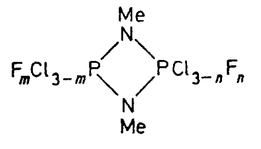
Preparative and Nuclear Magnetic Resonance Studies of Diazadiphosphetidines. Part VII.[1] Fluorine-19 and Phosphorus-31 Investigations of Chlorofluorodiazadiphosphetidines

By **Robin K. Harris** * and **Mohamed I. M. Wazeer**, School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ

Fluorine-19 and phosphorus-31 n.m.r. spectra have been obtained and analysed for a series of compounds of the type $\overline{PCl_{3-m}F_m{\cdot}NMe{\cdot}PCl_{3-n}F_n{\cdot}N}Me$, mostly under conditions of proton decoupling. The data are discussed in relation to substituent effects.

FLUORINATED diazadiphosphetidines have been the subject of a number of recent papers.[1] The most fruitful method of studying the geometry and intramolecular motion has proved to be n.m.r. spectroscopy. In previous papers in this series it was shown that n.m.r. parameters are very sensitive to changes in substituent and geometry. Here, it was decided to study the effects of substitution by chlorine, a second-row element, on the n.m.r. parameters. The compounds studied are of the general formula (I; $m,n = 0$—3). The ^{19}F n.m.r. spectrum of the fully fluorinated compound (I; $m = n = 3$) has been reported previously,[1a] as has[2] the ^{31}P chemical shift for the fully chlorinated compound (I; $m = n = 0$). Some information is presented here for all the other members of the series, although in certain cases the data are not complete because the species were present as minor components of a mixture. However, the range of results obtained is an improvement over those given earlier[1d] for the corresponding methyl and methoxy-cases. (Only four compounds in each of those series were available, apart from the fully fluorinated material.) The preparation of the chlorofluorodiazadiphosphetidines has been reported[3] earlier. In the present work, proton-decoupled ^{19}F and ^{31}P n.m.r. spectra were obtained and analysed to yield the relevant n.m.r. parameters. The ^{19}F, ^{31}P, and ^{1}H spectra of compound (I; $m = n = 1$) have been described by Binder,[4] but a proper spectral analysis was not carried out.



(I)

RESULTS

Spectral Analysis.—The spin systems[5] for the compounds studied, under conditions of proton-noise decoupling and rapid pseudo-rotation at both phosphorus atoms, are given in Table 1. The general appearance of the spectra was similar to those obtained for the methoxy-series.[1d] Two of the compounds (in addition to the fully fluorinated and fully chlorinated species) have symmetrical spin systems; the remaining molecules have unsymmetrical spin systems of the general type ABX_mY_n, where A and B are ^{31}P whereas X and Y are ^{19}F. Spectra of the type $[AX]_2$ are well known.[6] The system $[A[X]_2]_2$ with J_{AX} large, appropriate to the molecules considered here, has been described for the X region in Part II.[1b]

TABLE 1

Compounds $\overline{PCl_{3-m}F_m{\cdot}NMe{\cdot}PCl_{3-n}F_n{\cdot}N}Me$, (I), and their spin systems[5]

m	n	Spin system
3	2	ABX_3Y_2
2	2	$[A[X]_2]_2$
3	1	ABX_3Y
2	1	ABX_2Y
1	1	$[AX]_2$
3	0	ABX_3
2	0	ABX_2
1	0	ABX

For the unsymmetrical compounds $|\Delta\nu_{AB}|$ is in general comparable to $|J_{AB}|$ so that second-order characteristics result. However, $|\Delta\nu_{XY}|$ is in every case considerably greater than $|J_{XY}|$. Consequently, the spectra showed partial first-order characteristics in the ^{19}F region due to the 'X approximation' for phosphorus spin states $\alpha\alpha$ and $\beta\beta$. From these subspectra the ^{19}F chemical shifts and the magnitudes of the long-range (F,F) coupling constant, ($^4J_{FF}$), and of $|^1J_{PF} + {}^3J_{PF}|$ could be determined by inspection. The chemical shifts in the ^{19}F region between fluorines of PF_3, $PClF_2$, and PCl_2F groups are so large that there was no overlapping between signals of the different types, in spite of the large values of $^1J_{PF}$. However, there was very extensive overlapping in the ^{31}P region, entailing some difficulties in interpretation when mixtures of species were examined. In principle, the ^{31}P region of each unsymmetrical compound consists of a series of $(m + 1)(n + 1)$ *ab* subspectra and analysis is easy, although there can be ambiguities. In practice it proved feasible to measure $\Delta\nu_{AB}$ and $|J_{AB}|$ directly from the subspectra for all the unsymmetrical cases except $m = 3$, $n = 0$. In the case of compound (I; $m = 1$, $n = 0$), full spectral analysis was carried out by hand from ^{31}P and ^{19}F regions.[6] Of the two

