

MOLECULAR STRUCTURE OF $(\text{CH}_3)_3\text{PF}_2$ AN ELECTRON DIFFRACTION STUDY OF AN ANALOGUE OF ArF_2

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ABSTRACT

The molecule $(\text{CH}_3)_3\text{PF}_2$ is a trigonal bipyramid with freely rotating methyl groups at the equatorial sites. The principal structural parameters and estimated standard deviations are $r_g(\text{PF}) = 1.685(1) \text{ \AA}$, $r_g(\text{PC}) = 1.813(1) \text{ \AA}$, and $r(\text{CH}) = 1.114(6) \text{ \AA}$. Amplitudes of vibration were also determined. This investigation completes a study of the series $(\text{CH}_3)_n\text{PF}_{5-n}$, $0 \leq n \leq 3$, and $(\text{CH}_3)_3\text{PF}_2$ corresponds to the hypothetical molecule ArF_2 in the closely related series PF_5 , SF_4 , ClF_3 and ArF_2 . The stereochemistries and trends in structure parameters in both series are well accounted for by the Gillespie-Nyholm theory. A linear extrapolation suggests a bond length of 1.76 \AA for argon difluoride.

INTRODUCTION

Trigonal bipyramids continue to be popular subjects for investigation in studies of structure and intramolecular motions¹. As ambiguities in vibrational assignments are resolved² and as detailed molecular structures become available, the Valence-Shell-Electron-Pair Repulsion (VSEPR) model of Gillespie and Nyholm³ emerges as a simple and useful scheme to account for force fields, stereochemistry, and trends in bond lengths and bond angles in complexes not involving transition metals²⁻⁸. Consistent with this idea, it has been noted⁵ that structural features in the series PF_5 , CH_3PF_4 and $(\text{CH}_3)_2\text{PF}_3$ bear a striking similarity to those in the series PF_5 , SF_4 and ClF_3 . It was therefore thought worthwhile to proceed one step further to examine $(\text{CH}_3)_3\text{PF}_2$ which is formally analogous to the interesting hypothetical molecule ArF_2 (or the known molecule XeF_2). The scope of the present investigation is to determine the gas phase mole-

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cular structure and amplitudes of vibration of $(\text{CH}_3)_3\text{PF}_2$ by electron diffraction.

All members of the sequence PF_5 (ref. 9), CH_3PF_4 (refs. 10 and 11), $(\text{CH}_3)_2\text{PF}_3$ and $(\text{CH}_3)_3\text{PF}_2$ (refs. 11 and 12) have been studied by nuclear magnetic resonance and infrared spectroscopy. The observed spectra indicated that PF_5 and $(\text{CH}_3)_3\text{PF}_2$ have D_{3h} symmetry and CH_3PF_4 and $(\text{CH}_3)_2\text{PF}_3$ are trigonal bipyramids with C_{2v} symmetry. The first three members of the series have also been studied by electron diffraction^{4,5} which provided direct structural information confirming and augmenting the spectroscopic conclusions.

EXPERIMENTAL

A sample of $(\text{CH}_3)_3\text{PF}_2$ was received from Professor R. Schmutzler of the Technical University of Braunschweig, Germany. After its purity was checked by infrared analysis¹² the compound was used without further purification. Care was taken to remove possible traces of HF by keeping the liquid sample (b.p. 76°) over NaF in a vacuum line at room temperature. Before taking pictures, the sample was expanded into an evacuated 300-ml glass expansion bulb to an appropriate sample pressure (see Table 1). Diffraction patterns were recorded on 4×5 inch Kodak Electron Image plates using an electron diffraction apparatus¹³ equipped with an r^3 sector. Plates were developed at 68°F for three minutes with Kodak HRP developer. The experimental conditions under which the diffraction patterns were recorded using 40 kV incident electrons are given in Table 1.

Optical densities, measured with a digital microphotometer, were converted to exposures according to the expression

$$E = A(1 + 0.1A + 0.0133A^2 + 0.002A^3)$$

where A is the absorbance for a given reading, and E is the corresponding exposure. Five apparently flawless plates with absorbances between 0.25 and 0.9 from each camera distance were selected and used in the structure analysis.

TABLE I

EXPERIMENTAL CONDITIONS UNDER WHICH $(\text{CH}_3)_3\text{PF}_2$ DIFFRACTION PATTERNS WERE RECORDED

Camera distance (cm)	21.141	11.125
Sample pressure (torr)	50	50
Exposure time (sec)	10-12	25-32
Beam current (μA)	0.56	0.56
Throat diameter of Pt nozzle (cm)	0.017	0.017

ANALYSIS OF DATA

Experimental intensities were corrected for the measured sector irregularities and extraneous scattering before being leveled by division by the theoretical atomic intensity. The atomic scattering factors used were the tabulated elastic scattering factors of Schafer *et al.*¹⁴, and the inelastic scattering factors¹⁵ of Tavard *et al.* and Cromer in all phases of the analysis.

