Preparative and Nuclear Magnetic Resonance Studies of 1,3,2,4-Diazadiphosphetidines. Part IV.[1] Methyl- and Methoxy-fluorodiazadiphosphetidines

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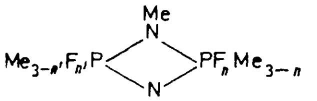
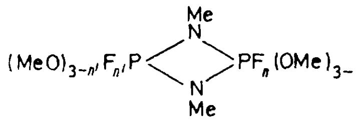
The preparation of a series of methyl- and methoxy-fluoro-1,3,2,4-diazadiphosphetidines [(I) and (II) respectively] has been accomplished, in many cases by substitution reactions on heavily fluorinated diazadiphosphetidines using organometallic reagents.

The $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ n.m.r. spectra of these compounds have been analysed, using subspectral techniques and iterative computer fitting. In only two cases axial $\rightleftharpoons$ equatorial exchange may be slowed on the n.m.r. time scale at low temperatures; the reason for this lies in the concerted pseudorotation nature of the exchange. The chemical shift and coupling constant data show the influences of substituents and geometry. It has been demonstrated that $^2J_{PP}$ is positive, and its values can be reproduced by a product of parameters characteristic of the environment of each phosphorus nucleus.

FLUORINATED 1,3,2,4-diazadiphosphetidines have been the subject of a number of recent papers.[1-7] The chemistry involved is relatively novel; the range of compounds available is rapidly increasing and now includes unsymmetrical[1] as well as symmetrical[2] species. The molecules are of particular interest because they contain two five-co-ordinate phosphorus atoms in a four-membered ring. It has been shown[1,2] that pseudorotation at these phosphorus atoms can occur in a concerted fashion, and for compounds of types (Ib) and (IIb) the molecular geometry is such that the existence of *gauche* and *trans* isomers [(III) and (IV)] can be demonstrated. The most fruitful method of studying the geometry and intramolecular motion of diazadiphosphetidines has proved to be n.m.r. spectroscopy;[1,2] the compounds are well suited to such study because the spin systems in most cases are such that the proton-decoupled spectra are amenable to complete analysis. In the symmetrical cases, such analysis can be carried out for the coupling constants either from $^{31}P\{^1H\}$ or $^{19}F\{^1H\}$ spectra. Some of the relative signs of the coupling constants can be obtained directly from the analysis; in other cases some signs can be found using heteronuclear double resonance. In previous papers in this series[1,2] it has been shown that some of the coupling constants are extraordinarily sensitive to changes in the substituents and to the molecular geometry. Differences between results for the *gauche* and *trans* isomers of the symmetrical tetrafluoro-compounds are remarkably large. In order more fully to understand these effects it was decided to study as large a range of compounds as possible in two series, one with relatively electropositive substituents [methyl groups, as in (I); the results for (Ib) have been reported earlier] and one with relatively electronegative substituents [methoxy groups, as in (II)]. It has not so far proved possible to prepare any of the compounds containing PMe_3 or $P(OMe)_3$ groups; nor have the compounds with $n = 3$, $n' = 1$ been prepared. This paper is concerned with the other four compounds in both series. A few of the preliminary results of this work have been recently reported.[1] The fully fluorinated compound has had its n.m.r. spectrum analysed some years ago.[3]

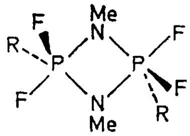


(I)

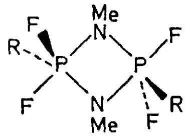


(II)

(a) $n' = 3$, $n = 2$
(b) $n' = n = 2$
(c) $n' = 2$, $n = 1$
(d) $n' = n = 1$



gauche isomer
(III)



trans isomer
(IV)

The known syntheses of diazadiphosphetidines normally involve the reactions of a halogenophosphorane with

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[1] Part III, O. Schlak, R. Schmutzler, R. K. Harris, and M. Murray, *J.C.S. Chem. Comm.*, 1973, 23.

[2] Part II, R. K. Harris, J. R. Woplin, R. E. Dunmur, M. Murray, and R. Schmutzler, *Ber. Bunsengesellschaft. Phys. Chem.*, 1972, **76**, 44.

[3] Part I, R. K. Harris and C. M. Woodman, *Mol. Phys.*, 1966, **10**, 437.

[4] L. G. Hoard and R. A. Jacobson, *J. Chem. Soc.* (*A*), 1966, 1203.

