included.

The possibility of the molecule having C_{2v} symmetry, and large amplitude torsional vibrations was then investigated. The model was modified so that the two torsion angles were replaced by a single parameter, δ, which was the root-mean-squared (r.m.s.) amplitude of PF_2 group torsion from C_{2v} symmetry. The two groups were assumed to vibrate independently and harmonically. The probability distributions for the two groups are therefore given by the equation below where

$$P(\varphi_1,\varphi_2) = Q^{-1}\exp[-(\varphi_1^2 + \varphi_2^2)/2\delta^2]$$

Q is a normalisation factor, and φ_1 and φ_2 are the angular displacements of the PF_2 groups. To represent the distribution of torsion-dependent distances, values of φ_1 and φ_2 equal to 0, $\pm 2\delta/3$, $\pm 4\delta/3$, and $\pm 2\delta$ were chosen, and all distances corresponding to pairs of angles φ_1 and φ_2 were calculated, and weighted by the appropriate probability term, $P(\varphi_1,\varphi_2)$. Using this model the five major parameters and amplitudes of vibration refined as before, with unchanged values. The r.m.s. torsional angle now refined to 22.3(24)°, and the lowest *R* factor obtained was 0.091, marginally higher than before. This probably reflects the fact that fewer amplitudes of vibration were refined. A single parameter was included to represent the contribution of vibrations, other than the torsions, to the long P ··· F distances, and a further similar ' framework ' amplitude of vibration was included for the long F ··· F distances.

The results of this refinement are given in Table 2, the scattering intensity data are shown in Figure 1(*a*), and the radial distribution curve is shown in Figure 2(*a*). The only major correlation between refining parameters was one of 0.75, between the angle SPF and the P ··· P amplitude of vibration.

Refinement of the $Se(PF_2)_2$ *Structure.*—The analysis of the structure of $Se(PF_2)_2$ followed essentially the same route as that of $S(PF_2)_2$, but there were two differences in the models used. At an early stage it became apparent that it was not possible to obtain large samples of $Se(PF_2)_2$ that were completely free of $PF_2H(Se)$. As the structure of the latter is known,[22] and as the main peak in its radial distribution curve is clear of any in the curve for $Se(PF_2)_2$, it was a straightforward matter to calculate the percentage impurity, and to modify the experimental data accordingly. The molar percentage of $PF_2H(Se)$ found was 15% for the 500-mm data set, and 27% for the 250-mm data set. The corrected intensity data were used in all subsequent refinements.

The second, minor, difference in the model used in the final refinements was that some of the long F ··· F distances that were very close together were grouped, and replaced by single distances of appropriate weight and distance. With this model, the parameters given in Table 2 were obtained, with an *R*

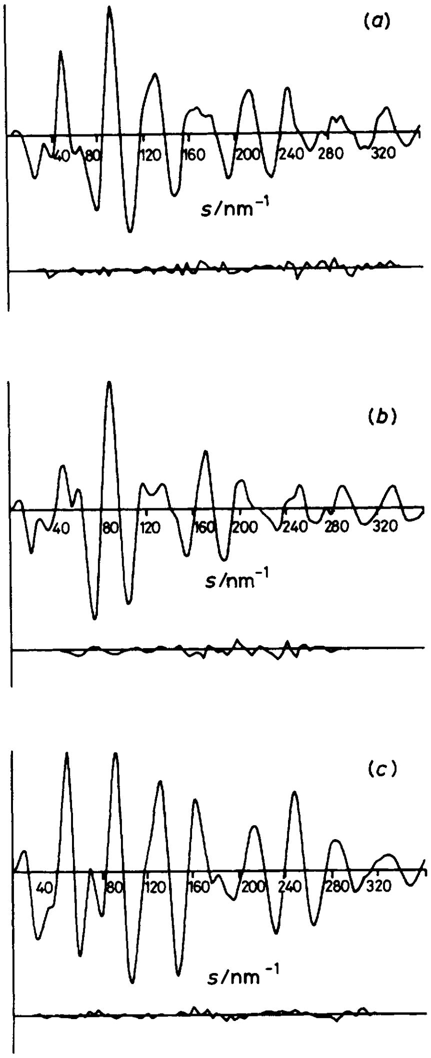

Figure 1. Observed and final weighted difference combined molecular-scattering intensity curves for (*a*) $S(PF_2)_2$, (*b*) $Se(PF_2)_2$, and (*c*) $PF_2(SMe)$

factor (R_G) of 0.158. This is significantly better than was achieved (0.179) with the simpler model, and overall C_2 symmetry.

