Gas-phase Molecular Structures of Bis(difluorothiophosphoryl)methane, $CH_2(PF_2S)_2$, and Bis(difluorothiophosphoryl) Ether, $O(PF_2S)_2$, determined by Electron Diffraction

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The molecular structures of the compounds bis(difluorothiophosphoryl)methane, $CH_2(PF_2S)_2$, and bis(difluorothiophosphoryl) ether, $O(PF_2S)_2$, have been determined by electron diffraction. The methane derivative has two conformers, *gauche-gauche* and *anti-gauche*, present in approximately equal amounts. Other important parameters (r_a) are r(P–C) 180.7(7), r(P=S) 187.9(3), r(P–F) 154.8(2) pm; FPF 101.8(7), FPC 103.2(4), SPC 115.0(10), and PCP 122.6(10)°. For the ether, all PF_2S groups have *gauche* conformations, but it was not possible to distinguish overall C_2 and C_s structures. For the best refinements, important parameters are r(P–O) 161.0(8), r(P=S) 186.5(5), r(P–F) 152.6(3) pm; FPF 101.9(47), FPO 100.2(24), SPO 116.5(33), and POP 130.9(35)°.

Recent structural studies of molecules containing two difluorophosphino-groups have shown that the most usual conformation adopted is one in which the bisectors of the FPF angles lie *trans* to the P–X bond of the other P atom. Thus, for example, the $-N(PF_2)_2$ parts of the molecules $N(PF_2)_2R$, where R is methyl,[1] silyl,[2] or germyl,[3] have C_{2v} symmetry. The ideal arrangement may not be possible if the molecule is crowded, as is found for $N(PF_2)_3$, which has overall C_{3h} symmetry.[4] The molecules $S(PF_2)_2$ and $Se(PF_2)_2$ also adopt C_{2v} conformations,[5] but $O(PF_2)_2$, which is certainly not crowded, has much more complicated conformational properties, and the best fit to the electron diffraction data was obtained using a mixture of four conformations.[6]

Relatively little is known about the conformations adopted by analogous phosphorus compounds with substituents other than fluorine. A study of bis(dimethylphosphino)methane[7] showed that it adopted a *gauche-gauche* structure with C_2 symmetry, and also that there was a wide PCP angle at the central carbon atom. We report here the structures of two molecules, each containing two difluorothiophosphoryl groups. In one structure, a wide PCP angle is again found; in both, the effect of the sulphur atoms is to force the adoption of predominantly *gauche* conformations for the PF_2S groups.

Experimental

A sample of $CH_2(PF_2S)_2$ was prepared by fluorination of $CH_2(PCl_2S)_2$[8] with antimony trifluoride, and $O(PF_2S)_2$ was prepared by the reaction of PF_2S_2H with $NMe_2(PF_2O)$.[9] Both samples were purified by fractional condensation *in vacuo*, and purities were checked spectroscopically.

Electron diffraction data were recorded photographically on Kodak Electron Image plates using a Balzers' KD.G2 apparatus.[10] Data were obtained in digital form using an automatic Joyce-Loebel microdensitometer. During diffraction experiments the samples were maintained at 228 K [for $O(PF_2S)_2$] or 320 K [for $CH_2(PF_2S)_2$] with nozzle temperatures of 295 K and 345 K respectively. Calculations were done on ICL 2970 and 2980 computers using data reduction[11] and least-squares refinement[12] programs. Weighting points, used in setting up the off-diagonal weight matrices, are given in Table 1, together with scale factors and correlation parameters. The electron wavelengths, also given in Table 1, were determined from the diffraction pattern of gaseous benzene. In all refinements, the scattering factors of Schäfer *et al.*[13] were used.

Refinement of $CH_2(PF_2S)_2$ *Structure.*—For the purpose of least-square refinements it was assumed that the two $C(PF_2S)$ units were identical, each having C_s symmetry, and that the P_2CH_2 group had local C_{2v} symmetry. With these assumptions the geometry was described by 11 parameters, chosen to be the P–C, P=S, P–F, and C–H bond distances, the FPF, FPC, PCP, SPC, and HCH valence angles, and the twist angles describing the orientations of the PF_2S groups. These last angles were defined to be zero when a P=S bond eclipsed a C–P bond, and their relative directions were chosen so that equal twist angles implied overall C_2 symmetry for the molecule. At later stages the option of including variable amounts of up to four conformers was added; the conformers were assumed to differ only in their twist angles.

