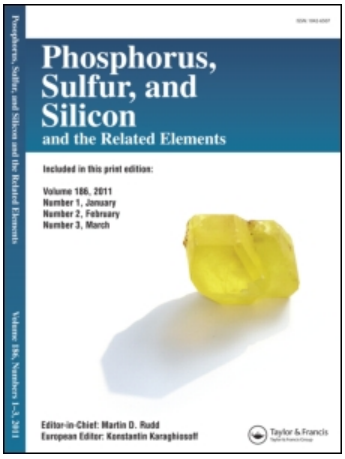

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MOLECULAR STRUCTURES OF PCl_4F, PCl_3F_2, AND PCl_2F_3: PURE CHLORINE NUCLEAR QUADRUPOLE RESONANCE AND LOW TEMPERATURE F^{19} NUCLEAR MAGNETIC RESONANCE SPECTRA

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MOLECULAR STRUCTURES OF PCl_4F, PCl_3F_2, AND PCl_2F_3: PURE CHLORINE NUCLEAR QUADRUPOLE RESONANCE AND LOW TEMPERATURE F^{19} NUCLEAR MAGNETIC RESONANCE SPECTRA[1,2]

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Chlorine nuclear quadrupole resonance spectra determined at 77°K. and F^{19} n.m.r. data obtained as a function of temperature for the molecular forms of PCl_4F, PCl_3F_2, and PCl_2F_3 were correlated with previous infrared and Raman spectra. The data support the trigonal bipyramid as the structural model for the halides with fluorine atoms showing a preference for axial positions. The symmetry of PCl_4F is C_{3v} and that of PCl_3F_2 is D_{3h}. For PCl_2F_3 the data are best interpreted in terms of the C_{2v} point group. Further, the data give no evidence for any significant variation in molecular structure between the gas, liquid, and solid states. Symmetry considerations and the F^{19} n.m.r. data support the presence of axial P—F π-bonding. The chlorine quadrupole data indicate a lesser importance of π-bonding in the P—Cl bonds.

Positional isomerization in the "low temperature" forms (moleculear forms[3]) of the phosphorus(V) chlorofluorides has been the subject of a recent infrared and low temperature Raman investigation[1] in this laboratory. Considering all likely possibilities for these five-coordinated molecules, the spectral data[1] have shown that the structure of PCl_3F_2 (D_{3h} symmetry) is a trigonal bipyramid wherein the fluorine atoms assume axial positions. The spectra[1] of PCl_4F were best interpreted in terms of the C_{3v} point group and consequently a trigonal bipyramidal structure in which the axial sites are occupied by a fluorine atom and a chlorine atom. The spectra further suggested that the three remaining equivalent chlorine atoms are not coplanar with the phosphorus atom; the extent or direction of deviation, however, was not evident. For PCl_2F_3 similar spectral analysis[1] ruled out the D_{3h} symmetry corresponding to the trigonal bipyramid having all equatorial fluorines. The latter structure had been proposed earlier on the basis of an electron diffraction study.[4] However, further analysis of the spectra did not allow a choice to be made among the remaining trigonal bipyramidal and tetragonal pyramidal models.

A chlorine nuclear quadrupole resonance investigation and a low temperature F^{19} nuclear magnetic resonance study[5,6] were undertaken concurrently with the infrared and Raman vibrational study[1] in order to firmly establish the structures of the molecular forms of the phosphorus(V) chlorofluorides and possibly to obtain insight into some of the bonding features peculiar to molecules possessing a co-

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ordination number of five. The results of these additional studies are the concern of the present paper.

EXPERIMENTAL

Materials

The mixed halides PCl_4F, PCl_3F_2, and PCl_2F_3 were prepared by the low temperature chlorination of PCl_2F, $PClF_2$, and PF_3, respectively, in a Pyrex glass vacuum system using a more convenient procedure[7] than that originally described.[5] Stopcocks were lubricated with Kel-F grease. The PCl_2F and $PClF_2$ were prepared and purified according to an earlier procedure.[5] PF_3 (Columbia Organic Chemicals Co.) was used after fractionation and in some cases was subjected to a chemical treatment which has been shown to remove small amounts of impurities yielding a mass spectroscopically pure product.[8]

Since all the molecular phosphorus(V) chlorofluorides do transform[3] slowly to solid modifications at room temperature, the purified samples were stored at $-78°$. No detectable change took place with time as observed by repeating all the chlorine quadrupole resonance measurements and the F^{19} determinations several months later.

