overlap populations (Table II) were derived by a Mulliken population analysis.[16]

Molecular Structure of ClF_3O. Chlorine trifluoride oxide is a distorted-trigonal-bipyramidal molecule with three different ligands in the equatorial plane: a single bond, a double bond, and a lone valence electron pair. The angles (Figure 3) between the axial bonds and the double bond are larger (by about 7°) than the angles between the axial bonds and the single bond or the lone electron pair; i.e., the axial fluorine atoms are bent away from the double bond into the sector between the single bond and the lone electron pair. This demonstrates that in the axial direction the steric repulsion of the double bond is larger than the repulsion from either the lone pair or the single bond. The angles in the equatorial plane, however, indicate that in the equatorial direction the repulsion by the lone pair is largest, followed by the double bond, with the single bond being smallest. This directional repulsion effect of double bonds, which has been pointed out previously,[6] correlates well with the different populations of the π-bond orbitals in the axial and the equatorial planes.[17] For ClF_3O, these populations (Table II) are almost equal.

The observed bond distances ($Cl{=}O = 1.405$ Å, $Cl{-}F_e = 1.603$ Å, $Cl{-}F_a = 1.713$ Å) agree well with previous estimates ($Cl{=}O = 1.42$ Å, $Cl{-}F_e = 1.62$ Å, $Cl{-}F_a = 1.72$ Å)[3] derived from the observed vibrational spectra and a comparison with related molecules. They confirm the conclusions, previously reached from the results of a normal-coordinate analysis,[3] that the chlorine–oxygen bond has double-bond character and that the axial Cl–F bond is significantly weaker than the equatorial one. These results support a previously outlined bonding scheme assuming mainly sp^2 hybridization for the bonding of the three equatorial ligands (ClF, ClO σ bond, and free valence electron pair) and the use of a chlorine p orbital for the bonding of the two axial fluorines by means of a semiionic three-center–four-electron bond pair.[3,7,18]

A comparison of the bond lengths in ClF_3O with those in closely related molecules (see Table III) also correlates well with the conclusions previously derived from force field computations.[3,7,18] These computations had shown that, if the bonds are separated according to the two possible types (i.e., mainly covalent and mainly semiionic 3c–4e), the bond strength within each type increases with increasing formal oxidation state of the central atom and decreases with increasing oxygen substitution. The first effect is due to an increase in the effective electronegativity of the central atom with increasing oxidation state. This increase causes the electronegativities of the central atom and the ligands to become more similar and therefore the bonds to become more covalent. The second effect is caused by oxygen being less electronegative than fluorine, thereby releasing electron density to the molecule and increasing the ionicity of the Cl–F bonds.[7,18] Although the previous force field computations clearly reflected these trends, the uncertainties in force constants, obtained from an underdetermined force field, were rather large and certainly are not as precise as the more reliable bond length measurements from this study.

Acknowledgment. H.O. wishes to express his appreciation to NATO for a research grant, and K.O.C. thanks the Office of Naval Research and the Army Research Office for financial support.

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Molecular Structures of Phosphorus Compounds. 10. Conformations and Structures of (Trifluoromethyl)fluorophosphoranes, $(CF_3)_nPF_{5-n}$ ($n = 1, 2, 3$), in the Gas Phase

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The molecular structures of CF_3PF_4, $(CF_3)_2PF_3$, and $(CF_3)_3PF_2$ have been studied by gas electron diffraction. For CF_3PF_4 a mixture of two conformers with equatorial (60 ± 10%) and axial CF_3 groups is found. In $(CF_3)_2PF_3$ both CF_3 groups occupy axial positions, while in $(CF_3)_3PF_2$ all three CF_3 groups occupy equatorial positions. Geometric parameters and vibrational amplitudes are given in the paper. The electron diffraction results are discussed in connection with earlier experimental studies, and an attempt is made to rationalize these results.

Introduction

The basic trigonal-bipyramidal framework of pentacoordinate phosphorus compounds with monofunctional substitutents has been confirmed by various experiments such as NMR, infrared, and microwave spectroscopy and X-ray or electron diffraction. Less certain is the location of various substituents in axial or equatorial positions. The initially suggested "electronegativity rule",[2] according to which more electronegative substituents prefer axial positions, has since been modified by the concept of "apicophilicity".[3] The following "apicophilicity" series, which indicates the relative tendency to occupy axial positions, has been suggested:[4,5]

$$F > Cl, Br > CF_3 > OR, SR, NR_2, R$$

Discrepancies exist in this series, which is based on NMR data and other experiments, when Cl and CF_3 groups compete for