On examination of the radial distribution curve (Figure 1) it was clear that the P–C and P=S peaks overlapped, at *ca.* 185 pm, and that the five major two-bond distances lay in the

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}							
$CH_2(PF_2S)_2$	250	4	72	84	280	288	0.326	0.556(8)	5.672
	500	2	34	40	146	152	0.429	0.692(9)	5.672
	1 000	1	18	20	70	72	0.444	0.536(9)	5.672
$O(PF_2S)_2$	190	4	80	88	288	300	0.280	0.441(16)	5.674
	580	2	24	28	128	134	0.496	0.730(20)	5.674

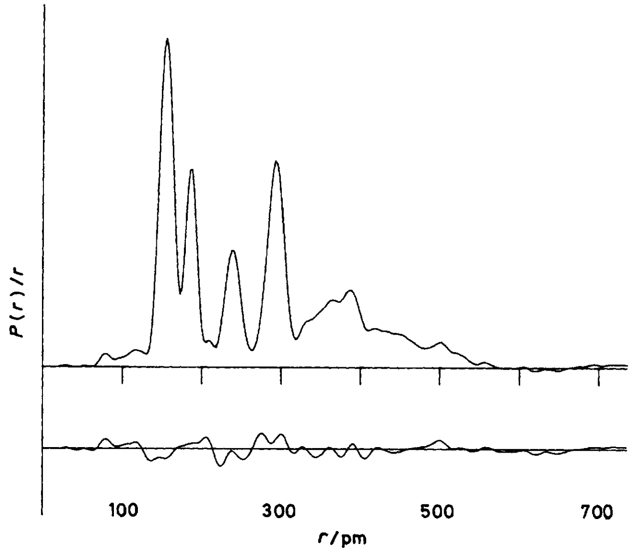

Figure 1. Observed and difference radial distribution curves, $P(r)/r$, for $CH_2(PF_2S)_2$. Before Fourier inversion the data were multiplied by $s \,.\, \exp[-0.000\,015\, s^2/(Z_P - f_P)(Z_F - f_F)]$

series of peaks and shoulders between 230 and 320 pm. In these circumstances it was not possible to refine all the important geometrical and vibrational parameters, and a number of constraints had to be applied. The parameters associated with hydrogen atom positions were fixed at reasonable values, and various groups of amplitudes were refined as single values. In particular, all amplitudes of vibration associated with pairs of atoms separated by three bonds were constrained to be equal, as were those for atoms separated by four bonds.

Table 2. Molecular parameters for $CH_2(PF_2S)_2$

	Distance/pm		Amplitude/pm
(*a*) Independent distances			
r_1(P–C)	180.7(7)		5.0 [a]
r_2(P=S)	187.9(3)		3.3(6)
r_3(P–F)	154.8(2)		3.5(4)
r_4(C–H)	105.4(33)		7.5 [a]
(*b*) Dependent distances [b]			
d_5(P · · · P)	317.0(18)		9.2(16)
d_6(C · · · F)	263.4(10)		8.5(11)
d_7(F · · · F)	240.3(12)		
d_8(C · · · S)	311.0(16)		7.5(4)
d_9(F · · · S)	290.9(4)		
	Conformer (I) [c]	Conformer (II) [c]	
d_{10}(P · · · F)	354.9(28)	354.9(28)	30.0(78)
d_{11}(P · · · F)		345.5(54)	
d_{12}(P · · · F)	435.4(16)	435.4(16)	
d_{13}(P · · · F)		336.9(37)	
d_{14}(P · · · S)	392.9(21)	392.9(21)	
d_{15}(P · · · S)		481.3(11)	
d_{16}(F · · · F)	486.6(20)	409.7(93)	14.7(11)
d_{17}(F · · · F)	523.9(22)	481.5(32)	
d_{18}(F · · · F)	424.7(51)	305.4(40)	
d_{19}(F · · · F)	466.6(20)	467.5(28)	
d_{20}(S · · · F)	518.9(18)	339.7(45)	
d_{21}(S · · · F)		419.6(87)	
d_{22}(S · · · F)	351.4(24)	519.0(32)	
d_{23}(S · · · F)		571.0(21)	
d_{24}(S · · · S)	478.0(50)	568.5(33)	
(*c*) Independent angles/°			
Angle 1 (F–P–F)	101.8(7)		
Angle 2 (F–P–C)	103.2(4)		
Angle 3 (P–C–P)	122.6(10)		
Angle 4 (S–P–C)	115.0(10)		
Angle 5 (H–C–H)	106.0 [a]		
Angle 6 (PF_2S twist) [d]	60.3(12)		
Angle 7 (FP_2S twist) [e]	184.6(40)		

