The Vibrational Spectra and Molecular Structures of Difluoro(isocyanato)phosphine and Difluoro(isothiocyanato)phosphine in the Gas Phase

By **D. W. H. Rankin,*** Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ
S. J. Cyvin, Institutt for Fysikalsk Kjemi, Norges Tekniske Høgskole, Trondheim, Norway

The i.r. and Raman spectra of difluoro(isocyanato)phosphine, F_2PNCO, and difluoro(isothiocyanato)phosphine, F_2PNCS, have been recorded. Assignments have been made of all the fundamental frequencies, and normal co-ordinate analyses have been carried out. Mean amplitudes of vibration and perpendicular amplitude correction coefficients have been derived from the spectroscopic data. The molecular structures of the two compounds have been determined by the sector-microphotometer method of electron diffraction, and the spectroscopic data have been used to determine average interatomic distances. The principal parameters (r_a) for F_2PNCO are: r(P–F) 1·563 ± 0·003, r(P–N) 1·683 ± 0·006, r(N–C) 1·256 ± 0·006, r(C–O) 1·168 ± 0·005 Å; ∠(P–N–C) 130·6 ± 0·8°. For F_2PNCS the parameters are: r(P–F) 1·566 ± 0·003, r(P–N) 1·686 ± 0·007, r(N–C) 1·221 ± 0·006 Å; ∠(P–N–C) 140·5 ± 0·7°. In each case the pseudohalide group is approximately *trans* to the bisector of the FPF angle, with the molecules possessing overall C_s symmetry.

RECENT electron diffraction studies of several compounds containing difluorophosphinyl groups [1,2] have shown that when the groups are bonded to nitrogen atoms, short phosphorus–nitrogen bonds and wide valence angles at nitrogen result. The effects, normally attributed to π-bonding involving vacant phosphorus *d* orbitals, have also been reported in similar compounds with silyl groups instead of phosphinyl groups.[3-5]

---

[1] G. C. Holywell, D. W. H. Rankin, B. Beagley, and J. M. Freeman, *J. Chem. Soc.* (*A*), 1971, 785.

[2] G. C. Holywell and D. W. H. Rankin, *J. Mol. Structure*, 1971, **9**, 11.

[3] C. Glidewell, D. W. H. Rankin, A. G. Robiette, and G. M. Sheldrick, *J. Mol. Structure*, 1970, **6**, 231.

[4] B. Beagley and A. R. Conrad, *Trans. Faraday Soc.*, 1970, **66**, 2740.

[5] D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, W. S. Sheldrick, B. J. Aylett, I. A. Ellis, and J. J. Monaghan, *J. Chem. Soc.* (*A*), 1969, 1224.

I.r.[6] and microwave studies[7,8] have shown that the SiNCX skeletons of silyl isocyanate and isothiocyanate are linear, contrasting with the methyl pseudohalides, which have CNC angles of 140 and 147° respectively.[9] It is therefore of interest to study the structures of difluorophosphine pseudohalides to discover whether the structural similarities of silyl and phosphinyl derivatives extend to this type of compound also. However, the situation is made more complicated by the fact that these pseudohalides have low-frequency bending vibrations, which make large shrinkage corrections necessary if electron diffraction data are to be accurately interpreted. Determination of these corrections depends on knowledge of the frequencies of the bending vibrations, and these have rarely been directly observed. Consequently a careful study of the vibrational spectra of difluoro(isocyanato)phosphine and difluoro(isothiocyanato)phosphine has been made. We report here the results of that study, and its application to the determination of the structures of the compounds.

EXPERIMENTAL

Samples of difluoro(isocyanato)phosphine and difluoro(isothiocyanato)phosphine were prepared by reaction of bromodifluorophosphine with the appropriate silver salts,[10] and were purified by fractional condensation *in vacuo*. Purities were checked by i.r. spectroscopy.

TABLE 1

Weighting functions, correlation parameters, and scale factors

	Camera height	Δs	$s_{\text{min.}}$	s_1	s_2	$s_{\text{max.}}$	p/h [a]	Scale factor [a]
F_2PNCO	250	0·4	4·8	5·4	24·5	30·0	0·4464	1·154 ± 0·018
	500	0·2	3·0	5·0	12·0	14·4	0·4984	0·759 ± 0·027
	1000	0·1	1·3	2·2	6·0	7·7	0·4999	0·867 ± 0·033
F_2PNCS	250	0·4	5·2	8·0	22·0	28·8	0·4084	1·085 ± 0·020
	500	0·2	3·4	6·0	12·5	15·0	0·4783	1·009 ± 0·085
	1000	0·1	1·3	2·2	6·0	7·2	0·4987	0·735 ± 0·035

[a] Scale factors and correlation parameters refer to refinements (A) in Tables 8 and 9.

I.r. spectra of the compounds in the gas phase were recorded in the range 5000—250 cm^{-1} on a Perkin-Elmer 225 spectrometer, using cells equipped with caesium iodide windows. Raman spectra of liquid samples were recorded in the range 2500—150 cm^{-1} on a Coderg PH1 laser instrument.

Electron diffraction scattering intensities were recorded photographically using Ilford N60 plates on a Balzers' KD.G2 apparatus,[11] and were transferred to paper tape using a Joyce–Loebl automatic microdensitometer. During the exposures the samples of compounds were maintained at 250 K (F_2PNCO) or 273 K (F_2PNCS), and the nozzle was kept at 313 K. The gas temperatures may be taken to be the means of these. Calculations on the vibrations of the molecules assumed gas temperatures of 298 K. Three plates were used for each compound, with nozzle-to-plate distances of 250, 500, and 1000 mm, giving ranges of *ca* 1—30 Å^{-1} in the scattering variable s. Values of the wavelength used (0·057 91 ± 0·000 03 Å) were obtained by direct measurement of the accelerating voltage, and from the diffraction pattern of powdered thallous chloride.

Electron diffraction calculations were carried out on the Edinburgh Regional Computing Centre's IBM 360/50 computer, using data reduction and least-squares refinement programmes described elsewhere.[1,12] Weighting points, correlation parameters, *etc.*, used in setting up the off-diagonal weight matrix are given in Table 1, together with camera heights and scale factors. The complex scattering factors of Cox and Bonham[13] were used in all refinements.

Calculations of force fields, amplitudes of vibration, perpendicular amplitude correction coefficients, and shrinkages were performed by standard methods.[14]

RESULTS AND DISCUSSION

Vibrational Spectra.—The observed i.r. and Raman frequencies for F_2PNCO and F_2PNCS are given in Tables 2 and 3. Assignments of most fundamentals could be made, assuming C_s symmetry, on the basis of Raman polarisation data, and by comparison with other fluorophosphines[15-17] and pseudohalides.[18,19] For each compound, three of the twelve fundamentals were not observed directly. Frequencies of about 180 cm^{-1} for the asymmetric F_2PN deformations satisfactorily accounted for several otherwise unassignable overtone or combination bands: similar modes in tetrafluorodiphosphine[16] and chlorodifluorophosphine[17] have been reported at 214 and 259 cm^{-1}.