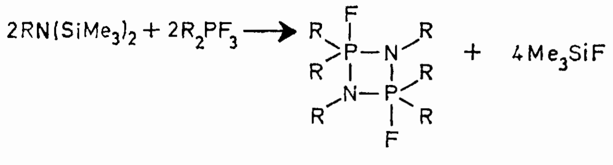
[5] J. W. Cox and E. R. Corey, *Chem. Comm.*, 1967, 123.

[6] A. Almenningen, B. Anderson, and E. E. Astrup, *Acta Chem. Scand.*, 1969, **23**, 2179.

[7] A. J. Downs, *Chem. Comm.*, 1967, 628.

the appropriate amine or silylamine[8-10] with loss of HX or R_3SiX (X = halogen); alternatively, the reaction of a phosphine with an azide[10,11] may be employed. With one exception,[1] only symmetrical diazadiphosphetidines are obtained in these reactions.

In some cases the reactivity of fluorophosphoranes towards Si–N compounds was insufficient to bring about cleavage of the Si–N bond. Thus, compound (Id) could not at first be obtained from Me_2PF_3 and $MeN(SiMe_3)_2$.[8] It was found, however, that the desired compound is formed in the presence of catalytic amounts of caesium fluoride,[12] although a complicated mixture of products is obtained. In such cases it was found useful to employ the appropriate lithium derivative,[12] *i.e.*



(Id; R=Me)

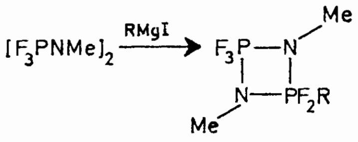
or

$$2\,RNLi_2 + 2R_2PF_3 \longrightarrow (Id) + 4LiF$$

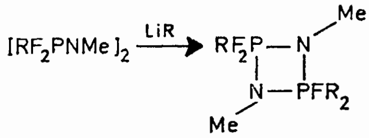
(R=Me)

Few substitution reactions on halogeno-diazadiphosphetidines are known, and they are restricted, essentially, to chlorine–fluorine exchange,[13-18] exchange of two halogen atoms for oxygen or sulphur,[10] aminolysis,[10,19] alcoholysis,[20,21] and hydrolysis.[22-24]

There are virtually no reported cases of substitution in halogenodiazadiphosphetidines with alcoholates,[21] and none with organometallic compounds. However, such reactions have now been found to permit the synthesis of symmetric and unsymmetric diazadiphosphetidines which were not accessible *via* any of the previously known preparative routes. The following examples are representative.



(Ia; R=Me)



(Ic; R=Me)

In contrast to previous experience, which seemed to exclude the existence of difluorodiazadiphosphetidines,[8,9] the compound $Ph_2FP(NMe)$, for example, being thought* to exist as the monomer,[25] rather than the dimer, the new compounds (Id) and (IId) are clearly the dimers, from both n.m.r. and mass-spectral evidence. Both compounds are stable thermally at temperatures in excess of 100°, and no tendency to dissociate to the monomeric fluorophosphine imides was noted. By contrast, the unsymmetrical diazadiphosphetidines are thermally unstable and some compounds undergo rearrangement to the symmetric species even at room temperature.

The geometry of the molecules is such that when n' or $n \geqslant 2$ it is not possible for all the fluorine nuclei to adopt the preferred axial position; the existence of the ring constrains the systems so that each bridging nitrogen atom is axial to one of the phosphorus atoms. At room temperature or above the axial $\rightleftharpoons$ equatorial process for two or more fluorine atoms attached to the same phosphorus is rapid on the n.m.r. time scale for all the compounds studied here. This process is not to be confused with the *gauche* $\rightleftharpoons$ *trans* interchange (III) $\rightleftharpoons$ (IV), which is, in general, slower than the axial $\rightleftharpoons$ equatorial exchange, but which is still rapid on the n.m.r. time scale at room temperature or above. The *gauche* and *trans* isomers can be separately studied at low temperature by n.m.r. in some cases.[2] Indeed, at temperatures below about +10 °C the spectrum of (Ib) showed the presence of *gauche* and *trans* isomers, as has already been described.[2] We were unable to slow the *gauche* $\rightleftharpoons$ *trans* process to observe separate spectra in the case of (IIb), even at the lowest temperature feasible (−120 °C, for a solution in vinyl chloride). However, it did prove possible to slow the axial $\rightleftharpoons$ equatorial exchange process for the PF_2 group of (Ic), as has been mentioned in a preliminary communication,[1] and correspondingly for (IIc). It must be noted that the assignment of the *gauche* and *trans* isomers of (Ib) is considered to be only tentative.[2]

SPECTRAL ANALYSIS

The spin systems relevant for the various molecules under conditions of proton noise decoupling are shown in

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* *Added at proof:* Recent evidence (R. K. Harris, M. I. M. Wazeer, O. Schlak, and R. Schmutzler, unpublished work), however, shows that this compound may also exist as a dimer.

