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Electron Diffraction Study of the Structure of PF_5[1a]

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The molecule PF_5 was found to be a trigonal bipyramid, in agreement with previous studies, but the greater resolving power in the present analysis revealed a significant difference between lengths of axial and equatorial bonds. Observed P–F bond lengths were $r_g(\text{eq}) = 1.534 \pm 0.004$ Å. and $r_g(\text{ax}) = 1.577 \pm 0.005$ Å. The P–F average length was 1.551 ± 0.001 Å. Root-mean-square l_g amplitudes found with the aid of an extension of Badger's rule were $(\text{P–F}_{\text{eq}}) = 0.041 \pm 0.002$ Å., $(\text{P–F}_{\text{ax}}) = 0.043 \pm 0.002$ Å., $(\text{F}_{\text{ax}}\cdots\text{F}_{\text{eq}}) = 0.059 \pm 0.003$ Å., $(\text{F}_{\text{eq}}\cdots\text{F}_{\text{eq}}) = 0.081 \pm 0.008$ Å., and $(\text{F}_{\text{ax}}\cdots\text{F}_{\text{ax}}) = 0.055 \pm 0.018$ Å. Results are consistent with a bonding scheme formulated several years ago by Rundle.

Introduction

The structure of phosphorus pentafluoride and the proper description of its bonding have been the subjects of a certain amount of controversy ever since the substance was discovered. Electron diffraction studies made over 25 years ago suggested that gaseous PF_5 molecules are trigonal bipyramids with all P–F bond distances equal in length.[2a] The nuclear magnetic resonance spectrum shows only one fluorine resonance,[2b] indicating that if nonequivalent sites exist, they are scrambled by molecular inversions during the long time scale of n.m.r. measurements.[3] Vibrational spectra are compatible with the electron diffraction D_{3h} symmetry.[4]

An electron diffraction analysis of the related compound PCl_5 has shown that it is also a trigonal bipyramid but that its axial bonds are distinctly longer than its equatorial bonds.[5] Such a difference between axial and equatorial bond lengths is a necessary consequence of the bonding scheme formulated by Rundle to describe interhalogen, rare gas, and analogous compounds.[6] It seemed worthwhile, then, to reinvestigate PF_5 by modern techniques to clarify its structure and to test Rundle's predictions about bond lengths.

Experimental

Experimental and interpretational procedures were similar to those published elsewhere.[7] Diffraction patterns were recorded on Kodak process plates. Intensity readings which were leveled through division by theoretical atomic intensities are plotted in Figure 1. The experimental radial distribution curve is shown in Figure 2.

Calibrations of the response of the photographic emulsions gave a value of about -0.1 for the constant c defined by[8]

$$E/D = (1 + cD)$$

Since the implied deviation from linearity is of a different sign and magnitude than we have obtained in the past, we accept the result with some reservation. Consequently, we have less confidence than usual in the derived value of the index of resolution, which depends on the assumed value of c. The index was unity to within experimental error. Although derived values of internuclear distances do not depend upon the assumed index of resolution, derived amplitudes of vibration may be sensitive to it. In the present case, however, independent analyses run at values of c differing by 0.1 gave almost identical distances and amplitudes.

The gas sample used in the determination was obtained through the courtesy of Dr. E. L. Muetterties of E. I. du Pont de Nemours and Co. Infrared spectra disclosed small amounts of POF_3 and PF_3. Although SiF_4 could not be detected in the infrared spectrum due to its small percentage and the masking of its main line by a line of PF_5, its presence in the sample had been reported by the suppliers. Impurities of POF_3, PF_3, and SiF_4 were estimated to be 1.5, 2, and 1%, respectively.

Corrections for the impurities were made by subtracting from the experimental intensity that portion which resulted from diffraction by POF_3, PF_3, and SiF_4. Estimates of these values were calculated from theoretical expressions for the intensities. Corrected experimental intensities were then used to compute the PF_5 radial distribution function.

Molecular parameters were obtained from the radial distribution curve by means of a new least-squares computer program due to Boates.[9] This program imposes constraints upon the internuclear distance parameters, r_g, requiring them to conform to certain geometric prerequisites. In contrast to our previous analyses in which all distances were fitted independently, the present analysis ensures that geometric consistency is maintained at all stages by allowing only a set of fully independent structural parameters to vary. The present radial distribution analysis essentially parallels the constrained intensity analysis of Hedberg, *et al.*,[10] although the computational technique for maintaining geometric consistency is quite different.

Corrections are introduced into the constrained analysis for "Bastiansen–Morino shrinkage effects"[11] in cases where the magnitudes are known or can be estimated. In the present study the shrinkages were estimated roughly from calculations by

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(1) (a) This work was performed under contract with the Atomic Energy Commission. Contribution No. 1743. Numerical electron intensity data have been deposited as Document No. 8582 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting \$1.25 for photoprints, or \$1.25 for 35-mm. microfilms. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress. (b) Author to whom correspondence concerning reprints should be addressed at the Department of Chemistry, University of Michigan, Ann Arbor, Mich.