[a] Fixed. [b] Non-bonded distances involving hydrogen were included, but are not listed here. [c] Percentage of both conformers (I) and (II) was 50% (see text). [d] Twist angle for both groups of conformer (I) and for one group of conformer (II). [e] Twist angle for one group of conformer (II) only.

Table 3. Portion of least-squares correlation matrix for $CH_2(PF_2S)_2$, showing all elements greater than 40%

		Angle								
r_2	1	3	4	6	7	u_2	u_3	u_5	k_1	
−51						58				r_1
	−54									r_4
		44	−60					−44		Angle 1
			−55					−44		Angle 2
			−46	−40						Angle 3
					−66					Angle 6
							68		73	u_2
									83	u_3

A preliminary study of the conformations adopted indicated that groups with twist angles of *ca.* 60 (*gauche*) and 180° (*anti*) could be present. Thus four conformers had to be considered: *anti-anti* (C_{2v} symmetry), *anti-gauche* (C_1), and *gauche-gauche* (C_s and C_2). After comparing the R factors obtained for refinements with a wide range of compositions, it was concluded that there was no evidence for the existence of the forms with C_{2v} or C_s symmetry. Considering then only the two remaining forms, the lowest R factor ($R_G = 0.110$) was obtained for a mixture containing 53% *gauche-anti* and 47% *gauche-gauche*: for the final refinements a 50 : 50 mixture was assumed, giving the parameters listed in Table 2, and the correlation matrix presented in Table 3. The intensity data are shown in Figure 2.

Refinement of $O(PF_2S)_2$ *Structure.*—For least-squares refinements it was assumed that the two $O(PF_2S)$ groups were identical, and that they had local C_s symmetry. The geometrical parameters chosen to describe the structure were the same as those used (with due alteration of details) for $CH_2(PF_2S)_2$, with those relating to the CH_2 group omitted.

The radial distribution curve (Figure 3) shows the P–F and P–O distances at 155 pm, the two-bond F · · · F and O · · · F distances with a single peak at 240 pm, and F · · · S, O · · · S,