[8] R. Schmutzler, *Halogen Chem.*, 1967, **2**, 55.

[9] M. Murray and R. Schmutzler, *Z. Chem.*, 1968, **8**, 241.

[10] A. F. Grapov, N. N. Mel'nikov, and L. V. Razvodovskaya, *Russ. Chem. Rev.*, 1970, **39**, 20.

[11] P. B. Hormuth and H. P. Latscha, *Z. anorg. Chem.*, 1969, **365**, 26.

[12] O. Schlak, Diplomarbeit, Braunschweig, 1971.

[13] B. S. Drach and I. N. Zhmurova, *Zhur. obshchei Khim.*, 1967, **37**, 892.

[14] P. Haasemann, Dissertation, Stuttgart, 1963.

[15] E. S. Kozlov and B. S. Drach, *Zhur. obshchei Khim.*, 1966, **36**, 760.

[16] B. S. Drach and I. N. Zhmurova, *Metody Poluch, Khim.*, Reaktivov Prep., No. 19 (1969), 65 (*Chem. Abs.*, 1971, **75**, 14164e).

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

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

[19] J. J. Harris and B. Rudner, *J. Org. Chem.*, 1968, **33**, 1392.

[20] I. N. Zhmurova, A. A. Kisilenko, and A. V. Kirsanov, *Zhur. obshchei Khim.*, 1962, **32**, 2580.

[21] I. N. Zhmurova, I. Yu. Voitekovskaya, and A. V. Kirsanov, *Zhur. obshchei Khim.*, 1961, **31**, 3741.

[22] I. N. Zhmurova and A. V. Kirsanov, *Zhur. obshchei Khim.*, 1960, **30**, 4648.

[23] I. N. Zhmurova and A. V. Kirsanov, *Zhur. obshchei Khim.*, 1969, **30**, 3044.

[24] I. N. Zhmurova and A. V. Kirsanov, *Zhur. obshchei Khim.*, 1963, **33**, 182.

[25] G. W. Adamson and J. C. J. Bart, *J. Chem. Soc.* (*A*), 1970, 1452.

TABLE 1

Spin systems for the diazadiphosphetidines (I) and (II) [a] under conditions of proton noise decoupling

Compounds	Spin system	
	Room temperature	Low temperature [b]
(Ia) and (IIa)	$[ABX_3Y_2]$	$[ABX_3Y_2]$
(Ib) and (IIb)	$[A[X]_2]_2$	$[B[Y]_2]_2 + [C[Z]_2]_2$
(Ic) and (IIc)	$[ABX_2Y]$	$[ABXYZ]$
(Id) and (IId)	$[AX]_2$	$[AX]_2$

[a] The notation of ref. 26 is used here. [b] The notation does not imply that such spectra have been observed in all cases.

Table 1. Spectra of the type $[AX]_2$ are well known.[27] Those of types $[ABX_3Y_2]$, $[ABX_2Y]$, and $[ABXYZ]$ can be handled fairly readily, even when not first order, by the principles of subspectral analysis.[28] 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.[2] The general appearance is sketched in Figure 1. The magnitudes of all the coupling parameters except $^2J_{FF}$ can be obtained by direct measurement, but the spectrum is only sensitive to some of the relative signs. Our general approach to the spectral analysis has been to obtain as much data as possible from direct measurement of the spectra, and then to use these results, together with the observed transitions, as input data to a suitable iterative computer program[29] for spectral analysis (LAOCOON, LACX, or UEANMRITR). This procedure optimises all the parameters. All the spectra were, in fact, second order. For the symmetrical compounds the second-order character arises from the chemical equivalence. The second-order nature of the spectra for the unsymmetrical compounds arises because the ^{31}P chemical shift difference, $|\Delta\nu_P|$, between the resonances of the different ^{31}P nuclei is of the same order as $|J_{PP}|$. The ratio $|\Delta\nu_P/J_{PP}|$ is smaller in the methoxy series than in the methyl series. In fact, however, $|^1J_{PF}|$ is so large that either $|\Delta\nu_P + {}^1J_{PF}|$ or $|\Delta\nu_P - {}^1J_{PF}|$ is considerably greater than $|^1J_{PP}|$. In consequence the spectra of (Ia), (Ic), (IIa), and (IIc) are actually partially first order. This is illustrated in Figure 2. This fact enables the relative signs of $^1J_{PF}$ and $^3J_{PF}$ to be readily obtained for the unsymmetrical compounds. The first-order patterns correspond to phosphorus spin states αα and ββ. These first-order patterns are observed nearer the Larmor frequency for each type of ^{19}F than the second-order lines, showing that $^1J_{PF}$ and $^3J_{PF}$ are opposite in sign. The relative signs of $^1J_{PF}$ and $^3J_{PF}$ were also obtainable from the spectra of the symmetrical compounds, by the usual procedures[2,27,28] of spectral analysis in such cases.