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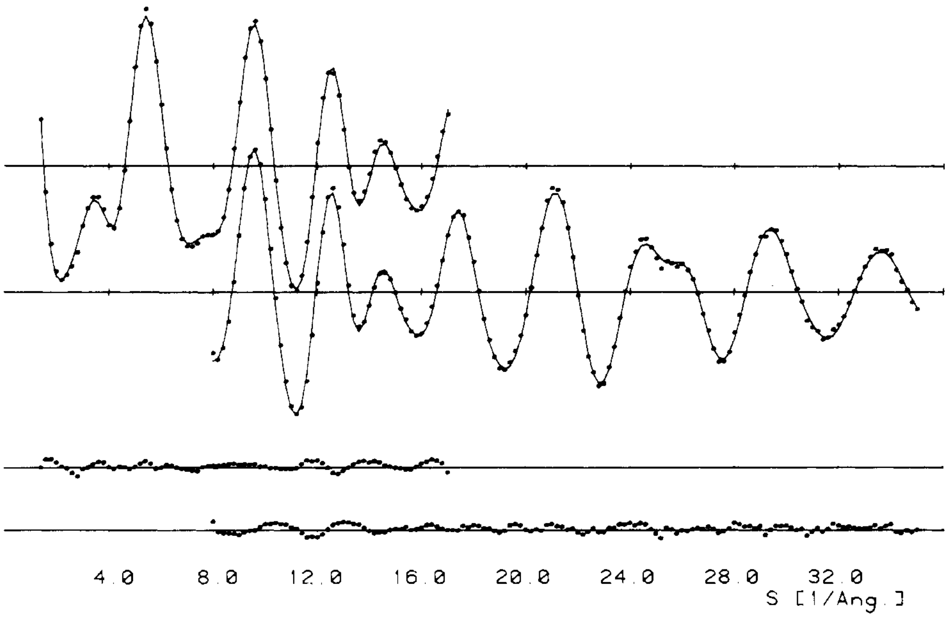
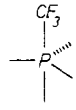


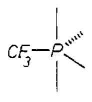
Figure 1. Experimental (points) and calculated (—) molecular intensities and differences for CF_3PF_4.

axial positions in the trigonal bipyramid. According to the interpretation of the NMR data (liquid phase) for such molecules,[4-6] chlorine tends toward axial positions, while infrared and Raman studies for CF_3PCl_4[7] (gas) and $(CF_3)_2PCl_3$[8] (gas, liquid, and solution) and an electron diffraction investigation on vapors[9] for $(CF_3)_2PCl_3$ and $(CF_3)_3PCl_2$ result in equatorial positions of the chlorine atoms. Thus, the suggested sequence of Cl and CF_3 in the "apicophilicity" series is questionable.

Various studies on the stereochemistry of (trifluoromethyl)fluorophosphoranes reveal further discrepancies about the sequence of F and CF_3. Muetterties et al.[2b] conclude from ^{19}F NMR chemical shifts for CF_3PF_4 that the CF_3 group occupies an axial position (I). This result is confirmed by a microwave study,[10] where a typical symmetric rotor spectrum (i.e., C_3 or higher symmetry) was observed. On the other hand, ^{13}C NMR data[5] and gas-phase infrared spectra[11] are interpreted in terms of equatorial conformation (II). MO calculations in the CNDO/2 approximation result in a difference of 23 kcal mol^{-1} for the bond energies, favoring clearly equatorial substitution in CF_3PF_4.[12] There is a similar discrepancy for $(CF_3)_2PF_3$. Here, ^{19}F NMR data[2] suggest axial CF_3 groups (III), while ^{13}C NMR data[5] are interpreted in terms of equatorial substitution (IV). Only for $(CF_3)_3PF_2$ do both ^{19}F and ^{13}C NMR studies result in the same conformation with all three CF_3 groups in equatorial positions (V). The aim of this study is the determination of the molecular geometries for $(CF_3)_nPF_{5-n}$ (n = 1, 2, 3), which may help to clarify some of the above discrepancies.



(I)



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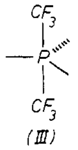

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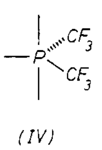
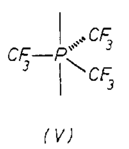


(IV)



(V)

Table I. Details of the Electron Diffraction Experiment

camera dist/cm	50	25
sample temp/°C (CF_3PF_4)	−88	−87
sample temp/°C ($(CF_3)_2PF_3$)	−68	−65
sample temp/°C ($(CF_3)_3PF_2$)	−52	−50
nozzle temp/°C	15	15
nozzle diam/mm	0.2	0.2
camera press./10^{-5} torr	<1.5	<2.0
exposure time/s	8-20	30-70
electron wavelength/Å	0.04875 (1)	0.04885 (1)
s range^a/Å^{-1}	1.4-17	8-35^b

^{a} $s = (4\pi/\lambda)\sin(\vartheta/2)$; λ = electron wavelength, ϑ = scattering angle. ^{b} 16-35 Å^{-1} for $(CF_3)_3PF_2$ (see text).

Experimental Section

The phosphoranes $(CF_3)_nPF_{5-n}$ (n = 1, 2, 3) are prepared by slightly modified literature procedures.[13] They can be obtained in good yields by fluorination of the corresponding chlorine derivatives $(CF_3)_nPCl_{5-n}$ or $CF_3PF_2Cl_2$ with freshly sublimed antimony trifluoride. The starting compounds have been synthesized by known methods.[14-16] According to NMR spectroscopic investigations the substances contain less than 0.5% impurities. For physical and chemical properties of the phosphoranes see ref 13.

The electron diffraction intensities were recorded with the Balzers gas diffratograph KD-G2[17] at 50- and 25-cm camera distances and an accelerating voltage of about 60 kV. Details of experiments are summarized in Table I (throughout this paper 1 Å = 100 pm, 1 torr = 101.325/760 kPa and 1 cal = 4.184 J). For each compound and camera distance four plates were exposed, two of which were selected for the structure analysis. All plates for the short camera distance