---

[1] (*a*) Part I, R. K. Harris and C. M. Woodman, *Mol. Phys.*, 1966, **10**, 437; (*b*) Part II, R. K. Harris, J. R. Woplin, R. E. Dunmur, M. Murray, and R. Schmutzler, *Ber. Bunsengesellschaft Phys. Chem.*, 1972, **76**, 44; (*c*) Part III, O. Schlak, R. Schmutzler, R. K. Harris, and M. Murray, *J.C.S. Chem. Comm.*, 1973, 23; (*d*) Part IV, R. K. Harris, M. I. M. Wazeer, O. Schlak, and R. Schmutzler, *J.C.S. Dalton*, 1974, 1912; (*e*) Part V, R. K. Harris, M. Lewellyn, M. I. M. Wazeer, J. R. Woplin, R. E. Dunmur, M. J. C. Hewson, and R. Schmutzler, *ibid.*, 1975, 61; (*f*) Part VI, R. K. Harris, M. I. M. Wazeer, O. Schlak, and R. Schmutzler, *ibid.*, in the press.

[2] E. Fluck, *Z. anorg. Chem.*, 1963, **320**, 64.

[3] K. Utvary and W. Czysch, *Monatsh.*, 1969, **100**, 681.

[4] H. Binder, *Z. anorg. Chem.*, 1971, **384**, 193.

[5] C. W. Haigh, *J. Chem. Soc.* (*A*), 1970, 1682.

[6] J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High-resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1969.

sets of parameters which fitted the observed spectral frequencies, one was rejected on the grounds of the incompatibility of ${}^3J_{PF}$ with the results for the other compounds. (A distinction between the two solutions using the transition intensities in the ${}^{31}P$ region was not possible.) Only a limited amount of information was obtainable for (I; $m = 2$ or 3, $n = 0$) (from the ${}^{19}F$ region only, for $m = 3$).

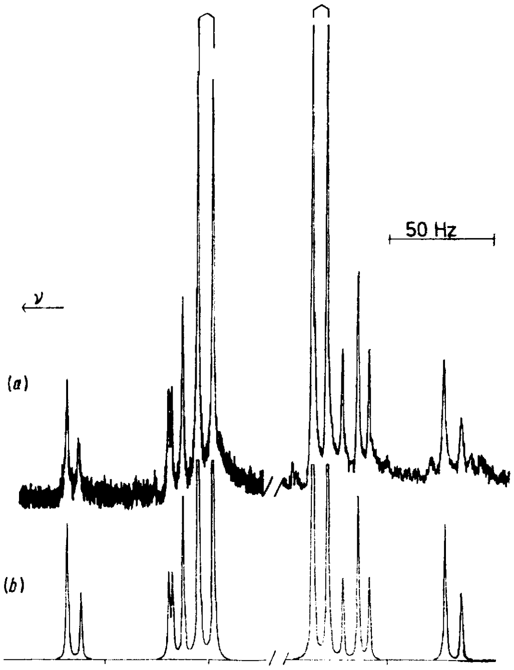


FIGURE 1 94.155 MHz ${}^{19}F-\{{}^1H\}$ spectra (PF_3 region) of compound (I; $m = 3, n = 1$): (a) observed; (b) calculated, showing the partial first-order characteristics (ax_3 subspectra) arising from phosphorus αα and ββ spin states. Some minor peaks in (a) are due to impurities. The four most intense peaks in (b) have been truncated