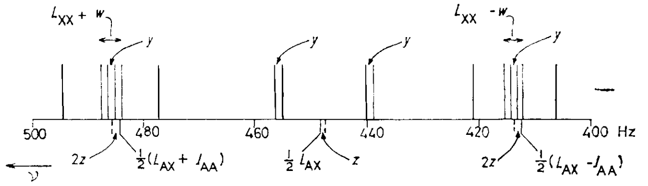

FIGURE 1 Diagrammatic representation of the high frequency half of the X region for an $[A[X]_2]_2$ spectrum characterised by large $|J_{AX}|$ (see ref. 2), as appropriate for compounds (Ib) and (IIb). The parameters w, y, and z are $J_{AA}L_{XX}/L_{AX}$, $J_{AA}N_{XX}/L_{AX}$, and $J_{AA}{}^2/8L_{AX}$ respectively. The intense line at $\nu_X + \frac{1}{2}N_{AX}$ has been omitted for clarity

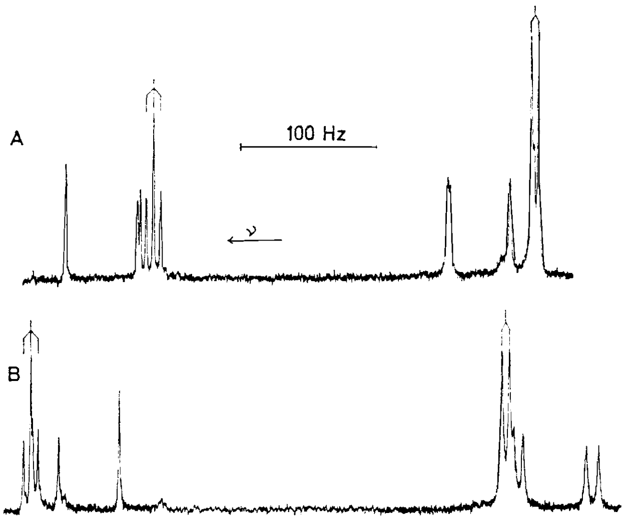

FIGURE 2 ^{19}F Spectrum of (IIc) (at high temperature) showing partial first-order characteristics (marked): A, high frequency half; B, low frequency half. In both A and B the high frequency part is due to $PF(OMe)_2$ and the low frequency part to PF_2OMe

None of the spectra are sensitive to the sign of $^2J_{PP}$, so heteronuclear triple resonance experiments were used for its determination (see below).

The low temperature spectra of (Ic) and (IIc) are the only ones which are sensitive to $^2J_{FF}$(ax, eq), since exchange between axial and equatorial fluorine nuclei is slowed so that there are separate resonances for the two types. The second-order nature of these spectra allows the relative signs of $^2J_{FF}$ and $^4J_{FF}$ to be determined. For both (Ic) and (IIc) the higher frequency resonance is assigned to the axial fluorine (see the Discussion section).

The data reported here for (Ic) are more accurate than the corresponding values presented in our preliminary note,[1] since the latter were from spectra obtained without the benefit of proton decoupling.

DISCUSSION

Discussion of the n.m.r. parameters for fluorinated diazadiphosphetidines must take account of at least five influences: (i) temperature variation (and possibly solvent effects also); (ii) the effect of substituents at phosphorus adjacent to the site of interest; (iii) effects from substituents at the more distant phosphorus atom;

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

[27] J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High-resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959.

[28] P. Diehl, R. K. Harris, and R. G. Jones, *Progr. N.M.R. Spectroscopy*, 1967, **3**, 1.

