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Molecular Structure of Phosphorus Trifluoride Studied by Gas Electron Diffraction

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Received September 9, 1968

The interatomic distances and the mean amplitudes for PF_3 have been determined by the sector–microphotometer method of gas electron diffraction to be $r_g(\text{P–F}) = 1.5700 \pm 0.0012$ Å, $r_g(\text{F} \cdots \text{F}) = 2.3643 \pm 0.0028$ Å, $l(\text{P–F}) = 0.0395 \pm 0.0025$ Å, and $l(\text{F} \cdots \text{F}) = 0.0653 \pm 0.0029$ Å. The average structure in the ground vibrational state has been calculated from the interatomic distances (r_g) by making correction for the effect of atomic displacements perpendicular to the equilibrium bond directions and for the centrifugal distortion. This average structure is in good correspondence with the rotational constant B_z calculated from the rotational constant B_0 obtained by microwave spectroscopy. The bond angle for PF_3, $\theta_\alpha(\text{F–P–F}) = 97.8 \pm 0.2°$, is found to be the smallest in the series of phosphorus trihalides reported so far, and, hence, one of the subrules proposed by Gillespie has to be modified.

Introduction

There have been appreciable differences among the structures of phosphorus trifluoride given in the literature. The structure was first reported to be $r(\text{P–F}) = 1.52$ Å and $\theta(\text{F–P–F}) = 104°$ by Brockway and his coworkers,[1,2] who used the visual method of electron diffraction, while the angle was later claimed to be much smaller ($r(\text{P–F}) = 1.537 \pm 0.04$ Å and $\theta(\text{F–P–F}) = 98.2 \pm 0.6°$) according to the sector study of Hersh.[3] Neither structure, however, was consistent with the rotational constant B_0 obtained by microwave spectroscopy.[4,5]

On the other hand, it has been difficult to determine the parameters directly by spectroscopic data alone, because both phosphorus and fluorine have single stable isotopes. Accordingly, the FPF angle had to be assumed in order to derive the P–F distance from the B_0 constant obtained by Gilliam, Edwards, and Gordy.[5] The FPF angles of 104, 102, 100, and 98° led to the P–F distances of 1.546, 1.551, 1.56, and 1.562 Å, respectively.[5–8] (Mirri, *et al.*,[4] pointed out that the P–F distance of 1.535 Å, given by Williams, *et al.*,[7] from the assumed FPF angle of 100°, was incorrect.)

In terms of the indirect evaluation of molecular geometry, Mirri[8] estimated the bond angle from the Coriolis coupling constant ζ_4 and the force constants using Meal and Polo's relation.[9] The upper limit for the estimated bond angle (98°) was smaller than that assumed in earlier studies[4,6,10] (102°); it was not only in agreement with Hersh's diffraction value[3] but also indicative of a force field, which brought the Coriolis coupling constants and the centrifugal distortion constants into good consistency.

Various structures reported so far are summarized in Figure 1. As has been discussed extensively by Gillespie,[11–13] Bartell,[14,15] and others, the structure of PF_3 is of basic importance in the stereochemistry of inorganic molecules. Accordingly, the present study has been undertaken to determine a more accurate structure by gas electron diffraction.

Experimental Section

A sample of PF_3 was prepared by the method cited by Brauer:[16] $PCl_3 + 3HF \rightarrow PF_3 + 3HCl$. The reaction vessels were made of brass. The system was filled with nitrogen gas and the product gas was sprayed on ice-cold water, into which hydrogen chloride was absorbed. The crude product trapped by liquid nitrogen contained a small amount of hydrogen chloride and silicon tetrafluoride. They were removed by another spray onto ice-cold water, which, however, caused considerable decomposition of PF_3. Upon redistillation under vacuum, no impurity band was observed in the infrared spectrum.