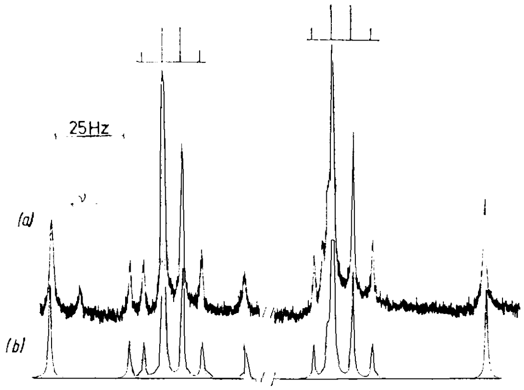


FIGURE 2 94.155 MHz ${}^{19}F-\{{}^1H\}$ spectrum (PCl_2F region) of compound (I; $m = 3, n = 1$): (a) observed; (b) calculated. The two most intense peaks in (b) have been truncated. Other details as in Figure 1

For the remaining unsymmetrical cases ($m = 3, n = 2$; $m = 3, n = 1$; and $m = 2, n = 1$) the spectra were simulated using the data obtained as described above (together with estimates of ${}^3J_{PF}$) with the UEA NMR computer program.[7] The program was then used in the iterative mode to fit the experimental spectra, employing ${}^{19}F$ transition frequencies only, and maintaining $\Delta\nu_{AB}$ and J_{AB} constant. (Although the ${}^{19}F$ spectra were very sensitive to $\Delta\nu_{AB}$ and J_{AB}, so iterations varying these parameters were also successful, the directly measured values were preferred.) The small difference in the magnetic fields used for recording the ${}^{31}P$ and ${}^{19}F$ spectra was ignored in the calculations. The experimental and calculated ${}^{19}F-\{{}^1H\}$ spectra for (I; $m = 3, n = 1$) are given in Figures 1 and 2. Partial first-order characteristics are clearly shown. No compound corresponding to (I; $m = 3, n = 1$) has been studied in the methyl or methoxy-series.[1d]

For the symmetrical compounds ($m = n = 1$ or 2) the parameters were mostly determined from the ${}^{19}F$ spectrum except for δ_P and J_{FF} in (I; $m = n = 1$). The ${}^{31}P$ chemical shift for (I; $m = n = 2$) was obtained readily from the ${}^{31}P$ spectrum, using the intense central peak; in fact this peak served as a convenient reference for all the ${}^{31}P$ chemical shifts. The relative signs of ${}^1J_{PF}$ and ${}^3J_{PF}$ were obtained from second-order characteristics in the spectra of the unsymmetrical compounds, and from the normal spectral analyses of (I; $m = n = 1$ or 2). It may be assumed that ${}^1J_{PF}$ is negative. The sign of ${}^2J_{PP}$ may be confidently asserted as positive, from previous work.[1d,f] The sign of ${}^4J_{FF}$ is similarly believed to be positive.

DISCUSSION

Chemical Shifts.—Table 2 lists the ${}^{19}F$ and ${}^{31}P$ chemical shifts observed for the compounds studied. The values for the parent compounds (I; $m = n = 0$ or 3) are also included for the purpose of comparison. The ${}^{19}F$ chemical shifts are spread over a wide range of 120 p.p.m., but each group has a characteristic region. Progressive substitution of F by Cl moves the fluorine resonance to higher frequency, *e.g.* $PF_3 \longrightarrow PClF_2$ gives a shift of *ca.* 45 p.p.m. and $PClF_2 \longrightarrow PCl_2F$ a shift of *ca.* 70 p.p.m. The changes in the chemical shifts are remarkable, compared to the effects observed in the methyl and methoxy-compounds discussed earlier.[1d] Similar variations in δ_F have been observed[8] for the chlorofluorophosphoranes. The axial–equatorial character of the fluorine is an important factor. However, as chlorine is the only second-row element present in the diazadiphosphetidines studied[1] to date, the large variations are attributed to this fact.

