Gas-phase Molecular Structure of Difluoro(isoselenocyanato)phosphine determined by Electron Diffraction

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The molecular geometry of $PF_2(NCSe)$ has been investigated in the gas phase by electron diffraction. Mean amplitudes of vibration and perpendicular amplitude-correction coefficients have been derived from previously published spectroscopic data, and used to determine the average (r_α) structure. The principal parameters (r_α) for $PF_2(NCSe)$ are: r(P–F) 153.0(4), r(P–N) 164.9(12), r(N=C) 121.2(8), and r(C=Se) 168.1(10) pm; angle P–N–C 149.0(15), F–P–N 98.8(8), and F–P–F 97.9(14)°. The overall symmetry is C_s with the pseudohalide group lying *trans* to the F–P–F angle bisector.

ELECTRON-DIFFRACTION structure determinations have previously been carried out on $PF_2(NCO)$ and $PF_2(NCS)$.[1] These molecules show short P–N bonds and wide angles at nitrogen characteristic of aminodifluorophosphines.[2] These features have been explained in terms of some π bonding between the lone pair of electrons on nitrogen and vacant *d* orbitals on phosphorus. It is therefore of interest to see whether the structure of $PF_2(NCSe)$ follows the pattern set by the two difluorophosphine pseudohalides.

In the cases of $PF_2(NCO)$ and $PF_2(NCS)$, complications arose because both molecules exhibit a significant shrinkage effect in the electron-diffraction (r_a) structure determination due to low-frequency bending modes. Spectroscopic data were used in these cases to calculate perpendicular amplitude coefficients and linear shrinkage corrections which yielded average (r_α) structures when applied to the refined electron-diffraction (r_a) structure. The i.r. spectrum of $PF_2(NCSe)$ [3] similarly exhibits a low-frequency bending mode, at 55 cm^{-1}, and in this case the necessary corrections from spectroscopic data were applied to the refining structure, as the computer programs used offer the facility to refine either r_a or r_α structures. We report here the results of our structural studies of $PF_2(NCSe)$ and comment on the major differences between the r_a and r_α structures refined from the same data.

EXPERIMENTAL

A sample of $PF_2(NCSe)$ was prepared by condensing $PBrF_2$ onto the silver pseudohalide salt,[3] the product being subsequently purified *in vacuo* and the purity checked by i.r. spectroscopy.

Electron-diffraction scattering intensities were recorded photographically using the Cornell/Edinburgh diffraction apparatus.[2,4] With an accelerating potential of 43 kV and nozzle-to-plate distances of 128 and 285 mm, several sets of data were obtained for s in the range 34—268 nm^{-1}. The sample and the nozzle were held at room temperature (293 K). The background pressure was 4×10^{-7} Torr † and during a run this increased to 2×10^{-6} Torr. The ion gauge used for the above measurements was situated in the main chamber but removed somewhat from the nozzle.

Photographic intensities were converted into digital form using a Jarrel–Ash double-beam microphotometer [5] with spinning plates. The electron wavelength was determined from the scattering pattern of gaseous benzene recorded immediately before the sample exposures. The weighting points used in the setting up of the off-diagonal weight matrix employed in the least-squares refinement program, together with correlation parameters and other experimental details, are shown in Table 1.

All calculations were done on the ICL 2970 computer at the Edinburgh Regional Computing Centre using established data-reduction [2] and least-squares refinement [6] programs.

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}				
128	4	60	80	200	268	0.014	0.919(31)
285	2	34	50	110	140	0.366	0.863(22)

† Correlation parameter, see ref. 6.

The scattering factors of Schäfer *et al.*[7] were used throughout.

Calculated Amplitudes of Vibration and K *Values.*—These were obtained using our program GTRIP, based on Schachtschneider's [8] GMAT routines for generating inverse kinetic energy matrices (G) for a molecular system or for each symmetry block. A versatile routine FGRUM calculates eigenvalues and allows an initial trial potential-energy matrix (F) to be modified interactively in one of three ways. (*a*) Specified F elements may be assigned new values. (*b*) Specified F elements may be included in a least-squares refinement based on the differences between observed and calculated frequencies and between observed and calculated isotope shifts; the required derivatives $\partial\nu/\partial F_{ij}$ are not calculated analytically but obtained numerically by altering F_{ij} to $F + \Delta F$ and rediagonalising to obtain eigenvalues $\lambda + \Delta\lambda$. (*c*) The entire F matrix may be altered in such a manner so as to fit the observed frequencies for one isotopic species by the so-called ' direct-fit ' procedure; this has the unfortunate property of leading to a solution with the same L vectors as the initial trial F matrix, so we have modified the procedure by eliminating any off-diagonal elements in the new F matrix below a specified threshold. The modified F matrix is then used as the starting point for a new ' direct-fit ' plus elimination cycle, and the process continues until convergence on the observed frequencies is achieved. It is

