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Molecular Structure of Thiophosphoryl Fluoride as Studied by Gas Electron Diffraction

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The molecular structure of SPF_3 has been determined by gas electron diffraction as follows: $r_g(P–F) = 1.538 \pm 0.003$ Å, $r_g(S–P) = 1.866 \pm 0.005$ Å and $\angle F–P–F(r_\alpha) = 99.6 \pm 0.3°$. The uncertainties represent estimated limits of error. The observed bond lengths and angle for this molecule have been compared with those for related molecules, and empirical equations representing the phosphorus–halogen bond lengths and the valence angles of phosphorus and the other group Vb atoms are obtained.

Introduction

The structure of thiophosphoryl fluoride was first reported to be r(P–F) = 1.51 ± 0.02 Å, r(S–P) = 1.85 ± 0.02 Å and ∠F–P–F = 99.5 ± 2° by the visual electron diffraction method by Stevenson and Russell[1]. Williams *et al.*[2] later determined the rotational constants for the $^{32}SPF_3$, $^{33}SPF_3$ and $^{34}SPF_3$ species by microwave spectroscopy. Since these rotational constants do not supply independent information for determining the three independent structural parameters, they assumed that r(P–F) = 1.53 ± 0.02 Å and obtained r(S–P) = 1.87 ± 0.03 Å and ∠F–P–F = 100 ± 2°. These parameters agreed within the limits of error with those given by electron diffraction. A lower value of r(P–F) was excluded since their rotational constants gave the other two parameters lying outside the error limits of electron diffraction.

The present study was undertaken to reinvestigate the structure of this molecule with accuracy comparable with those of related inorganic halide structures determined in recent studies (PF_3[3], PCl_3[4], PBr_3[5], $SPCl_3$[6], $OPCl_3$[6] and OPF_3[6]). Gas electron diffraction provides the most suitable method for this purpose for the following reasons: (i) since the radial distribution curve has four separate intense peaks corresponding to the four atomic pairs in SPF_3, the structure can be determined directly and accurately without assumptions or constraints; (ii) spectroscopy provides only limited information on the structure, since fluorine and phosphorus have single stable nuclides.

An accurate structure of SPF_3 should provide essential information for a quantitative comparison with its analogues listed above and for a discussion of bonding theory.

Experimental

A sample of SPF_3 (b.p. –52° C) was synthesized by refluxing $SPCl_3$ with an excess of SbF_3 in a sealed flask equipped with a dry ice–acetone trap. Commercial $SPCl_3$ and SbF_3 were purified by distillation and sublimation, respectively. The mixture was stirred for about one day at 40° C with a magnetic stirrer, and the crude product was trapped at liquid nitrogen temperature. The original product contained SPF_3, OPF_3, SiF_4 and SPF_2Cl, and after vacuum distillation an infrared spectrum[7] of the sample showed that a few percent of SPF_2Cl was the only impurity. The SPF_2Cl impurity was also estimated from the ratio of the vapor pressures[8] of SPF_2Cl and SPF_3 at –79° C to be at most 5%. It was used without further purification, and the presence of SPF_2Cl was taken into account in the analysis. However, the effect of this impurity was barely significant.

Electron diffraction photographs were taken[9] with an r^3-sector at the camera lengths of 107.86 ± 0.02 and 243.29 ± 0.02 mm. The electron wavelength (about 0.06 Å) was calibrated with reference to the r_a(C=O) distance of carbon dioxide (1.164_6 Å) measured under the same experimental conditions. The pressure of the sample gas was about 100 Torr, and the exposure times were about 7 and 3 s for the short and long camera lengths, respectively. The optical densities (0.26–0.64) were assumed to be proportional to electron intensities. Other experimental details are described elsewhere[9,10]. Molecular intensities in the ranges s = 3.5–18.8 and 7.9–33.6 $Å^{-1}$ were obtained*

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* For a listing of the experimental total intensity and background data, see NAPS document No. 02501 for 6 pages of supplementary material. Order from ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, NY 10016. Remit in advance for each NAPS accession number. Make checks payable to Microfiche Publications.