Electron diffraction photographs were taken with an apparatus[17,18] equipped with an r^3 sector at the camera lengths of 10.778 ± 0.002 and 24.322 ± 0.002 cm. The electron wavelength, 0.05969 Å, was calibrated with reference to the $r_a(\text{C=O})$ bond distance (1.1646 Å) of carbon dioxide measured under the same experimental condition. The gas stored in a 2-l. flask with a pressure of about 90 Torr at 22° was led into the diffraction chamber through a nozzle 0.2 mm in diameter. The pressure in the apparatus was less than 1×10^{-4} Torr during photographic exposure. Photographs were recorded on Fuji Process Hard plates with exposure times of about 30 sec and were developed at 20° for 5 min with ED-131 developer diluted twice.

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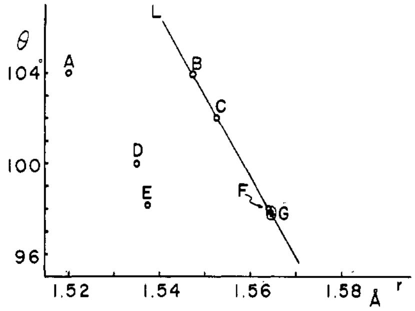

Figure 1.—Structural parameters for PF_3 (r for the P–F distance and θ for the F–P–F angle): (A) Pauling, *et al.*, ED;[2] (B) Gilliam, *et al.*, MW;[5] (C) Kisliuk, MW;[6] (D) Williams, *et al.*, MW;[7] (E) Hersh, ED;[3] (F) Mirri, MW;[8] (G) present study, ED (ED, electron diffraction; MW, microwave spectroscopy). A relation set by the rotational constant[4] B_z is shown by the line L.

Optical densities were measured by means of a microphotometer and an integrating digital voltmeter across the diameter of the plate with a regular interval of $\Delta q = 1$.[19] The optical densities (0.18–0.57) were assumed to be proportional to the electron intensities. Intensity data taken from four short-distance plates and two long-distance plates were analyzed by a standard least-squares method with a diagonal weight matrix[20] for the q values 15–120 using the elastic and inelastic scattering factors taken from the recent literature.[21–23] The observed and the best-fit molecular intensities are shown in Figure 2, and the corresponding error matrix is given in Table I.[24]

TABLE I

ERROR MATRIX[a]

	r(P–F)	r(F···F)	l(P–F)	l(F···F)	k
r(P–F)	0.0004	0.0000	−0.0000	0.0001	0.0001
r(F···F)		0.0017	0.0001	−0.0001	0.0004
l(P–F)			0.0007	0.0004	0.0022
l(F···F)				0.0015	0.0021
k					0.0093

[a] Units for the distance r_a and the mean amplitude are Å, while the index of resolution k (average 0.84) is dimensionless. Elements of the matrix are given by $\sigma_{ij} = \operatorname{sgn}[(B^{-1})_{ij}]\,[|(B^{-1})_{ij}|\cdot V^*PV/(n-m)]^{1/2}$, where the notations correspond to those by O. Bastiansen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, **27**, 1311 (1957). The diagonal element σ_{ii} represents the random standard error for the parameter i.

The r_a distances of P–F and F···F and their mean amplitudes derived from this analysis are listed in Table II. The limits of uncertainty (2.5σ) were estimated from the internal consistency and the reproducibility of the results including the consideration of systematic errors, among which the error in the scale factor was the only significant one for the distance parameters, while for the mean amplitudes those due to extraneous scattering and the correlation with the index of resolution were the most important contributors. The errors in the asymmetry parameters κ (κ_{P-F} and κ_{F-F} assumed to be 7×10^{-7} Å^3 and zero, respectively) were insignificant.

TABLE II

STRUCTURAL PARAMETERS AND MEAN AMPLITUDES FROM ELECTRON DIFFRACTION[a]

	P–F, Å	F···F, Å	θ(F–P–F), deg
r_a	$1.568_9 \pm 0.001_2$	$2.362_4 \pm 0.002_8$	(97.7)
r_g	$1.570_0 \pm 0.001_2$	$2.364_3 \pm 0.002_8$	(97.8)
r_α	$1.564_4 \pm 0.001_2$	$2.357_8 \pm 0.002_8$	97.8 ± 0.2
$r_\alpha{}^0$	$1.564_7 \pm 0.001_2$	2.358 ± 0.006[b]	97.8[b]
l_{obsd}	$0.039_5 \pm 0.002_5$	$0.065_3 \pm 0.002_9$	
l_{calcd}	0.041_2	0.069_8	

[a] See ref 17 for various definitions of the structure of a molecule exerting vibration and rotation. Convenient measures of structure may be "the thermal-average values of interatomic distances," r_g, and "the angles measured with regard to the average positions of atoms," θ_α and $\theta_\alpha{}^0$ for thermal and zero-point averages, respectively. [b] Estimated; see text.