Chlorine gas (The Matheson Co.) was dried over phosphorus pentoxide coated glass beads at $-78°$ *in vacuo* and fractionated before use. Isopentane (The Matheson Co., Chromatoquality reagent) had an analysis of 99 + mole %. It served as a solvent for some of the F^{19} n.m.r. measurements and was stored over CaH_2.

Nuclear Quadrupole Resonance Spectra

The instrument used for observing the quadrupole resonance signals was recently developed in this laboratory.[9] It is of the superregenerative type employing a wide-band feedback coherence control system which allows a radiofrequency searching band width as great as 30 Mc. Sensitivity is maintained very high and the spectrometer will scan unattended, thus allowing for overnight searching of signals in new substances. A full description of the circuitry and operational characteristics has been reported.[9]

Sample sizes of about 1 cc. of the phosphorus(V) chlorofluorides contained in 7-mm. diameter Pyrex glass tubing were used. The tubes were sealed under vacuum and placed in a finger dewar having a large liquid nitrogen reservoir. The sample coil was wound around the outside of the finger.

F^{19} Nuclear Magnetic Resonance Spectra

A Varian Associates HR-60 high resolution spectrometer operating at 56.4 Mc. and fitted with a low temperature probe was used to record the F^{19} spectra. Calibration was achieved by the audio side-band technique. Samples were contained in 5-mm. glass tubes sealed under vacuum. The spectra of the pure liquid phosphorus(V) chlorofluorides were recorded as well as those of samples diluted with

isopentane. The pure liquid samples were externally referenced with CCl_3F while the diluted samples were internally referenced with CCl_3F.

RESULTS AND DISCUSSION

The Cl^{35} quadrupole resonance frequencies observed for the phosphorus(V) chlorofluorides at 77°K. are given in Table I. In Table II the F^{19} nuclear magnetic resonance data are recorded for the phosphorus(V) chlorofluorides, $(CH_3)_2PF_3$[6] and $(CH_3)_3PF_2$.[6]

In both tables, values of resonances are listed separately for equatorial and axial halogen atoms. The manner in which these positional assignments are arrived at is outlined in the following section.

Structure

The infrared spectra of gaseous phosphorus(V) chlorofluorides and the Raman spectra of liquid phosphorus(V) chlorofluorides gave no indication of any structural change taking place on going from the gaseous to the liquid state. From an examination of the chlorine quadrupole data it seems reasonable to assume that no change in structure is taking place for these low melting chlorofluorides in going to the solid state. The latter follows from two primary considerations: (1) the interpretation of the chlorine quadrupole spectrum of PCl_4F and (2) the similarity in resonance values among the various chlorofluorides.

The chlorine quadrupole resonance spectrum of PCl_4F (Figure 1) shows as a function of increasing frequency, the higher intensity Cl^{37} line, the lower intensity Cl^{35} line, and the higher intensity Cl^{35} line. The intensities of the lowest and highest

TABLE I

Cl^{35} Nuclear Quadrupole Resonance Frequencies at 77°K

	Equatorial Cl^{35} Mc./sec.	Axial Cl^{35} Mc./sec.
PCl_4F	32.54[a]	28.99
PCl_3F_2	31.26	
	31.89	
PCl_2F_3	31.49	

[a] Three closely spaced lines centered at 32.54 Mc.

TABLE II

F^{19} Nuclear Magnetic Resonance Data

Temp., °C.		Chemical shift,[a] p.p.m. δF	δF_a	δF_e	Coupling constants, c.p.s. J_{P-F}	J_{P-F_a}	J_{P-F_e}
−144	PCl_2F_3[b]		−67.4	+41.5		1032	1092
−22	PCl_2F_3	−31.1			1048		
−140	PCl_3F_2		−123.0			1051	
−140	PCl_4F		−132			992	
	$(CH_3)_2PF_3$[c]		+4.8	+88.6		772	960
	$(CH_3)_3PF_2$[c]		+5.8			545	

[a] CCl_3F reference. [b] The $J_{F_a-F_e}$ coupling is 124 c.p.s. [c] Values taken from ref. 6 and adjusted to the present scale by adding 78.8 p.p.m. to take into account the chemical shift difference between CF_3COOH and CCl_3F.