In the final refinements there were some strong correlations between parameters (listed in the correlation matrix, Table 3), mainly arising from the overlap of the P–Se and F · · · F peaks near 230 pm, and it was necessary to refine just one amplitude of vibration for these two distances. The framework amplitudes of vibration for the long P · · · F and F · · · F distances were not refined.

The observed and final difference molecular scattering intensities are shown in Figure 1(*b*), and the radial distribution curve in Figure 2(*b*).

Refinement of the $PF_2(SMe)$ *Structure*.—During refinements of the structure of $PF_2(SMe)$ it was assumed that the PF_2S and SCH_3 groups had local C_s and C_{3v} symmetries respectively. The geometry was then defined by four bond lengths and four valence angles, as given in Table 4, and by the torsion angles defining the conformations of the CH_3 and PF_2 groups. The CH_3 twist angle was defined relative to zero for a *syn* H–C–S–P arrangement, and the zero PF_2 twist position was defined to be that in which the bisector of the FPF angle was *anti* to the S–C bond. Both angles were defined to be positive for clockwise rotations, when viewed from P or C to S.

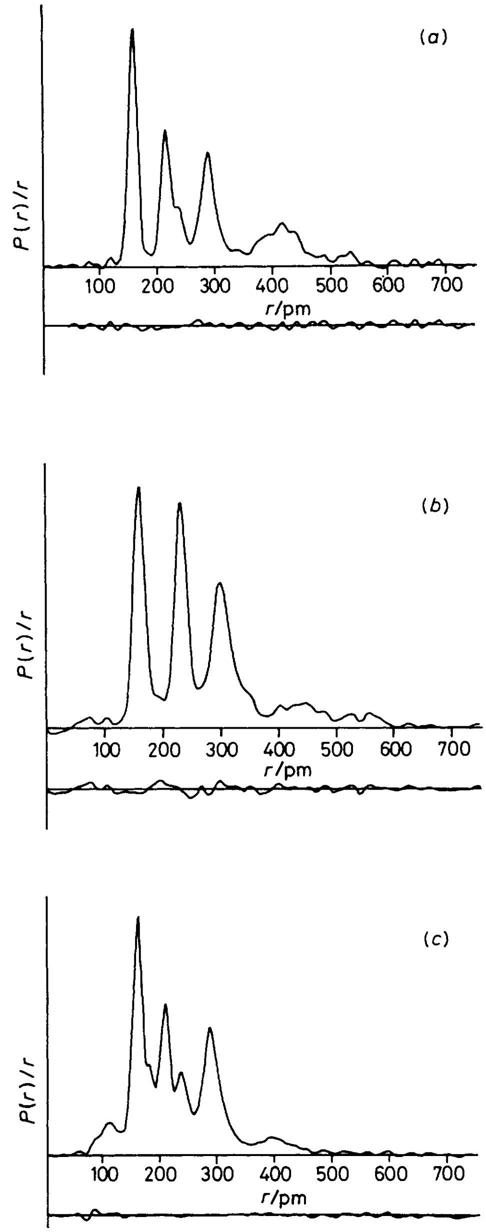

Figure 2. Observed and difference radial distribution curves, $P(r)/r$, for (*a*) $S(PF_2)_2$, (*b*) $Se(PF_2)_2$, and (*c*) $PF_2(SMe)$. Before Fourier inversion the data were multiplied by $s.\exp[-d.s^2]/(Z_P - f_P)(Z_F - f_F)$ where the damping factor, *d*, was 0.000 02 for (*a*) and (*c*), and 0.000 03 for (*b*)

The radial distribution curve [Figure 2(*c*)] shows clear peaks associated with the C–H, P–F, C–S, and P–S bonded distances. The next peak, at about 240 pm, contains contributions from F · · · F and S · · · H atom pairs, and the next, at *ca.* 290 pm, includes P · · · C and S · · · F components. It was therefore necessary to constrain some amplitudes of vibration to refine in groups, and even with these constraints there are some strong correlations between the parameters (valence angles) that depend on these distances. The correlation matrix is given in Table 5.