Determination of the P–N–C bending frequencies is important, as the interpretation of the electron dif-

---

[6] E. A. V. Ebsworth, R. Mould, R. Taylor, G. R. Wilkinson, and L. A. Woodward, *Trans. Faraday Soc.*, 1962, **58**, 1069.

[7] M. C. L. Gerry, J. C. Thompson, and T. M. Sugden, *Nature*, 1966, **211**, 846.

[8] D. R. Jenkins, R. Kewley, and T. M. Sugden, *Trans. Faraday Soc.*, 1962, **58**, 1284.

[9] R. G. Lett and W. H. Flygare, *J. Chem. Phys.*, 1967, **47**, 4730.

[10] G. G. Flaskerud, K. E. Pullen, and J. M. Shreeve, *Inorg. Chem.*, 1969, **8**, 728.

[11] B. Beagley, A. H. Clark, and T. G. Hewitt, *J. Chem. Soc. (A)*, 1968, 658.

[12] D. M. Bridges, G. C. Holywell, D. W. H. Rankin, and J. M. Freeman, *J. Organometallic. Chem.*, 1971, **32**, 87.

[13] H. L. Cox and R. A. Bonham, *J. Chem. Phys.*, 1967, **47**, 2599.

[14] S. J. Cyvin, 'Molecular Vibrations and Mean Square Amplitudes,' Universitetsforlaget, Oslo, and Elsevier, Amsterdam, 1968.

[15] R. W. Rudolph, J. G. Morse, and R. W. Parry, *Inorg. Chem.*, 1966, **5**, 1464.

[16] R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Amer. Chem. Soc.*, 1966, **88**, 3729.

[17] M. L. Dewaulle and M. F. Francois, *J. Chim. phys.*, 1949, **46**, 87.

[18] F. A. Miller and G. L. Carlson, *Spectrochim. Acta*, 1961, **17**, 977.

[19] J. Goubeau and J. Reyhing, *Z. anorg. Chem.*, 1958, **294**, 96.

fraction results depends on a knowledge of them. In the i.r. spectrum of the isocyanate, there are several bands near to the asymmetric NCO stretching mode at 2283 cm^{-1}, and none of them can be satisfactorily accounted for by any binary combination of known vibrational frequencies. However, if an A' vibration at 105 cm^{-1} is postulated (the frequency being given exactly by the difference band at 2178 cm^{-1}), the whole series may be explained, as well as two bands in other regions of the spectrum. This argument is further supported by the existence of similar bands in the i.r. spectra of other isocyanates.[18,20-22] Explanations of these bands in the literature have frequently been far-fetched, even including in- and out-of-phase vibrations for a molecule with but one isocyanate group.[10] Simple combinations with low frequency bends (or with their overtones, depending on symmetry [22]) would account for them all.

TABLE 2

I.r. and Raman spectra of F_2PNCO

I.r. (gas)	Raman (liquid)	Assignment
3780w		$\nu_1 + \nu_2 + \nu_8$
3750sh 3663mw		$\nu_1 + \nu_2$, $\nu_1 + 2\nu_4$
2988mw		$\nu_1 + \nu_4$
2881w		$\nu_1 + \nu_5$
2720w		$\nu_1 + \nu_6$
2599w		$\nu_1 + \nu_7$
2496vw		$\nu_1 + 2\nu_8$
2392ms		$\nu_1 + \nu_8$
2283vvs	2268w,p	ν_1
2178w		$\nu_1 - \nu_8$
2039vvw 1989vw 1959vw,br		?$\nu_2 + \nu_{10}$?$\nu_2 + \nu_5$
1839vw,br		$\nu_2 + \nu_6$
1707 1689 mw		$2\nu_3$, $2\nu_9$
1511mw		$\nu_2 + \nu_8$
1435ms 1405s	1434s,p	ν_2, $2\nu_4$
1308mw		$\nu_4 + \nu_5$
1221 1205 mw		$2\nu_{10}$, $\nu_5 + \nu_{10}$
1145w		$\nu_4 + \nu_6$
1043w		$\nu_5 + \nu_6$
970w		?$\nu_5 + 2\nu_{11}$
863sh 853vs 845sh	841m,p 827w,dp	ν_3 ν_9
718 714 s 710	706mw,p	ν_4
639 662 ms	*ca.* 620w,dp	ν_{10}
609 599 s	598ms,p	ν_5
498vw		$\nu_7 + \nu_{11}$
453 448 ms	444s,p	ν_6
358mw		$2\nu_{11}$
324mw	326ms,p	ν_7

s = strong, m = medium, w = weak, v = very, br = broad, p = polarised, dp = depolarised, sh = shoulder

Similar arguments may be applied to F_2PNCS, and a bending mode at 81 cm^{-1} may be postulated. However, the situation is complicated in this case by the possibility that the overtone of the C–S stretching mode may be in Fermi resonance with the N–C stretch. The two bands so formed (ν_1 and $2\nu_2$) would give rise to higher combinations in the same way as ν_1 and $\nu_1 + \nu_8$ would, and so the possibilities are not distinguishable. However, a fundamental near 80 cm^{-1} is also suggested by several other combination bands in the spectrum.

TABLE 3

I.r. and Raman spectra of F_2PNCS

I.r. (gas)	Raman (liquid)	Assignment
3941w		$2\nu_1$
3522w		$\nu_1 + \nu_2 + \nu_{10}$
2980w		$\nu_1 + \nu_2$
2660sh		$\nu_1 + \nu_4 + \nu_8$
2601mw		$\nu_1 + \nu_4$
2479vw		$\nu_1 + \nu_6 + \nu_8$
2408w		$\nu_1 + \nu_6$
2350w		$\nu_1 + \nu_7 + \nu_8$
2282w		$\nu_1 + \nu_7$
2208vvw		$\nu_1 + 3\nu_8$
2136mw		$\nu_1 + 2\nu_8$
2059s	2040w,p	$\nu_1 + \nu_8$, $2\nu_2$
1982vvs	1963m,p	ν_1
1901m,sh		$\nu_1 - \nu_8$
1688mw		$2\nu_3$
1560vw		$\nu_2 + \nu_{10}$
1387m		$\nu_3 + \nu_{10}$
1202vw		$\nu_2 + \nu_{11}$
1157 1134 vw		$\nu_7 + \nu_9$, $\nu_4 + \nu_{10}$
1092vw		$\nu_2 + \nu_8$
1028ms	1025m,p	ν_2
863sh 859sh 853vs	843m,p 829w,dp	ν_3 ν_9
701vw		$\nu_4 + \nu_8$
639mw,sh		?$\nu_5 + \nu_{11}$
622vs	614m,p	ν_4
531s	525w,dp	ν_{10}
500w		$\nu_6 + \nu_8$
480 473 ms	477w,p	ν_5
426ms	425s,p	ν_6
361m		$2\nu_{11}$
312mw	303s,p	ν_7

Good agreements of experimental and calculated P · · · C and P · · · O or P · · · S amplitudes of vibration for both isocyanate and isothiocyanate suggest that the bending frequencies used in the calculations are not far wrong.

No evidence about the torsion frequencies could be obtained from the vibrational spectra available. Rough estimates were made by comparison of experimental amplitudes of vibration from the electron diffraction data with those calculated assuming various torsional frequencies.

