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Pentacoordinated Molecules. XVI.[1] Molecular Structure of *tert*-Butyltetrafluorophosphorane. Infrared Spectrum, Raman Spectrum, and Gas-Phase Dipole Moment

By ROBERT R. HOLMES* and MANFRED FILD

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The vapor-phase infrared spectrum (4000–33 cm^{-1}) and liquid-state Raman displacements ($\Delta\nu$ = 100–3100 cm^{-1}) of *tert*-butyltetrafluorophosphorane are reported. Polarization measurements were obtained. Comparison of the infrared spectrum of the solid recorded at 77°K with the vapor-phase spectrum is made. The gas-phase dipole moment was obtained from a study of the temperature variation of the dielectric constant. The resulting value was 2.82 ± 0.03 D. Interpretation of the vibrational and dielectric data supports the conclusion that the structure of *tert*-butyltetrafluorophosphorane is a trigonal bipyramid with the *tert*-butyl group located in an equatorial position. Similar dielectric measurements on CH_3PF_4, $(CH_3)_2PF_3$, and $C_2H_5PF_4$ resulted in vapor-phase dipole moments for these substances. Electronic effects in this series of compounds are compared.

Introduction

A number of monosubstituted derivatives of PF_5 are now known whose structures have been established by vibrational analysis. These are $ClPF_4$,[2] CH_3PF_4,[3] CF_3PF_4,[4] and CCl_3PF_4.[1] In two cases, CH_3PF_4 and HPF_4, detailed structural parameters have been reported: the former from an electron diffraction study[5] and the latter from a microwave study.[6] In all of these reports the common structure is a trigonal bipyramid with the unique ligand located at an equatorial site.

A preliminary microwave study[7] of CF_3PF_4 shows it to be a symmetric-top molecule with the CF_3 group located in an axial position. The apparent discrepancy between the microwave[7] and vibrational interpretation[4] has been rationalized[4] in terms of the presence of isomeric conformations. For all of these substances nmr measurements[1,8–10] show one fluorine atom environment spin coupled to the phosphorus atom, indicative of rapid positional exchange. Except for $ClPF_4$[10] the ^{19}F chemical shifts for the XPF_4 compounds cited fall in a very narrow range, −10 to −31 ppm relative to CF_3CO_2H as a reference,[11] indicating a fluorine atom insensitivity to the nature of the coordinating ligand.

To extend the range of electronegativity of the ligands involved in structural investigations in the series XPF_4 and ascertain the effect of the presence of the bulky $(CH_3)_3C$ group, it was decided to study the structure of *tert*-butyltetrafluorophosphorane by means of infrared and Raman spectroscopy. Conceivably, stabilization of a square-pyramidal structure might result if a sufficiently large ligand were located in the axial position. Further, to obtain pertinent information about changes in charge distribution in these compounds, measurements of molecular dipole moments of CH_3PF_4, $C_2H_5PF_4$, *tert*-$(CH_3)_3CPF_4$, and $(CH_3)_2PF_3$ are reported. Dipole moment values for $ClPF_4$[2] and HPF_4[6] are available from earlier studies for comparison.

Experimental Section

Materials.—*tert*-Butyltetrafluorophosphorane, $(CH_3)_3CPF_4$, was prepared by allowing stoichiometric amounts of *tert*-butyldifluorophosphine[12] and chlorine (Matheson Co.) to react in a halogen-exchange reaction with antimony trifluoride (Fisher Technical grade) using a previous procedure.[12] The reaction was carried out in a steel cylinder at 110–120° for 10 hr. Purification of the liquid remaining after reaction was achieved by trap-to-trap distillation. The fractionation train contained traps held at −23, −50, −78, and −196°. The desired product was present in the trap cooled to −78° (vapor pressure 50.0 mm at 0°; bp 68–70° (lit. bp[12] 68–70°)).

The vapor pressure data obtained in the range −15 to +12° are governed by the relationship $\log p(\text{mm}) = (-1689.9/T) + 7.8816$.

Methyltetrafluorophosphorane, CH_3PF_4, was synthesized by the fluorination of CH_3PCl_4 with AsF_3 (Ozark-Mahoning Co.)

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[1] Presented in part at the Symposium on Fluorinated Organometallic Compounds, Division of Inorganic Chemistry, American Chemical Society–Canadian Institute of Chemists joint conference, Toronto, Canada, May 1970. Previous paper: R. Holmes and M. Fild, *J. Chem. Phys.*, **53**, 4161 (1970).

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[3] A. J. Downs and R. Schmutzler, *Spectrochim. Acta*, **21**, 1927 (1965).

[4] J. E. Griffiths, *J. Chem. Phys.*, **49**, 1307 (1968).

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[6] S. B. Pierce and C. D. Cornwell, *J. Chem. Phys.*, **48**, 2118 (1968).

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[8] E. L. Muetterties, W. Mahler, and R. Schmutzler, *ibid.*, **2**, 613 (1963).

[9] (a) R. R. Holmes and R. N. Storey, *ibid.*, **5**, 2146 (1966); (b) P. M. Treichel, R. A. Goodrich, and S. B. Pierce, *J. Amer. Chem. Soc.*, **89**, 2017 (1967).

[10] R. P. Carter, Jr., and R. R. Holmes, *Inorg. Chem.*, **4**, 738 (1965).

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according to the procedure of Komkov, *et al.*[13] CH_3PCl_4 was prepared[13] by the addition of chlorine to CH_3PCl_2 (Army Chemical Center, Md.). Both reactions were carried out in a steel cylinder.