[29] R. K. Harris and J. Stokes, 'A Library of Computer Programs for N.M.R. Spectroscopy,' Science Research Council (Atlas Computer Laboratory), Didcot, 1971.

(iv) the axial–equatorial character of substituents (especially the fluorine nucleus involved in a given n.m.r. parameter); (v) the *gauche–trans* isomer character for the $[MeNPF_2X]_2$ compounds, and geometric effects in the other compounds. Thus, even at an empirical level, the problem of rationalising the observations is not trivial. However, considerable progress can be made.

^{19}F *Chemical Shifts*.—Table 2 lists the results for the ^{19}F chemical shifts of the compounds studied. It may be seen that in nearly every case there are smooth trends with the extent of substitution at the adjacent ^{31}P atom, and, to a lesser degree, with substitution at the more distant phosphorus. It is clear from the Table that the substituent effect of Me is much greater than that of OMe, as might be expected. Thus the resonances for all the methyl compounds are at high frequency (deshielded) relative to those for the corresponding methoxy compounds. It has been suggested [30] for some fluorophosphoranes that π-bonding involving the fluorine is an important factor. π-Bonding involves back-donation of fluorine *p* electrons to certain vacant *d* orbitals of the phosphorus, and leads to deshielding, as observed. The oxygen atom of the methoxy group competes with this back-donation, thus increasing the shielding of the fluorine nucleus. However, objections may be offered to this explanation.

TABLE 2

^{19}F Chemical shifts [a] for the PF_nR_{3-n} group of the diazadiphosphetidines of types (I) and (II)

	Methyl series (I)			Methoxy series (II)		
n' \ n	3 [b]	2 [c]	1 [d]	3 [b]	2 [c]	1 [d]
3	−80·69	−59·82		−80·69	−79·43	
2	−76·20	−57·76	−23·35	−78·24	−78·43	−74·71
		[−51·81 t −55·90 g] [e]	−24·36 [f]			−75·3 [g]
1		−44·37	−21·88		−78·02	−73·50
		[−71·41 eq −34·46 ax] [f,h]			[−85·0 eq −68·9 ax] [g,h]	

[a] In p.p.m. relative to internal $CFCl_3$; a positive value indicates a high frequency shift for the sample with respect to the reference. [b] $\frac{1}{3}[2\delta_{F(eq)} + \delta_{F(ax)}]$. [c] $\frac{1}{2}[\delta_{F(eq)} + \delta_{F(ax)}]$. [d] $\delta_{F(ax)}$. [e] Results for separate *trans* (t) and *gauche* (g) isomers, obtained at low temperature (see ref. 2). [f] At −60 °C. [g] At −100 °C. [h] Results for the resonances of separate axial and equatorial fluorine nuclei, separable at low temperature.

The axial–equatorial character of the fluorine nucleus or nuclei is also important. The difference between the axial and equatorial fluorine chemical shifts is more marked for the methyl compounds than for the methoxy compounds. It has been suggested [31] that π-bonding to phosphorus is more favourable for the axial fluorine than the equatorial fluorine due to the differing orbital symmetries. This explains the deshielding of the axial fluorines relative to the equatorial fluorines. A similar argument regarding competition for π-bonding by the oxygen atom of methoxy groups can be invoked to explain the small difference in axial–equatorial fluorine chemical shifts for the methoxy compounds.

Since the room temperature result for (Ib) is outside the range of the separate values for the *gauche* and *trans* isomers, obtained at −60 °C, there are clearly substantial temperature effects for some cases [though not, apparently, for the $PFMe_2$ fluorine of (Ic)]. Such effects complicate comparisons of ambient temperature data for different compounds.

^{31}P *Chemical Shifts*.—^{31}P Chemical shifts have been explained [32] in terms of three parameters, bond angle, electronegativity, and π-bonding, amongst which somewhat inadequate inter-relationships have been established. For symmetrical five-co-ordinate phosphorus compounds, PZ_5, Van Wazer and Letcher's rather crude model suggests [32] that if effects from d_π electrons are ignored then increasing substituent electronegativity, χ, in the range $2{\cdot}2 < \chi < 4{\cdot}0$ should result in increasing shielding. However, d_π-bonding is supposed to reduce shielding. The observed overall effect for PZ_5 molecules appears to be [32] that shielding decreases in the order $PPh_5 > P(OEt)_5 > PF_5$. This is not the situation for the compounds studied here, where the general shielding effect for substituents is OMe > F > Me, and no simple explanation is likely to be valid. As would be expected from both electronegativity and π-bonding effects the

