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Pentacoordinated Molecules. VIII. Preparation and Nuclear Magnetic Resonance Study of PH_2F_3 and PHF_4[1a]

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Received May 27, 1966

Details of the synthesis of PH_2F_3 and PHF_4 from anhydrous hydrogen fluoride and the appropriate phosphorous acid are given. The compounds react with Pyrex and quartz. Proton, F^{19}, and P^{31} nmr spectra of the neat liquid and solutions suggest that both molecules are undergoing exchange with retention of P–H and P–F bonding at the lowest temperatures studied. The temperature dependence of the nmr spectra indicates that a self-association process is important for PH_2F_3 in the condensed state. Association is supported by other physical properties reported for this molecule. Similar data obtained for PHF_4 do not support self-association. In this case the nmr spectra at higher temperatures indicate the presence of an exchange process involving P–F bond breakage. The compounds are monomeric in the vapor. Infrared data are also reported. Analysis given elsewhere supports a trigonal bipyramidal structure for PH_2F_3 with the hydrogen atoms present in equatorial positions.

Various kinds of spectroscopic and dielectric data providing structural information have been accumulated on all members of the phosphorus(V) chlorofluoride series.[2] Spectroscopic[3] and electron diffraction[4] data have provided structural information on alkyl derivatives as well. To gain further information on phosphorus pentacoordinated molecules, the hydrogen ligand proves particularly attractive.

The preparation of both PH_2F_3 and PHF_4 from anhydrous hydrogen fluoride and the appropriate phosphorous acid was recently reported in the German patent literature;[5] however, little detail was given. This paper concerns the syntheses, measurement of some of the properties, and an nmr study of PH_2F_3 and PHF_4.

Experimental Section

Preparation.—The apparatus consisted of a copper vacuum system with Swagelok fittings, Hoke Monel bellows seal valves (480 series), and Kel-F U traps. To measure pressure the system incorporated a precision Heise Bourdon tube (8-in. diameter) made of stainless steel. Graduations were in millimeters covering the range 0–800 mm. The gauge was calibrated against a mercury manometer system and gave readings accurate to ±0.5 mm.

Hypophosphorous acid (Fisher, purified) obtained commercially is about a 50% solution. The water was removed from a 300-ml portion by vacuum transfer rather than the elaborate procedure of Jenkins and Jones.[6] After a 4-hr period, no further water was removed. Upon cooling the syrupy liquid that was left behind, immediate crystallization occurred. The product melted at 26.5° (lit.[6] 26.5°). It was stored in a desiccator which was placed in a refrigerator maintained at 0°.

For the preparation of PH_2F_3, approximately 2 g (0.030 mole) of solid hypophosphorous acid was allowed to warm to −78° with 5 g (0.25 mole) of anhydrous hydrogen fluoride (Matheson, 99.9%) in a Kel-F tube attached to the metal vacuum system. No noticeable reaction was evident and most of the solid was not in solution. After a few minutes the reaction mixture was allowed to warm slowly to −22° at which temperature it was maintained for 0.5 hr. At this point solution of the solid was complete. To ensure that the reaction was over, the mixture was warmed repeatedly to room temperature and condensed to −196°. Most of the unreacted hydrogen fluoride was retained by a trap cooled to −78°; the product was collected in a trap cooled to −111.6°. Small amounts of hydrogen fluoride contaminating the product were removed by further vacuum fractionation and treatment with sodium fluoride. A tensiometrically homogeneous product was obtained. The yield after fractionation is estimated to be 35%.

PHF_4 was prepared by an entirely analogous procedure from phosphorous acid (Fisher Certified reagent, 98.9%), used directly, and anhydrous hydrogen fluoride.

In a typical reaction about 2.6 g (0.13 mole) of hydrogen fluoride was condensed on 1.5 g (0.018 mole) of solid phosphorous acid. On warming no reaction was evident at −78°. Maintaining the reaction mixture at −50° for 0.5 hr caused solution of the phosphorous acid. The mixture was warmed to room temperature and condensed to −78° several times to ensure completion of the reaction. Repeated slow fractionation of the product through traps cooled to −95, −136, and −196° gave a sample free of HF impurity. The latter contaminant could not be removed with sodium fluoride as was done in the purification of PH_2F_3 because of apparent reaction between PHF_4 and the sodium fluoride. The yield was estimated to be 20%.