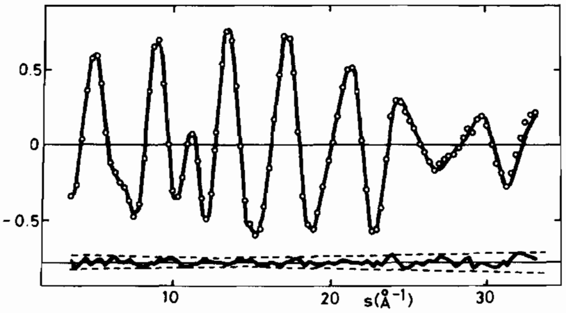

Figure 1. Experimental and thoretical molecular intensities for thiophosphoryl fluoride. Typical observed $sM(s)$ values are shown in open circles, and the best theoretical fit is shown in the solid curve. The indices of resolution are 0.93 ± 0.04 and 0.83 ± 0.03 for the short and long camera regions, respectively. The lower solid and broken curves represent the residuals and the error limites in the $sM(s)$ to a fractional error of 1×10^{-3} of the original photocurrent, respectively.

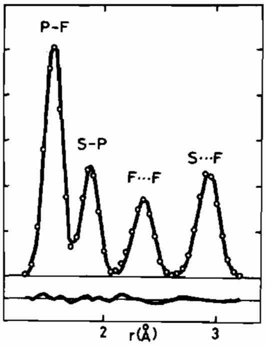

Figure 2. Experimental (open circles) and theoretical radial distribution curves for thiophosphoryl fluoride, the lower curve represents residuals. A damping factor, $\exp(-0.0020s^2)$, was used.

from the long and short distance data, respectively, by use of hand-drawn backgrounds. Since they agreed with each other in the overlapping region within experimental error, they were joined at $s = 11.9$ Å^{-1}. The elastic and inelastic scattering factors and the phase shifts were taken from the tables[11] prepared by Schäfer *et al.* The molecular intensity is illustrated in Figure 1, and the corresponding radial distribution curve is given in Figure 2. Most of the calculations were carried out on a HITAC 8800/8700 operating system in the Computer Center of the University of Tokyo.

Analysis

Since this molecule has C_{3v} equilibrium symmetry, three parameters, r(S–P), r(P–F) and ∠F–P–F, were selected to define the molecular geometry. Therefore, the three geometrical parameters, four mean amplitudes and the indices of resolution for the long and short camera regions were taken as independent parameters in the analysis. The asymmetry parameters[12] $\varkappa$ for the S–P and P–F bonds were estimated to be 6.2×10^{-7} and 7.7×10^{-7} Å^3, respectively, from the anharmonicity parameters[13] a_3 for SP and PF assumed to be 1.67 and 1.89 Å^{-1}, respectively. The parameters for nonbonded pairs were ignored since the observed radial distribution peaks of the nonbonded pairs were symmetric within estimated experimental error[5].

A least squares analysis was carried out with an empirical diagonal weight matrix[14]. The observed r_g distances and r_α angles determined in the analysis are shown in Table I. An alternative least squares analysis with four interatomic distances taken as independent variable parameters gave a consistent bond angle within the uncertainty quoted in Table I. The mean amplitudes and the vibrational corrections[15] calculated from the force constants[16] are listed in Table II, and the observed mean amplitudes are compared with the calculated amplitudes.

TABLE I. r_g Distances and r_α Angles of SPF$_3$[a].

r_g(S–P) = 1.866 ± 0.005 Å
r_g(P–F) = 1.538 ± 0.003 Å
r_g(F···F) = 2.346 ± 0.007 Å
r_g(S···F) = 2.922 ± 0.006 Å
∠F–P–F = 99.6 ± 0.3°
∠S–P–F = 117.9 ± 0.3°

[a] Uncertainties represent estimated limits of error.