(2) (a) H. Braune and P. Pinnow, *Z. physik. Chem.*, **B35**, 239 (1937); L. O. Brockway and J. Y. Beach, *J. Am. Chem. Soc.*, **60**, 1836 (1938); (b) H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

(3) S. Berry, *ibid.*, **32**, 933 (1960).

(4) J. E. Griffiths, R. P. Carter, and R. R. Holmes, *ibid.*, **41**, 863 (1964).

(5) M. Rouault, *Ann. Phys.*, **14**, 78 (1940).

(6) R. E. Rundle, *Acta Cryst.*, **14**, 585 (1961); *Rec. Chem. Progr.*, **23**, 195 (1962); *J. Am. Chem. Soc.*, **85**, 112 (1963); *Survey Progr. Chem.*, **1**, 81 (1963).

(7) L. O. Brockway and L. S. Bartell, *Rev. Sci. Instr.*, **25**, 569 (1954); R. A. Bonham and L. S. Bartell, *J. Chem. Phys.*, **31**, 702 (1959); L. S. Bartell, L. O. Brockway, and R. Schwendeman, *ibid.*, **23**, 1854 (1955).

(8) L. S. Bartell, K. Kuchitsu, and R. J. deNeui, *ibid.*, **35**, 1211 (1961).

(9) T. L. Boates and L. S. Bartell, to be published.

(10) K. Hedberg and M. Iwasaki, *Acta Cryst.*, **17**, 529 (1964).

(11) O. Bastiansen and M. Traetteberg, *ibid.*, **13**, 1108 (1960); Y. Morino, *ibid.*, **13**, 1107 (1960); Y. Morino, S. J. Cyvin, K. Kuchitsu, and T. Iijima, *J. Chem. Phys.*, **36**, 1109 (1962).

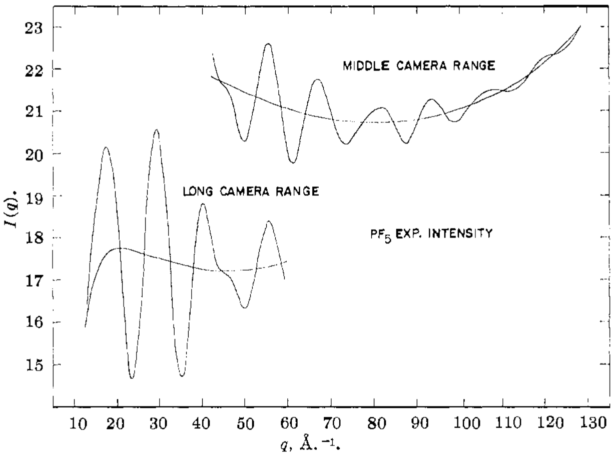

Figure 1.—A plot of the experimental total intensity and background functions of PF_5 for long and middle camera ranges.

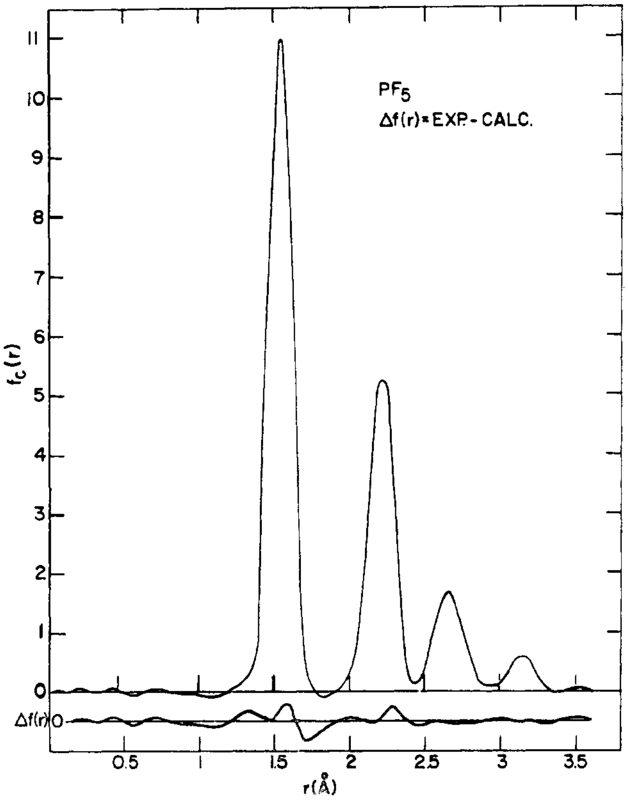

Figure 2.—A plot of the experimental radial distribution function of PF_5. The lower curve is a plot of the difference between the experimental and calculated radial distribution functions.