Results

Vapor Pressure.—The products were found to react rapidly with Pyrex and quartz; hence, the properties were studied in the metal vacuum system. As mentioned above, a calibrated Heise Bourdon tube was used to record pressures to ±0.5 mm. A platinum resistance thermometer was used to record the temperatures. Measurements were made from the melting point of −52°[5] to 0° for PH_2F_3 and from −80° to −45° for PHF_4. In contrast to the phosphorus chlorofluorides[1] no detectable changes in pressure took place with time. At each temperature a portion of the sample was removed to see if the pressure remained constant and thus to check on its homogeneity. No changes in pressure reading resulted. The equation governing the

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[1] (a) Presented in part before the Division of Inorganic Chemistry, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966. Previous paper: R. R. Holmes and R. P. Carter, Jr., *J. Chem. Phys.*, **43**, 1650 (1965). (b) Department of Chemistry, University of Massachusetts, Amherst, Mass. 01002.

[2] R. R. Holmes and R. P. Carter, Jr., *J. Chem. Phys.*, **43**, 1645 (1965), and references cited therein; A. A. Maryott, S. J. Kryder, and R. R. Holmes, *ibid.*, **43**, 2556 (1965).

[3] A. J. Downs and R. Schmutzler, *Spectrochim. Acta*, **21**, 1927 (1965), and references cited therein; (b) J. E. Griffiths, *J. Chem. Phys.*, **41**, 3510 (1964); **44**, 2686 (1966).

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

[5] B. Blaser and K. Worms, German Patent 1,106,736 (1961); *Angew. Chem.*, **73**, 76 (1961).

[6] W. A. Jenkins and R. T. Jones, *J. Am. Chem. Soc.*, **74**, 1353 (1952).

liquid–vapor equilibrium for PH_2F_3 obtained by a least-squares fit is $\log p(\text{mm}) = (-1473.0/T) + 8.1991$. The extrapolated boiling point is 3.8°. The heat of vaporization is 6.7 kcal/mole; Trouton's constant is 24.

The corresponding equation for PHF_4 is $\log p(\text{mm}) = (-1158.9/T) + 7.8290$. The boiling point (extrapolated) is −39.0°, the heat of vaporization, 5.30 kcal/mole, and Trouton's constant, 22.6. Table I lists the vapor pressure values.

TABLE I

VAPOR PRESSURES

PH_2F_3		PHF_4	
t, °C	p, mm	t, °C	p, mm
−49.58	36.2	−80.33	65.9
−36.32	93.5	−63.92	195.9
−22.94	198.5	−51.46	396.0
−6.69	478.0	−45.32	556.1
0.00	636.2		

Molecular Weight.—Vapor density measurements obtained by weighing samples of known p–v–t values gave slightly high results (102) for PH_2F_3 compared to the monomer molecular weight (calcd, 90.0). However, no trend in molecular weight was observed in the range 80–250 mm and no band shifts with pressure were present in the infrared spectrum. A monomer molecular weight (109.2) was obtained for PHF_4 (calcd, 108.0). The high value for PH_2F_3 may be a result of its greater reactivity compared to PHF_4 with the Pyrex vessel used in the measurements.

Nuclear Magnetic Resonance Spectra.—Owing to the reactivity of PH_2F_3 and PHF_4 with Pyrex and quartz, samples for nmr determinations were prepared in thin-wall Teflon tubes (FEP Type A). Sampling techniques involving vacuum transfer were similar to that reported by Reinhard.[7] Sample spinning was made possible by placing the Teflon tube inside an ordinary glass nmr tube.

For measurements involving external referencing $(CH_3)_4Si$ and CCl_3F were placed in the glass nmr tube along with the Teflon tube containing the sample. The glass tube was then sealed. Some measurements were made on samples in $CHCl_3$ and CCl_4 as solvents. P^{31} spectra were referenced by the substitution method using $(CH_3O)_3P$ as an external reference.

Spectra were recorded as a function of temperature using a Varian Associates HR-60 high-resolution spectrometer operating at 60 Mc/sec for protons, 56.4 Mc/sec for F^{19}, and 24.3 Mc/sec for P^{31}. Attempts to obtain spectra at temperatures lower than the melting points of PH_2F_3 and PHF_4 in an inert solvent were not successful. The compounds were found to be immiscible with most solvents tried, including isopentane, CCl_3F, and $CHCl_3$ (at lower temperatures), thus limiting the temperature range for investigation.