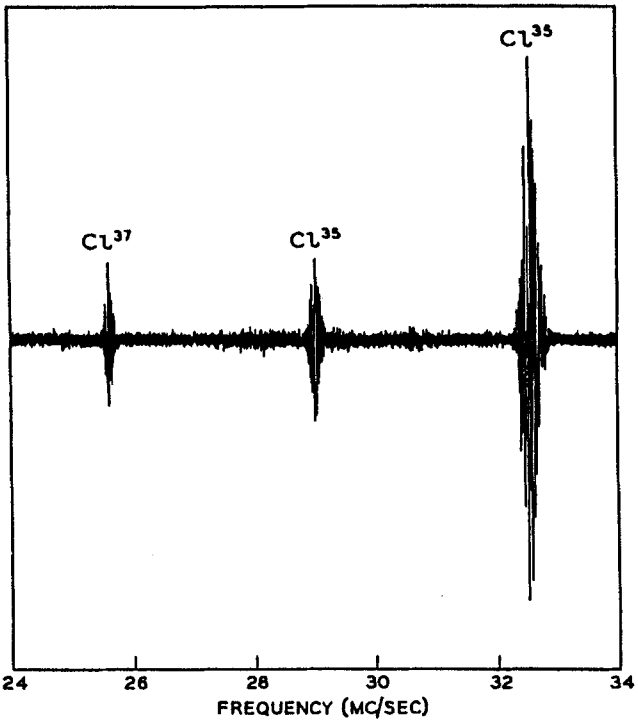


FIGURE 1 Pure chlorine n.q.r. spectrum of PCl_4F at 77°K.

frequency reflect the natural abundance of the chlorine isotopes, $Cl^{37}:Cl^{35} \simeq 1:3$. The fact that the intensity of the lower frequency Cl^{35} line closely approximates the intensity of the Cl^{37} line shows the presence of nonequivalent Cl^{35} environments in the ratio of 3:1. The large frequency separation of the Cl^{35} resonances, 3.56 Mc., as well as the 3:1 intensity ratio strongly suggest that the nonequivalence is due to the presence of positional nonequivalence in the free molecule and not to any nonequivalence introduced by intermolecular forces in the lattice. The magnitude of resonance splitting caused by intermolecular interactions in the solid for relatively nonpolar molecules such as these is of the order of a few tenths of a Mc.[10] The doublet observed in the Cl^{35} quadrupole spectrum of PCl_3F_2 with a separation of 0.63 Mc. is more realistically attributed to such an effect.

Infrared and Raman vibrational spectra show that PCl_3F_2 has the nonpolar trigonal bipyramidal structure (D_{3h} point group).[1] The latter structure is supported further by a study[7] of the dielectric behavior of the pure liquid as a function of temperature. The results showed a "zero" dipole moment. Thus with the reasonable assumption that the structure of PCl_3F_2 is retained in the solid as the quadrupole data suggest, the closely spaced Cl^{35} resonances are attributed to equatorial chlorine atoms.

The only reasonable pentacoordinated structure for PCl_4F having a chlorine ratio of 3:1 is the trigonal bipyramidal model (C_{3v} point group) having three equatorial and one axial chlorine atoms. This is also the structure suggested by the infrared and Raman vibrational spectra for this molecule.[1] The latter study, however, did

not definitely exclude the possibility of the trigonal bipyramidal structure bearing an equatorial fluorine atom (C_{2v} symmetry); hence in view of the present data more confidence may be associated with the model possessing a C_{3v} symmetry. In terms of this symmetry the Raman data provided some evidence that the three equivalent chlorine atoms are not coplanar with the phosphorus atom.[1] A dipole moment study[11] showed that PCl_4F possesses a very low value. Qualitative agreement with the latter value is achieved if the direction of distortion of the equatorial chlorine atoms is away from the axial fluorine atom.