Normal Co-ordinate Analysis.—(a) *Symmetry co-ordinates.* 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 $\Gamma = 8A' + 4A''$.

---

[20] J. Goubeau and H. Gräbner, *Chem. Ber.*, 1960, **93**, 1379.
[21] J. E. Griffiths, *J. Chem. Phys.*, 1968, **48**, 278.
[22] D. F. Koster, *Spectrochim. Acta*, 1968, **24**, 395.

The following set of symmetry co-ordinates was constructed.

$$\begin{aligned}
S_1(A') &= 2^{-\frac{1}{2}}(r_1 + r_2),\\
S_2(A') &= d,\\
S_3(A') &= s,\\
S_4(A') &= t,\\
S_5(A') &= R\alpha,\\
S_6(A') &= (RD/2)^{\frac{1}{2}}(\beta_1 + \beta_2),\\
S_7(A') &= (DS)^{\frac{1}{2}}\gamma,\\
S_8(A') &= (ST)^{\frac{1}{2}}\phi;\\
S_1(A'') &= 2^{-\frac{1}{2}}(r_1 - r_2),\\
S_2(A'') &= (RD/2)^{\frac{1}{2}}(\beta_1 - \beta_2),\\
S_3(A'') &= (RS)^{\frac{1}{2}}\tau,\\
S_4(A'') &= (ST)^{\frac{1}{2}}\theta.
\end{aligned}$$

Here R, D, S, and T designate the equilibrium distances of $R_{46} = R_{56}$, R_{36}, R_{23}, and R_{12} respectively (*cf.* Figure 1 for the numbering of atoms).

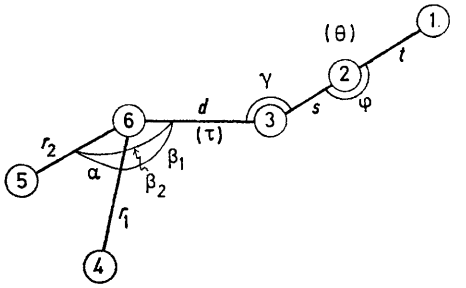

FIGURE 1 The *trans*-F_2PNCX model with linear NCX chain, symmetry C_s. Valence co-ordinates are indicated. ϕ is a linear bending in the symmetry plane, and θ is perpendicular to it. τ Is a twisting co-ordinate generated by two torsions as $2^{-\frac{1}{2}}(\tau_{2364} + \tau_{2365})$

(b) *Force constants.* Harmonic force fields for F_2PNCO and F_2PNCS were developed so as to fit exactly the observed vibrational frequencies. Tables 4 and 5 show the final results in terms of the symmetry F matrices for F_2PNCO and F_2PNCS respectively. As to the unobserved torsional frequency (ν_{12}) two alternatives were worked out: (i) ν_{12} equal to the lowest A' frequency (ν_8), and (ii) $\nu_{12} = 45$ and 50 cm^{-1} for F_2PNCS and F_2PNCO, respectively. The latter frequencies were estimated with the aid of mean amplitudes from the electron diffraction refinements. The two alternatives gave the largest percentage difference in force constants for $F_{33}(A'')$, but other A'' force constants were also affected. Tables 4 and 5 list the A'' blocks from the alternative (ii) only.

(c) *Potential energy distribution.* Tables 6 and 7 show the potential energy distribution terms as calculated from the developed force fields. In general these terms are fairly well consistent with the approximate descriptions of normal modes deduced from magnitudes of group frequencies. However, the potential energy distributions reveal considerable mixing of several vibration types and some substantial discrepancies. In particular the P–N stretching vibration gives contributions to several normal modes and shows especially in F_2PNCS a marked discrepancy between the potential-energy distribution and the approximate description. It seems inadequate to assign the P–N stretch to a definite normal mode; the large frequency shift from F_2PNCS to F_2PNCO (622 to 714 cm^{-1}) supports this conclusion.

Mean Amplitudes of Vibration and Related Quantities.—The force constants (Tables 4 and 5) were used to calculate the mean amplitudes of vibration.[14] The results are shown in Table 8 (F_2PNCO) and Table 9 (F_2PNCS). The Tables also include the calculated perpendicular amplitude correction coefficients or K values,[14] and shrinkage effects for the N=C=X chains.

TABLE 4

Symmetry force constants (mdyn/Å) for F_2PNCO

A'	1	3·88							
	2	0·03	3·96						
	3	0·53	−0·87	16·68					
	4	0·80	−1·35	1·40	11·28				
	5	0·08	0·00$_4$	−0·09	−0·02	0·83			
	6	−0·07	0·06	0·07	0·12	0·02	0·56		
	7	−0·07	−0·03	−0·04	−0·01	0·03	0·03	0·12	
	8	−0·11	0·04	0·17	0·21	−0·00$_4$	−0·01	0·09	0·49
A''	1	4·53							
	2	−0·08	0·14						
	3	0·01	0·03	0·02					
	4	−0·03	−0·04	−0·06	0·28				

TABLE 5

Symmetry force constants (mdyn/Å) for F_2PNCS

A'	1	3·53							
	2	0·28	3·18						
	3	0·44	−0·19	12·54					
	4	0·58	−0·49	0·53	7·69				
	5	0·04	−0·07	−0·09	−0·12	0·74			
	6	−0·05	0·22	0·21	0·17	−0·00$_2$	0·61		
	7	−0·11	−0·05	−0·05	−0·03	0·04	0·05	0·10	
	8	−0·19	−0·07	0·05	0·07	0·01	0·02	0·08	0·39
A''	1	4·55							
	2	−0·08	0·12						
	3	0·00$_3$	0·02	0·02					
	4	−0·01	−0·00$_2$	−0·03	0·17				

TABLE 6

Frequency assignment, potential energy distribution, and approximate description of normal modes for F_2PNCO

Species	Frequency (cm^{-1})	Potential energy distribution [a]	Approx. description
A′	2283	79s + 30t	C=N stretch
	ca. 1422 [b]	56t	C=O stretch
	853	23r + 22ϕ + 18d	sym.P–F stretch
	714	62r + 24d	P–N stretch
	604	46ϕ + 32d	NCO bend
	451	81α	PF_2 bend
	324	73β + 16d	PF_2 deform.
	105	111γ+ 42ϕ	PNC bend
A″	839 [c]	97r	asym.P–F stretch
	630	51θ	NCO bend
	183	80β + 40θ	PF_2 deform.
	50	215τ + 96θ + 50β	torsion

[a] Terms below 15 are omitted. For explanation of symbols, see Figure 1. [b] Estimated frequency. Fermi resonance with $2\nu_4$ moves band. [c] Estimated gas-phase frequency derived from liquid phase frequency observed in Raman spectrum.