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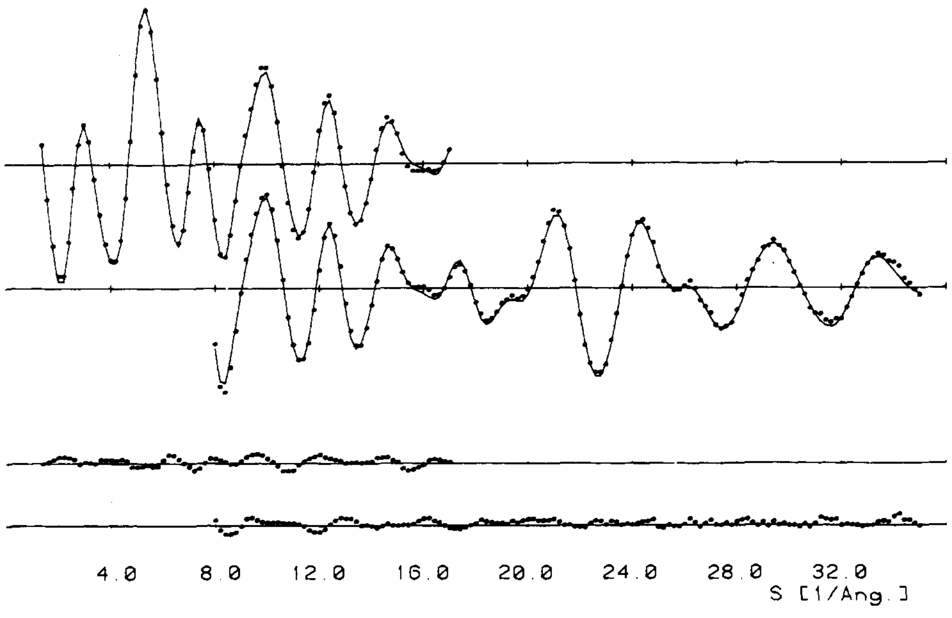

Figure 2. Experimental (points) and calculated (—) molecular intensities and differences for $(CF_3)_2PF_3$.

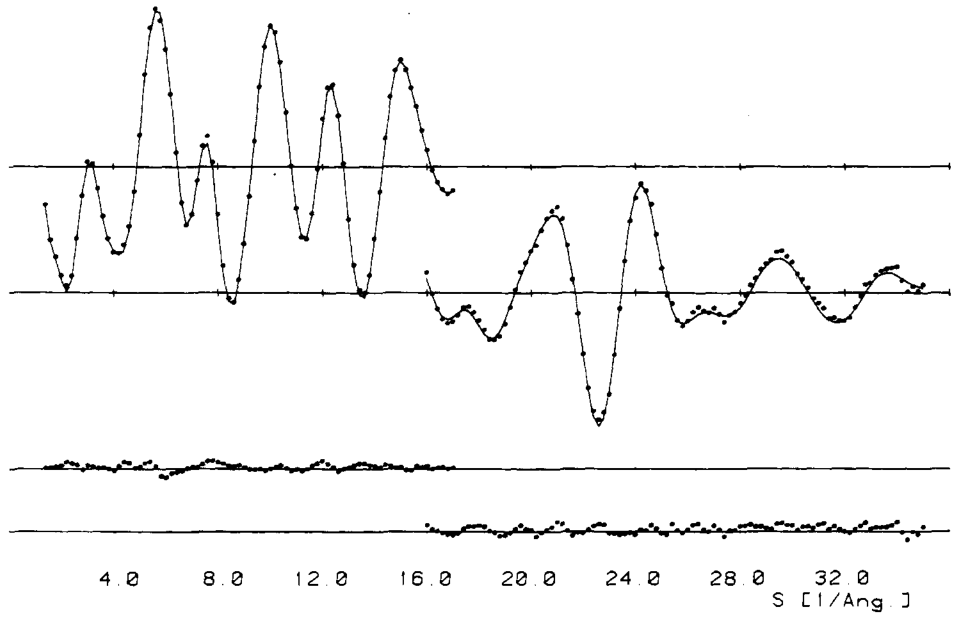

Figure 3. Experimental (points) and calculated (—) molecular intensities and differences for $(CF_3)_3PF_2$.

of $(CF_3)_3PF_2$ showed a weak halo in the inner part (from $s = 8$ to about 12 $Å^{-1}$), and data for these plates were used only for $s \geq 16$ $Å^{-1}$. The experiment was not repeated, since the small amount of remaining sample was kept for future vibrational studies. Processing of plates and data reduction procedures are described elsewhere.[18] Averaged modified molecular intensities for both camera distances are presented in Figures 1–3.[19] Theoretical intensities were calculated with the scattering amplitudes and phases of ref 20.

Structure Analysis

CF_3PF_4. Analysis of the experimental radial distribution function (Figure 4) for $r < 2$ Å results in preliminary values for bond distances. Model calculations for axial (curve A in Figure 4) and equatorial conformations (B) demonstrate that neither radial distribution function conforms with the experiment. Variations in bond angles within "reasonable" limits do not change the main features of the radial distribution functions. The torsional position of the CF_3 group in the equatorial conformation (one CF_3 fluorine atom eclipsing either an axial or equatorial fluorine or any intermediate position) has a minor effect on curve B. The most prominent differences between curves A and B are in the areas of the peaks at about 2.2, 2.6, and 3.1 Å: (1) The 2.2 peak is smaller than the 2.6 peak in curve A, and this ratio is reversed in curve B; both peaks have the same height in the experimental curve. (2) There is no peak at 3.1 Å in curve A but a distinct peak in curve B; in the experimental curve we observe a smaller peak (or shoulder). These two observations suggest the presence of a mixture of equatorial and axial conformers in the electron diffraction experiment. This is confirmed by model calculations, which give good agreement with the experiment for 60% equatorial and 40% axial contributions. The possibility of a tetragonal pyramid with all fluorine atoms in basal positions has to be rejected on the basis of model calculations.