In the outer region of the radial distribution curve there are the C $\cdots$ F, P $\cdots$ H, and F $\cdots$ H distances, which depend on the two torsional parameters, but the only distinct feature is a broad peak, centred at *ca.* 400 pm. A series of refinements was carried out with the PF_2 twist angle set at values in the range 0–180°. Three minima were found in the plot of *R* factor against angle, at angles of 15, 180, and 105°. Each of these was then investigated further, and the optimum value for the CH_3 twist angle was found in each case with another series of refinements. This angle was close to 60° (fully staggered) for two of the refinements, but close to 20° for the third. Finally, in each case, all the geometrical parameters, and as many amplitudes of vibration as possible, were refined simultaneously, to give the results listed in Table 4 as refinements A, B, and C, for PF_2 twist angles of 19(3), 171(5), and 106(9)° respectively. The final *R* factors (R_G) for these refinements were 0.0853, 0.0847, and 0.0823 respectively.

That there should be three, almost equally good, solutions with such disparate conformations is at first surprising. However, in refinement A, both C $\cdots$ F distances lie close to 400 pm; in refinement C, one of them does, and the other is hidden under the large peak near 300 pm, while P $\cdots$ H and F $\cdots$ H peaks make up the intensity near 400 pm; in refinement B, both C $\cdots$ F peaks lie near 300 pm, but there are four F $\cdots$ H and P $\cdots$ H contributions to the peak at 400 pm. The differences are therefore less than would be supposed, considering heavy atoms only, and indeed the difference intensity curves or radial distribution curves are almost indistinguishable by eye. The observed and final difference

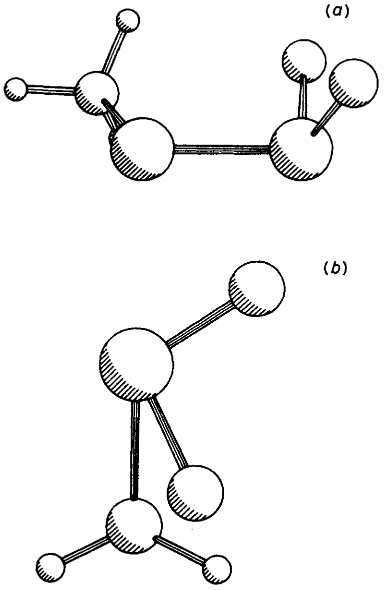

Figure 3. Perspective views of $PF_2(SMe)$ (refinement C) (*a*) perpendicular to the P–S bond, and (*b*) along the P–S bond

Table 3. Portion of least-squares correlation matrix for $Se(PF_2)_2$, showing all elements ≥40%

Angles							
1	2	3	u_1	u_2	u_4	k_2	
42	−51						r_2
	−72	−66					Angle 1
48	−48		71	41	42	46	k_1