There are some interesting trends for each group as the nature of the distant group is varied. Thus δ_F in each group increases as the distant group is varied from PF_3 to $PClF_2$ to PCl_2F as shown in Figure 3. The gradient of the plots decreases in the order $PF_3 > PClF_2 > PCl_2F$. In each case the final point is out of line, and for the groups PCl_2F and $PClF_2$ the change of the distant group from PCl_2F to PCl_3 actually results in a decrease in δ_F. These facts may be attributed qualitatively to the axial-equatorial natures of the shielded fluorine nuclei and of the distant fluorine substituents. It thus appears that replacement of a distant equatorial fluorine by chlorine deshields both axial and equatorial fluorines, the latter

---

[7] R. K. Harris and M. Kinns, 'A Library of Computer Programs for NMR spectroscopy,' Science Research Council (Atlas Computer Laboratory), 1974.

[8] R. R. Holmes and W. P. Gallagher, *Inorg. Chem.*, 1963, **2**, 433.

by more than the former. However, replacement of a distant axial fluorine by chlorine shields an axial fluorine, whereas an equatorial fluorine is deshielded by such a substitution.

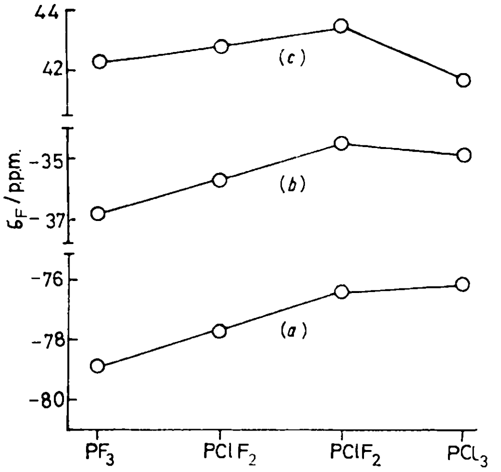


Figure 3 Variation in ^{19}F chemical shift with substitution pattern for the chlorofluorodiazadiphosphetidines. Groups: (*a*) PF_3, (*b*) $PClF_2$, (*c*) PCl_2F

pounds, and have been described by the theory of Letcher and Van Wazer.[9] There is a smooth variation in δ_P in each group as the distant group is varied in the order $PCl_3 < PCl_2F < PClF_2 < PF_3$, *i.e.* shielding is least when the distant group is PF_3, as might be expected on simple electronegativity grounds.

Coupling Constants.—The (P,F) coupling constants are given in Table 3. The values of $^1J_{PF}$ correspond to **33**, **50**, and **100%** axial character for the fluorines of the PF_3, $PClF_2$, and PCl_2F groups respectively. The trend in the variation of $^1J_{PF}$ in these compounds (*i.e.* $|^1J_{PF}|$ generally increasing in the order $PF_3 < PClF_2 < PCl_2F$) is the reverse of that found for the methyl and methoxy-compounds.[1] A similar trend is, however, observed [8,10,11] for the chlorofluorophosphoranes.

There are two effects to be considered: the axial–equatorial character of the bond, and the electronegativity (and/or bulk) effects of the substituents at phosphorus. It is well known that $|^1J_{PF}|$ is greater for equatorial than for axial fluorines (the axial bonds have less *s* character than the equatorial bonds). The sign of $^1J_{PF}$ is negative, so the algebraic value of $^1J_{PF}$ decreases as the axial character increases. It is not clear whether the Fermi-contact term is dominant for $^1J_{PF}$. For the $PF_2(OMe)-PF(OMe)_2$ compound in the methoxy-series the difference between $^1J_{PF}(ax)$ and $^1J_{PF}(eq)$ was found to be 144 Hz, and therefore changes in axial–equatorial character could account for a large part of the F ⟶ OMe substituent effect. However, clearly other effects dominate for the present series of compounds, since $^1J_{PF}$ increases as the axial character increases. Two features of the published data on chlorofluorophosphoranes are relevant. First,