Resonance signals very much broadened were observed for PH_2F_3 in both the F^{19} and proton high-resolution nmr measurements in the neat liquid as well as in $CHCl_3$ solution. The proton spectrum of PH_2F_3 in CCl_4 solution (Figure 1b) was more resolvable showing a basic doublet (a result of P–H coupling), each component of which is split into a quartet having a 1:3:3:1 intensity distribution (that expected from spin coupling of hydrogen atoms with three fluorine atoms which are apparently magnetically equivalent). The F^{19} spectrum in CCl_4 (Figure 1d) appears as a broadened doublet, thus showing the phosphorus–fluorine spin coupling but not the hydrogen–fluorine coupling.

The nmr spectra of neat PH_2F_3 (Figure 1a and c) are similar to that of the CCl_4 solution except that the proton spectrum is less resolved. In $CHCl_3$ solution a broad doublet was present in the proton spectrum, and only a single, very broad band was present in the F^{19} spectrum.

In addition, band shifts with changes in temperature were present particularly in the case of the neat liquid. In all spectra sharp peaks due to the references, $CHCl_3$, $(CH_3)_4Si$, and CCl_3F, were observed; hence the broadened signals would not be a result of the use of Teflon nmr tubes. The data are summarized for PH_2F_3 in Table II.

Figure 2 shows proton and F^{19} nmr spectra for PHF_4. Considerably lower temperatures for investigation were available for this molecule because of its low melting point (∼−100°) and slight miscibility with isopentane. Exchange effects are clearly evident.

In the proton spectra observed at −114°, a basic doublet is seen (a result of P–H spin coupling), each component of which is split into a quintet of 1:4:6:4:1 intensity distribution (a result of F–H spin coupling proven by radiation at the fluorine resonance frequency and observing the collapse of the quintet structure, Figure 2e). On warming, the quintet structure is lost and the remaining doublet sharpens. As with PH_2F_3 the F^{19} spectrum shows no F–H spin coupling. A doublet of low resolution collapses to a single, broadened resonance signal on warming from −112 to −38°. In both spectra no change in chemical shift with temperature is evident. The data are summarized in Table III.

P^{31} nmr measurements on neat PH_2F_3 and a CCl_4 solution (∼20% by volume) showed only a single broad resonance signal over the same temperature range reported for the proton and F^{19} spectra for this molecule. The signal was somewhat more pronounced from the CCl_4 solution, having a half-width at half-height of about 2 kc/sec. The chemical shift was approximately 180 ppm upfield from $(CH_3O)_3P$ (obtained by superposition of the maximum in the resonance from PH_2F_3 and the center of the resonance pattern from $(CH_3O)_3P$ as seen on the oscilloscope screen). Since the maximum in the broad resonance of PH_2F_3 was difficult to locate, considerable uncertainty exists in the chemical shift.

In contrast to PH_2F_3, the P^{31} spectrum of the PHF_4 molecule (neat) is well resolved at the lowest tempera-

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[7] R. R. Reinhard, *Rev. Sci. Instr.*, **36**, 549 (1965). See also C. A. Wamser and B. B. Stewart, *ibid.*, **36**, 397 (1965).