Table 4. Molecular parameters [a] for $PF_2(SMe)$

	Refinement A		Refinement B		Refinement C	
	Distance (pm)	Amplitude (pm)	Distance (pm)	Amplitude (pm)	Distance (pm)	Amplitude (pm)
(*a*) Independent distances						
r_1(C–H)	110.6(14)	9.5(17)	111.0(14)	9.2(18)	111.0(14)	9.2(17)
r_2(C–S)	182.4(5)	4.8(6)	181.8(6)	5.5(7)	182.2(5)	5.1(6)
r_3(P–F)	159.0(3)	3.9(3)	158.8(3)	3.5(4)	158.9(3)	3.8(4)
r_4(P–S)	208.4(3)	4.9(3)	208.6(3)	4.7(4)	208.5(3)	4.7(3)
(*b*) Dependent distances						
d_5(H $\cdots$ H)	178.4(33)	12.0 [b]	177.2(36)	12.0 [b]	181.3(33)	12.0 [b]
d_6(S $\cdots$ H)	245.3(22)	9.7(15)	247.0(18)	8.2(16)	242.9(29)	10.1(12)
d_7(F $\cdots$ F)	235.2(8)	6.1 [c]	235.1(6)	5.1 [c]	235.4(9)	6.3 [c]
d_8(P $\cdots$ C)	303.9(13)	8.4(15)	302.9(12)	9.6(6)	304.2(21)	9.4(5)
d_9(S $\cdots$ F)	285.6(5)	7.9(5)	285.1(6)	8.0 [d]	285.7(7)	7.9 [d]
d_{10}(C $\cdots$ F)	425.6(17)	17.5(71)	321.5(47)	15.6(73)	404.4(49)	26.1(55)
d_{11}(C $\cdots$ F)	391.8(30)		297.2(37)		287.7(25)	
d_{12-14}(P $\cdots$ H)	314/324/406	15.0 [b]	291/359/396	15.0 [b]	316/317/405	15.0 [b]
d_{15-20}(F $\cdots$ H)	372/436/443	20.0 [b]	262/266/312	20.0 [b]	251/293/391	20.0 [b]
	460/482/516		390/403/405		397/447/495	
(*c*) Independent angles (°)						
Angle 1 (P–S–C)	101.9(7)		101.6(6)		102.0(12)	
Angle 2 (S–C–H)	111.4(22)		112.8(22)		109.4(29)	
Angle 3 (CH_3 twist)	54.8(160)		22.3(86)		60.5(150)	
Angle 4 (S–P–F)	101.2(2)		100.9(2)		101.2(3)	
Angle 5 (F–P–F)	95.4(5)		95.5(4)		95.6(6)	
Angle 6 (PF_2 twist)	19.2(30)		170.7(48)		105.7(88)	

[a] Errors quoted in parentheses are estimated standard deviations obtained in the least-squares analyses, increased to allow for systematic errors. [b] Fixed. [c] Tied to u_6. [d] Tied to u_8.

Table 5. Portion of least-squares correlation matrix for $PF_2(SMe)$ (refinement C), showing all elements $\geqslant 40\%$

		Angle											
r_1	r_2	2	3	4	5	6	u_2	u_3	u_4	u_6	u_8	k_1	
	42						−47	47				48	r_3
		−50	74	80		86							Angle 1
			−63		−66					−63			2
				73		60							3
						77							4
										66			5
	54						−63		68		43	90	u_3
							−58				40	77	u_4
42	48						−64	−64			48		k_1
40	45						−48	64	52			64	k_2

intensity curves for refinement C are given in Figure 1(*c*), and the radial distribution curves for refinement C are shown in Figure 2(*c*).

Discussion

The parameters associated with the PF_2S groups in $S(PF_2)_2$, $PF_2(SMe)$, and $PF_2(SGeH_3)$ are compared in Table 6. Most striking is the great variation in P–S distances, from 208.5(3) pm in $PF_2(SMe)$, to 213.2(4) pm in $S(PF_2)_2$. The expected distance, calculated from covalent radii derived from bond lengths in C_2H_6,[24] PF_2Me[25] and SMe_2,[26] is 208.9 pm, or 210 pm using the Schomaker–Stevenson rule,[27] so it would appear that this bond is exceptionally long in $S(PF_2)_2$. Similar calculations for P–Se bonds, using data for $SeMe_2$,[28] give expected lengths of 222.9 or 224 pm, compared with the observed length of 227.3(5) pm, and support the idea that the bonds in $S(PF_2)_2$ and $Se(PF_2)_2$ are exceptionally long. It should be noted that the Ge–S bond in $PF_2(SGeH_3)$ [29] is *ca.* 5 pm longer than in $S(GeH_3)_2$,[5] and that the S–C bond in $PF_2(SMe)$ is 2 pm longer than in SMe_2.[26] Thus it seems that the effect of the difluorophosphino group is primarily to *lengthen* the *further* bond to sulphur or selenium. In contrast to this, it has been observed that in trifluorosilylphosphine [30] the *nearer, i.e.* Si–P, bond is *ca.* 4 pm *shorter* than in other silylphosphines,[31] the difference being ascribed to the inductive effect of the SiF_3 group.