Table 2

^{19}F and ^{31}P chemical shifts [a] for the chlorofluorodiazadiphosphetidines

	δ_F			δ_P			
Distant group	PF_3	$PClF_2$	PCl_2F	PF_3	$PClF_2$	$PClF_2$	PCl_3
PF_3	−78.91 [b]	−36.77	42.30	−8.13 [c]	1.63	5.41	*d*
$PClF_2$	−77.71	−35.64	42.82	−9.70	0.0	3.73	−15.62
PCl_2F	−76.35	−34.35	43.49	−11.27	−1.53	2.35	−16.99 [e]
PCl_3	−76.14	−34.78	41.71	*d*	−3.02	1.48	−17.86 [f]

[a] δ_F Values are in p.p.m. with respect to $CFCl_3$ and are accurate to ±0.05 p.p.m. The δ_P values are in p.p.m. with respect to the signal for (I; $m = n = 2$) and are ±0.1 p.p.m. Calculations based on absolute resonance frequencies [1d] indicate that the chemical shift of (I; $m = n = 2$) is −60.5 ± 0.5 p.p.m. with respect to external 85% H_3PO_4. For both δ_F and δ_P a positive sign indicates that the sample resonates to high frequency of the reference. [b] Ref. 1*a* gives −80.7 p.p.m. [c] Ref. 1*a* gives −69 p.p.m. from external 85% H_3PO_4. [d] Not obtained. [e] Ref. 4 gives −59.3 p.p.m. from external 85% H_3PO_4. [f] Ref. 2 gives −78.2 p.p.m. from external 85% H_3PO_4.

Table 3

(P,F) Coupling constants (Hz) [a] for the chlorofluorodiazadiphosphetidines

	$^1J_{PF}$ [b]			$^3J_{PF}$ [b]		
Distant group	PF_3	$PClF_2$	PCl_2F	PF_3	$PClF_2$	PCl_2F
PF_3	−922 [c]	−966	−966	32 [c]	22	7
$PClF_2$	−929	−970	−973	26	16	2
PCl_2F	−935	−975	−978 [d]	22	13	−3 [d]
PCl_3	*e*	−978 [f]	−971	*e*	8 [f]	−2

[a] (±1 Hz). [b] Coupling involving the fluorines of the group shown and the distant phosphorus. [c] Ref. 1*a*. Our measurements give $|^1J_{PF} + {}^3J_{PF}|$ 891 Hz. [d] Binder [4] gave 970 Hz for J_{PF}, but he presumably meant $|^1J_{PF} + {}^3J_{PF}|$. [e] Not obtained separately, but $|^1J_{PF} + {}^3J_{PF}|$ 924 Hz. [f] From ^{31}P data only; ^{19}F measurements led to $|^1J_{PF} + {}^3J_{PF}|$ 973 Hz.

The π bonding between phosphorus and fluorine seems to dominate the ^{31}P chemical shifts more than direct-substituent electronegativity effects. Thus the value of δ_P increases in the order $PCl_3 < PF_3 < PClF_2 < PCl_2F$, *i.e.* it shows a maximum for PCl_2F. Such effects are commonly observed for series of phosphorus com-

---

[9] J. H. Letcher and J. R. Van Wazer, *Topics Phosphorus Chem.*, 1967, **5**, 75.

[10] R. R. Holmes, R. P. Carter, jun., and G. E. Peterson, *Inorg. Chem.*, 1964, **3**, 1748.

[11] R. P. Carter, jun., and R. R. Holmes, *Inorg. Chem.*, 1965, **4**, 738.

the difference, ${}^1J_{PF}(ax) - {}^1J_{PF}(eq)$, is[10] only 60 Hz for PCl_2F_3. Secondly, the series $PCl_2F_3 \longrightarrow PCl_3F_2 \longrightarrow PCl_4F$ has[10] coupling constants, ${}^1J_{PF}(ax)$, of −1 032, −1 051, and −992 Hz; this shows that the substitution F ⟶ Cl at an equatorial site increases $|{}^1J_{PF}(ax)|$ whereas at an axial site it decreases $|{}^1J_{PF}(ax)|$. The evidence from ${}^1J_{PF}$ for the series PF_5 (−930),[8] $PClF_4$ (−1 000),[11] and PCl_2F_3 (average −1 048 Hz) [10] suggests that F ⟶ Cl substitution at an equatorial site also increases the equatorial $|{}^1J_{PF}|$. Our data are therefore consistent with the chlorofluorophosphorane results. It may be noted that the increase in $|{}^1J_{PF}|$ shown in Table 3 for $PClF_2 \longrightarrow PCl_2F$ is substantially smaller than that for $PF_3 \longrightarrow PClF_2$, consistent with a 50% increase in axial character for the former change compared to 17% for the latter. However, the above discussion ignores the effects of geometry on ${}^1J_{PF}$; for the methyl analogue of (I; $m = n = 2$) the values of ${}^1J_{PF}$ for the *gauche* and *trans* forms differ [1d] by 40 Hz.