The CH_3PF_4 was purified by vacuum fractionation through traps maintained at −41, −50, −78, and −196°. The CH_3PF_4 was collected at −78°. To facilitate separation it proved useful to use slightly less than the stoichiometric amount of AsF_3 in the preparation and to use a small quantity of NaF in the first trap in the purification sequence to remove traces of HF. The vapor pressure of the product was 51.2 mm at −41.6° (lit. value[14] 50.2 mm at −41.9°) and the infrared spectrum agreed well with the published[3] spectrum.

The preparation of dimethyltrifluorophosphorane $(CH_3)_2PF_3$ by the fluorination of tetramethylbiphosphine disulfide $(CH_3)_2P(S)P(S)(CH_3)_2$ with SbF_3 has been described elsewhere.[15] The disulfide was prepared according to Reinhardt, *et al.*,[16] by treating thiophosphoryl chloride (Alfa Inorganics) with methylmagnesium chloride (Alfa Inorganics). The desired product $(CH_3)_2PF_3$ was distilled from the reaction mixture, bp 62° (lit. bp[15] 62°). Vacuum fractionation and condensation on sodium fluoride further purified the product. Repeated fractionations through traps cooled to −30, −50, −63, and −196° gave samples in the −63° trap that were tensiometrically homogeneous, vapor pressure at 0°, 50.6 mm.

The vapor pressure data obtained in the range −32 to 0° are governed by the relationship $\log p(\text{mm}) = (-1707.6/T) + 7.9476$.

The ethyl derivative, $C_2H_5PF_4$, was prepared using exactly the same procedure as described above for the CH_3PF_4. Starting materials were $C_2H_5PCl_2$ (Orgmet Inc.), chlorine, and AsF_3. In preparing a second sample, $C_2H_5PCl_2$ was fluorinated with SbF_3 by adding the chloride dropwise to SbF_3 as described elsewhere.[17] Both samples were transferred to a vacuum system and distilled, fractionation being effected by traps held at −41, −63, −95, and −196°. The pure product was collected at −95°; vapor pressure at −23.7° was 55.1 mm (lit. value[14] 54.9 mm at −23.9°).

In both the dielectric and spectroscopic studies several samples of each compound were used. In each case the samples were refractionated prior to use.

Dielectric Measurements.—Dielectric measurements of gaseous CH_3PF_4, $C_2H_5PF_4$, *tert*-$(CH_3)_3CPF_4$, and $(CH_3)_2PF_3$ were performed using a dielectric measuring assembly and operational procedure already described.[2,18]

The temperature range studied extended from room temperature to 85°. This range allowed sufficient volatility for the samples under investigation. At each temperature capacitance readings were obtained as a function of sample pressure up to about 200 mm. Capacitance values were easily recorded to the nearest 0.001 pF. Temperature equilibrium was reached in 1 min or so on introduction of the gaseous samples. Noticeable changes in capacitance took place with the compounds other than CH_3PF_4, particularly at the higher temperatures and pressures, if they were allowed to remain in the dielectric cell for periods of about 15 min or more. The temperature was held constant to ±0.01° and determined with a Pt-resistance thermometer. The pressure readings were good to ±0.01 mm.

The Nesa coating on the Pyrex cell served as a shield from external capacitive coupling in the three-terminal system used. The replaceable capacitance of the cell (C_0), determined with gaseous dimethyl ether, was 179.3 pF. For the calculation, the value of the dipole moment of dimethyl ether was taken as 1.29 D and the temperature-independent polarization as 14.2 cm^3.[18] The same experimental procedure was used in determining C_0 as was used in obtaining the dipole moments of gaseous compounds.

Spectra.—The gas-phase infrared spectrum of $(CH_3)_3CPF_4$ was recorded in the range 4000–33 cm^{-1} using a Beckman IR 11-12 spectrophotometer. The region 4000–400 cm^{-1} was studied at a variety of pressures using a 10-cm Monel Metal gas cell fitted with AgCl windows. For the far-infrared region the same cell with polyethylene windows was employed. The solid-state spectrum was also recorded in the range 3100–200 cm^{-1}. For this purpose the sample was formed by slowly depositing the vapor on a CsI window maintained at 77°K in a Sulfrian helium cryostat system.

For all spectra atmospheric water vapor was removed by flushing the instrument with dry nitrogen. The far-infrared region was calibrated with rotational lines of HF, HCl, and H_2O vapor. The higher range was calibrated with CO_2 and H_2O vapor.

Raman displacements from the 4358-Å Hg line were recorded with a Cary Model 81 spectrophotometer and are considered accurate to ±3 cm^{-1} for the sharper lines. Weak and broad instrument ghosts appear at about 145 and 170 cm^{-1} with the latter being the stronger of the two. The $(CH_3)_3CPF_4$ sample was present in the liquid state at ambient temperatures in a 7-mm o.d. Pyrex tube. Qualitative polarization measurements were obtained with the use of cross and axial Polaroid cylinders.

Results

Dipole Moments.—Table I lists the total molar polarization P for CH_3PF_4, $(CH_3)_2PF_3$, $C_2H_5PF_4$, and $(CH_3)_3CPF_4$ as a function of temperature. Calculation of the dipole moments from a least-squares treatment of the variation of the polarization with the reciprocal of the absolute temperature gave the results in Table II.