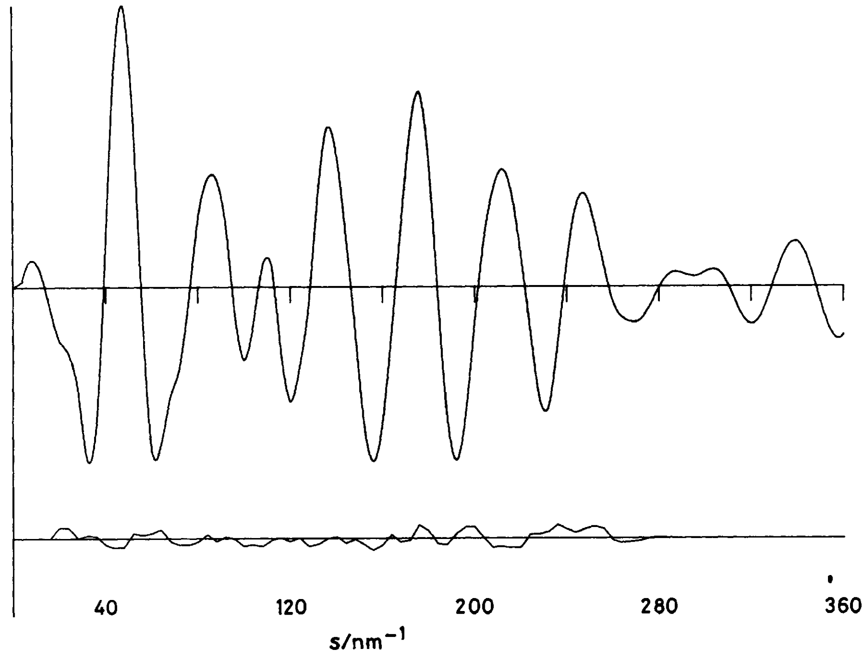

Figure 2. Observed and final weighted difference combined molecular-scattering intensity curves for $CH_2(PF_2S)_2$

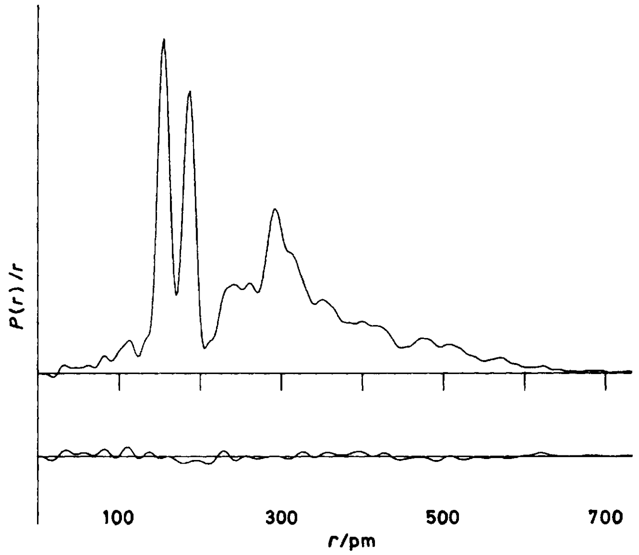

Figure 3. Observed and difference radial distribution curves, $P(r)/r$, for $O(PF_2S)_2$. Before Fourier inversion the data were multiplied by $s \, . \, \exp[-0.000\,015\, s^2/(Z_P - f_P)(Z_F - f_F)]$

and P ··· P peaks all overlapping at 290 pm. Thus in this case it was necessary to fix several amplitudes of vibration, and to refine others in groups. The amplitudes given in Table 4 for the large groups of distances between atoms separated by three or four bonds were obtained in early refinements but not included in the final cycles.

Even with these several constraints there were strong correlations between refining parameters, and the estimated standard deviations are correspondingly high. Nevertheless, all the geometrical parameters were included in the final stages of the refinements.

Careful study of the conformations adopted by the molecule indicated that the P=S bonds were *gauche* with respect to the P–O bonds (*i.e.* the twist angles were *ca.* 60 or −60°) and there was no evidence for any other conformation. Thus there could be two conformers present, one with C_2 symmetry and one with C_s symmetry. Results for both forms are given in Table 4. Refinement B (C_s) gave an R factor (R_G) of 0.141 compared with 0.143 for refinement A (C_2) but the difference is not large enough to be significant. The fit to the experimental data was not significantly improved by having a mixture of the two forms.

The least-squares correlation matrix for refinement B is given in Table 5, and the molecular scattering intensity and difference curves are shown in Figure 4.

Discussion

In Table 6 the parameters relating to the PF_2S groups of the compounds studied are compared with those for PF_3S [14] and other related compounds.[15] There is a noticeable correlation between P–F or P=S distances and the electronegativity of the fourth substituent at phosphorus, and so both these distances are at the short end of the observed range for the ether, and near to the long end for the methane derivative. The SPF angles, and other angles at phosphorus, are much as would be expected, but the FPF angles for both compounds are fairly large.

The P–C distance in $CH_2(PF_2S)_2$ [180.7(7) pm] is similar to those in other four-co-ordinate phosphorus compounds. The slight shortening compared with PMe_3S [16] [181.8(2) pm] again probably arises from the electronegative nature of the fluorine substituents. The P–O distance in $O(PF_2S)_2$ [161.0(8) pm] is shorter than in $O(PF_2)_2$[6] [163.1(10) pm], a change that is typically found when the co-ordination number of phosphorus increases from three to four. The distance lies between those reported for $PCl_2(OMe)S$ [17] and $PCl(OMe)_2S$,[18] of 162.8(6) and 158.0(5) pm respectively.