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† Throughout this paper: 1 Torr ≈ (101 325/760) Pa; 1 dyn = 10^{-5} N.

usually convenient to begin with a high threshold (1.0 or 0.5 mdyn Å^{-1}) and to reduce it progressively if convergence is slow; in this way most of the changes are forced into the diagonal F elements, and only a limited number of non-zero off-diagonal elements remain in the final F matrix, which now has L vectors that may differ substantially from those of the original trial.

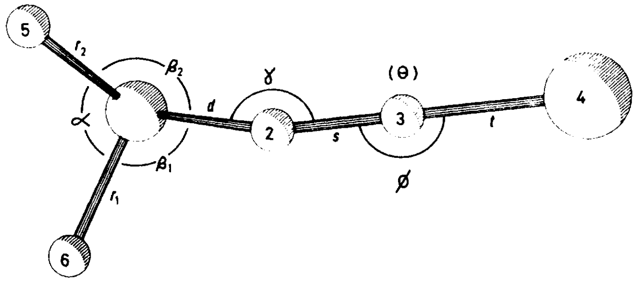

FIGURE 1 The *trans*-$PF_2(NCSe)$ model with linear NCSe chain, symmetry C_s. Valence co-ordinates are indicated; ϕ is a linear bending in the symmetry plane, and θ is perpendicular to it. The twisting co-ordinate, τ, is generated by two torsions as $2^{-\frac{1}{2}}(\tau_{3216} + \tau_{3215})$

The L matrix corresponding to the final F matrix, chosen to reproduce observed frequencies and isotope shifts (where available), is then used to generate the mean-square Cartesian displacements for specified pairs of atoms. These are summed over all symmetry species and finally converted into u and K values by co-ordinate rotations appropriate to the atom pair. The amplitudes are calculated for 0 K and any specified higher temperature. GTRIP also includes facilities for calculation of Coriolis coupling terms and centrifugal distortion constants for symmetric top molecules.

Normal-co-ordinate Analysis.—The published values [3] for the fundamental vibration frequencies of $PF_2(NCSe)$ were used in the normal-co-ordinate analysis. Figure 1 shows the applied molecular model and definition of valence co-ordinates. The normal modes of vibration are distributed into the symmetry species of the C_s symmetry group according to $\Gamma = 8A' + 4A''$. The set of symmetry co-ordinates S_1—S_{12} was constructed. Here R, D, S, and T

TABLE 2

Non-zero symmetry force constants ($\times$ 10^{-2}, N m^{-1}) for $PF_2(NCSe)$

A'	1	5.72							
	2	1.10	13.50						
	3	−0.06		5.32					
	4	0.01			4.22				
	5					0.73			
	6				0.48		0.12		
	7				0.12			0.58	
	8				−0.05				0.18
A''	1	4.58							
	2		0.64						
	3		−0.01	0.23					
	4				0.01				

$S_1(A') = t$

$S_2(A') = s$

$S_3(A') = d$

$S_4(A') = 2^{-\frac{1}{2}}(r_1 + r_2)$

$S_5(A') = R\alpha$

$S_6(A') = (RD/2)^{\frac{1}{2}}(\beta_1 + \beta_2)$

$S_7(A') = (DS)^{\frac{1}{2}}\gamma$

$S_8(A') = (ST)^{\frac{1}{2}}\phi$

$S_9(A'') = 2^{-\frac{1}{2}}(r_1 - r_2)$

$S_{10}(A'') = (RD/2)^{\frac{1}{2}}(\beta_1 - \beta_2)$

$S_{11}(A'') = (ST)^{\frac{1}{2}}\theta$

$S_{12}(A'') = (RS)^{\frac{1}{2}}\tau$

designate the equilibrium distances of $R_{15} = R_{16}$, R_{12}, R_{23}, and R_{34} respectively (see Figure 1 for the atom numbering).