Only one Cl^{35} resonance frequency is observed in the spectrum of PCl_2F_3. Its value of 31.49 Mc. is very near the average Cl^{35} frequency for PCl_3F_2, suggesting that here too we are "seeing" equatorial chlorine atoms only. The infrared and Raman vibrational study[1] of PCl_2F_3 was able to rule out the D_{3h} symmetry corresponding to the symmetrical trigonal bipyramidal structure having axial chlorine atoms. The latter structure was the one proposed on the basis of electron diffraction study.[4] That this structure is erroneous is confirmed further by establishing that PCl_2F_3 possesses a dipole moment.[11] However, no decision among remaining trigonal bipyramidal or tetragonal bipyramidal models was possible on the basis of the vibrational spectral study.[1] The quadrupole data suggest the trigonal bipyramidal structure having two axial and one equatorial fluorine atoms (C_{2v} point group).

The presence of the nonequivalence of fluorine atoms is fully demonstrated by observing the F^{19} n.m.r. spectrum of PCl_2F_3 (m.p. $-124°$) in isopentane solution at $-143°$. The F^{19} spectrum as a function of temperature[6] (Figure 2b) is typical of that observed for a molecule undergoing intramolecular exchange. Both P—F and F_a—F_e coupling are present at $-143°$. The low field pair of doublets arises from the axial fluorine atoms (the splitting caused by the phosphorus and equatorial fluorine atoms) and has an over-all intensity of twice that of the higher field pair of triplets (the splitting caused by the phosphorus and two axial fluorine atoms). At $-22°$ only a sharp doublet is seen, *i.e.*, the P—F coupling is retained. However, the weighted average chemical shift at $-143°$ is exactly the same, -31.1 p.p.m.,

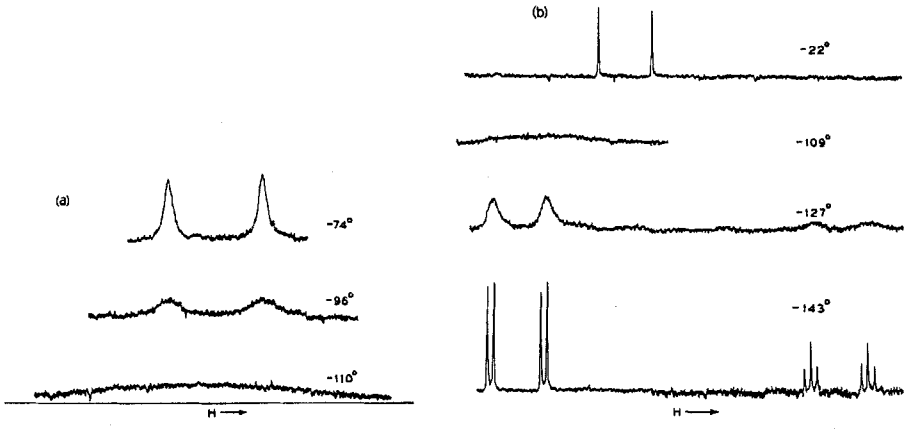
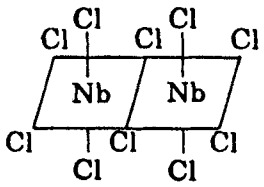


FIGURE 2 F^{19} n.m.r. spectra of PCl_2F_3: (a) pure liquid; (b) isopentane solutions, 20% by volume at $-22°$ and 30% by volume at the other temperatures listed.

as that observed for the molecule undergoing exchange at $-22°$ (Table II). Hence even though exchange is occurring, the molecule retains at higher temperatures the structure it possesses at $-143°$. The latter is in agreement with the Raman vibrational spectra,[1] which showed no detectable change from -40 to $-144°$ in a solution containing 25% by volume of PCl_2F_3 in isopentane or from -20 to $-120°$ in a sample of the pure liquid PCl_2F_3.