The POP angle found for $O(PF_2S)_2$ (134 and 131° in refinements A and B) is fairly similar to that reported for $O(PF_2)_2$,[6] and is associated with a non-bonded P ··· P distance of 296 or 293 pm respectively, very similar to those in many

Table 4. Molecular parameters for $O(PF_2S)_2$

	Refinement $A(C_2)$		Refinement $B(C_s)$	
	Distance/pm	Amplitude/pm	Distance/pm	Amplitude/pm
(*a*) Independent distances				
r_1(P–O)	160.9(8)	4.2 *	161.0(8)	4.2 *
r_2(P=S)	186.5(4)	4.1(6)	186.5(5)	4.0(6)
r_3(P–F)	152.6(3)	4.9 *	152.6(3)	4.9 *
(*b*) Dependent distances				
d_4(O ··· F)	238.6(20)	8.9(9)	240.6(43)	8.6(15)
d_5(F ··· F)	239.6(42)		237.1(76)	
d_6(P ··· P)	296.1(32)	10.0 *	293.0(34)	10.0 *
d_7(O ··· S)	297.7(36)	6.2(12)	295.9(59)	6.7(14)
d_8(F ··· S)	290.0(9)		290.5(19)	
d_9(P ··· F)	298.6(20)	13.7 *	335.1(31)	15.6 *
d_{10}(P ··· F)	343.0(27)	13.7 *	400.0(34)	15.6 *
d_{11}(P ··· S)	379.7(20)	13.7 *	377.0(18)	15.6 *
d_{12}(F ··· F)	442.8(48)	21.0 *	303.8(64)	19.3 *
d_{13}(F ··· F)	435.2(40)	21.0 *	444.9(34)	19.3 *
d_{14}(F ··· F)	458.7(78)	21.0 *	444.9(34)	19.3 *
d_{15}(F ··· F)	442.8(48)	21.0 *	466.6(112)	19.3 *
d_{16}(S ··· F)	359.4(43)	21.0 *	442.4(36)	19.3 *
d_{17}(S ··· F)	509.3(25)	21.0 *	505.3(51)	19.3 *
d_{18}(S ··· S)	443.2(51)	21.0 *	336.4(37)	19.3 *
(*c*) Independent angles/°				
Angle 1 (F–P–F)	103.4(26)		101.9(47)	
Angle 2 (F–P–O)	99.1(10)		100.2(24)	
Angle 3 (P–O–P)	133.9(33)		130.9(35)	
Angle 4 (S–P–O)	117.8(20)		116.5(33)	
Angle 5 (PF_2S twist)	47.9(15)		55.7(66)	

* Fixed.

Table 5. Portion of least-squares correlation matrix for $O(PF_2S)_2$ (refinement B), showing all elements greater than 40%

	Angle							
r_3	2	3	4	5	u_4	u_7	k_1	
−44		−55	47				66	r_1
		−40						r_2
							−43	r_3
	−96			−71	82			1 Angle
				81	−83	40		2 Angle
			−79			68		3 Angle
				−79		−91		4 Angle
					−68	76		5 Angle

Table 6. Bond lengths and angles in some derivatives of fluorophosphine sulphide

	Distances/pm		Angles/°		
Compound	r(P=S)	r(P–F)	SPF	FPF	Ref.
PF_3S	186.5(5)	153.6(3)	118.1(8)	99.6(3)	14
PF_2HS	187.6(3)	155.1(3)	115.9(2)	98.3(4)	15
$PBrF_2S$	188.1(4)	154.3(3)	118.2(10)	98.3(10)	15
$PClF_2S$	186.4(8)	153.5(2)	116.2(9)	100.5(8)	15
$CH_2(PF_2S)_2$	187.9(3)	154.8(2)	115.8(4)	101.8(7)	
$O(PF_2S)_2$	186.5(5)	152.6(3)	117.2(8)	101.9(47)	