TABLE II. Mean Amplitudes and Vibrational Corrections for SPF$_3$ (Å).

	l_{obs}[a]	l_{calc}[b]	d[c]
P–F	0.042 ± 0.003	0.0396	0.0024
S–P	0.042 ± 0.005	0.0386	0.0017
F–F	0.064 ± 0.007	0.0644	0.0020
S–F	0.071 ± 0.006	0.0684	0.0007

[a] Observed mean amplitudes. Uncertainties represent estimated limits of error. [b] Mean amplitudes calculated from force constants taken from ref. 16. [c] Vibrational corrections, $d = r_g - r_\alpha$, calculated from force constants.

The random errors σ_1 and σ_2 in the r_g distances and the r_α angles were estimated by use of their standard deviations and discrepancies among the parameters derived from different plates[14], respectively. Since the σ_1 and σ_2 values were comparable with each other, the larger of them was assumed to be the random error for each parameter. The systematic error in the scale factor was estimated to be ±0.06%. Uncertainties in the harmonic terms of the vibrational corrections were estimated to be negligible. Changes of ± 100% in the $\varkappa$ parameters for the bonded pairs and changes of $\pm 1.0 \times 10^{-6}$ Å^3 for the nonbonded pairs caused no significant systematic errors in the distances.

The effect of the sample impurity (SPF_2Cl) on the index of resolution was estimated to be about 1%, *i.e.*, about one-third of the experimental uncertainty of the index of resolution. The effect of electron scattering of the P–F and S–P pairs in SPF_2Cl seems to be the most important, because the P–F and S–P distances in SPF_2Cl are nearly equal to those in SPF_3. The P–F and S–P distances in SPF_2Cl were estimated from those in related compounds[6], and the effect of the pairs on the corresponding distances in SPF_3 were estimated to be about 0.0002 Å for each distances, *i.e.*, an order of magnitude smaller than the experimental error of each distance. The effect of the S–F pair in SPF_2Cl was also unimportant because the S–F distance is relatively large. The P–Cl pair in SPF_2Cl causes a "ghost" peak of about 2% of the peak height of P–F pair comparable to the noise level of the radial distribution curve. In addition to these estimates, the following experimental facts showed that the effect of the SPF_2Cl impurity was negligible: (i) the observed mean amplitudes, which can be affected by the presence of impurity, agree with the corresponding theoretical estimates within experimental error, as shown in Table II; (ii) a least squares analysis with four interatomic distances taken as independent parameters gave a consistent result with another analysis for the r(P–F), r(S–P) and ∠F–P–F parameters; (iii) the residuals in the radial distribution curve are within the estimated error level (Figure 2); (iv) the structural parameters derived from the diffraction intensities are consistent with the rotational constants determined by microwave spectroscopy.

The error limits quoted in Table I include 2.5 times the random errors plus the systematic errors estimated above. A typical error matrix is shown in Table III.

In order to examine the accuracy of the present structure, the rotational constants were calculated and compared with those determined by microwave spectroscopy[2]. The interatomic distances r_g were converted into the r_α distances by use of the vibrational corrections in Table II. The r_α parameters were extrapolated to zero Kelvin by a diatomic approximation for the bonded parameters and the temperature dependence of the angle parameters was ignored[15]. The rotational constants $B_\alpha{}^0$ calculated from the $r_\alpha{}^0$ parameters[15] are listed in Table IV, where the rotational constants B_0 for $^{32}SPF_3$, $^{33}SPF_3$ and $^{34}SPF_3$ are also given. The B_0 constants were transformed into the average rotational constants[17] B_z. The uncertainties in the B_z constants are those in the B_0 to B_z corrections, and the uncertainties in the $B_\alpha{}^0$ constants correspond to those of the r_g distances and the r_α angle quoted in Table I. The systematic errors originating from the r_α to $r_\alpha{}^0$ conversion are not included in the error limits of $B_\alpha{}^0$. The $B_\alpha{}^0$ and B_z constants shown in Table IV agree within the error limits of the former. The rotational constants were not used jointly in the analysis of diffraction intensities since, in the present case, a slight increase in the precision of the structural parameters is offset