This preliminary result was refined by a least-squares procedure based on the molecular intensities. A diagonal-weight matrix was used with the elements given in ref 18. As the experimental data do not allow the simulataneous deter-

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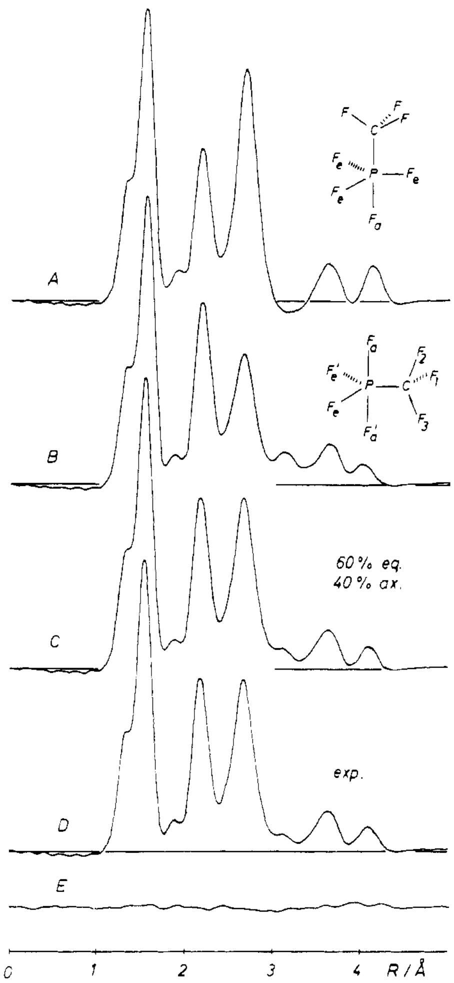

Figure 4. Radial distribution functions for CF_3PF_4: (A) axial, (B) equatorial, (C) mixture of equatorial and axial, (D) experiment, (E) difference (curve C − curve D).

mination of geometric parameters and vibrational amplitudes for both conformers, several constraints were imposed: (1) Common parameters (C–F, P–F_e, P–F_a, FCF, and vibrational amplitudes) have the same values for both conformers. (2) The P–C bond length in the axial conformer is set to 1.90 Å. Variation of this parameter by ±0.02 Å results in a significant increase in the sum of the errors squared. (3) The angles F_aPF_e were fixed at 90° in both conformers. Refinements of these angles converged toward 90°—within the standard deviations—independent of the starting values (85° or 95°). (4) Vibrational amplitudes for the equatorial conformer that cause large correlations between parameters or that are poorly determined by the electron diffraction experiment were constrained to the spectroscopic values (see the Appendix). For the axial conformer, common amplitudes were transferred from $(CF_3)_2PF_3$ (see below). Only the $(F_e\cdots F)_{gauche}$ amplitude was refined. Some important fixed vibrational amplitudes were varied systematically within "reasonable" limits in a series of least-squares runs. This demonstrates that these constraints have a very small effect on the geometric parameter, except for the F_ePF_e angle. (5) C_s symmetry was assumed for the equatorial conformer. Only the result for the F_ePF_e angle depends on the rotational position of the CF_3 group (C_s plane either equatorial or axial).

Table II. Results of the Least-Squares Analysis for CF_3PF_4[a]

(a) Geometric Parameters (r_a Values in Å and Deg)

	equatorial	axial		equatorial	axial
C-F	1.332 (3)	1.332^b	FCF	108.0 (0.5)	108.0^b
P-F_e	1.537 (5)	1.537^b	F_ePF_e	117.4 (3.4)	120.0^b
P-F_a	1.573 (7)	1.573^b	F_aPF_e	90.0^b	90.0^b
P-C	1.881 (8)	1.90^b	ratio	60 (10)%	40 (10)%

(b) Electron Diffraction and Spectroscopic Vibrational Amplitudes for the Equatorial Conformer (Å)

	ed	spectr[c]		ed	spectr[c]
C-F	0.050 (3)	0.046	$F_a\cdots F_a'$	0.055^b	0.053
P-F_e	$0.039\ (6)^d$	0.040	$F_e\cdots F_e'$	0.100^b	0.098
P-F_a	$0.043\ (6)^d$	0.043	$F_1\cdots F_a$	0.250^b	0.241
P-C	0.045 (11)	0.049	$F_1\cdots F_e$	0.075^b	0.074
$F_1\cdots F_2$	0.066 (7)	0.055	$F_1\cdots F_e'$	0.150^b	0.145
$F_a\cdots F_e$		0.062	$F_2\cdots F_e$	0.180 (83)	0.191
P···F	0.073 (8)	0.062	$F_2\cdots F_e'$	0.151 (79)	0.157
C···F_e	0.122 (56)	0.091	$F_2\cdots F_a$	0.170^b	0.173
C···F_a	0.075^b	0.073	$F_2\cdots F_a'$	0.105 (37)	0.122

(c) Agreement Factors (%)

$R_{50} = 4.8$ $R_{25} = 6.5$

[a] Atom numbering for the equatorial conformer is indicated in Figure 4. For an estimate of error limits see text. [b] Value not refined. [c] See the Appendix. [d] Ratio $l(P\text{-}F_e)/l(P\text{-}F_a)$ was fixed to the spectroscopic value.