Taken alone the F^{19} n.m.r. data for PCl_2F_3 are in agreement with several likely models, the trigonal bipyramid of C_{2v} symmetry supported by the quadrupole data and the tetragonal pyramids having axial fluorine atoms.[6] A dimer molecule containing bridging chlorine bonds might also be considered, analogous to the structure of $NbCl_5$, which is a trigonal bipyramid in the vapor[12] but a dimer in the solid.[13]



To obtain agreement with the F^{19} data in this case it would have to be assumed that spin-spin coupling through the bridging chlorine atoms is not observed. The latter structural possibility was eliminated from consideration by a cryoscopic study[7] in isopentane solution as a function of concentration of PCl_2F_3. The data showed a monomer formulation.

Examination of the F^{19} n.m.r. spectra of PCl_4F and PCl_3F_2 showed simple doublets (P—F coupling) which remained invariant in pattern and chemical shift to less than 1 p.p.m. as a function of temperature in the range -22 to $-140°$. For these molecules the F^{19} spectra would be the same whether exchange is occurring or not since the fluorine atoms are equivalent in PCl_3F_2 and PCl_4F has only one such atom. Such a process would be expected to have a decreased rate as fluorine atoms are replaced by heavier chlorine atoms if one envisions an intramolecular inversion mechanism similar to that proposed by Berry.[14] In any event the fact that the chemical shift remains unaltered as the temperature is changed argues for the presence of one molecular species for each.

For PCl_3F_2, known to have axial fluorine atoms in a symmetrical trigonal bipyramidal structure from vibrational spectra[1] of the gas and liquid state, a chemical shift of -123.0 p.p.m. relative to CCl_3F was observed. For PCl_4F, suggested to have an axial fluorine atom in a distorted trigonal bipyramidal structure from the vibrational spectral study[1] and supported from the chlorine quadrupole data for the solid state, a similar chemical shift of -132 p.p.m. was observed. It then seems reasonable to assign the higher field line, $+41.5$ p.p.m., representing one fluorine atom in PCl_2F_3 to an equatorial position and the lower field line, -67.4 p.p.m., representing two fluorine atoms to axial positions, thus giving the structure supported by the quadrupole data for the solid.

An argument of this type would not eliminate from consideration the tetragonal pyramidal models with axial fluorine atoms. However, with all structural evidence supporting trigonal bipyramids in molecular PCl_4F and PCl_3F_2 as well as PF_5[1,4,15]

in the vapor and liquid states and molecular PCl_5[16] it seems highly unlikely that PCl_2F_3 should assume a different structural environment.

Bonding

Figure 3 shows F^{19} chemical shift data (relative to CF_3COOH) for a series of mixed phosphorus halides where the phosphorus atom has coordination numbers ranging from three to six. Some related to F^{19} data also are included for halides of other central atoms.[17] Figure 4 shows Cl^{35} nuclear quadrupole resonance data for members of the series PCl_xF_{3-x},[18] $POCl_xF_{3-x}$, and PCl_xF_{5-x}, and some related compounds.[19]

The data exhibit a number of significant features: (1) both the trends in F^{19} chemical shifts in the series $POCl_xF_{3-x}$ and PCl_xF_{5-x} and the trend in Cl^{35} resonance frequencies in the series PCl_xF_{3-x} are in a direction opposite to that expected on the basis of electronegativity considerations; (2) F^{19} chemical shifts for axial fluorine atoms are found to be significantly lower compared to the shift observed for the equatorial atoms in a given molecule; (3) the Cl^{35} resonance frequency for the axial chlorine atoms in PCl_4F or CF_3PCl_4 is several Mc. lower than that observed for the corresponding equatorial chlorine atoms in these molecules.

Some of the results may be correlated adequately from an examination of the make-up of the F^{19} chemical shift expression and the related expression describing quadrupole coupling constants.