TABLE IV. Rotational Constants for SPF_3 (MHz).[a]

	$B_0{}^b$	$B_z{}^c$	$B_\alpha{}^{0\,d}$
$^{32}SPF_3$	2657.63 (4)	2655.7 (2)	2654 (8)
$^{33}SPF_3$	2614.73 (4)	2612.9 (2)	2614 (8)
$^{34}SPF_3$	2579.77 (4)	2577.9 (2)	2576 (8)

[a] Uncertainties attached to the last significant digits are given in parentheses. [b] Observed rotational constants taken from ref. 2. [c] Average rotational constants calculated from B_0 with corrections for vibrational effects. The limits of error are estimated from the uncertainties in the quadratic force constants used for calculating the corrections. [d] Rotational constants calculated from $r_\alpha{}^0$ parameters determined in the present electron diffraction study. The systematic errors originating from r_α to $r_\alpha{}^0$ corrections are not included in the error limits.

TABLE III. Error Matrix for SPF_3.[a]

	$k_1{}^b$	$k_2{}^c$	r(S–P)	r(P–F)	∠F–P–F	l(P–F)	l(S–P)	l(F···F)	l(S···F)
k_1	127								
k_2	56	206							
r(S–P)	12	−27	11						
r(P–F)	−5	15	−3	5					
∠F–P–F	15	−33	9	−5	18				
l(P–F)	15	49	−7	4	−8	13			
l(S–P)	12	55	−8	4	−9	14	19		
l(F···F)	19	41	−4	3	−6	10	11	20	
l(S···F)	19	42	−5	3	−6	10	11	9	18

[a] Units ($\times 10^{-4}$) for the distances are Å, that for the angle is rad, those for the indices are dimensionsless. [b] Index of resolution for the long camera region. [c] Index of resolution for the short camera region.

by an additional systematic error introduced in the joint analysis.

Discussion

In the light of the structure of SPF_3, systematic variations in the structures of PX_3 and YPX_3 molecules summarized in ref. 6 can be re-evaluated. The experimental data[3–6, 18–24] of r(P–X), r(Y–P) and the bond angles are listed in Tables V–VII, respectively.

TABLE V. Observed and Calculated r_g(P–X) Distances (Å).

	Obs[a]	Calc[b]	Ref.
PF_3	1.570 ± 0.001	1.570	3
SPF_3	1.538 ± 0.003	1.538	c
OPF_3	1.524 ± 0.003	1.525	6
PCl_3	2.040 ± 0.001	2.040	4
$SPCl_3$	2.011 ± 0.003	2.008	6
$OPCl_3$	1.993 ± 0.003	1.995	6
PBr_3	2.220 ± 0.003	2.224	5
$SPBr_3$	d	2.192	–
$OPBr_3$	d	2.179	–
PI_3	d	2.476	–

[a] Observed r_g(P–X) distances taken from Refs. [b] Calculated from Eq. (1) with the following values of covalent radii (r) and electronegativities (E): $r_P = 1.10$, $r_F = 0.718$, $r_{Cl} = 0.994$, $r_{Br} = 1.140$, $r_I = 1.333$ Å; $E_F = 4.0$, $E_{Cl} = 3.0$, $E_{Br} = 2.8$, $E_S = 2.5$, $E_O = 3.5$ and E_Y for PX_3 are assumed to be zero. [c] Present study. [d] Accurate structures are not known.

TABLE VI. S–P and O–P Distances (Å).

	$YPCl_3$	YPF_3	$YP(CH_3)_3$
S–P	1.885 ± 0.005[a]	1.866 ± 0.005[b]	1.940 ± 0.002[c]
O–P	1.449 ± 0.005[a]	1.436 ± 0.006[a]	1.475 ± 0.002[c]

[a] r_g structure taken from ref. 6. [b] r_g structure determined in the present study. [c] r_a structure taken from ref. 23.