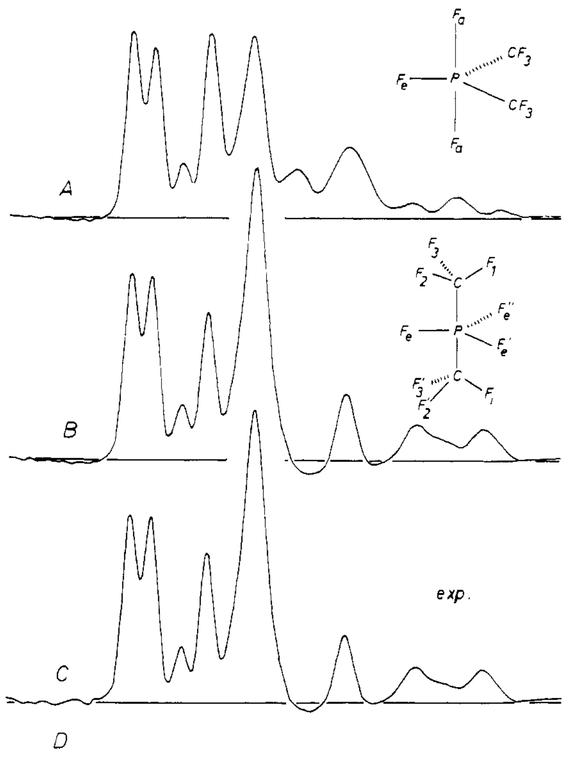

Figure 5. Radial distribution functions for $(CF_3)_2PF_3$: (A) equatorial–equatorial, (B) axial–axial, (C) experiment, (D) difference (curve C − curve B).

Since the refinement of the relative ratio of the two conformers caused large correlations with some vibrational amplitudes, a series of least-squares runs was carried out with different but fixed ratios. The final value is obtained from the minimum of the sum of the errors squared, and the error limit is based on a 15% increase. With these constraints the following correlation coefficients have values >0.6: P–F_e/P–F_a = 0.90, C–F/FCF = 0.63, P–C/FCF = 0.61, P–F_e/l(P–F_e) = 0.81 and P–F_a/l(P–F_e) = 0.91. The results of the final least-squares analysis are summarized in Table II. Error limits are in general 3σ values. Systematic errors due to constraints 4 and 5 and a scale error of 0.1% for the bond lengths are included. For the $(F_e\cdots F)_{gauche}$ vibrational amplitude in the axial conformer a value of 0.131 (14) was obtained. The geometric parameters for the axial conformer

Table III. Results of the Least-Squares Analysis for $(CF_3)_2PF_3$ (Axial-Axial Conformation)[a]

(a) Geometric Parameters (r_a Values in Å and Deg)

C–F	1.334 (3)	P–C	1.884 (6)
$P–F_e$	1.559 (3)	FCF	108.3 (0.3)

(b) Vibrational Amplitudes (Å)

C–F	0.043 (3)	$C\cdots F'$	0.108 (19)
$P–F_e$	0.041 (3)	$F_e\cdots F_1$	0.077 (7)
P–C	0.048 (8)	$F_e\cdots F_2$	0.133 (28)
$F_1\cdots F_2$	0.050 (4)	$F_1\cdots F_1'$	0.110 (36)
$P\cdots F$	0.075 (7)	$F_1\cdots F_2\cdot$	0.126 (33)
$F_e\cdots F_e'$	0.058 (15)	$C\cdots C'$	0.055[b]
$C\cdots F_e$	0.084 (10)		

(c) Agreement Factors (%)

$R_{50} = 7.2$ $R_{25} = 8.3$

[a] Atom numbering is indicated in Figure 5. For an estimate of error limits see text. [b] Value not refined.

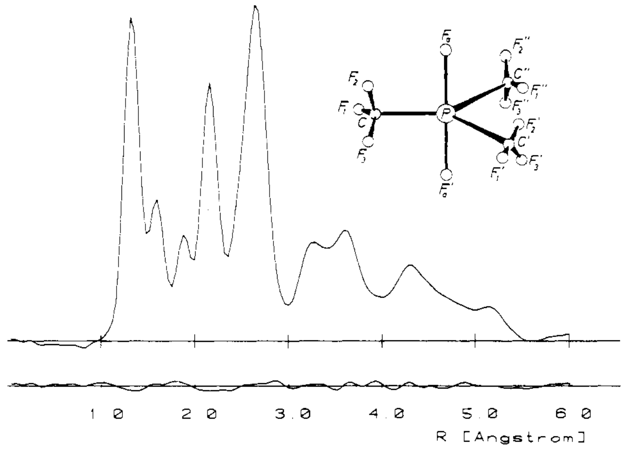

Figure 6. Experimental radial distribution function and difference curve for $(CF_3)_3PF_2$.

reproduce the microwave rotational constant B^{10} to within 1 MHz (B = 1182.039 MHz vs. B_0 = 1183.026 (1) MHz).

$(CF_3)_2PF_3$. Figure 5 demonstrates that the radial distribution function in the range $r > 2$ Å is very characteristic for the conformation of this molecule. The function for an axial–equatorial conformation, which is not shown in Figure 5, is also very characteristic and different from the experiment. In the model calculation for the equatorial–equatorial conformer, C_{2v} symmetry and a CPC angle of 124° were assumed. These assumptions do not affect the main features of curve A. Good agreement between experiment (curve C) and model is observed only for the axial–axial conformation. Thus, in the least-squares refinement the presence of only this conformer with D_{3h} symmetry was assumed. On the basis of the electron diffraction experiment we can not exclude small contributions from other conformers, but they are estimated to be certainly <10%. With one vibrational amplitude ($C\cdots C'$) fixed in the least-squares analysis, 4 geometric parameters and 12 amplitudes were refined simultaneously. Two correlation coefficients had values >0.6: C–F/FCF = 0.62 and $l(P\cdots F)/l(F_e\cdots F_e')$ = 0.82. The results of the least-squares refinement are listed in Table III. Error limits are 3σ values plus a scale error of 0.1% for bond distances.