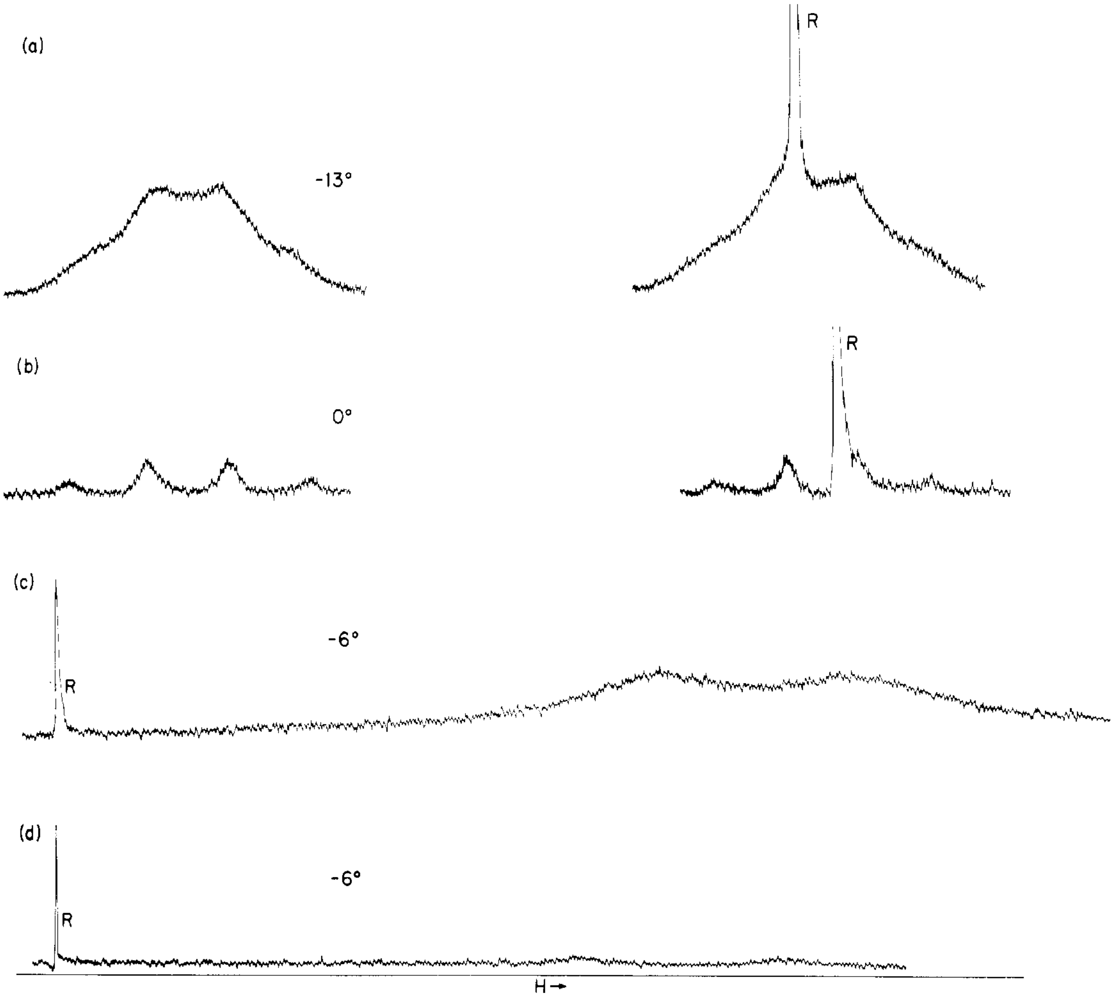

Figure 1.—Proton nmr spectra of PH_2F_3 as (a) neat liquid at −13° and (b) 20% CCl_4 solution at 0°. Fluorine-19 nmr spectra of PH_2F_3 as (c) neat liquid at −6° and (d) 20% CCl_4 solution. R = reference signal.

TABLE II[a]

F^{19} Nmr Data for PH_2F_3

Temp, °C	Solvent	Ref	δ, ppm	J_{P-F}, cps
−34	Neat	CCl_3F (ext)	29.1	770
−6	Neat	CCl_3F (ext)	54.2	824
−6	CCl_4 (20%)	CCl_3F (int)	48.0	860

Proton Nmr Data for PH_2F_3[b]

Temp, °C	Solvent	Ref	δ, ppm	J_{P-H}, cps	J_{H-F}, cps	δ_{H-F},[c] ppm
0	CCl_4 (20%)	$(CH_3)_4Si$ (int)	−7.26	841	80	No HF
−13	Neat	$(CH_3)_4Si$ (ext)	−7.15	908	63	−6.17
0	Neat	$(CH_3)_4Si$ (ext)	−6.90	878	58	−5.75
−33	$CHCl_3$ (20%)	$CHCl_3$	−7.32	891	Broadened	−6.43
−13	$CHCl_3$ (20%)	$CHCl_3$	−7.27	888	Broadened	−6.10
−33	$CHCl_3$ (50%)	$CHCl_3$	−7.28	894	Broadened	−6.75

[a] Concentrations are expressed in approximate per cent by volume. [b] The chemical shifts are reported relative to $(CH_3)_4Si$. The chemical shift difference between $(CH_3)_4Si$ and $CHCl_3$ was taken as 7.71 ppm and this value was subtracted from shifts relative to $CHCl_3$. [c] A sharp line of weak intensity attributable to HF was observed in some of the proton spectra.