For each group (axial–equatorial character unchanged) the changes in ${}^1J_{PF}$ shown in Table 3, which are quite substantial, must be accounted for by changes in the substituents at the distant phosphorus. A decrease in the electronegativity of the substituents at the distant phosphorus decreases ${}^1J_{PF}$ algebraically, but compound (I; $m = 3$, $n = 0$) is anomalous in this respect. Again, the behaviour for the Cl series is the opposite of that of the methyl and methoxy-compounds. The ${}^3J_{PF}$ values also follow the same trend as that of ${}^1J_{PF}$, *i.e.* as the axial character of the fluorine increases ${}^3J_{PF}$ decreases and, for a constant axial character, ${}^3J_{PF}$ decreases with decreasing electronegativity of the substituents at phosphorus. For the fluorine in the PCl_2F group, ${}^3J_{PF}$ actually becomes negative as the substituents at the distant phosphorus are changed from $PClF_2$ to PCl_2F. It should be noted that for ${}^3J_{PF}$, in contrast to ${}^1J_{PF}$, the patterns for the Cl, Me, and OMe series are similar. However, the magnitude of the subsituent effect for Cl is as close to that for Me as to that for OMe, so clearly it is not just substituent electronegativity that is important.

The ${}^2J_{PP}$ values for the compounds are listed in Table 4. As for the methyl and methoxy-compounds,[1d] J_{PP} can be expressed in terms of the parameters *a* for the groups PF_3, $PClF_2$, and PCl_2F [equation (1)]. The

$$J_{PP'} = a_P a_{P'} \qquad (1)$$

values of *a*, obtained from the symmetrical compounds, are 14.49, 13.64, and 12.49 Hz$^{\frac{1}{2}}$ for the groups PF_3, $PClF_2$, and PCl_2F respectively. The values of J_{PP} for (I; $m = 2$, $n = 0$) then gives *a* 10.70 Hz$^{\frac{1}{2}}$ for PCl_3. These parameters do not vary smoothly with the extent of chlorine substitution, either in arithmetic or in geometric progression (the value for $PClF_2$ ignores complications due to the existence of isomers). Some discrepancies are to be expected in view of the pronounced effect of stereochemistry on J_{PP} which has been established for other diazadiphosphetidines.[1b,e,f] The deviations from additivity in the substituent effect on J_{PP} are in the same sense fo Cl as for OMe, but in the opposite direction for Me. However, if a geometric progression is assumed, the deviations are all in the same sense; the value of *a* for PF_2X is higher than anticipated from the values of *a* for PF_3 and PFX_2. Deviations from additivity effects for coupling constants are well known, and have been explained [12] within an assumption of dominance by the Fermi-contact mechanism. The values calculated for compounds (I; $m = 3$, $n = 1$ or 2; $m = 2$, $n = 1$; $m = 1$, $n = 0$), using the group parameters, are also given in Table 4. Agreement with the observed values is reasonable, though a relatively large discrepancy is observed for compound (I; $m = 3, n = 1$). (In the methyl and methoxy-series the corresponding compound was not available for comparison.[1d])

TABLE 4

(P,P) and (F,F) coupling constants for the chlorofluorodiazadiphosphetidines, (I)

		$J_{PP}{}^{a,b}$/Hz		
m	n	obs.	calc.	${}^4J_{FF}{}^{b,c}$/Hz
3	3	210 [d]		8.7
3	2	198	198	8.0
2	2	186		N_{FF} 14.5 L_{FF} 5 ± 2
3	1	188	181	7.2
2	1	172	170	6.0
1	1	156		3 ± 2
2	0	146		
1	0	129	134	

[a] ±2 Hz. [b] J_{PP} and ${}^4J_{FF}$ are assumed to be positive (see previous papers in this series). [c] ±0.5 Hz except where otherwise indicated. [d] Ref. 1*a*.