$(CF_3)_3PF_2$. Comparison between calculated radial distribution functions for various conformations and experiment (Figure 6) demonstrates, more obviously than in the previous case, that only the conformation with all CF_3 groups in equatorial positions conforms with the experiment. Again small contributions from other conformers (certainly <10%) can not be excluded definitely. In the least-squares refinement C_{3h} symmetry (i.e., one fluorine atom of each CF_3 group lies in the equatorial plane) and local C_{3v} symmetry for the CF_3 groups were assumed. Furthermore, some vibrational amplitudes (see Table IV) were fixed. The final results are listed in Table IV. Error limits are estimated according to the analysis for $(CF_3)_2PF_3$.

Table IV. Results of the Least-Squares Analysis for $(CF_3)_3PF_2$ (All CF_3 Groups in Equatorial Positions)[a]

(a) Geometric Parameters (r_a Values in Å and Deg)

C–F	1.331 (3)	P–C	1.888 (4)
$P–F_a$	1.600 (4)	FCF	108.3 (0.2)

(b) Vibrational Amplitudes (Å)

C–F	0.048 (4)	$C\cdots F_2''$	0.120 (18)
$P–F_a$	0.050 (4)	$F_1\cdots F_1'$	0.150[b]
P–C	0.051 (5)	$F_1\cdots F_2'$	0.167 (30)
$F_1\cdots F_2$	0.061 (4)	$F_1\cdots F_2''$	0.300[b]
$P\cdots F$	0.079 (3)	$F_2\cdots F_2'$	0.165 (26)
$F_a\cdots F_a'$	0.055[b]	$F_2\cdots F_3'$	0.210 (42)
$C\cdots F_a$	0.087 (12)	$F_1\cdots F_a$	0.303 (55)
$C\cdots F_1'$	0.150[b]	$F_2\cdots F_a$	0.236 (31)
$C\cdots F_2'$	0.256 (86)	$F_3\cdots F_a$	0.200[b]
$C\cdots F_1''$	0.150[b]		

(c) Agreement Factors (%)

$R_{50} = 4.2$ $R_{25} = 8.3$

[a] Atom numbering is indicated in Figure 6. For an estimate of error limits see text. [b] Value not refined.

Discussion and Results

The result of the electron diffraction experiment for CF_3PF_4, i.e., the presence of a mixture of axial and equatorial conformers, neither confirms nor contradicts any of the previous studies. We have to ascertain, however, that our result is compatible with the previous experimental data. (1) In the microwave spectrum transitions for the axial conformer only were observed. Transitions for the equatorial conformer are expected to have much lower intensities due to a smaller dipole moment and an unfavorable partition function. CNDO/2 calculations result in μ_a = 0.6 D and μ_e = 0.2 D, i.e., $(\mu_e/\mu_a)^2 \approx 0.1$. Although dipole moments calculated by this semiempirical method are in general not very reliable, the relative magnitude should be correct. A further reason for low intensities of the equatorial conformer was pointed out by Cohen and Cornwell:[10] this conformer is expected to have a low sixfold barrier to internal rotation of the CF_3 group, and consequently its spectrum is weakened by being split into a large number of lines. This low barrier is qualitatively confirmed by the electron diffraction experiment where a rough estimate for V_6 = 0.24 kcal mol^{-1} is obtained (see the Appendix). For the axial conformer the microwave analysis results in a threefold barrier with V_3 = 5.0 ± 1.5 kcal mol^{-1}. Finally, the lifting of the K degeneracy in an asymmetric rotor (equatorial conformer) reduces intensities of the observed transitions. Nevertheless, a careful search with a spectrometer of high sensitivity should succeed in observing the rotational spectrum for the equatorial conformer as well. (2) In the gas-phase infrared spectrum[11] the great number of bands could be assigned only on the basis of a low symmetry species (C_{2v} or C_s), i.e., an equatorial conformer. The gas-phase spectrum, however, is certainly compatible with a mixture of both conformers, since no drastic differences in the infrared spectra of the two conformers are expected, except for the number of bands. A matrix infrared spectrum should definitely show the presence of both conformers. (3) The interpretation of the NMR spectra depends on the information considered: ^{19}F data[2b] are interpreted as "typical" for axial positions of the CF_3 group, while ^{13}C data[5] are interpreted as "typical" for equatorial positions. Since both conformers are present and the NMR spectra show only one CF_3 group, we must conclude that the CF_3 group participates in pseudorotation as do the fluorine atoms, even at temperatures as low as −150 °C and does not form the "pivot" in a Berry type exchange mechanism.