TABLE I

TEMPERATURE VARIATION OF THE MOLAR POLARIZATION

CH_3PF_4		$(CH_3)_2PF_3$		$C_2H_5PF_4$		$(CH_3)_3CPF_4$	
Temp, °C	P, cm^3	Temp, °C	P, cm^3	Temp, °C	P, cm^3	Temp, °C	P, cm^3
31.14	146.01	55.04	117.71	29.66	173.09	42.03	188.40
38.01	142.97	61.72	114.52	39.91	168.27	58.12	180.94
44.69	140.32	72.07	112.33	49.61	164.59	64.93	178.68
52.19	138.93	85.30	109.67	62.39	157.37	72.01	174.92
63.01	134.33			71.04	155.14	79.55	172.09
70.01	130.76						

TABLE II

GAS-PHASE ELECTRIC DIPOLE MOMENTS AND INDUCED POLARIZATION VALUES

	μ, D	$P_E + P_A$, cm^3	Temp, °C
$ClPF_4$[a]	0.78 ± 0.01	13.7 ± 0.4	−68 to −2
HPF_4[b]	1.32 ± 0.02		
CH_3PF_4[c]	2.55 ± 0.04	16.2 ± 3.8	31 to 70
$C_2H_5PF_4$[c]	2.77 ± 0.05	19.4 ± 5.6	30 to 78
$(CH_3)_3CPF_4$[c]	2.82 ± 0.03	35.2 ± 3.3	42 to 80
Cl_2PF_3[d]	0.68 ± 0.02	23.4 ± 0.5	−30 to 19
$(CH_3)_2PF_3$[c]	2.22 ± 0.10	25.9 ± 7.8	55 to 86

[a] Reference 2. [b] Reference 6. [c] This work. [d] Reference 18.

Values of the temperature-independent polarizations $P_E + P_A$ and the temperature range studied are listed for each compound. The limits of uncertainty for the dipole moments are those associated with the standard deviation in the slope of the least-squares line. Correspondingly, the uncertainty in the temperature-independent part of the polarization is the standard deviation in the intercept. In addition to the dipole moments for compounds in this study, Table II lists values for related substances to be compared later.

Infrared and Raman Spectra.—The top portion of Figure 1 shows the gas-phase spectrum of $(CH_3)_3CPF_4$ at room temperature, and the lower portion, the infrared spectrum of the solid at 77°K. Figure 2 shows the far-infrared spectrum of the vapor while the Raman spectrum of the liquid is displayed in Figure 3. The frequencies, relative intensities, states of polarization, and suggested assignments are listed in Table III.

The assignments for the skeletal frequencies corresponding to the CPF_4 framework are made on the basis

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[13] I. P. Komkov, S. Z. Ivin, K. V. Karavanov, and L. J. Smirnov, *Zh. Obshch. Khim.*, **32**, 301 (1962); see also R. Schmutzler, *Halogen Chem.*, **2**, 31 (1967).

[14] R. A. Goodrich and P. M. Treichel, *Inorg. Chem.*, **7**, 694 (1968).

[15] R. Schmutzler, *ibid.*, **3**, 421 (1964).

[16] H. Reinhardt, D. Bianchi, and D. Mölle, *Chem. Ber.*, **90**, 1656 (1957).

[17] R. Schmutzler, *Inorg. Chem.*, **3**, 410 (1964).

[18] R. R. Holmes and R. P. Carter, Jr., *J. Chem. Phys.*, **43**, 1645 (1965).

TABLE III

VIBRATIONAL SPECTRUM OF (CH$_3$)$_3$CPF$_4$[a]