TABLE 3

^{31}P Chemical shifts [a] for the PF_nR_{3-n} group of the diazadiphosphetidines of types (I) and (II)

	Methyl series (I)			Methoxy series (II)		
n' \ n	3	2	1	3	2	1
3	−69	−51·2		−69	−70·6	
2	−67·3	−50·3	−60·5 [b]	−67·6	−69·3	−71·8 [b]
		[−51·2 t −47·4 g] [c]				
1		−47·5 [b]	−59·3		−68·2 [b]	−70·6

[a] In p.p.m. relative to external 85% H_3PO_4 (see the Experimental section). A positive value indicates a high frequency shift for the sample with respect to the reference. [b] No observable change down to −60 °C for (Ic) and to −100 °C for (IIc). [c] See footnote *e* of Table 2.

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

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

[32] J. R. Van Wazer and J. H. Letcher, *Topics in Phosphorus Chem.*, 1967, **5**, 169.

variations caused in the ^{31}P chemical shifts of diazadiphosphetidines by substituting OMe for F are much less marked than variations in the methyl series (I). The effects in the methoxy series (II) are reasonably additive, but they are markedly non-additive for the methyl compounds, where the shielding actually shows a minimum for the PF_2Me group. Such non-additivity is well known for three- and four-co-ordinate phosphorus compounds, and has been explained[32] on the basis of a mixture of π- and σ-bonding effects. Geometry variation may be an added factor of importance for the diazadiphosphetidines.

Atom or groups other than those directly attached to the phosphorus atom can have remarkable effects on the chemical shift, as seen[33] for compounds containing the P(:X)NP(:X) group with X = O or S. The Table shows there is a correlation in the chemical shift of PF_3, PF_2X, and PFX_2 groups with variation in the number of substituents at the distant phosphorus atom, for both the present series of compounds, (I) and (II). The exact origin of these effects is not clear.

Short-range (P,F) *Coupling*, $^1J_{PF}$.—Table 4 lists our results for $|^1J_{PF}|$ (all values are presumably[34] negative).

TABLE 4

$|^1J_{PF}|$/Hz for the PF_nR_{3-n} group of the diazadiphosphetidines of types (I) and (II)

	Methyl series (I)			Methoxy series (II)		
n' \ n	3[a]	2[a]	1[a]	3[a]	2[a]	1[a]
3	922·0	899·0		922·0	875·2	
2	918·2	891·5	663·8	909·7	867·8	797·6
		[908·2 g 868·0 t] [a]	654·8 [a]			810 [a]
1		885·8	636·7		866·2	779·5
		[803·6 ax 959·2 eq] [a]			[805 ax 949 eq] [a]	

[a] See the appropriate footnotes to Table 2.

The values of $^1J_{PF}$ correspond to 33, 50, and 100% axial character for the fluorines of PF_3, PF_2, and PF groups respectively. The axial–equatorial character of the fluorine is clearly important, since $|^1J_{PF(ax)} - {}^1J_{PF(eq)}|$ is measured at low temperature to be 155·6 Hz and 144 Hz for (Ic) and (IIc), respectively. The difference is larger for the methyl series than for the methoxy series, in agreement with earlier work[35] on $RR'PF_3$ compounds, which demonstrated that $^1J_{PF(ax)}$ approaches $^1J_{PF(eq)}$ as the electron-withdrawing powers of the R and R′ groups are increased. It has been suggested[35] that this effect arises because axial and equatorial bonds tend to have equal *s* character as the electronegativity of the equatorial substituents increases. However, this assumes dominance of the Fermi contact contribution to coupling, and it must be recalled that $^1J_{PF}$ is negative. In acyclic systems of the type R_2PF_3 the value of $|^1J_{PF(ax)} - {}^1J_{PF(eq)}|$ is 100 to 140 Hz,[8] which is somewhat smaller than the differences observed here for the RPF_2 groups; this is not entirely consistent with the postulated electronegativity influence mentioned above, but the variation may be due to the cyclic nature of our compounds.