A harmonic force field for $PF_2(NCSe)$ was developed which exactly fitted the observed vibrational frequencies. Table 2 shows the final results in terms of the symmetry F matrix. Table 3 gives the potential-energy distribution terms calculated from the developed force fields,[1] together with approximate descriptions of the normal modes of vibration, although mixing is so pronounced in some cases as to make simple assignments inadequate. Table 4 shows the calculated mean amplitudes of vibration for the normal modes of $PF_2(NCSe)$ at 0 and 298 K, together with calculated K values at 298 K as used in the following r_α structure determination.

Refinement.—Molecular model. The molecule was assumed to have local C_s symmetry for the PF_2N group with the geometry being defined by the P–F, P–N, N=C, and C=Se distances, the angles F–P–F, F–P–N, P–N=C, and N=C=Se, and a torsion angle. The last was defined as zero when the F–P–F angle bisector was *trans* to the N=C bond.

TABLE 3

Frequency assignment, potential-energy distribution, and approximate description of normal modes for $PF_2(NCSe)$

Species	Frequency/ cm^{-1}	Potential-energy distribution *	Approximate description
A'	1 972	$90s$	N=C str.
	920	$23t + 29d + 42r$	C=Se str.
	851	$26t + 72d + 49r$	P–F sym str.
	569	$22t + 41d + 49\beta$	P–N str.
	429	80α	NCSe bend
	396	$21\gamma + 66\phi$	PF_2 bend
	262	$15t + 20d + 49\beta$	PF_2 def.
	77	$74d + 156\gamma + 21\phi$	PNC bend
A''	851	$95r$	P–F asym str.
	490	$39\beta + 52\theta$	NCSe bend
	347	$54\beta + 41\theta$	PF_2 def.
	54	91τ	torsion

* For explanation of symbols see Figure 1 in ref. 1.

Initial refinements of the r_a structure indicated that the N=C=Se angle could lie anywhere between 170 and 180°, and that it was strongly correlated with the P–N=C angle, which lay between 139 and 145°. This showed that there could be a large shrinkage arising from bending at nitrogen and carbon. The predominance of the P $\cdots$ Se peak in the radial-distribution curve (Figure 2) would ensure that this effect was pronounced. Therefore it was decided to concentrate on refinements of the r_α structure. This would also take account of the effects of the torsional vibration on any apparent distortion from C_s symmetry.

Average structure parameters (r_α) are related to those measured in the electron-diffraction experiment (r_a) by the expression (1) where u is the root-mean-square amplitude of vibration and K is the perpendicular amplitude-correction coefficient. Thus, using r_a instead of r_e in the second term, and calculated values for u and K, we have been able to refine the r_α structure directly.

$$r_\alpha = r_a + (u^2/r_e) - K \qquad (1)$$

The final r_α parameters found for $PF_2(NCSe)$, together with r_a values for all distances, are shown in Table 5. The P–N=C angle has widened from the r_a value (144°) to 149°. In the r_α structure the twist angle refined to zero and the symmetry now became exactly C_s with the N=C=Se chain exactly linear, and so only seven parameters were subsequently used to define the molecular geometry.

TABLE 4

Calculated amplitudes of vibration and K values at 0 and 298 K

	u/pm		K/pm	
Distance	0 K	298 K	0 K	298 K
P–F	4.10	4.18	0.37	1.78
P–N	4.59	5.39	0.45	2.31
N=C	3.67	3.69	0.54	1.18
C=Se	3.83	3.98	0.46	2.06
F · · · F	6.03	6.77	0.37	2.36
F · · · N	6.15	7.42	0.61	3.72
F · · · C	7.07	11.98	0.28	1.39
F · · · Se	7.79	17.30	0.02	0.04
P · · · C	5.14	6.80	0.20	0.62
P · · · Se	5.50	10.73	0.03	0.14
N · · · Se	3.91	4.15	0.38	2.35

In the final stages of the refinement, all independent geometrical parameters and amplitudes of vibration, with the exceptions of u(P–N) [= 1.2 u(C–Se)] and u(F · · · F) [= 1.0 u(F · · · N)], were free to refine.

Table 5 shows the final parameter set (r_α) for the PF_2(NCSe); the least-squares correlation matrix is given in Table 6, and the observed and difference molecular scattering curves are shown in Figure 3.