Ir (gas)		Ir (solid)		Raman (liq)[b]			
Cm^{-1}	*I*	Cm^{-1}	*I*	Cm^{-1}	*I*	Pol	Assignment, cm^{-1}
				150	2	dp	$\nu_2 - \nu_4 = 139$, torsion
183	vw						ν_9(b$_1$) (CPF$_4$)
208	w						ν_5(a$_1$) (CPF$_4$)
271	vw			272	1	dp	ν_{24}(e) (*tert*-C$_4$H$_9$)
283	w	280	vw				$\nu_{10} - \nu_4 = 286$ (CPF$_4$)
		304	vw				
308	w	310	w	309	3	dp	ν_{23}(e) (*tert*-C$_4$H$_9$)
329	vw						$\nu_{10} - \nu_4 = 335$ $\nu_1 - \nu_{11} = 327$ (CPF$_4$)
355	w	350	w	340	1	(p)	ν_8(a$_1$) (*tert*-C$_4$H$_9$)
376	w	376	m				ν_{12}(b$_2$) (CPF$_4$)
390	sh, w	395	sh, w				ν_{22}(e) (*tert*-C$_4$H$_9$)
				425	1		ν_6(a$_2$) (CPF$_4$)
435	w	436	vw				ν_8(b$_1$) (CPF$_4$)
		504	s				
511	vs	510	s	512	3	p	ν_4(a$_1$) (CPF$_4$)
560	vs	557	s	557	0		ν_{11}(b$_2$) (CPF$_4$)
583 Q	m	577	w	581	1	p	ν_3(a$_1$) (CPF$_4$)
589 R	m						
646 P	s	642	m				
650 Q	s	646	m	648	10	p	ν_2(a$_1$) (CPF$_4$)
654 R	s						
				815	2	(p)	ν_6(a$_1$) (*tert*-C$_4$H$_9$)
		811	vs				
846	vs	836	vs				ν_{10}(b$_2$) (CPF$_4$)
		879	s				
887	vs	890	s	876	1	p	ν_1(a$_1$) (CPF$_4$)
964		939	vs	949	2	dp	ν_7(b$_1$) (CPF$_4$)
		988	m				
		995	m				
1028	m	1026	m	1032	0	dp	ν_{20}(e) (*tert*-C$_4$H$_9$)
1035	sh						$2\nu_4 = 1022$ (CPF$_4$)
1093	w						$\nu_4 + \nu_{11} = 1094$ (CPF$_4$)
1157	w						ν_5(a$_1$) (*tert*-C$_4$H$_9$)
1218	w			1215	1	dp	ν_{19}(e) (*tert*-C$_4$H$_9$)
		1326	w				
		1371	w				
		1376	w				
1380	m	1380	w				ν_{18}(e) (*tert*-C$_4$H$_9$)
1406 P	m						
1410 Q	m	1408	w	1414	0	(p)	ν_4(a$_1$) (*tert*-C$_4$H$_9$)
1417 R	m						
1446	sh						$\nu_1 + \nu_{11} = 1447$ (CPF$_4$)
		1460	w	1456	2	dp	ν_{17}(e) (*tert*-C$_4$H$_9$)
		1476	m	1472	2	dp	ν_{16}(e) (*tert*-C$_4$H$_9$)
1489	s	1488	w				ν_3(a$_1$) (*tert*-C$_4$H$_9$)
		1494	m				
1537	w						$\nu_1 + \nu_2 = 1537$ (CPF$_4$)
1698	w						$2\nu_{10} = 1692$ (CPF$_4$)
1734	w						$\nu_1 + \nu_{10} = 1733$ (CPF$_4$)
1777	w						$2\nu_1 = 1774$ (CPF$_4$)
1845	w						$\nu_6 + \nu_{20} = 1843$ (*tert*-C$_4$H$_9$)
							$\nu_1 + \nu_7 = 1851$ (CPF$_4$)
1922	w						$2\nu_7 = 1928$ (CPF$_4$)
2034	w						$\nu_6 + \nu_{19} = 2033$ (*tert*-C$_4$H$_9$)
2194	w						$\nu_6 + \nu_{18} = 2195$ (*tert*-C$_4$H$_9$)
2324	w						$2\nu_5 = 2314$ (*tert*-C$_4$H$_9$)
		2348	vw				
2424	w						$\nu_4 + \nu_{20} = 2438$ (*tert*-C$_4$H$_9$)
2606	w						$\nu_3 + \nu_5 = 2603$ (*tert*-C$_4$H$_9$)
2676	w						$\nu_{17} + \nu_{19} = 2674$ (*tert*-C$_4$H$_9$)
2747	w			2744	1	p	$2\nu_{18} = 2760$ (*tert*-C$_4$H$_9$)
				2789	0		
2818	w			2811	1	p	$2\nu_4 = 2809$ (*tert*-C$_4$H)
2892	m	2890	vw	2890	3	p	$\nu_4 + \nu_{16} = 2899$; $2\nu_3 = 2892$ (*tert*-C$_4$H$_9$)
2926	m			2924	6	p	ν_2(a$_1$) (*tert*-C$_4$H$_9$)
		2958	vw	2950	6	p	ν_1(a$_1$) (*tert*-C$_4$H$_9$)
2977	s						ν_{15}(e) (*tert*-C$_4$H$_9$)
		2990	vw	2988	6	dp	ν_{14}(e) (*tert*-C$_4$H$_9$)
3006	s	3000	w	3004	sh	dp	ν_{13}(e) (*tert*-C$_4$H$_9$)
		3010	w				

[a] p denotes polarized; dp, probably depolarized; sh, shoulder; s, strong; m, medium; w, weak; v, very; parentheses, for states of polarization, uncertain. [b] Raman intensities are relative to that of the strongest line being equal to 10.

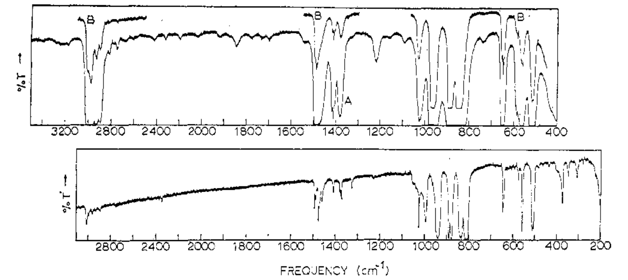

Figure 1.—Infrared spectrum of $(CH_3)_3CPF_4$: top, vapor at 25°, (A) p = 11.2 cm, (B) p = 1.3 cm, l = 10 cm, AgCl windows; bottom, solid film at 77°K, CsI windows.

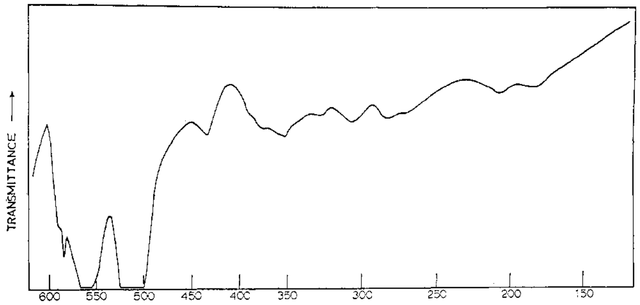

Figure 2.—Far-infared spectrum of $(CH_3)_3CPF_4$ vapor at 25°; p = 8.1 cm, l = 10 cm, polyethylene windows.

of C_{2v} symmetry, the justification of which is cited below. For all practical purposes the $(CH_3)_3C$ group vibrations may be treated according to selection rules appropriate for C_{3v} local symmetry although the molecular symmetry is undoubtedly lower.

The pertinent structural models to consider are shown in Figure 4. They are the trigonal bipyramid and the tetragonal pyramid, both equatorially and axially substituted. In addition idealized point group symmetries are listed for both high and low barrier cases with regard to the internal rotation of the $C(CH_3)_3$ group relative to the PF_4 group. While an intermediate barrier might be expected, it is not certain to what degree the selection rules may be modified.[19] Table IV lists the point group symmetries and corresponding selection rules for the models shown in Figure 4.