Considering the original theory of Ramsey,[20] Saika and Slichter[21] concluded that the paramagnetic term dominates F^{19} chemical shifts and obtained a useful cor-

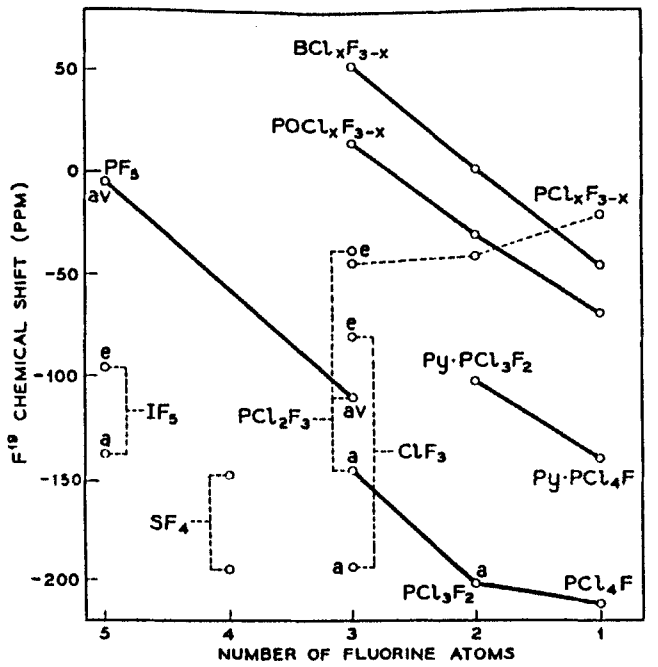


FIGURE 3 F^{19} chemical shifts relative to CF_3COOH *vs.* number of fluorine atoms.

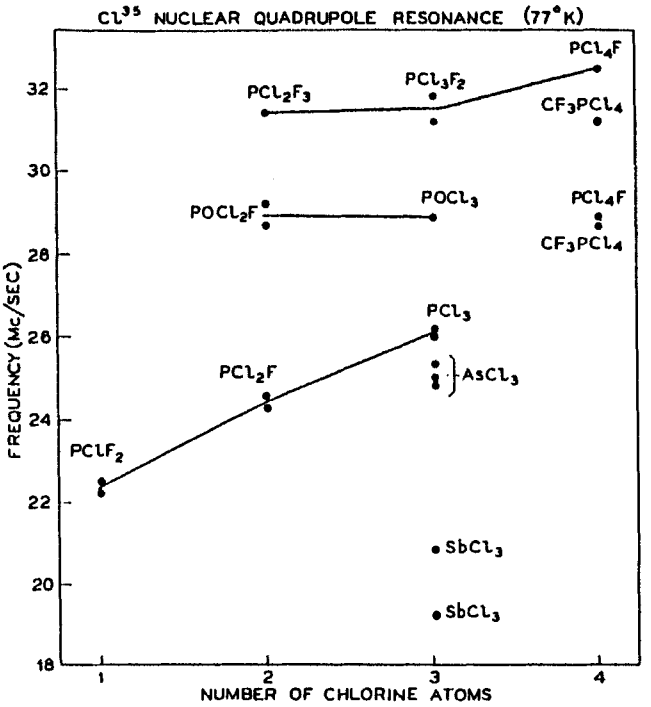


FIGURE 4 Cl^{35} n.q.r. frequencies (Mc.) *vs.* number of chlorine atoms.

relation with ionic character for binary halides. Recently Karplus and Das[22,23] employing a molecular orbital wave function further divided up the F^{19} chemical shift expression in terms of ionic character, I, hybridization, S, and double bond character, π. It has been pointed out that the contributions from other atoms do not contribute significantly to the chemical shift for fluorine atoms.[22-24]

Specializing to the case of an axially symmetrical cone-shaped charge distribution about the bond axis (*i.e.*, $\pi_x = \pi_y = \pi$) the relation of Karplus and Das[22] expressed in terms of the gross orbital populations on the fluorine atom becomes

$$\sigma = \sigma_0 \left[1 - S - I + IS + \pi + \pi(I + S - IS) - \frac{\pi^2}{2} \right] \tag{1}$$

where σ_0 (a negative quantity) may be interpreted as the difference between the shielding for the fluorine atom in a purely covalent single bond and that for the fluoride ion.

From the theory of Townes and Dailey[25] concerning quadrupole coupling constants for the bond type under consideration one has the result expressed in terms of the electric field gradient

$$q = q_0[1 - S - I + IS - \pi] \tag{2}$$

where q_0 is the field gradient for the atom.

If square terms are neglected as an approximation, it is seen that expressions 1 and 2 are analogous except, as pointed out by Karplus and Das,[22] for the opposite

dependency of σ and q on double bonding. When considering trends in series where double bonding may be significant, F^{19} data should prove more readily interpretable than quadrupole coupling constants.