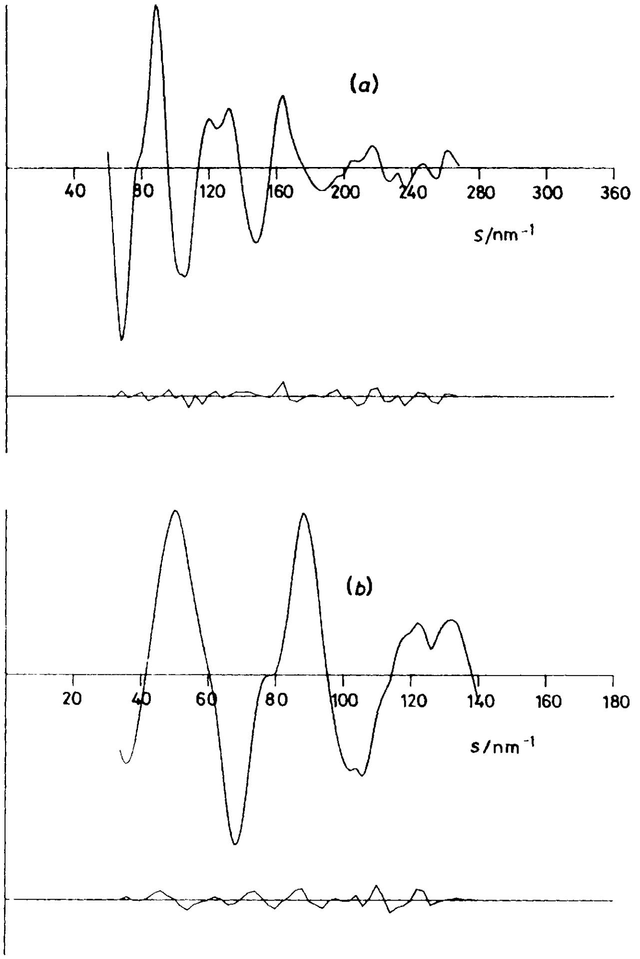

FIGURE 2 Observed and final weighted difference molecular scattering intensities for nozzle-to-plate distances of (a) 128 and (b) 285 mm

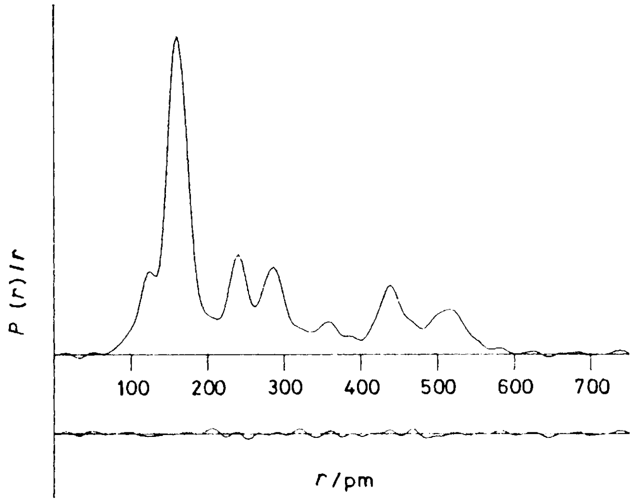

FIGURE 3 Observed and difference radial-distribution curves, $P(r)/r$, for PF_2(NCSe). Before Fourier inversion the data were multiplied by $s\{\exp[(-0.000\,02\ s^2)/(Z_{Se} - f_{Se})(Z_F - f_F)]\}$

DISCUSSION

In most structure determinations carried out on compounds containing the PF_2N group [1,2,9,10] the P–F and P–N distances are so close that refinement of all four parameters associated with these bonded distances is impossible, and u(P–F) and u(P–N) are usually constrained to refine together. In the case of PF_2(NCSe), r(P–F) and r(P–N) are comparatively well resolved, whereas r(C=Se) overlaps with r(P–N) and the two amplitudes associated with these distances were refined as a single parameter. The relation between r(P–N) and r(C=Se) is clearly shown in the least-squares correlation matrix (Table 6). The correlation would have been more severe but for the fact that the sum of r(C=N) and