TABLE IV
ACTIVITY OF FUNDAMENTAL MODES FOR VARIOUS MODEL STRUCTURES FOR THE CPF_4 FRAMEWORK

Point group	Fundamentals	Raman	Ir	Raman–ir coincidences
C_{4v}	9	9 (3p)	6	6
C_{3v}	8	8 (4p)	8	8
C_{2v}	12	12 (5p)	11	11
C_s	12	12 (8p)	12	12

In deciding on a possible structure for a complex molecule like $(CH_3)_3CPF_4$ from vibrational data, considerable simplification results by first examining available assignments for the *tert*-butyl group. Some of these assignments are summarized by Mann, Acquista, and Lide[20] for $(CH_3)_3CX$ molecules of C_{3v} molecules. For this symmetry, the fundamentals break up to give 8 of species a_1 and 12 of species e, all infrared and Raman active. There are 4 symmetry-forbidden a_2 vibrations.

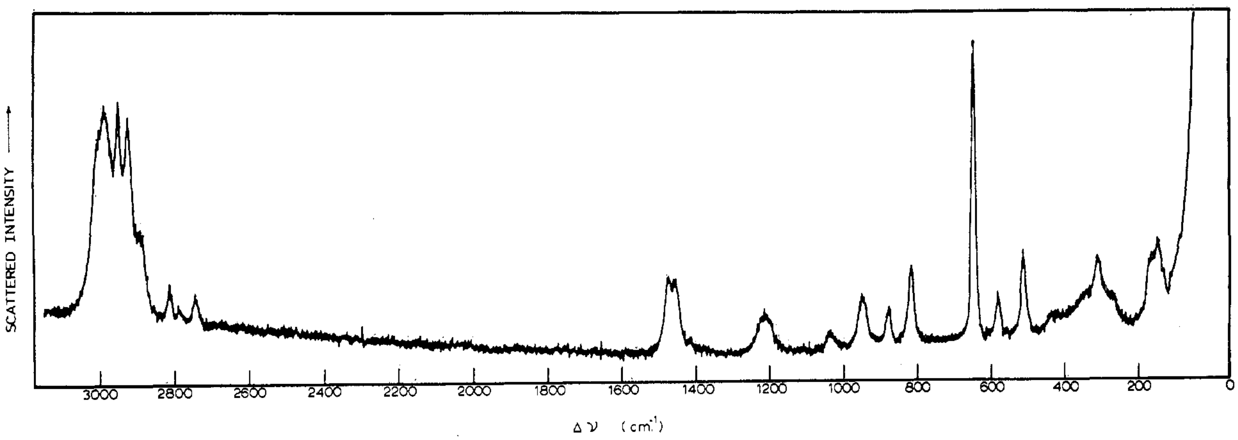

Figure 3.—Raman spectrum of liquid $(CH_3)_3CPF_4$ at 25°; 10-cm^{-1} slit, 735 amplitude, single beam.

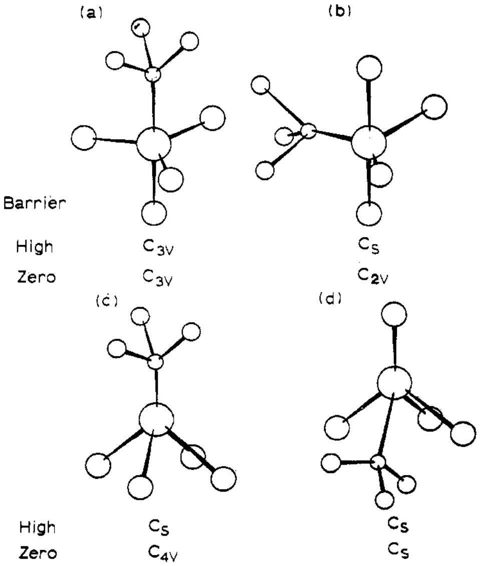

Figure 4.—Structural models for $(CH_3)_3CPF_4$.

Of the 20 active fundamentals, 10 are internal vibrations of the CH_3 groups, 5 are stretches, and 5 are bends. The CH stretches appear characteristically at about 3000 cm^{-1} while the CH bending vibrations are grouped near 1450 and 1380 cm^{-1}. Most of these vibrations are readily identified in the spectra recorded in Figures 1 and 3. The Raman spectrum shows an intense band in the 3000-cm^{-1} region with four components attributed to fundamentals. The corre-

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(19) D. F. Eggers, Jr., H. E. Wright, and D. W. Robinson, *J. Chem. Phys.*, **35**, 1045 (1961).

(20) D. E. Mann, N. Acquista, and D. R. Lide, Jr., *J. Mol. Spectrosc.*, **2**, 575 (1958).

sponding infrared absorption consists of three closely spaced lines, two of which (3006 and 2926 cm^{-1}) overlap with Raman lines at 3004 and 2924 cm^{-1}, respectively. When these results are combined with polarization data, the assignment in Table III was obtained.

No Raman lines appeared between the CH stretching and bending region while weak infrared bands are seen in Figure 1 attributable to combination and overtone bands of the *tert*-butyl group and CPF_4 skeletal frame.

Two bands in the infrared spectrum (at 1410 and 1489 cm^{-1}) are counted as fundamentals in the CH bending region. The band at 1410 cm^{-1} has a counterpart in the Raman spectrum at 1414 cm^{-1}. Two additional Raman bands at 1456 and 1472 cm^{-1}, both depolarized, have no counterpart in the infrared. Thus four bands are assigned as CH bending vibrations in this region in Table III. An infrared band of medium intensity appearing at 1380 cm^{-1} with no corresponding Raman band is counted as the fifth CH bend. Two of the Raman bands are depolarized and hence listed as e species. The infrared band appearing at 1489 cm^{-1} and the low-intensity Raman band at 1414 cm^{-1}, polarized, are assigned as a_1 species. The species designations are considered somewhat tenuous, however.