The thermal averages of the instantaneous internuclear distances r_g were calculated by[25]

$$r_g = r_a + (l^2/r_a) \tag{1}$$

The mean amplitudes are compared in Table II with those calculated from the quadratic force constants which were determined by Mirri[8] from vibrational frequencies, centrifugal distortion, and Coriolis coupling constants. The agreement is within the errors in the experimental and theoretical values, the latter being estimated to be about ±0.003 Å. Similar values for the amplitudes have been calculated by several authors.[26–28]

Molecular Structure

Average Structure ($r_\alpha{}^0$) from Electron Diffraction.—In order to compare the structure determined in the present analysis with spectroscopic results, the zero-point average distances[29] ($r_\alpha{}^0$) were derived from r_g by the use of the quadratic force constants. Following the usual steps, the r_α and $r_\alpha{}^0$ distances were calculated by[17]

$$r_\alpha = r_g - [(\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle)/2r] - \delta r \tag{2}$$

$$r_\alpha{}^0(\text{P–F}) = \lim_{T \to 0°\text{K}} r_\alpha(\text{P–F}) = r_\alpha(\text{P–F}) - \Delta\langle \Delta z \rangle \tag{3}$$

where

$$\begin{aligned} \Delta\langle \Delta z \rangle &\equiv \Delta z \text{ (room temperature)} - \langle \Delta z \rangle (0°\text{K}) \\ &= {}^3/_2 a \Delta \langle \Delta z^2 \rangle - [\Delta(\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle)/2r] \end{aligned} \tag{4}$$

The parameter a characterizing the anharmonicity of the P–F bond stretching vibration was assumed to be equal to that of the PF diatomic molecule,[30] 1.89 Å^{-1}. Minor corrections for the centrifugal distortion, δr,

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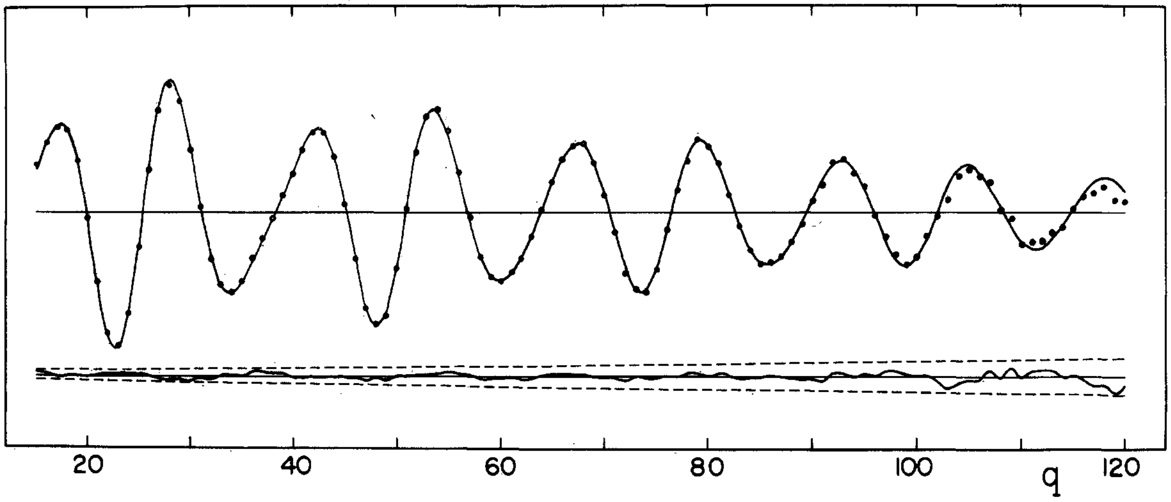