Phosphorus–Halogen Bond Lengths

The P–X (X = F, Cl) bond lengths change in accordance with Gillespie's valence shell electron pair repulsion (VSEPR) model[25–31]: for the P–Cl distances, $PCl_3 > SPCl_3 > OPCl_3$, and for the P–F distances, $PF_3 > SPF_3 > OPF_3$. The differences between r_g(P–Cl) and r_g(P–F) in PX_3, 0.470 ± 0.002 Å, in SPX_3, 0.473 ± 0.004 Å, and in OPX_3, 0.469 ± 0.004 Å, are equal to one another within their experimental error. This trend results in two parallel straight lines a and b illustrated in Figure 3. A similar diagram was presented in ref. 6 (Figure 6), but the curve corresponding to the present line b was appreciably deformed since a precise structure of SPF_3 was not available when the diagram was drawn.

TABLE VII. Bond Angles (r_α or r_z) of Group Vb Halides (deg).

	Obs[a]	Calc[b]	Ref.
NF_3	102.2 ± 0.3[c]	100.7	18
NCl_3	107.1 ± 0.5	102.9	19
PF_3	97.8 ± 0.2	97.5	3
SPF_3	99.6 ± 0.3	100.0	d
OPF_3	101.3 ± 0.2	101.0	6
PCl_3	100.3 ± 0.1[e]	99.8	4
$SPCl_3$	101.8 ± 0.2	102.3	6
$OPCl_3$	103.3 ± 0.2	103.3	6
PBr_3	101.0 ± 0.4	101.0	5
$SPBr_3$	f	103.5	–
$OPBr_3$	f	104.5	–
AsF_3	96.2 ± 0.2	96.5	20
$AsCl_3$	98.6 ± 0.4	98.7	20
$AsBr_3$	99.7 ± 0.3	99.9	24
SbF_3	f	94.6	–
$SbCl_3$	97.2 ± 0.9	96.9	21
$SbBr_3$	98.2 ± 0.6	98.1	22

[a] Observed angles taken from Refs. [b] Calculated from Eq. (2) with the following covalent radii (r): $r_N = 0.74$, $r_{As} = 1.22$ and $r_{Sb} = 1.43$ Å. See footnote b of Table V for the other r and electronegativities (E). [c] r_0 structure. [d] Present study. [e] r_a structure. [f] Accurate structures are not known.

The observed P–X distances are systematically shorter than the sum of their covalent radii[32, 33]. The difference, $(r_P + r_X) - r_g(\text{P–X})_{obs}$, versus the electronegativities of the X atoms (E_X)[33] are shown in Figure 4, where the covalent radii for phosphorus and halogen atoms are assumed to be 1.10 (r_P), 0.718 (r_F), 0.994 (r_{Cl}) and 1.140 Å (r_{Br}). The figure is a quantitative representation of the Stevenson–Schomaker correction[33] to the sum of covalent radii. The relations given in Figures 3 and 4 lead to the following empirical equation (in Å units),

$$r_g(\text{P–X}) = r_P + r_X - \{(0.194E_X + 0.013E_Y) - 0.528\} \quad (1)$$

where E_Y represents the electronegativity of the Y atoms, and the E_Y for PX_3 is assumed to be zero. The observed r_g(P–X) distances are compared in Table V with those calculated by use of Eq. (1). In almost all cases the latter values reproduce the former to within experimental error.