ture available for investigation, −110° (Figure 3a). The structure collapses on warming to −85° where a single, broad resonance is observed. No change in line shape is detected on further warming to −40°. The low-temperature pattern shown in Figure 3a was obtained with the integrator in the circuit and shows side bands at 1969 cps. The chemical shift relative to $(CH_3O)_3P$ as an external reference obtained as described above is +191 ppm at −110°. At −85° the shift which has a considerable degree of uncertainty was calculated to be approximately +200 ppm. A CCl_4 solution (30% by volume) of PHF_4 at −17° also showed a single, broad resonance line shifted about +180 ppm from $(CH_3O)_3P$.

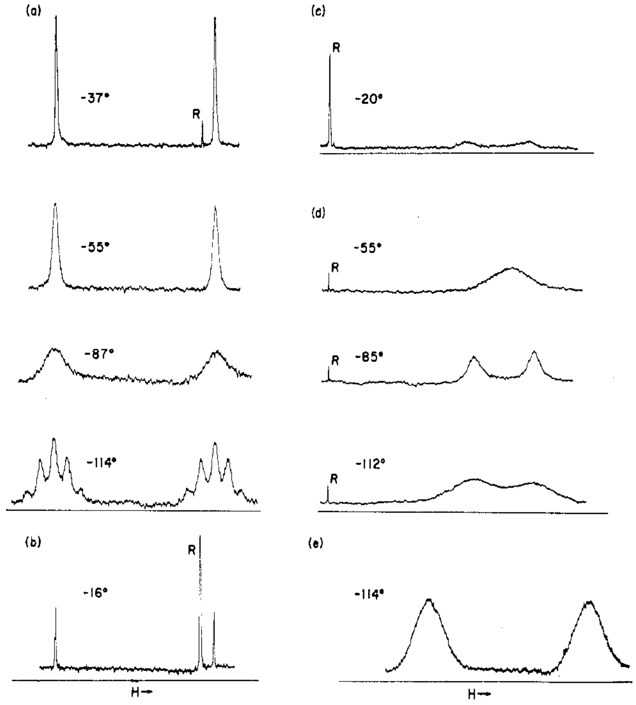

Figure 2.—Proton nmr spectra of PHF_4 as (a) neat liquid as a function of temperature and (b) 30% CCl_4 solution at −16°. Fluorine-19 nmr spectra of PHF_4 in (c) 30% CCl_4 solution at −20° and (d) neat liquid as a function of temperature. (e) Proton nmr spectrum of PHF_4 at −114° while irradiating at the fluorine resonance frequency. R = reference signal.

TABLE III

F^{19} Nmr Data for PHF_4

Temp, °C	Solvent	δ,[a] ppm	J_{P-F}, cps	Remarks
−112	Neat[b]	49.6	892[f]	Doublet
−101	Neat[b]	49.6	980	Doublet
−85	Neat[b]	49.5	953	Doublet
−50	Neat[b]	50.2	. . .	Single peak
−38	Neat[b]	49.6	. . .	Single peak
−20	CCl_4 (30%)	47.1	944[f]	Doublet

Proton Nmr Data for PHF_4

Temp, °C	Solvent	δ,[c] ppm	J_{P-H}, cps	J_{H-F}, cps	δ_{H-F},[e] ppm
−114	Neat[b]	. . .[d]	1092	91	
−85	Neat[b]	. . .	1093		
−55	Neat[b]	−7.52	1084		−6.38
−37	Neat[b]	−7.51	1080		−6.10
−16	CCl_4 (30%)	−7.38	1075		−7.13

[a] Fluorine chemical shifts are relative to CCl_3F as an internal reference except for the CCl_4 solution where CCl_3F was an external reference. [b] The neat liquid contained a small amount of dissolved isopentane in addition to the internal references. [c] Proton chemical shifts are internally referenced relative to $(CH_3)_4Si$. [d] The chemical shifts are not available for lack of solubility of the internal reference. [e] A sharp line of weak intensity attributed to HF was observed in some of the proton spectra. [f] Considerable uncertainty exists due to the broadness of the peaks.