compounds with two adjacent PF_2 groups, such as $N(PF_2)_3$ [4] and $NH(PF_2)_2$.[19] It is therefore very surprising to find the PCP angle in $CH_2(PF_2S)_2$ to be 122.6(10)°, with the P ··· P distance as large as 317 pm. We have therefore checked very carefully to ensure that the refinements have not reached a false minimum, but any attempt to reduce this angle results in greatly increased *R* factors. It should be noted that the other distances around 300 pm (291 pm for F ··· S and 311 pm for C ··· S) are entirely resonable. The wide angle is probably caused by long-range F ··· S and F ··· F interactions; although none is less than the sum of the appropriate van der Waals radii, they would certainly become so if the PCP angle was significantly reduced. There is precedent for a wide PCP angle associated with a long P ··· P distance; in $CH_2(PMe_2)_2$ [7] the P ··· P distance is 313 pm.

For both $CH_2(PF_2S)_2$ and $O(PF_2S)_2$ the only conformers found have the PF_2S groups in staggered positions relative to the C–P or O–P bond of the other P atom. The staggered arrangement, which is to be expected, given the sizes of the atoms involved, can then give four conformers, with C_2, C_s, C_{2v}, and C_1 symmetry, and multiplicities of 2, 2, 1, and 4. For $CH_2(PF_2S)_2$, the C_2 and C_1 conformers are found (53 and 47% respectively) and this suggests that the C_2 form is the more stable by 1.7 kJ mol^{-1}. It is therefore not surprising that the C_{2v} form is not observed, as it would involve both groups being in the less stable *anti* configuration. The C_s form is

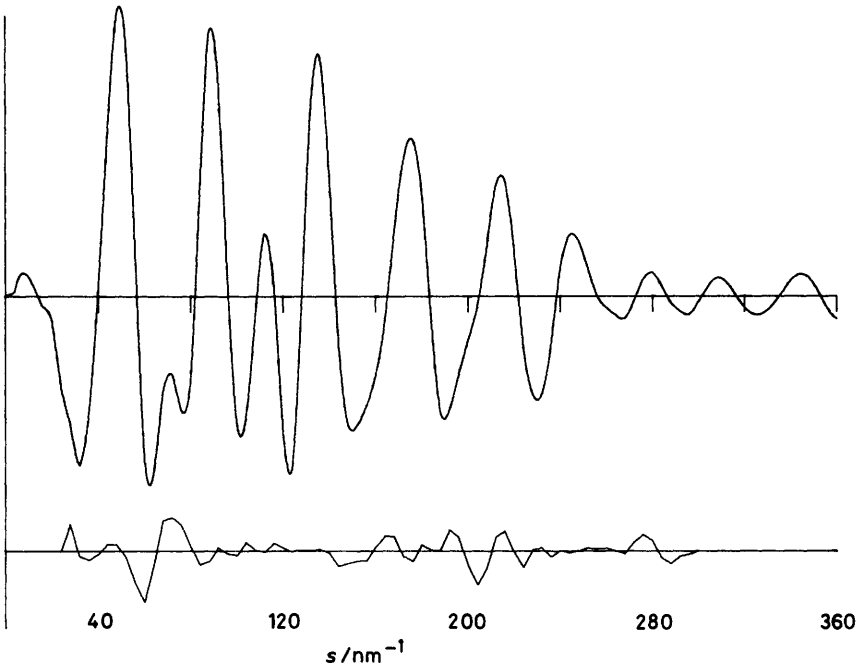

Figure 4. Observed and final weighted difference combined molecular-scattering intensity curves for $O(PF_2S)_2$

probably less favoured than the C_2 form as it will have substantial dipole–dipole interactions.

In the case of the ether, no conformer containing a PF_2S group in an *anti* configuration is found: such a species would have a P · · · F distance of *ca.* 320 pm, slightly less than the sum of van der Waals radii for phosphorus and fluorine. The two all-*gauche* forms unfortunately cannot be distinguished. Of the two, the C_s form gives a marginally better fit to the experimental data.

Acknowledgements

We thank Professor D. W. J. Cruickshank and Dr. B. Beagley of the University of Manchester Institute of Science and Technology for the provision of experimental facilities and the S.R.C. for a research studentship (to M. R. T.).

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Received 30*th March* 1982; *Paper* 2/548