Oxygen–Phosphorus and Sulfur–Phosphorus Bond Lengths

The O–P and S–P distances in the fluorides are significantly shorter than those in the corresponding chlorides (Table VI). The differences between the r_g(S–P) and r_g(O–P) distances in YPF_3 and $YPCl_3$ molecules, 0.430 ± 0.007 Å and 0.436 ± 0.007 Å respectively, are nearly equal. The situation is also

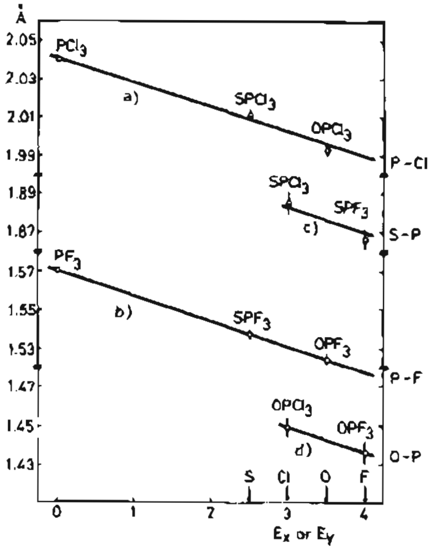

Figure 3. Variations of the P–X and Y–P bond lengths in YPX_3 with the electronegativities (E) of the Y and X atoms, respectively. Lines a, b, c and d represent the variations of the P–Cl, P–F, S–P and O–P bond lengths, respectively. For PX_3 the parameter E_Y is arbitrarily set equal to zero. The values of the electronegativities are listed in footnote b of Table V.

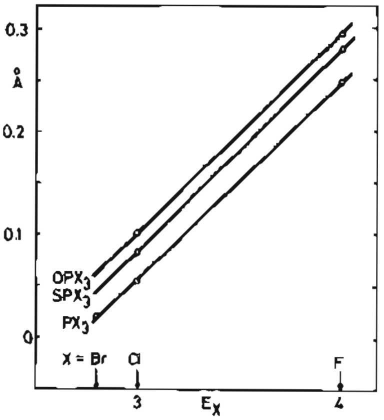

Figure 4. Variations of the differences between the sum of covalent radii (r_P+r_X) and the observed r_g(P–X) bond lengths with the electronegativities of the X atoms. The values of the covalent radii and the electronegativities are listed in footnote b of Table V.

illustrated in Figure 3 as two parallel straight lines c and d.

The O–P and S–P distances in the halides are significantly shorter than those in the corresponding trimethylphosphine compounds determined in the recent electron diffraction study of Hagen *et al.*[23] (Table VI), who discussed systematic variations in the Y–M bond distance (Y = O, S; M = P, As and Sb) in terms of bond polarities and force constants. The difference between r(S–P) and r(O–P) in $YP(CH_3)_3$ and that between r(S–As) and r(O–As) in $YAs(CH_3)_3$ are 0.465 ± 0.003 Å and 0.428 ± 0.004 Å, respectively.

Valence Angles in Phosphorus and Other Group Vb Atoms

The regular trends observed for the valence angles ∠X–M–X in MX_3 (M = N, P, As and Sb) are summarized[6,34] as follows:* (i) the valence angles decrease with the increasing atomic number of M; (ii) the valence angles in chlorides are significantly larger than those in the corresponding fluorides; (iii) coordination of an oxygen or sulfur atom to the lone pair of PX_3 makes the X–P–X angle increase, and the tendency is stronger for the oxygen atom than for the sulfur atom. The present investigation has confirmed that the above mentioned systematic trends (ii) and (iii) are also applicable to SPF_3.

Konaka and Kimura recently proposed[22] an empirical relation for the valence angles in YMX_3 expressed in terms of the electronegativities of the X, M and Y atoms. On the other hand, valence angles may also be represented by the following equation (in degrees):

$$\angle X\text{–}M\text{–}X = 101.3+8.2r_X-8.8r_M+E_Y \qquad (2)$$

where the covalent radii[32] are assumed to be 0.74 (r_N), 1.22 (r_{As}) and 1.43 (r_{Sb}). The observed angles are compared in Table VII with the angles calculated by Eq. (2). The agreement is almost within experimental error except for nitrogen compounds.

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* These features were discussed in terms of the VSEPR model in ref. 6. Recently, Nakatsuji[35–37] has developed the force concept on the basis of the Hellmann–Feynman theorem[38,39]. His electrostatic force theory is consistent with the observed trends and enables an intuitive and qualitative interpretation of molecular shapes.

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