Of the ten remaining fundamentals associated with the *tert*-butyl group, four are external CH_3 modes, three are rocking, and one is a CH_3 torsion. The rocking modes normally appear in the 900–1150-cm^{-1} region. The weak infrared band at 1157 cm^{-1} in Figure 1 is assigned as one of the rocking vibrations of a_1 species by comparison with assignments on related molecules.[20,21] The infrared band at 1028 cm^{-1}, appearing as a depolarized line at 1032 cm^{-1} in the Raman spectrum, is counted as a rocking mode while the third such mode, expected to be of weak intensity, undoubtedly is buried in the intense P–F absorption at 964 cm^{-1} in the infrared spectrum (949 cm^{-1} in the Raman spectrum). The CH_3 torsion usually appearing around 250 cm^{-1} and of low intensity is tentatively associated with the very weak infrared band at 271 cm^{-1} (272 cm^{-1} in the Raman spectrum).

Two CC stretches and two CC bends are expected for the *tert*-butyl group under C_{3v} symmetry. The Raman band at 815 cm^{-1}, apparently polarized, with no infrared counterpart and the weak infrared band at 1218 cm^{-1} (1215 cm^{-1} in the Raman spectrum) appear in the expected regions for CC stretches and are so assigned. Two weak infrared bands at 355 and 390 cm^{-1} are assigned as CC bending fundamentals. The latter frequencies are very close to assignments for these bending fundamentals in $(CH_3)_3CX$ molecules[20,21] and form the main basis for the present assignment. The 355-cm^{-1} band in the infrared spectrum has a Raman counterpart, possibly polarized, at 340 cm^{-1} while no corresponding Raman band appears for the infrared shoulder at 390 cm^{-1}.

Finally, two fundamentals associated with the phosphorus atom are expected for C_{3v} symmetry of the $(CH_3)_3CP$ grouping, a PC stretch and a PC bend. The PC stretching vibrations in other compounds appear to vary over a wide range, 700–800 cm^{-1} for methyl dichlorophosphines[22,23] and around 425–575 cm^{-1} for chloro- and fluorophosphines[23,24] containing the CF_3 group. Considerable mixing of modes in the latter compounds has been indicated[24] and may result in the much lower frequencies than seen in the methyl compounds. In any event, this band invariably appears medium to strong in the infrared spectrum and normally much weaker in the Raman spectrum.

After assignment of PF stretching fundamentals characteristic of the PF_4 group, to be discussed below, the frequency of the PC stretch is strongly indicated to be one of the remaining bands lower than 650 cm^{-1}. The infrared band of moderate intensity at 583 cm^{-1} serves as the PC stretch for $(CH_3)_3CPF_4$, particularly in view of the presence of the low-intensity, polarized Raman counterpart at 581 cm^{-1}. Here again, coupling may be significant but most likely with CC modes.

The PC bending mode is tentatively assigned to the weak infrared band at 308 cm^{-1} (309 cm^{-1} in the Raman spectrum) and is close to the corresponding vibration in *tert*-butyl chloride[21] (301 cm^{-1}). The comparison here is based on the closeness in mass of chlorine and phosphorus atoms.

In fact, the frequencies (summarized in Table V) for the $(CH_3)_3CP$ unit of $(CH_3)_3CPF_4$ more closely parallel those of *tert*-butyl chloride[21] than any of the other members of the $(CH_3)_3CX$ series of molecules. Evans and Lo[21] have given a more detailed assignment for *tert*-butyl chloride than reported previously.[20] Their assignment is compared with the *tert*-butyl vibrations reported here (Table V). The assignments warrant further confidence when compared with spectra ob-

TABLE V

$(CH_3)_3C$ FREQUENCIES

No.	Mode description	Freq, cm^{-1} $(CH_3)_3CP^a$	Freq, cm^{-1} $(CH_3)_3CCl^b$
	a_1 Species		
1	CH str	2950	2981
2	CH str	2926	2937
3	CH_3 def	1489	1448
4	CH_3 def	1410	1375
5	CH_3 rock	1157	1155
6	CC str	815	818
7	PC str	560	585
8	CCC bend	355	372
	a_2 Species		
9	CH str	...	...
10	CH_3 def	...	...
11	CH_3 rock	...	...
12	CH_3 torsion	...	...
	e Species		
13	CH str	3006	2993
14	CH str	2988	2981
15	CH str	2977	2937
16	CH_3 def	1472	1480
17	CH_3 def	1456	1456
18	CH_3 def	1380	1375
19	CC str	1218	1241
20	CH_3 rock	1028	1030
21	CH_3 rock	...[c]	927
22	CCC bend	390	408
23	PC bend	308	301
24	CH_3 torsion	271	~290[d]

[a] Frequencies are those from the gas-phase infrared spectrum except ν_6, ν_{16}, and ν_{17} which are taken from the liquid-phase Raman spectrum. [b] See ref 21. [c] See text. [d] Estimated. See ref 21.

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(21) J. C. Evans and G. Y.-S. Lo, *J. Amer. Chem. Soc.*, **88**, 2118 (1966).

(22) J. R. Durig, F. Block, and I. W. Levin, *Spectrochim. Acta*, **21**, 1105 (1965).

(23) J. E. Griffiths, *ibid.*, **21**, 1135 (1965).