Figure 2.—Reduced molecular intensity $qM(q)$ for PF_3. The observed and the best-fit values from one of the photographic plates are shown by dots and a solid curve, respectively. The lower solid and broken curves represent the residual and the error in the $qM(q)$ due to the relative error of 1×10^{-3} in the original photocurrent, respectively.

were calculated by the method of Iwasaki and Hedberg[31] to be 4×10^{-4} Å for P–F and F · · · F.

The zero-point average angle, θ_α^0, was set equal to the temperature-average angle, θ_α, for the following reason. It seems plausible, as a first-order approximation, to assume a linear and additive relation in regard to the angle corresponding to the average positions of atoms for a certain vibrational state $v(v_1, v_2, v_3, v_4)$, designated as

$$\theta_z^v = \theta_e + \sum_{i=1} \beta_i(v_i + d_i/2) + \ldots \qquad (5)$$

where d_i represents degeneracy. Since the θ_α angle is essentially equal to the Boltzmann average of θ_z^v, it follows that

$$\theta_\alpha \approx \sum_v \theta_z^v w_v(T) \approx \theta_e + \sum_i \beta_i d_i T_i/2 \qquad (6)$$

where

$$w_v(T) = \exp(-E_{\text{vib}}(v)/kT)/\sum_v \exp(-E_{\text{vib}}/kT) \qquad (7)$$

and

$$T_i = \coth\,(hc\nu_i/2kT) \qquad (8)$$

Accordingly, the difference is shown to be

$$\theta_\alpha - \theta_\alpha^0 \approx \sum_i \beta_i d_i(T_i - 1)/2 \qquad (9)$$

One may further assume that substantial contributions come from bending modes ν_2 (487 cm^{-1}) and ν_4 (344 cm^{-1})[32] and that the orders of magnitude of β_2 and β_4 are equal. Then the difference may be estimated in terms of that between the zero-point average and equilibrium angles.

$$\theta_\alpha - \theta_\alpha^0 \approx 0.37(\theta_z - \theta_e) \qquad (10)$$

While the $\theta_z - \theta_e$ for PF_3 is unknown, it can be estimated from analogous molecules to be only a small fraction of 1°. (For example, the corresponding differences are +6′ and +2′ for OF_2 and SO_2, respectively.[33]) Consequently, it seems plausible to regard the θ_α^0 as equal to θ_α to within the experimental uncertainty of the latter (±0.2°). The r_α^0(F · · ·F) distance was derived from the r_α^0(P–F) distance and the θ_α^0 angle.

Various average distances and angles are listed in Table II.

Rotational Constant from Spectroscopy.—The rotational constant B_z, which corresponds to the average structure in the ground vibrational state, was calculated from the rotational constant for the ground vibrational state B_0 by correcting for rotation–vibration interactions.[17] The difference between B_z and B_0 was found to be -5.70×10^{-3} cm^{-1}. Thus the rotational constant B_0 (7819.99 MHz) obtained by Mirri, *et al.*,[4] gave a B_z constant of 7802.9 MHz.

Average Structure.—The rotational constant B_z sets a relation between the r_z(P–F) distance and the θ_z(F–P–F) angle. This is illustrated in Figure 1 as a nearly straight line L. No unique r_z structure can be obtained from spectroscopy alone since the other rotational constant C_z is yet unknown.

On the other hand, the r_α^0 structure, which should be essentially equivalent to the spectroscopic r_z structure,[17] derived from electron diffraction is shown by G with an estimated uncertainty indicated by an ellipse. Since the point G is very closely on the line L, the result of electron diffraction is consistent with the rotational constant B_z. This consistency may be restated from a slightly different standpoint. The θ_z angle can be obtained from B_z based on spectroscopy and the r_α^0(P–F) distance based on electron diffraction. The resulting θ_z, 97.9 ± 0.3°, agrees with θ_α, 97.8 ± 0.2°, within experimental uncertainties, and, hence, the above-mentioned

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estimation, $\theta_\alpha^0 \approx \theta_\alpha$, within a few tenths of 1°, is justified.