It was suggested previously[5] that increasing π-bonding per fluorine bond as the number of fluorine atoms decreases along the series PCl_xF_{5-x} could account for the trend in F^{19} chemical shifts. In view of the structural information now accumulated showing that axial positions are preferred positions for fluorine atoms in these molecules and considering the symmetry of d orbitals in relation to the equatorial and axial positions in the trigonal bipyramid, an explanation based on π-bonding becomes even more attractive.

As was pointed out in an early paper by Kimball,[26] the d_{xz} and d_{yz} orbitals of the phosphorus atom are potentially capable of forming strong π-bonds in the trigonal bipyramid. An axially symmetrical cone-shaped charge distribution is expected about the P—F axial bond (regarded as coinciding with the Z axis) when these d orbitals overlap with the occupied p_x and p_y orbitals of the fluorine atom. If the d_{xz} and d_{yz} orbitals are used for π-bonding with fluorine atoms in equatorial positions, only the p_z orbital of each equatorial fluorine atom would participate effectively in π-bonding. Consequently, axial π-bonding would be considerably stronger than equatorial π-bonding. With axial π-bonding concentrated in the d_{xz} and d_{yz} orbitals, equatorial fluorine atoms probably π-bond more favorably with the d_{xy} and $d_{x^2-y^2}$ orbitals of the phosphorus atom but again such bonding would not be expected to be highly effective because of limited overlap, and, as Kimball[26] pointed out, the fact that these d orbitals may be involved partially with σ-bonding in the equatorial plane.

On the basis of symmetry π-bonding is expected to be greater for axial than equatorial atoms but equatorial atoms may have some measure of π-bonding.

Although F^{19} shifts for axial positions in molecules such as PCl_2F_3, SF_4,[27] and ClF_3 are lower than the shifts for the respective equatorial positions, it is not clear that the difference reflects greater axial π-bonding. This is because the nature of axial σ-bonding in trigonal bipyramids is somewhat speculative at present, particularly regarding the extent of d orbital participation of the central atom in hybridization schemes.[28] Consequently, if the σ-bonding to the two positions differs significantly, the interpretation of the internal F^{19} shifts becomes complex.

However, evidence that axial π_{d-p}-bonding exists to an appreciable extent in the phosphorus(V) chlorofluorides is provided more directly by comparing the downfield trends in axial F^{19} shifts for the series PCl_xF_{5-x} with the similar downfield shifts in the series $POCl_xF_{3-x}$ and BCl_xF_{3-x}. In the latter two series the problem of d orbital σ-bonding does not arise. The trend in F^{19} shift in the BCl_xF_{3-x} series has been interpreted[29] in terms of increasing π-bonding per B—F bond as x increases and appears entirely justified in view of the accumulation of evidence[30] supporting the greater importance of π_{p-p}-bonding in B—F bonds compared to B—Cl bonds.

For the $POCl_xF_{3-x}$ series P—F π-bonding has been considered to be more important than P—Cl π-bonding on the basis of respective bond-shortening values.[31] For molecules in a tetrahedral conformation such as these Cruickshank[32] following Kimball's[26] method represents the d_{z^2} and $d_{x^2-y^2}$ orbitals of the phosphorus atom as the ones most favorably oriented for π_{d-p}-bonding.

The fact that similar trends in F^{19} shifts are seen in series whose central atoms

have coordination numbers ranging from three to six shows that the paramagnetic shift is not peculiar to the trigonal bipyramid environment and suggests a common explanation. Thus, in accordance with the interpretation of the chemical shift expression for F^{19}, increasing importance of axial P—F π-bonding is supported in the series $PCl_2F_3 < PCl_3F_2 < PCl_4F$.