Table V. Bond Lengths for Some Related Phosphoranes (Å)

	position of CH_3 or CF_3	$P-F_e$	$P-F_a$	$P-C_e$	$P-C_a$
PF_5 [a]		1.534 (4)	1.577 (5)		
CH_3PF_4 [b]	eq	1.543 (4)	1.612 (4)	1.780 (5)	
$(CH_3)_2PF_3$ [b]	eq, eq	1.553 (6)	1.643 (3)	1.798 (5)	
$(CH_3)_3PF_2$ [c]	eq, eq, eq		1.685 (1)	1.813 (1)	
$(CF_3)_2PCl_3$ [d]	ax, ax				1.950 (11)
$(CF_3)_3PCl_2$ [d]	ax, ax, eq			1.938 (31)	1.946 (14)
CF_3PF_4 [e]	eq	1.537 (5)	1.573 (7)	1.881 (8)	
CF_3PF_4 [e]	ax	(1.537)	(1.573)		(1.90)
$(CF_3)_2PF_3$ [e]	ax, ax	1.559 (3)			1.884 (6)
$(CF_3)_3PF_2$ [e]	eq, eq, eq		1.600 (4)	1.888 (4)	

[a] r_g structure from ref 23. [b] r_g structure from ref 24. [c] r_g structure from ref 25. [d] r_a structure from ref 9. [e] r_a structure from this work.

If the CF_3 group changes position, chemical shifts and coupling constants can no longer be typical for any position. Thus, none of the previous experimental data are really incompatible with the presence of a mixture of axial and equatorial conformers. The semiempirical MO calculations in the CNDO/2 approximation,[12] which predict a difference in bonding energies of 23 kcal mol^{-1} in favor of the equatorial conformer, are seriously in error. From the relative ratio of the two conformers in the electron diffraction experiment we obtain a difference in free enthalpy of $\Delta G = 0.2 \pm 0.2$ kcal mol^{-1}. For $(CF_3)_2PF_3$ the interpretation of the NMR spectra depends to a large extent on the actual barrier to pseudorotation, which is unknown. Muetterties et al. concluded from the fact that only one type of P–F fluorine environment is observed down to −120 °C[2b,21] that both CF_3 groups occupy axial positions (structure III) and no positional exchange occurs. This observation is confirmed by Cavell et al.[5] down to even lower temperatures, but these authors interpret the ^{19}F and ^{13}C NMR spectra in terms of equatorial substitution (structure IV) with fast permutational exchange of the fluorine atoms. This interpretation is based on $^1J_{PC}$ and $^2J_{PF}$ coupling constants. Since the electron diffraction experiment confirms structure III for this phosphorane, we must conclude that coupling constants are not in all cases typical for the position of a substituent. The only alternative explanation for the discrepancy between this interpretation of the NMR spectra and the electron diffraction result would be different conformations in the gas phase and in solution. Only in the case of $(CF_3)_3PF_2$ does interpretation of ^{19}F and ^{13}C NMR spectra and electron diffraction result in the same conformation with three equatorial CF_3 groups (structure V).

Various concepts have been proposed to predict the stereochemistry of phosphoranes. According to both the electronegativity rule and apicophilicity series, fluorine has the highest tendency for the axial positions. Luckenbach[22] argues that trifluoromethyl has powerful *−I/−M* effects and is a considerably stronger electron-withdrawing moiety than a single fluorine atom with *−I/+M* characteristics. Therefore, CF_3 should have a higher tendency for axial positions than fluorine. None of these concepts, however, predict the correct stereochemistry for all three (trifluoromethyl)fluorophosphoranes considered here. The surprising result of the electron diffraction study, i.e., three CF_3 groups in a fluorophosphorane occupy the equatorial positions, two CF_3 groups occupy the axial positions, and one CF_3 group can occupy either position with nearly equal probability, can possibly be rationalized in the following way: the position of a ligand depends on two effects, (1) the bonding energy and (2) steric interaction with the rest of the molecule. Following Luckenbach's argumentation, we suppose bonding energy to be slightly lower for axial CF_3 groups. In CF_3PF_4 steric repulsion between the CF_3 group and the PF_4 remainder is estimated to be higher for the axial position (3 neighbors at a 90° angle), compensating the difference in bonding energy for axial and equatorial CF_3 groups. Consequently, we observe a mixture of both conformers. In $(CF_3)_2PF_3$ the axial–axial conformer is favored by bonding energy and steric repulsion, which would be considerably higher for equatorial–equatorial or axial–equatorial conformers. In $(CF_3)_3PF_2$ steric interaction between the CF_3 groups is lowest for all CF_3 groups in equatorial positions (with 120° angles between them). Any other conformer would imply two 90° contacts between CF_3 groups with strong steric repulsion. Thus, the loss in bonding energy is overcompensated by the gain in steric interaction, if all three CF_3 groups occupy equatorial positions.

Table V summarizes P–F and P–C bond lengths for some related phosphoranes that have been studied in the gas phase. The following trends are observed: (1) Equatorial P–F bond lengths increase only slightly upon substitution of equatorial or axial fluorine atoms by CH_3 or CF_3 groups. (2) Axial P–F bond lengths increase much more strongly when equatorial fluorine atoms are replaced by less electronegative substitutents (1.577 (5) Å in PF_5 vs. 1.600 (4) Å in $(CF_3)_3PF$ vs. 1.685 (1) Å in $(CH_3)_3PF_2$). The difference between equatorial and axial P–F bond lengths is about 0.04 Å for PF_5 and CF_3PF_4 and increases with insertion of electropositive ligands in the equatorial positions (0.09 Å in $(CH_3)_2PF_3$). (3) P–C bond lengths vary over a wide range, from 1.780 Å in CH_3PF_4 to 1.950 Å in $(CF_3)_2PCl_3$, showing a strong CH_3/CF_3 substitution effect (1.780 Å in CH_3PF_4 vs. 1.881 Å in CF_3PF_4) and F/Cl substitution effect (1.884 Å in $(CF_3)_2PF_3$ vs. 1.950 Å in $(CF_3)_2PCl_3$). Within the two families of (trifluoromethyl)phosphoranes, $(CF_3)_nPF_{5-n}$ ($n = 1, 2, 3$) and $(CF_3)_nPCl_{5-n}$ ($n = 2, 3$), equatorial and axial P–C bond lengths are equal within their error limits. This last observation may explain why, for these cases, coupling constants are no longer typical for the position of the CF_3 group.