Meisingseth and Cyvin[12] on octahedral fluorides. The values used were 0.0007 Å. for $F_{ax}\cdots F_{eq}$, 0.0025 Å. for $F_{ax}\cdots F_{ax}$, and 0.006 Å. for $F_{eq}\cdots F_{eq}$.

The positions and areas of the four well-resolved peaks in the experimental radial distribution function are in excellent accord with a trigonal bipyramidal structure. They are inconsistent with the structure of a tetragonal pyramid. A rigid PF_5 trigonal bipyramid with axial and equatorial bonds of unequal length would possess five distinct internuclear distances. Thermal amplitudes of vibration in the actual molecule, however, cause the axial and equatorial distributions to overlap so severely that it is not feasible to determine the difference $[r_g(\text{ax}) - r_g(\text{eq})]$ from the unresolved P–F peak alone. Despite this difficulty the centers of gravity of the components can be resolved. Since the four observed peaks depend upon only two distance parameters, the analysis with geometric constraints readily converges to a solution containing distinct axial and equatorial mean bond lengths.

TABLE I

STRUCTURAL PARAMETERS AND ESTIMATED STANDARD ERRORS FOR PF_5

	$r_g(0)$, Å.	l_g, Å.
P–F (mean dist.)	$1.551 \pm 0.001_1$	
$P{-}F_{eq}$	$1.534 \pm 0.003_7$	0.041 ± 0.002
$P{-}F_{ax}$	$1.577 \pm 0.005_0$	0.043 ± 0.002
$F_{ax}\cdots F_{eq}$	$2.199 \pm 0.002_4$	0.059 ± 0.003
$F_{eq}\cdots F_{eq}$	$2.656 \pm 0.008_7$	0.081 ± 0.008
$F_{ax}\cdots F_{ax}$	$3.152 \pm 0.019_2$	0.055 ± 0.018

$(P{-}F_{ax}) - (P{-}F_{eq}) = 0.043 \pm 0.008$ Å.

In determining the amplitudes of vibration of the axial and equatorial P–F components, it is again not possible to establish values from the single P–F peak. Amplitudes were therefore determined by assuming that the slightly larger axial bond has an amplitude 0.002 Å. greater than that of the equatorial bond. This difference was estimated as explained elsewhere[13] by combining an expression for mean amplitudes of diatomic molecules with Badger's rule,[14] which relates force constants to bond length. The shift Δl in amplitude attending a small shift Δr in bond length can be expressed as

$$\Delta l = (3/4)[l/(r - \delta)]\Delta r$$

where δ is a Badger's rule constant equal to 0.9 Å. for P–F bonds. This relationship was observed to hold reasonably well in comparisons of bridge and terminal bonds in B_2H_6 and B_2D_6.[13] It is likely to be followed even more accurately in PF_5, where the two types of bonds compared are more similar to each other.

Results and Discussion

The structural parameters for PF_5 obtained in this investigation are given in Table I. It is confirmed that the molecule is a trigonal bipyramid. The equatorial bonds (1.534 Å.) are surprisingly close in length to the 1.53_5 Å. bonds observed in PF_3.[15] All bonds are distinctly shorter than 1.67 Å., the value given by the Pauling–Schomaker–Stevenson rule for lengths of P–F single bonds.[16]

Of most interest is the observation that the axial P–F bond is longer than the equatorial bond by about 0.043 Å. This result agrees quite closely with the unpublished finding of Brockway and Hersh, who recently made an independent electron diffraction study.[17] The axial–equatorial difference is smaller than the difference of 0.15 ± 0.06 Å. reported by Rouault for PCl_5.[5] It is also smaller than the analogous differences found in SF_4[18] and ClF_3.[19] It is in the direction predicted by Rundle's scheme and comparable in magnitude to the value of 0.056 Å. suggested by the simplest counting of bonds if s and p orbitals are used but d orbitals are neglected. A more detailed discussion of these points will be given in the following paper on the structure and bonding of the compounds $PF_{5-n}(CH_3)_n$.[20]

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(12) E. Meisingseth and S. J. Cyvin, *Acta Chem. Scand.*, **16**, 2452 (1962); *ibid.*, **17**, 1805 (1963).

(13) L. S. Bartell and B. L. Carroll, *J. Chem. Phys.*, **42**, 1135 (1965).

(14) R. M. Badger, *ibid.*, **2**, 128 (1934).

(15) Q. Williams, J. Sheridan, and W. Gordy, *ibid.*, **20**, 164 (1952).

(16) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 228.

(17) L. O. Brockway and O. Hersh, private communication.

(18) W. M. Tolles and W. D. Gwinn, *J. Chem. Phys.*, **36**, 1119 (1962).

(19) R. D. Burbank and F. N. Bensey, *ibid.*, **21**, 602 (1953); D. F. Smith, *ibid.*, **21**, 609 (1953).

(20) L. S. Bartell and K. W. Hansen, *Inorg. Chem.*, **4**, 1777 (1965).