The effect of the decreased electronegativity of the methyl group compared to the chlorine atom is clearly evident, on comparing the higher fluorine resonances for $(CH_3)_2PF_3$[6] compared to PCl_2F_3 (Table II). It is also noteworthy that little change in F^{19} shift for axial fluorine atoms is seen between $(CH_3)_2PF_3$ and $(CH_3)_3PF_2$ assuming, as the authors[6] suggest, that the latter structure is a trigonal bipyramid of D_{3h} symmetry. Since a saturated carbon atom is expected to π-bond less effectively than a chlorine atom, P—F π-bonding in $(CH_3)_2PF_3$ should be maximized to a greater extent than in PCl_2F_3. Consequently, in going to $(CH_3)_3PF_2$ one expects a lower percentage change in axial P—F π-bonding compared to the corresponding change in the chlorofluorides. Accompanied again with the greater electron-releasing ability of an added methyl group, the similarity in axial fluorine resonances between $(CH_3)_2PF_3$ and $(CH_3)_3PF_2$ is rationalized as a consequence of the cancellation of the opposing influences.

The possibility of a steric effect caused by substitution of larger chlorine atoms in place of fluorine atoms being the cause of the trend in F^{19} shifts in the series PCl_xF_{5-x} has been discussed previously[5] and considered of minor importance. In this regard it is interesting to note that X-ray data have shown pentaphenylphosphorus to have a trigonal bipyramidal configuration, whereas the corresponding structure involving the larger antimony atom is a square pyramid in the solid state.[33]

A parallel behavior in the available Cl^{35} quadrupole data (Figure 4) also is seen between the $POCl_xF_{3-x}$ and PCl_xF_{5-x} series. Apparently changes in ionic character more nearly compensate for changes in P—Cl π-bonding as indicated by the small variations in Cl^{35} frequencies from member to member in each series.[34] If P—Cl π-bonding changes dominated, decreasing quadrupole resonance frequencies should be observed as the number of chlorine atoms per molecule decreased. That this does not occur supports the greater importance of P—F compared to P—Cl π_{d-p}-bonding.

Using expressions similar to (2) for the quadrupole coupling constant, estimations of ionic character have been made in the past,[10] usually by assuming a standard percentage S hybridization and estimating double bond character, empirically, with the aid of bond distance values. It is felt that such a calculation has little validity in the present instance. There is over a 20-Mc. variation in the coupling constant for chlorine atoms involved in the various P—Cl bonds (Figure 4) and no convenient way of assigning absolute π-bonding values from series to series.

On a qualitative basis through the general variations from series to series are understandable if it is assumed that they are primarily a result of changes in group electronegativities. Then the observed increase in the magnitude of the coupling constant in going from PCl_3 to $POCl_3$ or PCl_3F_2 is reasonable since the added oxygen or fluorine atoms bond the electron pair in σ-bonding and as a consequence cause an electron drift away from the chlorine nuclei, two fluorine atoms being more effective than a single oxygen atom in reducing the ionicity. However, little can be said about the difference between equatorial and axial chlorine coupling constants in PCl_4F.

The PCl_xF_{3-x} series deserves some comment. The changes in F^{19} shift show small variations along the series in a direction expected from electronegativity effects, while changes in Cl^{35} quadrupole frequencies in the series are in a direction opposite from that expected on the basis of electronegativity considerations. The reasons for the observed changes are not entirely clear. The presence of the lone electron pair as previously[5] pointed out is suspected to introduce considerably more bond flexibility in these molecules compared to the $POCl_xF_{3-x}$ series. However, further information is needed in order to understand these variations.

Considering the gain in stabilization energy resulting from the presence of greater axial P—F π-bonding compared to equatorial P—F π-bonding, a partial explanation is seen for the structure of PCl_2F_3 having C_{2v} symmetry (for which strong support has been given) compared to the more symmetrical D_{3h} model.[35] A more complete explanation must await the assessment of relative energy differences in P—F and P—Cl σ-bonds in the two positions of the trigonal bipyramidal structure. It is noteworthy that recent F^{19} n.m.r. data indicate that fluorine atoms prefer axial positions in molecules such as $CCl_3PF_2Cl_2$ and $CCl_3PF_2Br_2$.[36] It would be interesting to compare F^{19} n.m.r. data for additional series involving the phosphorus atom and other electronegative ligands with the results reported here. Reduced axial π-bonding is expected for ligands like —OR and $—NR_2$ since these groups each may have only one suitably oriented p orbital available for such bonding compared to the two available for fluorine.[37]

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