TABLE 5

Molecular parameters for PF_2(NCSe) *

Independent distances (pm)		Angles (°)	
r_α(P–F)	153.0(4)	F–P–F	97.9(14)
r_α(P–N)	164.9(12)	F–P–N	98.8(8)
r_α(N=C)	121.2(8)	P–N–C	149.0(15)
r_α(C=Se)	168.1(10)		

		u/pm	
		Electron diffraction	Vibrational spectroscopy
(a) Independent distances, r_a/pm			
r(P–F)	154.7(4)	4.7(11)	4.2
r(P–N)	167.0(12)	3.6(17)	5.4
r(C=N)	122.0(8)	5.9(12)	3.7
r(C=Se)	170.0(10)	3.0 (tied to u2)	4.0
(b) Dependent distances (pm)			
d(Se · · · N)	291.3(9)	6.7(17)	4.2
d(Se · · · P)	438.7(8)	12.8(8)	10.7
d(Se . . . F)	513.5(14)	21.4(13)	17.3
d(C · · · P)	276.4(11)	5.5(23)	6.8
d(C · · · F)	353.2(13)	17.3(23)	12.0
d(N · · · F)	245.0(11)	7.2(21)	7.4
d(F · · · F)	233.2(11)	7.2 (tied to u10)	6.8

* Estimated standard deviations derived from the least-squares analysis, increased to allow for systematic errors, are given in parentheses.

TABLE 6

Least-squares correlation matrix, multiplied by 100

				Angle														
r_1	r_2	r_3	r_4	1	2	3	u_1	u_2	u_3	u_5	u_6	u_7	u_8	u_9	u_{10}	k_1	k_2	
100								76										r_1
	100	53	−74		−62	−66												r_2
		100			−58	−67												r_3
			100							−70			−63					r_4
				100											89			1 Angle
					100										−56			2 Angle
						100	58											3 Angle
							100	84								74	65	u_1
								100								63	55	u_2
									100									u_3
										100			79					u_5
											100							u_6
												100						u_7
													100					u_8
														100				u_9
															100			u_{10}
																100	66	k_1
																	100	k_2

Only elements with absolute values greater than 0.5 are included.

TABLE 7

Comparison of geometric parameters of two-co-ordinate nitrogen compounds

	$PF_2(NCO)$ [a]	$PF_2(NCS)$ [a]	$PF_2(NCSe)$	$C(NPF_2)_2$ [b]	$SiH_3(NCSe)$ [c]
r_a(P–N)/pm	168.3(6)	168.6(6)	167.0(12)	168.0(6)	
r_a(P–F)/pm	156.3(3)	156.6(3)	154.7(4)	156.2(2)	
r_a(N=C)/pm	125.6(6)	122.1(6)	122.0(8)	124.0(5)	118.1(8)
r_a(C=Se)/pm			170.0(10)		175.9(7)
Angle MNC(r_α)/°	134.8(8)	144.0(7)	149.0(15)		180.0
Angle MNC(r_a)/°	130.6(8)	140.5(7)	143.9(13) [d]	132.8(5)	158.9(6)

[a] Ref. 1. [b] Ref. 12. [c] A. Fraser, G. S. Laurenson, and D. W. H. Rankin, unpublished work. [d] Linear N=C=Se assumed.

r(C=Se) is well defined by the N · · · Se distance in the linear pseudohalide moiety. Thus r(C=Se) is equal to d(Se · · · N) − r(C=N).

The angle found at nitrogen [149.0(15)°] is the widest yet reported for two-co-ordinate nitrogen bound to phosphorus,[11] but this value is not unexpected when compared to those for $PF_2(NCO)$, $PF_2(NCS)$, and $C(NPF_2)_2$.[12] In fact, all r_α structural parameters and r_a distances yield values consistent with those found for the two comparable pseudohalides. Parameters for $PF_2(NCSe)$, $PF_2(NCS)$, $PF_2(NCO)$, and $C(NPF_2)_2$, together with those for $SiH_3(NCSe)$, are compared in Table 7. Most amplitudes of vibration are found to be within experimental error of those calculated in the normal-co-ordinate analysis, despite the fact that this was undertaken prior to the gas-phase structure investigation and utilised slightly different parameters.

The final R_G and R_D factors [2] were 0.10 and 0.08 respectively. These are somewhat higher than usual for structures of small molecules undertaken at Edinburgh. This can be attributed to the rapid decay with increasing angle in the short-distance intensity data arising from destructive interference caused by the superposition of scattering from many differing interatomic distances of comparable scattering power, a feature illustrated by the form of the radial-distribution curve (Figure 3). However, the R factors compare well with those obtained in the analyses of $PF_2(NCO)$ and $PF_2(NCS)$.

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