Prior to the determination of the molecular structure, several assumptions were made. A quantity defined as $\Delta = I_{P-C} - I_{P-F}$ was adopted and fixed during analyses since I_{P-F} and I_{P-C} were too highly correlated to allow independent refinement. The quantity Δ was taken to be 0.005 Å based on a rough estimation from the spectroscopic data¹². Also, the analysis was insufficiently sensitive to the angle PCH to justify its free variation in structure refinements. Therefore, the angle was fixed at a value of 111.4° estimated from the corresponding angles of 111.5° for CCH in C_2H_6 (ref. 16) and 111.9° for BCH in $\text{B}(\text{CH}_3)_3$ (ref. 17).

Molecular parameters were refined by comparing the experimental and calculated reduced intensity function, $M(s)$, by a least-square procedure. Initially, data for each camera distance were interpolated to integral q values and treated separately until the background was refined and the experimental $M(s)$ of the overlap region matched well. A blended experimental intensity was constructed by merging data from these two camera distances. The scattering variable s , experimental intensity $I_0(s)$, and background intensity $B(s)$ for the two camera distances are available from ASIS*.

The apparent indices of resolution were 0.878 and 0.836 for the 21- and 11-cm camera distances, respectively, the values for these and other patterns recorded on electron image plates being significantly lower than those previously obtained with process plates.

A radial distribution function was calculated using a damping factor [$\exp(-0.0021s^2)$], making the usual corrections for scattering by planetary electrons¹⁸ and integral termination errors¹⁹. Asymmetry constants of 2.0 Å⁻¹ were adopted for both bonded and nonbonded distances except in the case of C-H bonded distances where a value of 2.4 Å⁻¹ was taken. The nonbonded distances were also corrected for Bastiansen-Morino shrinkage effects²⁰. The principal corrections were estimated to be 0.0006 Å for F ··· C, 0.0019 Å for F ··· F and 0.002 Å for C ··· C nonbonded distances.

RESULTS

Experimental and calculated intensities $sM(s)$ are compared in Fig. 1. The experimental radial distribution is shown in Fig. 2 and is compared with the

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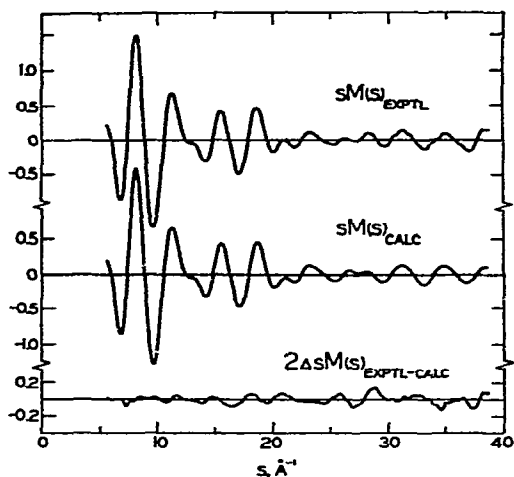


Fig. 1. Comparison of experimental and calculated molecular intensity functions for $(\text{CH}_3)_3\text{PF}_2$. $\Delta sM(s) = sM(s)_{\text{exptl}} - sM(s)_{\text{calc}}$.

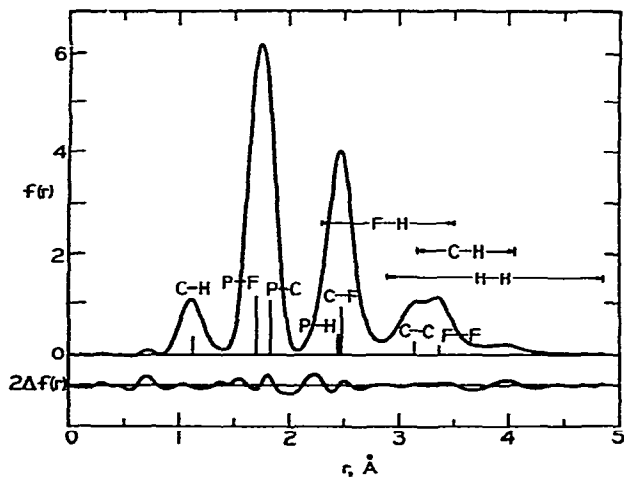


Fig. 2. Experimental radial distribution function for $(\text{CH}_3)_3\text{PF}_2$. $\Delta f(r) = f(r)_{\text{exptl}} - f(r)_{\text{calc}}$.

theoretical distribution function corresponding to free rotation of the methyl groups. Table 2 gives the structure parameters and their estimated standard errors which were derived from a least-squares analysis of the composite molecular intensity. In the course of the least-squares refinements on $sM(s)$, a diagonal weight matrix was adopted with constant elements. The corresponding parameter correlation coefficients for the molecular parameters are given in Table 3.

TABLE 2

STRUCTURAL PARAMETERS^a AND ESTIMATED STANDARD ERRORS^b FOR (CH₃)₃PF₂

Parameter	r_z	l_z
C-H	1.114±0.006	0.076±0.006
P-F	1.685±0.001	0.048±0.001 ^c
P-C	1.813±0.001	0.053±0.001
F···F	3.368±0.002	0.063±0.005
C···C	3.138±0.002	0.095±0.006
C···F	2.474±0.001	0.087±0.002

^a Units for distances and amplitudes are in Å. (Angle P-C-H was fixed at 111.4°.)^b The effects of both random and systematic errors were included in calculated standard errors according to ref. 21.^c $l(\text{P-C})$ and $l(\text{P-F})$ were constrained to have a constant difference $\Delta = 0.005$ Å. The estimated standard errors for $l(\text{P-C})$ and $l(\text{P-F})$ did not include the uncertainty in Δ .