(24) (a) J. E. Griffiths, *ibid., Part A*, **24**, 303 (1968); (b) *ibid., Part A*, **24**, 115 (1968).

tained on *tert*-butyldifluorophosphine and *tert*-butyldichlorophosphine to be reported elsewhere.[25]

There remain twelve infrared bands in the region below 1000 cm^{-1} attributable to the skeletal frequencies of the CPF_4 framework. Two of these are counted as difference bands. The band at 283 cm^{-1} disappears in the infrared spectrum of the solid at 77°K (Figure 1, bottom) while the 329-cm^{-1} band is extremely weak in the gas-phase spectrum (Figure 1, top). The PC stretch, which has already been discussed, is common to both the $(CH_3)_3CP$ and CPF_4 groupings. Consequently, eleven infrared-active bands are assignable as fundamentals for the CPF_4 framework. Table IV indicates that the point group symmetry is C_{2v} for this number of infrared-active fundamentals. However, the strongest evidence against either the C_{4v} or the C_{3v} point group, each of which has three infrared stretching fundamentals associated with it, is the observance of four intense infrared bands in the PF stretching region.

Eight Raman-active fundamentals are assignable to the CPF_4 group, three of which are polarized. Twelve are expected for C_{2v} or C_s symmetry indicating that several weak bands were not observed. The fact that eleven instead of twelve infrared-active vibrations are considered as fundamentals does not eliminate C_s symmetry from contention; however, the low number of polarized bands present provides some evidence against the C_s point group.

With these considerations in mind the assignments listed in Table III for the CPF_4 group correspond to those expected for the C_{2v} point group. The structure then is indicated to be a trigonal bipyramid with the *tert*-butyl group located in an equatorial position. The details of these assignments follow.

The four PF stretching vibrations in the infrared spectrum are seen as intense absorptions at 964, 887, 846, and 650 cm^{-1}. The corresponding Raman frequencies are at 949, 876, 844, and 648 cm^{-1}, respectively. The most intense Raman line is the 648-cm^{-1} frequency, strongly polarized, and hence is listed under a_1 species. The 876-cm^{-1} line in the Raman spectrum is also polarized. The latter band is in the region ascribed[1-4] to the equatorial PF_2 stretch in other XPF_4 molecules while the Raman line at 648 cm^{-1} is characteristic of a PF_2 symmetric axial stretching mode. The higher frequency of the two remaining PF stretches, the 964-cm^{-1} band in the infrared spectrum, is undoubtedly the asymmetric equatorial stretching fundamental (b_1 species). The equatorial asymmetric PF stretch is then assigned to the infrared band at 846 cm^{-1} (844 cm^{-1} in the Raman spectrum) as a b_2 species.

Two bending modes of a_1 species remain to be assigned. One is readily identified as the polarized band at 512 cm^{-1} in the Raman spectrum, the infrared counterpart of which appears as the intense absorption at 511 cm^{-1}. Comparison with related molecules[1-4] suggests that the weak infrared band at either 183 or 208 cm^{-1} is associated with the other PF bending mode of a_1 symmetry. Neither has a complementary Raman line. An additional PF bending mode of b_1 symmetry is also expected in this low-frequency region. These assignments are listed in Table III ascribing the 183-cm^{-1} band to a_1 species and the 208-cm^{-1} band to b_1 species. However the reverse may just as well be the case.

An intense infrared band at 560 cm^{-1} (low intensity in the Raman spectrum at 557 cm^{-1}) is indicated to be the out-of-plane bending motion (b_2 species). This motion appears higher than rocking motions in more symmetric trigonal bipyramids.[26] For example, in PF_5[27] the rocking vibration is located at 514 cm^{-1} while the out-of-plane motion is assigned to a frequency at 579 cm^{-1}. For the $(CH_3)_3CPF_4$ molecule under consideration the weak infrared band at 376 cm^{-1} with no Raman counterpart is assigned to a rocking motion of b_2 symmetry. The much lower frequency of this motion compared to that in PF_5[27] implies that the *tert*-butyl group participates in the mode to a considerable extent; whereas the equatorial out-of-plane bend is largely associated with motion of the fluorine atoms.

A nearby Raman line at 425 cm^{-1} with no corresponding infrared absorption is indicated as an a_2 species vibration. The latter mode is expected to be infrared inactive under C_{2v} symmetry. For D_{3h} symmetry, as in PF_5, this mode would be degenerate with the rocking vibration just discussed. The splitting under the lower symmetry is not expected to be great and, accordingly, the 425-cm^{-1} line is assigned as a PF twisting motion.

The only vibrations remaining to be assigned are the weak infrared band at 435 cm^{-1} with no corresponding Raman line and the low-intensity Raman line at 150 cm^{-1} with no corresponding infrared band. The band at 435 cm^{-1} would logically be associated with a PF bending mode of b_1 species. This frequency would be degenerate under D_{3h} symmetry with the PF bend assigned at 511 cm^{-1} in the infrared spectrum. Comparison with other molecules of the type XPF_4 shows[1-4] that the splitting seen here of 76 cm^{-1} is not unreasonable. The Raman line at 150 cm^{-1} may be a difference band or possibly a torsional mode about the PC bond. However little information is known about such motions and additional work is needed on this point.

While the assignment is reasonably satisfactory in terms of C_{2v} symmetry, the C_s symmetry is not entirely ruled out. Whether or not the barrier to rotation about the PC bond is sufficiently high to alter appreciably the selection rules and lower the symmetry to C_s is not readily discernible in this study.

The assignments of fundamental frequencies for the skeletal framework of $(CH_3)_3CPF_4$ are summarized in Table VI.

Discussion

Analysis of the vibrational spectra suggests a trigonal-bipyramidal structure for $(CH_3)_3CPF_4$ with the *tert*-butyl group located in an equatorial position. This structure is consistent with that found for a variety of XPF_4 molecules.[1-6] Only in the case of CF_3PF_4 has a different structure been reported,[7] that of an axially substituted trigonal bipyramid from microwave work at −78°.