The ${}^4J_{FF}$ values are also given in Table 4. It was shown for methyl and methoxy-compounds [1d] that there is a substantial geometry effect for the (F,F) coupling constants across the ring. The pattern for the chloro-compounds follows that of the methoxy-series in that ${}^4J_{FF}$ for (I; $m = n = 1$), presumably involving two axial fluorines, appears to be the smallest; this is the reverse of the case for the methyl compounds.

EXPERIMENTAL

Compounds (I) were obtained as two mixtures of overall compositions 'Cl_2F_4' and 'Cl_3F_3' respectively, and were examined as such without separation; (I; $m = n = 2$ and $m = 3$, $n = 1$) were the major components in 'Cl_2F_4', while (I; $m = 1$ or 2, $n = 1$) were the principal species in 'Cl_3F_3'. The n.m.r. tubes used were of 5 mm outside diameter. Some $CFCl_3$ and C_6D_6 were added to the neat liquid mixtures to provide field-frequency locks for ${}^{19}F$ and ${}^{31}P$ n.m.r. resonances respectively. After measurements on the spectra of compounds (I) were complete, small amounts of $[NMe(PF_3)]_2$ and $[NMe(PCl_3)]_2$ were added to separate samples of 'Cl_3F_3' in order to confirm the ${}^{31}P$ chemical shifts of these species. All samples were degassed using the freeze–pump–thaw technique with a vacuum line.

94.155 MHz ${}^{19}F$–$\{{}^1H\}$ and 40.5 MHz ${}^{31}P$–$\{{}^1H\}$ spectra were recorded on Varian HA-100 and XL-100 n.m.r. spectrometers, respectively, at ambient probe temperature in the frequency-sweep mode (continuous wave, CW, for ${}^{19}F$ and either CW or Fourier transform, FT, for ${}^{31}P$).

---

[12] R. Ditchfield, M. A. Jensen, and J. N. Murrell, *J. Chem. Soc.* (*A*), 1967, 1674.

Proton decoupling was carried out to eliminate the broadening or splitting effects of long-range coupling to the NMe protons. The $^{19}F-\{^1H\}$ experiments were carried out using a double-tuned transmitter circuit discussed elsewhere.[1d] $^{31}P-\{^1H\}$ Spectra obtained in the CW mode involved multiscan averaging. The ^{31}P chemical shifts were measured relative to the shift of (I; $m = n = 2$) and were related to other scales as follows:[1d] the ^{31}P resonance frequency of (I; $m = n = 2$) was obtained using a radiofrequency (r.f.) counter, converted into the equivalent frequency for a magnetic field such that the protons in $SiMe_4$ resonate at exactly 100 MHz, the corresponding scaled ^{31}P frequency for 85% H_3PO_4 (40 480 720 Hz) was subtracted, and the result converted into p.p.m. In addition to the above, the ^{19}F spectra of (I; $m = 3, n = 2$; $m = 1, n = 0$ or 1) were obtained without proton decoupling using a Varian HA 100 spectrometer at 94.155 MHz at the University of Sussex.

We thank Dr. K. Utvary (Technische Hochschule, Wien) for generous gifts of the compounds investigated, Dr. J. F. Nixon of the University of Sussex for the ^{19}F spectra of compounds (I; $m = 1, n = 0$ or 1 and $m = 3, n = 2$), Dr. G. Hägele (University of Düsseldorf) for obtaining and analysing the ^{19}F spectrum of (I; $m = n = 2$) and for valuable discussions, the Commonwealth Scholarship Commission for a scholarship (to M. I. M. W.), Miss E. M. McVicker and Mr. P. W. Haylett for assistance with recording some of the spectra, and Dr. P. Anstey for help with the computations.

[5/994 *Received, 28th May*, 1975]