Infrared Spectrum.—Gas-phase infrared spectra were recorded using Perkin-Elmer Model 421 and 21 spectrophotometers in the region 250–4000 cm⁻¹. The spectra were calibrated with NH_3 and CO_2. Samples were contained in a 10-cm Monel metal gas cell. AgCl and CsI windows were used. The windows were held in place in a vacuum-tight seal with Kel-F gaskets. No changes in spectra with time or band shifts with pressure in the range of 2–500 mm were noted and no impurities were detected. The principal lines are recorded in Table IV and serve to characterize the compounds.

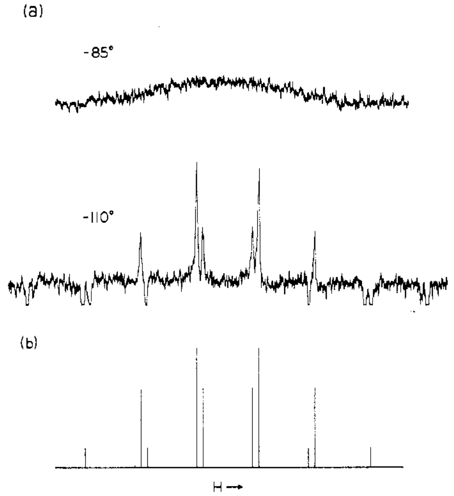

Figure 3.—Phosphorus-31 nmr spectra of PHF_4 as (a) neat liquid (side bands at 1969 cps are present) and (b) predicted (simple first order) for structure with equivalent fluorine atoms showing P–H and P–F spin coupling.

TABLE IV

INFRARED SPECTRA[a]

Cm⁻¹	Intens	Cm⁻¹	Intens	Cm⁻¹	Intens
		PH_2F_3			
320[b]	m	787	m	1103[b]	w
341	m	823[b]	vs	1121[b]	w
388	w	856	m	1291[b]	w
472[b]	m	871	m	1448	m
635	w	915	w	1459	m
665[b]	w	945[b]	w	2435	m
720	w	999	vs	2482[b]	m
766	s	1013	vs	2550[b]	m
		PHF_4			
313	m	667	w	1192[b]	w
318	m	762	w	1302[b]	w
346	m	792	w	1377	m
388[b]	m	832	s	1386	m
485[b]	m	866[b]	vs	1531	m
508	m	881	s	1539	m
532	s	890	s	1930	w
538	s	936[b]	m	2478	m
628[b]	m	991	m	2585	w
649[b]	m	1027[b]	s		

[a] s, strong; m, medium; w, weak. [b] Band heads.

Thermal Stability.—In contrast to the molecular forms of the phosphorus(V) chlorofluorides which slowly transform to solid modifications[8] at room temperature, PH_2F_3 and PHF_4 show no evidence of such behavior. No changes were seen in the infrared spectrum of a sample held in the cell for several hours and no changes were evident in the vapor pressure measure-

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(8) (a) R. R. Holmes, *J. Chem. Educ.*, **40**, 125 (1963); (b) T. Kennedy and D. S. Payne, *J. Chem. Soc.*, 1228 (1959); (c) L. Kolditz, *Z. Anorg. Allgem. Chem.*, **284**, 144 (1956); **286**, 307 (1956).

ments. In contact with Pyrex, however, catalytic decomposition occurs producing SiF_4 and other products with PH_2F_3 reacting more rapidly than PHF_4.

Discussion

Molecular weight data show that PH_2F_3 is nearly monomeric in the vapor. Coupled with this information, vibrational analysis[9] of the gas phase infrared data rules out the D_{3h} symmetry which would be representative of the most symmetrical trigonal bipyramidal structure with equatorial fluorine atoms. The vibrational data are consistent with a trigonal bipyramidal structure (C_{2v} symmetry) with one equatorial and two axial fluorine atoms, analogous to the structure of the PCl_2F_3 molecule strongly supported by a variety of information.[2]

The proton nmr spectrum of PH_2F_3 in CCl_4 solution (pair of quartets, somewhat broadened) shows the spin–spin coupling of the phosphorus atom and secondary coupling with three fluorine atoms acting in an apparent magnetically equivalent fashion. In view of the conclusions from the spectroscopic study[9] it seems unlikely that the most symmetrical structure should be present in the liquid state. Consequently the nmr data are best interpreted in terms of an exchange process similar to that occurring in PCl_2F_3.[10]

In the latter molecule the two fluorine atom environments are seen at temperatures below $-120°$ (a pair of sharp doublets of twice the intensity of a pair of sharp triplets) giving a spectrum in agreement with the gas phase structure suggested by vibrational analysis.[11] The pattern changes over to a sharp doublet above $-70°$. Thus equatorial and axial fluorine atoms undergo exchange with retention of P–F bonding. However, no experimental information is available on the exact mechanism involved.