The differences in the values for the methyl and methoxy series are not simply matters of electronegativity, however. It has been shown[36] that for compounds of the type FP(:S)XY, $|^1J_{PF}|$ *decreases* approximately linearly with the electronegativities of X and Y (when these contain first-row elements bonded to the phosphorus) but that groups containing carbon as the bonded element are anomalous, giving significantly higher values of $|^1J_{PF}|$ than expected. The same effect appears to be present for the diazadiphosphetidines of the type $[MeNPF_2X]_2$ where $|^1J_{PF}|$ (the average for axial and equatorial fluorines) for X = NEt_2[2] is less than that for X = OMe, whereas that for X = Me is higher. The individual values for axial and equatorial fluorine nuclei, obtained for the compounds (Ic) and (IIc), show that the anomaly is present for both positions, though, as remarked above, the difference $|^1J_{PF(ax)} - {}^1J_{PF(eq)}|$ follows an expected pattern. Interestingly, the anomalous effect of carbon-containing substituents seems to be absent for the PFR_2 group in diazadiphosphetidines; the values of $|^1J_{PF}|$ for this group in (Ic) and (Id) are *ca.* 140 Hz less than in (IIc) and (IId) respectively. Table 4 shows that the effects of substituent changes at the distant phosphorus are small but consistent; as the Me or OMe is progressively substituted for F the value of $|^1J_{PF}|$ decreases. The variable temperature measurements show that $^1J_{PF}$ is sensitive to this parameter also, as has been demonstrated[37] in other cases. A detailed study of the ^{19}F resonance of the $PFMe_2$ group for (Ic) shows that $|^1J_{PF}|$ decreases from 673 Hz at 160 °C to 670 Hz at 40 °C for the neat liquid and from 663 Hz at 60 °C to 652 Hz at −80 °C for a solution in CH_2Cl_2. The same series of experiments indicated a dependence of $^1J_{PF}$ on solution conditions. The low temperature results for (Ib) show that molecular geometry has a surprisingly large influence on $^1J_{PF}$; the values for the *gauche* and *trans* isomers differ by 40 Hz. In view of this fact it is surprising that the average value falls neatly into the pattern of results for the other compounds.

Long-range (P,F) *Coupling*, $^3J_{PF}$.—The results for $^3J_{PF}$ are given in Table 5 and plotted against the number of substituents for the methoxy series in Figure 3. The signs are given with respect to that of $^1J_{PF}$ being negative. The same influences act on $^3J_{PF}$ as on $^1J_{PF}$, but the effects are often proportionately greater. Thus, the substituent effect of the Me group is sufficient to change the sign of $^3J_{PF}$ for heavily methylated compounds. The geometry effect is enormous and also produces[2] coupling constants of opposite sign for the *gauche* and *trans* isomers of (Ib); so does the axial–equatorial effect as shown by the low temperature results for (Ic) [though $^3J_{PF(eq)}$ is, within experimental error, zero]. It may be

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[33] R. K. Harris, R. Keat, and M. I. M. Wazeer, unpublished work.

[34] C. Schumann, H. Dreeskamp, and O. Stelzer, *Chem. Comm.* 1970, 619.

[35] G. Mavel, *Progr. N.M.R. Spectroscopy*, 1966, **1**, 283.

[36] R. K. Harris, J. R. Woplin, M. Murray, and R. Schmutzler, *J.C.S. Dalton*, 1972, 1590.

[37] J. Grosse and R. Schmutzler, unpublished work.

reasonably suggested that the variations in ${}^1J_{PF}$ and ${}^3J_{PF}$ have the same theoretical origin; but *if* the contact term is dominant the sign change for ${}^3J_{PF}$ makes it clear that variations in *s*-electron densities are not the major effect; changes in the mutual polarisability must predominate (the average energy approximation cannot, however, be valid, because of the negative signs of ${}^1J_{PF}$ and ${}^3J_{PF}$, so a simple relation of the variations to orbital *s*-characters would be surprising). However, substantial contributions from terms other than the Fermi contact one may be expected.[38,39]

TABLE 5

Values of ${}^3J_{PF}$/Hz for diazadiphosphetidines of types (I) and (II) [a]

n' \ n	Methyl series (I)			Methoxy series (II)		
	3 [b]	2 [b]	1 [b]	3 [b]	2 [b]	1 [b]
3	+32	+14·9		+32	+27·3	
2	+15·7	+5·2 $\begin{bmatrix} -6{\cdot}1\ \text{g} \\ +18{\cdot}7\ \text{t} \end{bmatrix}$ [b]	−9·2 [c]	+30·4	+26·0	+22·0 +19·8 [b]
1		−4·0 $\begin{bmatrix} -8{\cdot}0\ \text{ax} \\ +0{\cdot}1\ \text{eq} \end{bmatrix}$ [b]	−5·5		+24·5 $\begin{bmatrix} +22{\cdot}6\ \text{ax} \\ +24{\cdot}7\ \text{eq} \end{bmatrix}$ [b]	+19·8

[a] Involving the fluorine nucleus of the PF_nX_{3-n} group. [b] See the appropriate footnotes to Table 2. [c] No observable change down to −60 °C.