Discussion

In the light of the structural parameters determined in the present investigation, the long-standing confusion in regard to the PF_3 structure may be elucidated in the following way.

(a) The initial study of Brockway and Wall[1] by means of visual intensity measurements (r(P–F) = 1.65 Å and θ(F–P–F) = 99°) estimated the structure nearly correctly. However, a subsequent study of Pauling and Brockway[2] by the radial distribution method gave a different set of parameters including much larger errors (r = 1.47 Å and θ = 110°). Unfortunately, the latter authors recommended average values of the above two with equal weights (r = 1.52 Å and θ = 104°). Similar situations are encountered in the structures of PCl_3, $AsCl_3$, and Cl_2O.

(b) Hersh's study,[3] on the other hand, estimated the bond angle correctly, whereas an appreciable systematic error (about 2%) involved in the scale factor caused the bond distance to appear unreasonably short. This is probably the reason for a similar systematic shortening in the P–F bond distances of PF_5 studied contemporaneously by Hersh in comparison with the corresponding distances reported more recently by Hansen and Bartell.[14]

(c) The P–F distance of 1.535 Å, which was presented by Williams, *et al.*,[7] as derived from the rotational constant B_0 by assuming the bond angle of 100° and which has frequently been referred to,[34] is in fact incompatible with the rotational constant, as first pointed out by Mirri.[4] This value was compared by Hansen and Bartell[14] with the axial and equatorial P–F distances in PF_5, where the latter bond (1.534 Å) was thought to be "surprisingly close to the P–F bond in PF_3." It turns out, however, that a more correct P–F bond distance in PF_3 (1.570 Å) is apparently much closer to the *axial* P–F distance (1.577 Å). The P–F bond of PF_3BH_3 measured by Kuczkowski and Lide[35] is shorter than that of PF_3 by about 0.03 Å, while the P–F bond in HPF_2[36] is longer by 0.01 Å. The latter increase has been discussed by Kuczkowski,[36] although he cited Hersh's value for the P–F bond in PF_3.

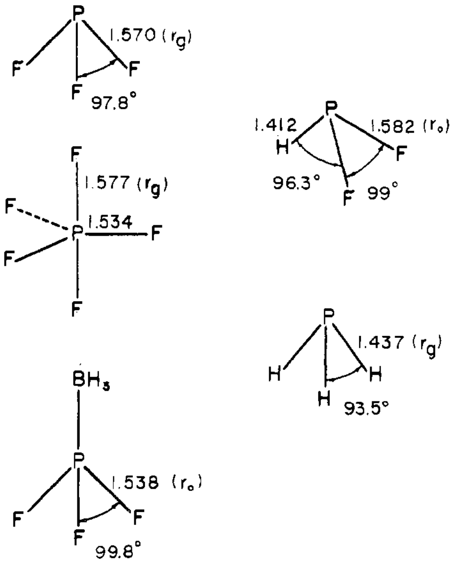

Figure 3.—Comparison of the structures of phosphorus–fluorine compounds. All bond lengths are in Å.

The above differences in the P–F bond distances for related molecules (Figure 3) may be understood systematically in terms of the structural characteristics of PF_5, CH_3PF_4, and $(CH_3)_2PF_3$, as discussed by Bartell and Hansen[15] and by Gillespie.[12,37] The P–F bond distance in PF_3BH_3 should be shorter than that in PF_3 as a result of the diminution of the lone-pair repulsion by BH_3 coordination, which should cause an increase in the FPF angle at the same time. A similar shortening has been observed for the equatorial P–F bond in PF_5, where the unshared pair in PF_3 is replaced by two axial P–F bonds. As for HPF_2, substitution of a fluorine atom in PF_3 by hydrogen should increase the remaining P–F bonds, since the repulsion of the P–H bonding electron pair is larger than that of the P–F pair because of the lower electronegativity of hydrogen in comparison with that of fluorine. A similar relation holds for the P–H bond distances of PH_3[38] and HPF_2. Table III lists the bond angles in group V trihalides, which increase from fluorides to iodides and decrease from nitrogen to antimony compounds.[39–51] These systematic changes in bond angles have been accounted for by Gillespie[11–13] on the basis of his valence-shell electron-pair repulsion theory. In his table, however, the angles of 104 and 102° for PF_3 and AsF_3, respectively, were cited, and, hence, it seemed as if phosphorus and arsenic trifluorides had shown anomalously large angles. In order to explain this behavior, Gillespie invoked a subrule (postulate 5 in ref 11) assuming a