In these compounds there are substantial variations in the valence angles at sulphur, which range from 91.3(11)° in $S(PF_2)_2$, to 102.0(12)° in $PF_2(SMe)$, the widest angles being associated with the shortest P–S bonds. In $P(SMe)_3$[32] the PSC angle was reported to be 115.3(7)°, but in other refinements this angle was in the range 98—103°, and these seem to be much more reasonable. Otherwise the parameters are in good agreement with those reported for related compounds, and call for no particular comment.

The conformations adopted by these molecules are interesting. In the case of $PF_2(SMe)$, it is not possible to be absolutely certain which of the three conformers described in Table 4 is present, or whether a mixture may exist. However, we prefer refinement C, as this not only gave the lowest *R* factor, but also gave the most reasonable values for other refining parameters, particularly those relating to the positions of the hydrogen atoms. These determined positions would be expected to be sensitive to imperfections in the molecular model. In refinement C, the PF_2 group is twisted 106° from the position in which the FPF angle bisector is *anti* to the S–C bond, with the result that the methyl group lies close to one fluorine atom. The shortest F · · · H distance is calculated to be 251 pm, slightly less than the sum of the van der Waals radii for fluorine and hydrogen. In $PF_2(SGeH_3)$ [24] the corresponding twist angle is 162°, but the Ge–S bond is much longer than the S–C bond in $PF_2(SMe)$, so that again the shortest F · · · H distance (271 pm) is comparable to the sum of van der Waals radii. As with $PF_2(OMe)$ [33] and other fluorophosphine derivatives,[21,34] the favoured conformation is one in which there are weak interactions between fluorine and hydrogen atoms.

Table 6. Bond lengths (pm) and angles (°) in some difluoro(thio)phosphines

	$S(PF_2)_2$	$PF_2(SMe)$	$PF_2(SGeH_3)$ *
r(P–F)	157.2(2)	158.9(3)	159.0(9)
r(P–S)	213.2(4)	208.5(3)	211.5(8)
Angle FPF	97.4(5)	95.6(6)	97.0(10)
Angle SPF	100.2(4)	101.2(3)	99.9(4)
Angle PSX	91.3(11)	102.0(12)	99.0(6)

* Ref. 29.

In $S(PF_2)_2$ and $Se(PF_2)_2$, there can be no such interactions, and as with $N(PF_2)_3$,[35] the average structure has a high degree of symmetry, but there are large amplitude torsional vibrations. Thus the predictions based on the large PP coupling constants [10] are borne out. In the average structure, the axes of the phosphorus lone pairs of electrons lie in the P(S/Se)P plane, and because the angle at the central atom is small, the lone pairs are to some extent directed towards each other, whereas in $O(PF_2)_2$, with a wide central angle, they are directed away from each other. The interaction between the lone pair and the neighbouring phosphorus atom is believed to be responsible for the large PP coupling constant, and the increasing amplitude of torsional vibration with increasing temperature leads to a reduced interaction and a concomitant decrease in the coupling constant. Using the observed r.m.s. torsion angles, and assuming that the vibrations are purely harmonic, we have calculated the frequencies of the torsion vibrations to be 25(3) cm^{-1} for $S(PF_2)_2$, and 27(5) cm^{-1} for $Se(PF_2)_2$, which can be compared with frequencies of 30 cm^{-1} for $N(PF_2)_3$[35] and 55 cm^{-1} for $NMe(PF_2)_2$.[35,36] We have collected data for the sulphur and selenium compounds with a nozzle temperature of 368 K, but the structures obtained were insignificantly different from those determined at the lower temperature, and the data were of much poorer quality. The expected increase in r.m.s. torsion angles is only 2—3°.

Acknowledgements

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