TABLE 7

Frequency assignment, potential energy distribution, and approximate description of normal modes for F_2PNCS

Species	Frequency (cm^{-1})	Potential energy distribution [a]	Approx. description
A′	1982	81s + 21t	C=N stretch
	1028	52t + 27d	C=S stretch
	859	26r + 16ϕ	sym.P–F stretch
	622	67r + 21ϕ	P–N stretch
	476	41d + 37ϕ + 34β	NCS bend
	426	83α	PF_2 bend
	312	53β + 21d	PF_2 deform.
	81	122γ + 48ϕ	PNC bend
A″	845 [b]	97r	asym.P–F stretch
	531	42θ + 18τ	NCS bend
	181	70β + 26θ	PF_2 deform.
	45	165τ + 89θ + 55β	torsion

[a] See note *a* to Table 6. [b] See note *c* to Table 6.

TABLE 8

Calculated mean amplitudes of vibration (u), perpendicular amplitude correction coefficients (K), and linear shrinkage effect (δ) for F_2PNCO; Å units. ν_{tors} = 50 cm^{-1}

Distance	u $T = 0$	u $T = 298$	K $T = 298$ K
P–F (1·565)	0·0428	0·0442	0·0199
P–N (1·697)	0·0441	0·0462	0·0099
N=C (1·257)	0·0348	0·0349	0·0146
C=O (1·165)	0·0378	0·0380	0·0412
F · · · F (2·360)	0·0605	0·0674	0·0305
F · · · N (2·491)	0·0744	0·1137	0·0219
F · · · C (3·589)	0·0865	0·1791	0·0041
F · · · O (4·679)	0·1022	0·2459	0·0027
P · · · C (2·690)	0·0625	0·0999	0·0028
P · · · O (3·754)	0·0803	0·1469	0·0144
N · · · O (2·422)	0·0414	0·0419	0·0457
δ(N · · · O)	0·00573	0·01009	

Note: Parenthesised values show the interatomic separations calculated from the structural data adopted for the equilibrium structure in the spectroscopic calculations. For this purpose they are not required with particularly great accuracy, and no special significance should be attached to the given figures. The values are included here in order to facilitate the identification of the various distances.

TABLE 9

Calculated mean amplitudes of vibration (u), perpendicular amplitude correction coefficients (K), and linear shrinkage effect (δ) for F_2PNCS; Å units. ν_{tors} = 45 cm^{-1}

Distance	u $T = 0$	u $T = 298$	K $T = 298$ K
P–F (1·567)	0·0435	0·0451	0·0262
P–N (1·693)	0·0462	0·0494	0·0167
N=C (1·230)	0·0371	0·0374	0·0085
C=S (1·553)	0·0382	0·0388	0·0361
F · · · F (2·390)	0·0622	0·0703	0·0411
F · · · N (2·451)	0·0745	0·1164	0·0336
F · · · C (3·559)	0·0839	0·1729	0·0126
F · · · S (5·040)	0·0966	0·2470	0·0005
P · · · C (2·756)	0·0604	0·0972	0·0047
P · · · S (4·229)	0·0733	0·1466	0·0063
N · · · S (2·783)	0·0419	0·0433	0·0334
δ(N · · · S)	0·00557	0·01118	

See note to Table 8.

All the calculated mean amplitudes seem to have reasonable values. In particular, the u(P–F) and u(F · · · F) magnitudes are comparable with the corresponding ones in PF_3; *cf.* Table 10. These two types maintain fairly characteristic values through a series of mixed halides,[23,24] u(P–F) being around 0·042 Å and u(F · · · F) being about 0·07 Å. The same orders of magnitude are also found in OPF_3 and SPF_3 in spite of different bonding properties of the phosphorus atom. Mean amplitudes for PF_3 from electron diffraction [25] agree well with the calculated values. The mean amplitudes pertaining to the N=C=X chains are compared with corresponding data for different molecules in Table 11. The u(N=C) values are seen to vary between 0·035 and 0·038 Å. They are of the same order of magnitude as u(N≡C),[14] which in CH_3CN is 0·0343 Å.[26] The mean amplitudes for the carbonyl bond, C=O, in different molecules have been studied systematically.[27] 0·035 Å is reported as the normal value in a =C=O conformation. The u(N · · · X) values calculated here agree well with the corresponding ones in H_3SiNCX, but are significantly lower than those of HNCX. The latter values (for HNCO and HNCS) were obtained by Cyvin [14] from data of Venkateswarlu *et al.*,[28] and seem not to be necessarily correct.

TABLE 10

Comparison of mean amplitudes for the P–F and F · · · F distances in different molecules; Å units, T = 298 K

Molecule	u(P–F)	u(F · · · F)	Reference
PF_3	0·0413	0·0700	23,*a*
OPF_3	0·0390	0·069	*b*
SPF_3	0·0396	0·0645	*c*
F_2PNCO	0·0442	0·0674	This work
F_2PNCS	0·0451	0·0703	This work

[a] S. J. Cyvin, B. N. Cyvin, and A. Müller, *J. Mol. Structure*, 1969, **4**, 341. [b] A. Müller, B. Krebs, A. Fadini, O. Glemser, S. J. Cyvin, J. Brunvoll, B. N. Cyvin, I. Elvebredd, G. Hagen, and B. Vizi, *Z. Naturforsch.*, 1968, **23**a, 1656. [c] S. J. Cyvin, B. Vizi, A. Müller, and B. Krebs, *J. Mol. Structure*, 1969, **3**, 173.

---

[23] S. J. Cyvin, *Kgl. Norske Videnskab. Selskabs Skrifter*, **1971, 1.**

[24] I. Elvebredd, B. Vizi, S. J. Cyvin, A. Müller, and B. Krebs, *J. Mol. Structure*, 1968, **2**, 158.

[25] Y. Morino, K. Kuchitsu, and T. Moritani, *Inorg. Chem.*, 1969, **8**, 867.

[26] S. J. Cyvin and V. Devarajan, *J. Mol. Structure*, in the press.

[27] S. J. Cyvin and B. Vizi, *Acta Chim. Hung.*, in the press.

[28] K. Venkateswarlu and V. Malthy Devi, *Proc. Indian Acad. Sci.*, 1965, *A*, **61**, 272.

TABLE 11

Comparison of mean amplitudes for the N=C=X chain in different molecules; Å units, T = *ca.* 298 K

Molecule	u(N=C)	u(C=O)	u(C=S)	u(N ··· O)	u(N ··· S)	Reference
HNCO	0·03789	0·03501		0·05626		14, 28
HNCS	0·03758		0·03982		0·05696	14, 28
CH_3NC	0·0351					*a*
SiH_3NCO	0·035	0·037		0·041		35
SiH_3NCS	0·036		0·040		0·043	35
F_2PNCO	0·0349	0·0380		0·0419		This work
F_2PNCS	0·0374		0·0388		0·0433	This work

[a] S. J. Cyvin and V. Devarajan, *Acta Chem. Scand.*, 1971, **25**, 2363.

Refinement of Molecular Structures.—(a) *Molecular model*. In the early refinements, both the compounds were assumed to have C_s symmetry, with linear NCX groups *trans* to the PF_2 groups. The structures were then each defined by four bonded distances, and the FPF, FPN, and PNC angles. At a later stage, rotation about the PN bond was also permitted, giving a total of 8 structural parameters.