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TABLE III

BOND ANGLES IN GROUP V TRIHALIDES[a]

Halide	N		P		As		Sb	
	Angle, deg	Method	Angle, deg	Method	Angle, deg	Method	Angle, deg	Method
F	102.17 ± 0.04	MW[39]	97.8 ± 0.2	ED[b]	96.1 ± 0.2	ED[40]	(88)	XD[42]
					95.8 ± 0.7	ED[41]		
Cl	...		100.27 ± 0.09	ED[43]	98.7 ± 0.3	ED[45]	99.5 ± 1.5	MW[6]
			100.1	MW[44]	98.4	MW[44]		
Br	...		(101.5)	ED[46]	99.66 ± 0.26	ED[47]	(97)	ED[48 49]
I	...		(102)	ED[49]	100.2 ± 0.4	ED[50]	99.1 ± 2	ED[51]

[a] Abbreviations: ED, electron diffraction; MW, microwave spectroscopy; XD, X-ray diffraction (crystal). [b] Present study.

considerable contribution of double-bond character for the fluorides; according to his argument,[12] the above anomaly may be attributed to "the unshared pairs of fluorine having a strong tendency to delocalize into the incomplete shell of the central atom, thereby giving the bonds some double-bond character and, therefore, increasing the size of the bonding orbitals and hence the bond angle." From the present result for PF_3, along with the recent results for AsF_3 by Bartell and Clippard[40] and by Konaka and Kimura,[41] their bond angles fit in regular series, so that the rules governing the bond angles in group V trihalides can be simplified.

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The Characterization of Metal–Oxygen Bridge Systems[1]

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Received October 17, 1968

The vibrational spectra of various types of metal–oxygen bridge systems are assigned by normal-coordinate analysis and discussed in terms of geometry. The results of this analysis are shown to be a powerful tool for the characterization of metal–oxygen bridged complexes. The synthesis of a new dioxo-bridged molybdenum(V) complex is described and a structure is proposed on the basis of its infrared spectrum.

Introduction

In the course of our work on molybdenum(V) chemistry we have frequently been faced with the problem of distinguishing between the several types of oxygen-bridged dimers that occur in this system.[2–4] Infrared spectral measurements were thought to be the solution to this problem.

However, the ir spectral characteristics of metal-to-oxygen multiply bonded systems have been discussed in detail only for those compounds in which the oxo ligand is in a terminal position.[5–7] An abbreviated analysis of monooxo bridged systems, both linear and bent, was discussed by Cotton and Wing,[6] and Hewkin and Griffith[8] have tabulated a considerable amount of infrared and Raman data for compounds containing a single oxo bridge.

It is the purpose of this paper to present a general analysis of the mono- and dioxobridged systems and to illustrate how infrared spectra in the bridge metal–oxygen region (*ca.* 850–200 cm^{-1}) can be used to predict structures. Of prime importance in a consideration of these bridge systems is the fact that the vibrational frequencies are strongly sensitive to the M–O–M bond angle. It is in fact this angular dependence which permits one to distinguish between mono- and dioxo-bridged systems.

Normal-Coordinate Analyses and Angular Dependence of Frequencies

The general monooxo-bridged metal dimer, treated for simplicity as a three-body system, is bent at an angle ϕ and exhibits two bridge vibrations. Such a system can be characterized by a two-constant potential field. The first constant pertains to the metal–oxygen

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[1] Supported in part by the National Science Foundation under Grant GP-8055.

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