TABLE 3

MATRIX OF CORRELATION COEFFICIENTS^a FOR (CH₃)₃PF₂

	$r_{\text{P-F}}$	$r_{\text{P-C}}$	$r_{\text{C-H}}$	$l_{\text{P-F}}^b$	$l_{\text{C-H}}$	$l_{\text{C}\cdots\text{F}}$	$l_{\text{F}\cdots\text{F}}$	$l_{\text{C}\cdots\text{C}}$	R
$r_{\text{P-F}}$	1.0	0.32	-0.26	-0.08	-0.03	-0.16	-0.02	0.01	-0.18
$r_{\text{P-C}}$		1.0	-0.32	0.08	0.06	0.06	0.01	0.01	0.21
$r_{\text{C-H}}$			1.0	0.03	-0.03	0.16	0.01	-0.02	0.06
$l_{\text{P-F}}$				1.0	0.11	0.30	0.04	0.04	0.55
$l_{\text{C-H}}$					1.0	0.11	0.02	0.01	0.21
$l_{\text{C}\cdots\text{F}}$						1.0	0.04	0.03	0.55
$l_{\text{F}\cdots\text{F}}$							1.0	0.16	0.08
$l_{\text{C}\cdots\text{C}}$								1.0	0.07
R									1.0

^a Based on the expression for the matrix elements $\rho_{ij} = (\mathbf{B}_{ij}^{-1}/\mathbf{B}_{ii}^{-1}\mathbf{B}_{jj}^{-1})^{1/2}$ taken from O. Bastiansen, L. Hedberg and K. Hedberg, *J. Chem. Phys.*, 27 (1957) 1311.^b $l_{\text{P-C}}$ constrained to be $l_{\text{P-F}} + 0.005$ Å.

DISCUSSION

The radial distribution curve constructed from a model simulating free rotation agrees satisfactorily with the experimental curve (Fig. 2) consistent with the small barrier expected for such a structure²²⁻²⁴.

The observed variations in the structures of the series PF₅, CH₃PF₄, (CH₃)₂PF₃ and (CH₃)₃PF₂ are summarized in Fig. 3. In all cases the least electronegative ligands go to equatorial sites. The steepness of Curve A in Fig. 3 portrays the marked weakening suffered by the axial P-F bond as the number of methyl substituents increases⁵⁻⁷. The comparative flatness of curves B and C for equatorial ligands in Fig. 3 supports the Gillespie-Nyholm model^{3,6-8} in which the axial-equatorial VSEPR in a trigonal bipyramid substantially exceed the equa-

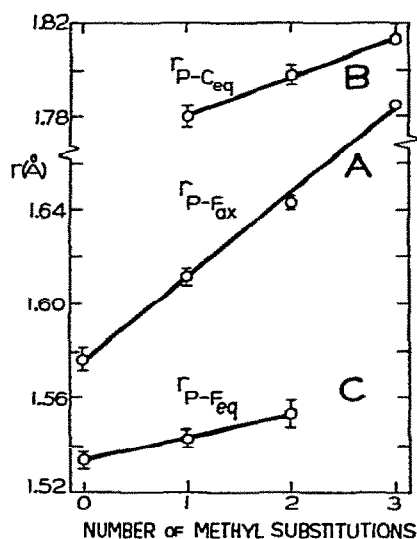


Fig. 3. Trends of $P-C_{eq}$, $P-F_{ax}$ and $P-F_{eq}$ bond lengths in the series $(CH_3)_nPF_{5-n}$.

torial-equatorial repulsions. The stereochemistry and structural deformations, then, conform to the VSEPR model in which the magnitudes of the bond repulsions increase as ligand electronegativity decreases and in which valence shell repulsions increase in the order $F_{eq}-F_{eq} < F_{eq}-(CH_3)_{eq} < (CH_3)_{eq}-(CH_3)_{eq} < F_{ax}-F_{eq} < F_{ax}-(CH_3)_{eq}$. Furthermore, the lengthening of the axial $P-F$ bonds in the series correlates nicely with the increase in $P-F$ amplitudes of vibration and the decrease in the mean $P-F$ stretching frequencies reported by Griffiths *et al.*⁹ and by Downs and Schmutzler¹⁰.

A linear extrapolation of the axial bond lengths^{4, 25} in PF_5 , SF_4 , and ClF_3 analogous to the middle curve in Fig. 3 suggests a bond length of about 1.76 Å in ArF_2 , the hypothetical molecule isoelectronic, in the VSEPR sense, with $(CH_3)_3PF_2$. It is not unlikely that ArF_2 , if formed, would be stable with respect to atomization. Its stability with respect to decomposition into Ar and F_2 is not yet resolved²⁶.

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