(b) *Refinements*. It was found to be possible to refine all seven original structural parameters for the isocyanate, as well as most of the amplitudes of vibration. Where several interatomic distances were very similar, one or more of the associated vibrational amplitudes could not be refined. The situation was similar for the isothiocyanate, with the exception that the C–S distance was always kept fixed at either 1·553 or 1·563 Å. This was necessary because of the similarity of the P–F, P–N, and C–S distances. The distance chosen was the difference between the refined N ··· S and N–C distances, with a small shrinkage correction. Under these conditions, the minimum R factor obtained was 0·13 for each compound.

The conformations of the PF_2 groups were then studied. For each compound, a series of refinements was done with the dihedral angle (between the NCX group and the PF_2 bisector) fixed at various angles between 0 and 180°. The possibility of free or only slightly restricted rotation was also investigated. These refinements indicated approximately *trans*-configurations, so further refinements were performed with the dihedral angles between 0 and 30°. Figure 2 shows the variations in R factors that were found, together with various percentage confidence limits.[29] For each compound, the minimum R factor was for a

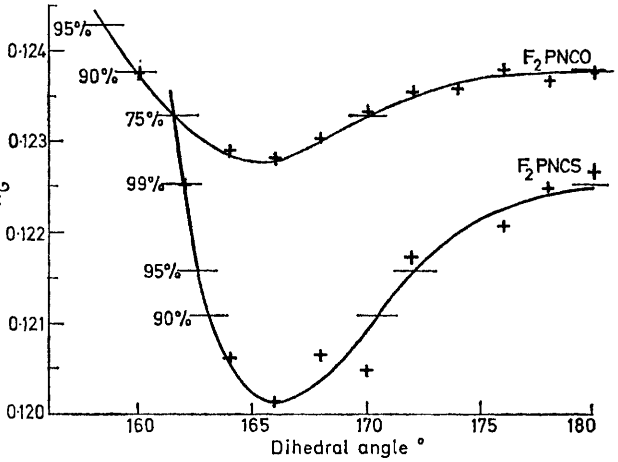

FIGURE 2 Variation of $R_G = (U'WU/I'WI)^{\frac{1}{2}}$ for F_2PNCO and F_2PNCS with dihedral angle, showing percentage confidence limits

TABLE 12

Molecular parameters for F_2PNCO

	Refinement (A)		Refinement (B)		Refinement (C)		Spectroscopic
	r_a	u_a	r_a	u_a	r_a	u_a	u_a (298 K)
P–F	1·563(3)	0·055(3)	1·563(3)	0·053(3)	1·565(3)	0·044(F)	0·044
P–N	1·683(6)	0·046(F)	1·689(6)	0·046(F)	1·697(6)	0·046(F)	0·046
N–C	1·256(6)	0·035(F)	1·258(6)	0·035(F)	1·257(7)	0·035(F)	0·035
C–O	1·168(5)	0·038(F)	1·163(6)	0·038(F)	1·165(6)	0·038(F)	0·038
F ··· F	2·358	0·064(12)	2·349(8)	0·066(10)	2·345(9)	0·067(F)	0·067
F ··· N	2·480	0·110(F)	2·463(11)	0·110(F)	2·47³(9)	0·104(F)	0·101 [a] 0·114 [b]
F ··· C	3·491 3·644	0·227(31) 0·227(31)	3·481(23)	0·197(28)	3·504(24)	0·202(29)	0·119 [a] 0·179 [b]
F ··· O	4·543 4·769	0·180(22) 0·180(22)	4·723(18)	0·208(15)	4·721(19)	0·205(16)	0·146 [a] 0·246 [b]
P ··· C	2·675	0·083(12)	2·664(9)	0·078(11)	2·655(12)	0·099(F)	0·100
P ··· O	3·733	0·162(16)	3·760(16)	0·128(15)	3·757(24)	0·146(F)	0·147
N ··· O	2·415	0·042(F)	2·418(F)	0·042(F)	2·407(11)	0·042(F)	0·042
∠FPF	97·9(8)						
∠FPN	99·5(7)						
∠PNC	130·6(8)						
∠dihedral	14(F)						

Note: E.s.d.'s are given in parentheses. Parameters that were fixed in a refinement are marked (F). [a] Assuming ν_{tors} = 105 cm^{-1}. [b] Assuming ν_{tors} = 50 cm^{-1}.

---

[29] W. C. Hamilton, *Statistics in Physical Science*, Ronald Press, New York, 1964.

dihedral angle of 14°. The shallower minimum for the isocyanate merely reflects the smaller amount of scattering by F · · · O atom pairs than by F · · · S pairs.

The results of refinements with dihedral angles of 14° are given as refinements (A) in Tables 12 and 13.

At this stage, refinements were done in which C_s structures were assumed, and the eleven different interatomic distances could be refined independently. Some amplitudes of vibration were allowed to refine, the remainder being fixed at calculated values. The results are given as refinements (B) in Tables 12 and 13. Further refinements (C) were performed with all amplitudes fixed at spectroscopic values, with the exception of those for the F · · · C and F · · · X distances. These were allowed to refine because single distances in the C_s model represent what in reality should be pairs of distances. Also, these amplitudes are strongly dependent on the torsional frequences, which were not determined spectroscopically. Instead, the amplitudes of vibration for these distances, as determined from refinements (A), were used to give rough estimates of the torsion frequencies.

TABLE 13

Molecular parameters for F_2PNCS

	Refinement (A)		Refinement (B)		Refinement (C)		Spectroscopic
	r_a	u_a	r_a	u_a	r_a	u_a	u_a (298 K)
P–F	1·566(3)	0·058(4)	1·566(3)	0·056(3)	1·567(3)	0·045(F)	0·045
P–N	1·686(7)	0·049(F)	1·689(7)	0·049(F)	1·693(7)	0·050(F)	0·049
N–C	1·221(6)	0·037(F)	1·233(6)	0·055(10)	1·230(7)	0·037(F)	0·037
C–S	1·553(F)	0·039(F)	1·553(F)	0·039(F)	1·553(F)	0·039(F)	0·039
F · · · F	2·384	0·097(17)	2·381(40)	0·100(36)	2·373(11)	0·070(F)	0·070
F · · · N	2·447	0·107(F)	2·445(34)	0·107(F)	2·454(10)	0·106(F)	0·103 [a] 0·116 [b]
F · · · C	3·604 3·478	0·179(21) 0·179(21)	3·553(20)	0·189(18)	3·549(21)	0·178(19)	0·124 [a] 0·173 [b]
F · · · S	5·119 4·917	0·208(20) 0·208(20)	5·052(20)	0·222(14)	5·051(21)	0·216(15)	0·155 [a] 0·247 [b]
P · · · C	2·743	0·133(7)	2·660(23)	0·129(F)	2·650(13)	0·098(F)	0·097
P · · · S	4·207	0·136(9)	4·222(11)	0·134(7)	4·221(14)	0·149(F)	0·147
N · · · S	2·764	0·058(7)	2·769(7)	0·049(9)	2·778(7)	0·043(F)	0·043
∠FPF	99·4(9)						
∠FPN	97·7(8)						
∠PNC	140·5(7)						
∠dihedral	14(F)						

Note: E.s.d.'s are given in parentheses. Parameters that were fixed in a refinement are marked (F). [a] Assuming $\nu_{tors} = 81$ cm^{-1}. [b] Assuming $\nu_{tors} = 45$ cm^{-1}.