Both the C_{4v} and C_{3v} symmetries were readily ruled out. Much simpler spectra were expected for these cases than that observed.

Even though a fairly detailed spectral assignment of

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(26) R. R. Holmes, R. M. Deiters, and J. A. Golen, *Inorg. Chem.*, **8**, 2612 (1969).

(27) J. E. Griffiths, R. P. Carter, Jr., and R. R. Holmes, *J. Chem. Phys.*, **41**, 863 (1964).

TABLE VI

SKELETAL FREQUENCIES (CPF_4) OF *tert*-BUTYLTETRAFLUOROPHOSPHORANE[a]

No.	Mode description[b]	Species	Freq,[e] cm^{-1}
1	PF_2 str	a_1	887
2	PF_2' str		650
3	PC str[c]		583
4	PF_2–PF_2' bend[d]		511
5	PF_2–PF_2' bend[d]		183
6	PF_2F_2' twist	a_2	425
7	PF_2 str	b_1	964
8	PF_2–PF_2' bend[d]		435
9	PF_2–PF_2' bend[d]		208
10	PF_2' str	b_2	846
11	CPF_2 out-of-plane bend		560
12	CPF_4 rock		376

[a] Frequencies are gas-phase infrared values except ν_6 which is taken from the liquid-phase Raman spectrum. [b] Primes refer to axial atom. [c] The PC stretch is listed here and in Table V. [d] At present there is uncertainty in characterizing these equatorial–axial bending motions: L. S. Bartell, *Inorg. Chem.*, **9**, 1594 (1970); R. R. Holmes and J. A. Golen, *ibid.*, 9, 1596 (1970). [e] In addition to the fundamental frequencies listed here and in Table V for $(CH_3)_3CPF_4$ there is a torsion of the *tert*-butyl group about the PC bond. A Raman frequency at 150 cm^{-1} might possibly be attributed to this mode although it appears to be too high a value.

$(CH_3)_3CPF_4$ was made, it was not possible to rule out models of C_s symmetry completely. The likely models that were considered, are the high-barrier cases for the equatorially substituted trigonal bipyramid and the axially substituted square pyramid. The small number of polarized bands seen in the Raman indicated the unlikelihood of C_s symmetry.

Examination of the results of dipole moment measurements in Table II provides additional evidence against an axially substituted square pyramid. A regular increase in dipole moment is seen as the electronegativity of the equatorial ligand is decreased. The small increase in gas-phase dipole moments over the series of ligands methyl, ethyl, and *tert*-butyl supports a common structure. If there was a structural change from the equatorially substituted trigonal bipyramid observed[5] for CH_3PF_4 to an axially substituted square pyramid for $(CH_3)_3CPF_4$, a larger dipole moment might be expected. The axial F–P–F bond angle near 180° in the former would be closer to 120° in the latter structure. With a PF bond moment estimated[18] at approximately 1.2 D, the resultant moment along the C_4 axis should be nearer to 4 D instead of the 2.8-D value observed for $(CH_3)_3CPF_4$. Thus, it is concluded that the structure is an equatorially substituted trigonal bipyramid with only a modest distortion toward a square-pyramidal conformation.

Although the equatorially substituted trigonal bipyramid is decidedly the favored structure on the basis of the vibrational analysis and dipole data, little can be said about the barrier to rotation of the *tert*-butyl relative to the PF_4 group about the PC bond. As pointed out, the extent to which selection rules might be modified in going from a low to an intermediate barrier is not well understood.[19]

Some evidence is provided on the lower limit to rotation from nmr spectroscopy. In view of the C_{2v} structure indicated for $(CH_3)_3CPF_4$, the ^{19}F spectrum[12] showing one fluorine atom environment spin coupled to the phosphorus atom suggests intramolecular exchange similar to that postulated in CH_3PF_4,[8] CF_3PF_4,[4] $ClPF_4$,[10] PF_5,[28] and others.[11,29,30] To explain nmr equivalence in molecules like CF_3PF_4 and $(CH_3)_3CPF_4$, rotation about the PC bond is required in addition to a Berry-type process.[28] In the case of $(CH_3)_3CPF_4$, the fluorine atom equivalence[31] is maintained down to −150° where the compond begins to settle out of the isopentane solvent. As the temperature is lowered, no perceptible increase in line width is observed. Thus, on an nmr time scale at least, the rotation about the PC bond required to give ^{19}F equivalence in an intramolecular exchange is considered rapid. However, relative to a vibrational time scale, this motion may be insufficient to alter, in particular, polarizations of Raman bands.

Examination of the infrared spectrum of the solid film at 77°K (Figure 1, bottom) shows no features attributable to the presence of any new isomeric conformation such as that discussed in the case of CF_3PF_4.[4] As expected, considerable sharpening of the bands is seen and some of the bands, particularly those at 1489, 1380, 887, and 846 cm^{-1} in the gas phase, undergo splitting in the solid. The latter is no doubt associated with crystal lattice effects. The most noticeable band shifts seen in the solid occur for the very strong asymmetric PF equatorial and axial stretching vibrations at 964 and 846 cm^{-1}, respectively. The former shifts to 939 cm^{-1} and the latter to the doublet at 836 and 811 cm^{-1}. Only minor changes are associated with the symmetric PF stretches, each splitting into a doublet.

The group electronegativity of the CF_3 unit estimated[32] at about 3.2 allows a prediction of the dipole moment of the C_{2v} form of CF_3PF_4 of a few tenths of 1 D. The presence of such a low value for an asymmetric-top molecule might preclude the detection of this form of CF_3PF_4 in the microwave study[6] as suggested by Griffiths.[4] On the other hand, it is not easy to rationalize the lack of detection of the C_{3v} form in the temperature-dependent infrared study.[4]

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