Appendix: Spectroscopic Calculations

An approximate force field was derived for CF_3PF_4 with use of the vibrational assignment of Griffiths.[7] Starting values for force constants were transferred from PF_5[26] and CH_3PF_4.[27] The experimental frequencies were fitted with an average deviation of 9 cm^{-1}. The force constants are deposited as supplementary data.[19] The force field was used for calculating vibrational amplitudes (Table II). The force constant for CF_3 torsion was adjusted until approximate agreement between spectroscopic and electron diffraction values for torsion-de-

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pendent F···F vibrational amplitudes ($F_2 \cdots F_e$, $F_2 \cdots F_e'$, and $F_2 \cdots F_a'$) was obtained. This allows a rough estimate of the torsional force constant f_τ = 0.03 (+0.04, −0.015) mdyn Å. With the assumption of a V_6 cosine potential the barrier to internal rotation is estimated to V_6 = 0.24 (+0.32, −0.12) kcal mol^{-1}. All spectroscopic calculations were performed with the program NORCOR.[28]

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Registry No. CF_3PF_4 (ax), 79549-38-5; CF_3PF_4 (eq), 79549-39-6; $(CF_3)_2PF_3$ (ax, ax), 79549-40-9; $(CF_3)_3PF_2$ (eq, eq, eq), 79549-41-0.

Supplementary Material Available: Tables of total electron scattering intensities for CF_3PF_4, $(CF_3)_2PF_3$, and $(CF_3)_3PF_2$ and force constants for CF_3PF_4 (7 pages). Ordering information is given on any current masthead page.

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Molecular Structure of Fluoro Derivatives of Anionic Pentacoordinated Germanium. A New Geometrical Form for Germanium[1,2]

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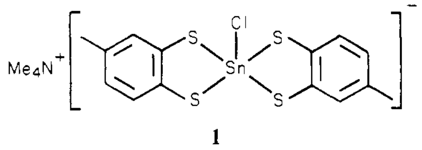
The X-ray structures of tetraethylammonium bis(1,2-benzenediolato)fluorogermanate, $[(C_2H_5)_4N]^+[(C_6H_4O_2)_2GeF]^-$ (**3**), and the related monosolvate of methyltriphenylphosphonium bis(4-methyl-1,2-benzenedithiolato)fluorogermanate, $[(CH_3)PPh_3]^+[(C_7H_6S_2)_2GeF]^- \cdot CH_3CN$ (**4**), lie along the Berry C_{2v} coordinate connecting the idealized trigonal bipyramid with the rectangular pyramid. The structure of **3** is placed about 81% along this coordinate toward the rectangular pyramid and that for **4** is about 40% along this coordinate. **3** crystallizes in the monoclinic space group $P2_1/c$ with a = 12.886 (2) Å, b = 14.870 (2) Å, c = 10.912 (1) Å, β = 100.29 (1)°, and Z = 4. **4** crystallizes in the monoclinic space group $P2_1/n$ with a = 17.108 (6) Å, b = 10.566 (3) Å, c = 20.630 (6) Å, β = 114.01 (2)°, and Z = 4. The final conventional unweighted residuals were 0.035 and 0.058 for **3** and **4**, respectively. The greater displacement of the pentacoordinated oxa compound **3** toward the RP is rationalized in terms of reduced electron-pair-repulsion effects.

Introduction

Most prevalent among pentacoordinated compounds of main group 4 elements are those of tin.[3] However, most of these contain relatively weak inter- or intramolecular tin dative bonds. A few examples are known that are anionic derivatives which have been characterized structurally as trigonal bipyramidal.[4-7] Recently, we reported[8] the first example of a discrete pentacoordinated anionic tin(IV) compound that has a rectangular pyramidal geometry (**1**). As observed in our studies on phosphoranes,[9] we found that the rectangular or square-pyramidal geometry may form when a spirocyclic system is present containing unsaturated five-membered rings having like atoms bonded to the central atom in any one ring.



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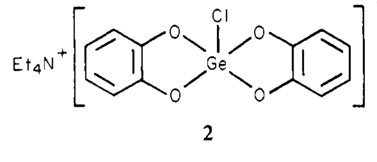

2

In an extension of our structural studies to related anionic germanium species, we synthesized the first pentacoordinated Ge(IV) compound[10] existing as a square pyramid $[(C_6H_4O_2)_2GeCl]^-Et_4N^+$ (**2**). Previously, pentacoordination for Ge(IV) was confined, primarily, to germatranes containing relatively long Ge–ligand dative bonds.[11] In one case, the crystal structure of an *N*-germylphosphinimine,[12] $[Cl_3GeN{=}PMe_3]_2$, revealed a dimeric formulation containing pentacoordinated germanium. For the latter germyl derivative as well as for the germatranes, X-ray analysis showed only the trigonal-bipyramidal geometry.

Since our preliminary report on **2**,[10] we have prepared a range of new anionic pentacoordinated germanium(IV) complexes.[2,13] Reported herein are the crystal structures of two fluoro derivatives, **3** and **4**, containing, respectively, ring oxygen and sulfur atoms. These structures are compared with the chloro derivative **2** and with related main group 4 compounds. The synthesis and characterization of **2**–**4** have been reported.[13]

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