The intensity data, and final weighted differences for refinements (A), are shown in Figures 3 and 4. Uphill curves are available from the authors on request.

The lowest R factors obtained [R_G (ref. 1)] were 0·109 (F_2PNCO) and 0·102 (F_2PNCS).

Determination of Average Structures.—The calculated amplitudes of vibration and shrinkages given in Tables 8 and 9 are derived from $r_g \equiv r_g(0)$ distances.[30] The $r_a \equiv r_g(1)$ distances obtained by electron diffraction may be converted to r_g distances by means of the approximate formula $r_g = r_a + L$ where L, the parallel amplitude correction coefficient, may be identified with u^2/r. Calculated values of L from the present spectroscopic analysis are included in Table 14. The Table also contains the distances of the average structure.[25,31-34] r_α, obtained using the formula

$$r_\alpha = r_g - K = r_a + L - K$$

where K is the perpendicular amplitude correction coefficient, as given in Tables 8 and 9. The ' observed ' shrinkage effect for F_2PNCO, as obtained from the r_g values, amounts to 0·0064 Å for the N=C=O chain. Thus the experimental shrinkage is consistent with the calculated value within their error limits.

TABLE 14

Parallel amplitude correction coefficients (L) and different types of distances

	F_2PNCO			F_2PNCS		
	r_a	L(298 K)	r_α	r_a	L(298 K)	r_α
P–F	1·565	0·0012	$1{\cdot}546_3$	1·567	0·0013	$1{\cdot}542_1$
P–N	1·697	0·0013	$1{\cdot}688_4$	1·693	0·0014	$1{\cdot}677_7$
N–C	1·257	0·0010	$1{\cdot}243_4$	1·230	0·0011	$1{\cdot}222_6$
C–X	1·165	0·0012	$1{\cdot}125_0$	1·553	0·0010	$1{\cdot}517_9$
F · · · F	2·345	0·0019	$2{\cdot}316_4$	2·373	0·0021	$2{\cdot}334_0$
F · · · N	2·473	0·0052	$2{\cdot}456_3$	2·454	0·0055	$2{\cdot}425_9$
F · · · C	3·504	0·0089	$3{\cdot}508_8$	3·549	0·0084	$3{\cdot}544_8$
F · · · X	4·721	0·0129	$4{\cdot}731_2$	5·051	0·0121	$5{\cdot}062_6$
P · · · C	2·655	0·0037	$2{\cdot}655_9$	2·650	0·0034	$2{\cdot}648_7$
P · · · X	3·757	0·0057	$3{\cdot}748_3$	4·221	0·0051	$4{\cdot}219_8$
N . . . X	2·407	0·0007	$2{\cdot}362_0$	2·778	0·0007	$2{\cdot}745_3$

It is possible, using the r_α values of Table 14, to calculate average values for the PNC angles in these molecules. Using the P–N, P · · · X, and N · · · X distances, the angles obtained are 134·8 and 144·0° for F_2PNCO and F_2PNCS respectively. Thus the effect of the bending vibration is to lower the apparent angles at nitrogen by only *ca*. 4°, much less than in the corresponding silyl compounds.[35]

---

[30] L. S. Bartell, *J. Chem. Phys.*, 1955, **23**, 1219.

[31] K. Kuchitsu and S. Konaka, *J. Chem. Phys.*, 1966, **45**, 4342.

[32] K. Kuchitsu, *J. Chem. Phys.*, 1968, **49**, 4456.

[33] K. Kuchitsu, *J. Chem. Phys.*, 1966, **44**, 906.

[34] Y. Morino, K. Kuchitsu, T. Fukuyama and M. Tanimoto, *Acta Cryst.*, 1969, *A*25, S217.

[35] S. J. Cyvin, J. Brunvoll, and A. G. Robiette, *Chem. Phys. Letters*, 1971, **11**, 263.

Discussion of Structures.—The least-squares correlation matrices for F_2PNCO and F_2PNCS (Tables 15 and 16) show a number of fairly large correlations, attributable to the overlapping of peaks in the radial distribution curves (Figures 5 and 6). For both compounds, the phosphorus–fluorine and phosphorus–nitrogen distances are similar, and so are strongly correlated, as are the FPF and FPN angles, dependent on the F $\cdots$ F and F $\cdots$ N distances at *ca.* 2·4 Å. Similarly, the N–C and C–O bond lengths in the isocyanate differ by less than 0·1 Å. In all these cases, attempts to refine amplitudes of vibration can lead to unacceptable values,[36] and so at least one of each pair of amplitudes was fixed at the value determined from the spectroscopic data.

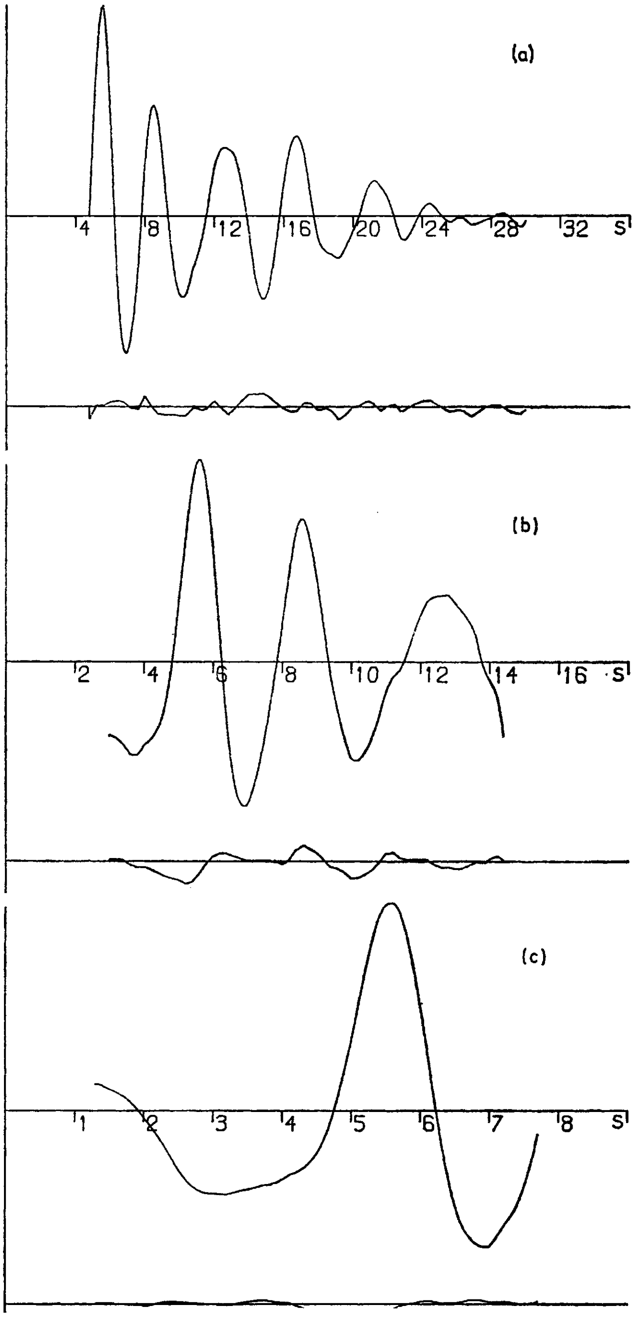

FIGURE 3 Observed and final weighted difference molecular scattering intensities for F_2PNCO at nozzle-to-plate distances of (a) 250, (b), 500, and (c) 1000 mm [differences for refinement (A)]