In addition to the averaging of fluorine environments discussed above, the exchange appears more complicated in PH_2F_3. The F^{19} nmr spectrum of the neat liquid shows a broad doublet (spin coupling between phosphorus and fluorine atoms) which shifts downfield on lowering the temperature. A single, broad resonance is present in the P^{31} spectrum. A shift of 25 ppm for a temperature change of 28° is seen in the F^{19} spectrum (Table II). A smaller change in the same direction is evident in the proton spectra. No shift in the F^{19} spectra of the corresponding doublet pattern in the phosphorus(V) chlorofluorides was observed.[10a]

The reasons for the changes are not clear, but one plausible explanation suggested by other physical properties and consistent with the shift, at least in the proton spectrum, is that association caused by hydrogen bonding is present. It is significant that the most resolvable proton spectra were obtained in CCl_4 solution where association would be expected to be reduced. Formation of associated species of varying degrees in solution would contribute to line broadening as well as the onset of any atom exchange which may very well accompany such a process. The presence of small amounts of HF (Table II) could easily catalyze an exchange process.

Evidence supporting self-association of PH_2F_3 is seen from its immiscibility with solvents and the unusually high melting point compared to that of PCl_2F_3 (Table V[12]). It is also noteworthy that PHF_4 is more volatile and has a much lower melting point than PH_2F_3. The PHF_4 molecule shows no tendency for self-association. The chemical shifts are seen to be temperature independent in both F^{19} and proton spectra (Table III) which is the same as that observed in the F^{19} spectrum of PCl_2F_3.[10a]

Table V

Physical Properties of PHF_4, PH_2F_3, and PCl_2F_3

	Mp, °C	Bp, °C	ΔH_{vap}, kcal/mole	Trouton's constant
PHF_4	(-100)	-39.0	5.30	22.6
PH_2F_3	-52^a	3.8	6.7	24
PCl_2F_3	-124	2.5	6.23	22.6

[a] See ref 5.

The proton spectrum of PHF_4 at $-114°$ (Figure 2a), a doublet with a resolved quintet structure, shows the spin–spin coupling between the phosphorus and hydrogen atoms (1092 cps) and secondary coupling between the hydrogen and four fluorine atoms acting in an apparent magnetically equivalent fashion. Correspondingly, at $-110°$ both phosphorus–hydrogen (J_{P-H} = 1086 cps) and phosphorus–fluorine spin couplings (J_{P-F} = 975 cps) are evident in the P^{31} spectrum of PHF_4 (Figure 3a). Because P–F and P–H coupling constants are similar the spectrum consists of two interpenetrating quintets.

With the use of the integrator, the marker frequency at 1969 cps at almost twice the frequency of the phosphorus–fluorine coupling constant serves to alter the intensity of the lines in the P^{31} spectrum and causes the lack of observance of the four weakest lines expected for PHF_4 having four equivalent fluorine atoms attached to phosphorus (Figure 3b).

The only reasonable model having four equivalent fluorine atoms would be a tetragonal pyramid of C_{4v} symmetry. However, analysis[9] of the infrared spectrum rules out such a structure. Consequently, an exchange mechanism involving retention of P–F and P–H bonding is implied at this temperature.

On warming, though, the quintet structure in the proton spectrum is lost and the resulting doublet sharpens. Correspondingly, in the F^{19} spectrum of PHF_4 the doublet collapses to a singlet on warming and the fine structure in the P^{31} spectrum changes to a single, broad resonance. These changes are consistent with a process in which the onset of P–F bond breakage takes place on warming but P–H bonding is

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(9) R. R. Holmes, to be published.

(10) (a) R. R. Holmes, R. P. Carter, Jr., and G. E. Peterson, *Inorg. Chem.*, **3**, 1748 (1964); (b) E. L. Muetterties, W. Mahler, and R. Schmutzler, *ibid.*, **2**, 613 (1963).

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

(12) Similar data on the other chlorofluorides are recorded in ref 1a.