The phosphorus–nitrogen and phosphorus–fluorine bond lengths in these two compounds are similar to those found in aminodifluorophosphine, dimethyl-

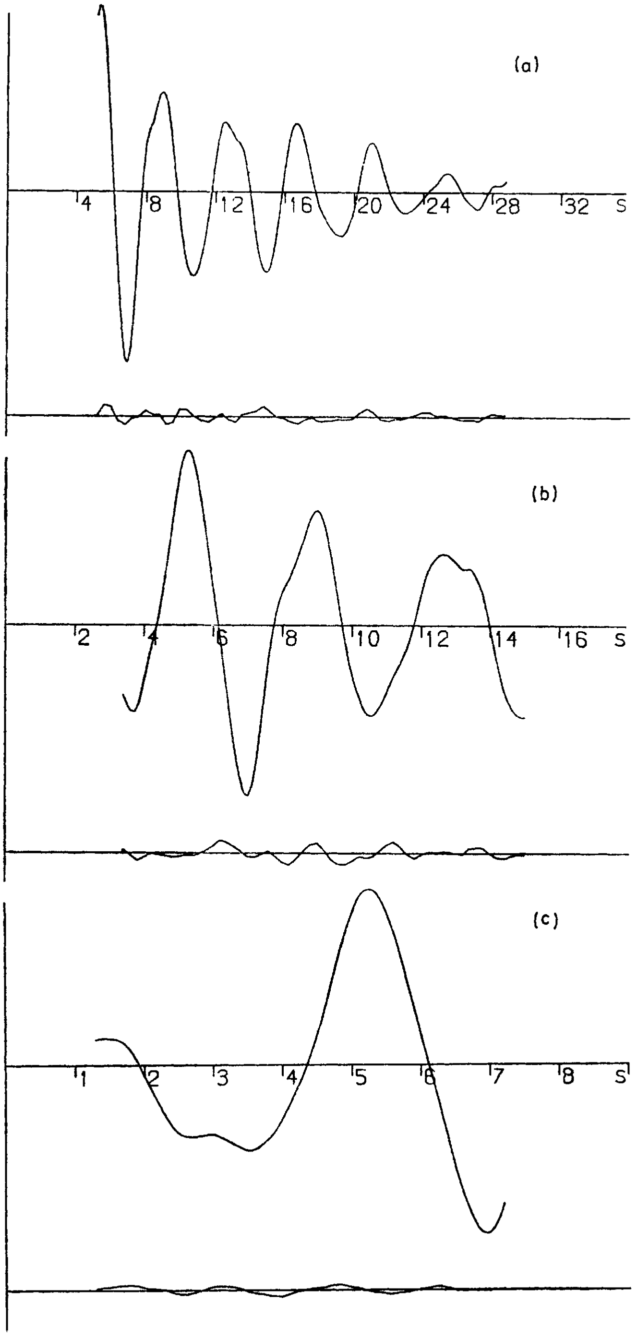

FIGURE 4 Observed and final weighted difference molecular scattering intensities for F_2PNCS at nozzle-to-plate distances of (a) 250, (b), 500, and (c) 1000 mm [differences for refinement (A)]

---

[36] F. B. Clippard and L. S. Bartell, *Inorg. Chem.*, 1970, **9**, 805.

TABLE 15

Least-squares correlation matrix for F_2PNCO (refinement A), multiplied by 1000

*R*1	*R*2	*R*3	*R*4	<1	<2	<3	*U*1	*U*5	*U*7	*U*9	*U*11	*U*12	*K*1	*K*2	*K*3	
1000	173	37	158	−35	−163	−38	−209	57	−61	−52	−21	−28	−161	−24	27	*R*1
	1000	206	−54	416	−180	−430	−504	213	116	39	80	30	427	149	172	*R*2
		1000	−136	340	129	−560	−44	−103	103	−29	26	48	229	30	19	*R*3
			1000	−111	−83	24	−89	−225	−205	−31	−94	−42	−258	−63	−111	*R*4
				1000	−218	−744	−284	89	307	−7	−154	−194	46	3	35	<1
					1000	−358	156	−507	175	−118	599	117	47	−22	−53	<2
						1000	223	130	−402	85	−227	112	−180	−29	−48	<3
							1000	14	63	40	−2	35	203	21	−9	*U*1
								1000	116	91	−264	−70	327	125	157	*U*5
									1000	−148	66	−270	288	101	184	*U*7
										1000	−65	−132	132	54	54	*U*9
											1000	97	104	21	33	*U*11
												1000	113	54	34	*U*12
													1000	179	188	*K*1
														1000	70	*K*2
															1000	*K*3

TABLE 16

Least-squares correlation matrix for F_2NCS (refinement A), multiplied by 1000

*R*1	*R*2	*R*3	<1	<2	<3	*U*1	*U*5	*U*7	*U*9	*U*12	*U*13	*K*1	*K*2	*K*3	
1000	81	128	−50	−76	82	−182	0	−52	14	−30	−15	−180	−85	14	*R*1
	1000	192	201	−251	33	−483	178	95	89	36	128	316	283	101	*R*2
		1000	155	275	−682	−71	40	30	−247	34	15	125	43	−35	*R*3
			1000	−760	205	−61	604	46	131	63	−109	102	125	51	<1
				1000	−769	65	−702	−30	−357	−41	17	−114	−201	−132	<2
					1000	33	441	17	418	−17	26	27	139	123	<3
						1000	117	56	49	72	59	440	158	3	*U*1
							1000	74	246	69	59	309	253	112	*U*5
								1000	113	−213	−36	172	154	19	*U*7
									1000	−144	30	130	172	88	*U*9
										1000	33	135	89	0	*U*12
											1000	207	100	56	*U*13
												1000	349	75	*K*1
													1000	51	*K*2
														1000	*K*3

aminodifluorophosphine,[1] and cyanodifluorophosphine,[2] as are the interbond angles at phosphorus. It is perhaps significant that the silicon–nitrogen bonds in silyl pseudohalides [8,37] are *ca.* 0·02 Å shorter than those in silyl amines,[4] consistent with *sp* nitrogen hybridisation instead of sp^2. The bond length evidence suggests that the nitrogen hybridisations in the fluorophosphinyl-amines and -pseudohalides are roughly equivalent.

It seems probable that the observed torsional deviations from C_s symmetry can be accounted for by assuming average structures with the NCX groups *trans* to the PF_2 bisectors, with fairly low-frequency torsional vibrations leading to apparent distortion.

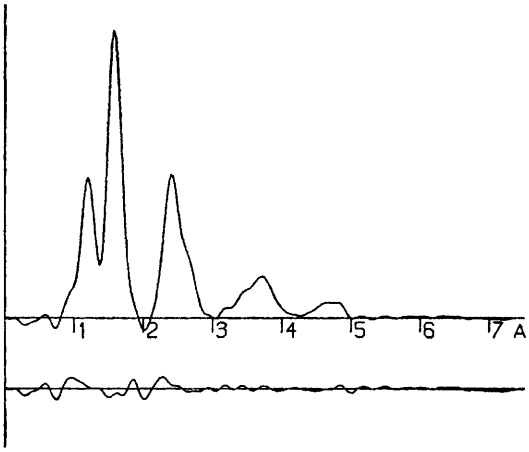

FIGURE 5 Radial distribution curve, $P(r)/r$, for F_2PNCO. Before Fourier inversion, the data were multiplied by $s\,.\,\exp(-0{\cdot}0015\,s^2)/(z_P - f_P)(z_F - f_F)$. The difference curve is for refinement (A)

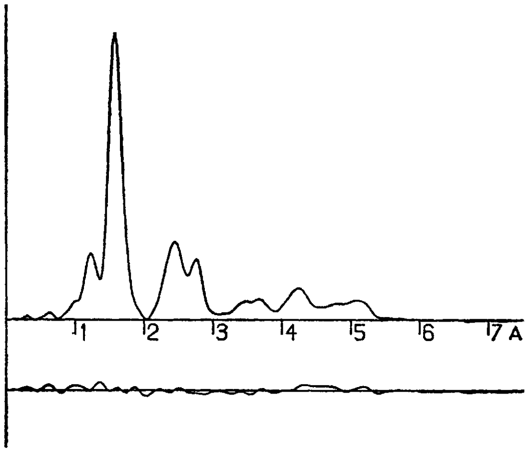

FIGURE 6 Radial distribution curve, $P(r)/r$, for F_2PNCS. Before Fourier inversion the data were multiplied by $s\,.\,\exp(-0{\cdot}0015\,s^2)/(z_P - z_P)(z_F - f_F)$. The difference curve is for refinement (A)

---

[37] A. G. Robiette and C. Glidewell, personal communication.

We have observed that in methyl pseudohalides[38] there is a tendency for one of the hydrogen atoms to be eclipsed with respect to the pseudohalide group, and therefore staggered with respect to the lone pair of electrons. In the substituted fluorophosphines, therefore, the predominant repulsive effect is probably between the phosphorus and nitrogen lone pairs.

TABLE 17

XNC Angles in some isocyanates and isothiocyanates

Compound	Method[a]	Angle[b]		Ref.	Compound	Method[a]	Angle[b]		Ref.
		θ_a	θ_α				θ_a	θ_α	
HNCO	MW		128·1(5)	*c*	HNCS	MW		130·3(3)	*d*
						MW		135	*e*
					DNCS	MW		132·3(3)	*d*
CH_3NCO	MW		140·0(10)	9	CH_3NCS	MW		147·5(10)	9
	ED	140·3(4)		38		ED	142·8(9)		38
SiH_3NCO	MW		180	7	SiH_3NCS_3	MW		180	8
	ED	151·7(12)		37		ED	163·8(26)		37
$(CH_3)_3SiNCO$	ED	150(3)		*f*	$(CH_3)_3SiNCS$	ED	154(2)		*f*
SiF_3NCO	ED	161		*g*					
$SiCl_3NCO$	ED	138·0(4)		*h*					
$SiCl_2(NCO)_2$	ED	136(1)		*h*					
$SiCl(NCO)_3$	ED	145(2)		*h*					
$Si(NCO)_4$	ED	146·4		*i*	$Si(NCS)_4$	X		172·5(8)	*j*
					$P_3N_3(NCS)_6$	X		mean 152(10)	*k*
F_2PNCO	ED	130·6(8)	134·8	This work	F_2PNCS	ED	140·5(7)	144·0	This work
ClNCO	MW		123·7(10)	39					

[a] ED = Electron diffraction, MW = microwave, X = *X*-ray diffraction. [b] θ_a = Apparent angle derived from r_a values, θ_α = average angle. [c] L. H. Jones, J. N. Shoolery, R. G. Shulman, and D. M. Yost, *J. Chem. Phys.*, 1950, **18**, 990. [d] G. C. Dousmanis, T. M. Sanders, C. H. Townes, and H. J. Zeiger, *J. Chem. Phys.*, 1953, **21**, 1416. [e] R. Kewley, K. V. L. N. Sastry, and M. Winnewisse, *J. Mol. Spectroscopy*, 1963, **10**, 418. K. Kimura, K. Kitada, and S. H. Bauer, *J. Amer. Chem. Soc.*, 1966, **88**, 416. [g] W. C. Airey, C. Glidewell, A. G. Robiette, and G. M. Sheldrick, to be published. [h] R. L. Hilderbrandt and S. H. Bauer, *J. Mol. Structure*, 1969, **3**, 325. [i] K. E. Hjortaas, *Acta Chem. Scand.*, 1967, **21**, 1381. [j] G. M. Sheldrick and W. S. Sheldrick, *Acta Cryst.*, in the press. [k] J. B. Faught, T. Meeller, and I. C. Paul, *Inorg. Chem.*, 1970, **9**, 1656.

The angles at nitrogen in some isocyanates and isothiocyanates are listed in Table 17. From the tabulated data, it can be seen that any isothiocyanate has a wider angle than its isocyanate analogue, but apart from this, there are no systematic trends. It is possible that the average structures of all the compounds include linear SiNC groups, but this cannot at present be confirmed, in view of current uncertainty about shrinkage corrections in these molecules. But even if these compounds do not have linear SiNC groups, they have wider angles than the methyl compounds, a feature that has been attributed to (*p*–*d*) π-bonding. The angles found in phosphorus compounds are therefore somewhat surprising, as similar possibilities for multiple bonding exist. However, the differences between observed phosphorus–nitrogen bond lengths in these pseudohalides and the length predicted by the Schomaker–Stevenson rule[39] are generally smaller than the corresponding differences for silicon pseudohalides. Thus the evidence suggests that π-bonding is less important for phosphorus than for silicon. That this trend is continued across the periodic table is suggested by work on chloride isocyanate,[40] which has a small ClNC angle and a long chlorine–nitrogen bond.

We are grateful to Professor D. W. J. Cruickshank and Dr. B. Beagley (University of Manchester Institute of Science and Technology), Dr. M. J. Smyth (The Royal Observatory, Edinburgh), and Dr. M. J. Mays and Dr. G. M. Sheldrick (University of Cambridge) for the provision of experimental facilities for electron diffraction and Raman work. D. W. H. R. thanks Imperial Chemical Industries Ltd. for a research fellowship.

[1/1935 *Received*, 21*st October*, 1971]

---

[38] D. W. W. Anderson, D. W. H. Rankin, and A. Robertson, unpublished observations.

[39] V. Schomaker and D. P. Stevenson, *J. Amer. Chem. Soc.*, 1941, **63**, 37.

[40] W. H. Hocking and M. C. L. Gerry, *Chem. Comm.*, 1970, 448.