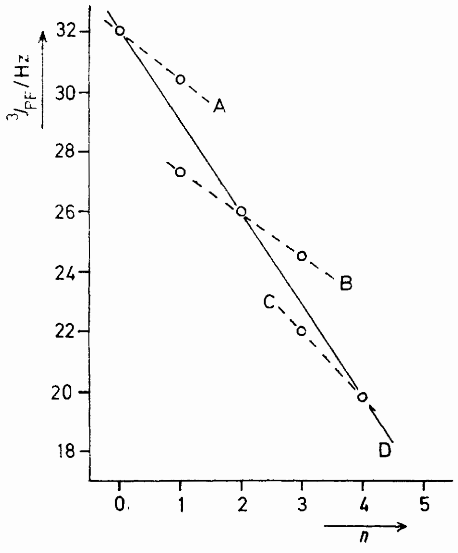

FIGURE 3 ${}^3J_{PF}$ in $P_2F_{6-n}(OMe)_n(NMe)_2$ *vs.* n; A, coupling to PF_3, involving $\frac{1}{3}[2J_{PF(eq)} + J_{PF(ax)}]$; B, coupling to $PF_2(OMe)$, involving $\frac{1}{2}[J_{PF(eq)} + J_{PF(ax)}]$; C, coupling to $PF(OMe)_2$, involving $J_{PF(ax)}$; D, coupling in symmetrical compounds

The result for (Id) is surprising and as yet unexplained; the pattern of the remaining data would suggest a value for this compound *ca.* 10—15 Hz lower.

(P,P) *Coupling Constants.*—It has been shown[2] that ${}^2J_{PP}$ in diazadiphosphetidines of the type $[XF_2PNMe]_2$ is sensitive to the electronegativity of the substituents X. The data for the present series of compounds, given in Table 6, show that the effect of multiple substitution on ${}^2J_{PP}$ is progressive but not additive. It is possible to express the coupling constant as in equation (1), where a_P and $a_{P'}$ are group parameters for the PF_nX_{3-n} and $PF_{n'}X_{3-n'}$ groups respectively. The values of a_P

$$ {}^2J_{PP'} = a_P \, . \, a_{P'} \qquad (1) $$

derived from the symmetrical compounds are given in Table 7. The values of ${}^2J_{PP'}$ for the unsymmetrical compounds, predicted from the group parameters using equation 1 are given in Table 6. Agreement with the observed values is good, particularly in view of the effects of geometry.[2] In actual fact our original approach for the methyl series (I) was not as described above, because there was ambiguity between J_{PP} and J_{FF} from the spectral analysis of (Id). Therefore the parameter for the $PFMe_2$ group was derived from (Ic) and J_{PP} estimated for (Id) using equation (1). The calculated value was 24 Hz compared to the two possible experimental values of 23 and 14 Hz; the assignment was then obvious.

The group parameters follow the substituent electronegativities qualitatively, as expected from Bent's rule[40] (that electronegative substituents use little *s*-character) if the dominant contribution to coupling comes from the contact term. However the effects are not additive; *e.g.* the change from $a(PF_3)$ to $a(PF_2Me)$ is 5·8 $Hz^{\frac{1}{2}}$ but that from $a(PF_2Me)$ to $a(PFMe_2)$ is only 3·8 $Hz^{\frac{1}{2}}$ (interestingly, the reverse effect is seen for the methoxy series). Clearly a plot of ${}^2J_{PP}$ against the sum of the electronegativities of all six substituents at phosphorus outside the ring is non-linear. A similar situation has been found for ${}^1J_{CH}$ and ${}^1J_{SiH}$, where pairwise substituent parameters were introduced to take account of the phenomenon, which has been explained in theoretical terms within the contact contribution.

As has been mentioned previously,[2] the results for the isomers of (Ib) show there is a pronounced geometry effect on ${}^2J_{PP}$. Triple resonance experiments on (Ic), in which the ${}^{31}P$ resonance of the PF_2Me group was observed while the protons were noise decoupled and the ${}^{19}F$ resonance of the $PFMe_2$ group was tickled (see Figure 4), indicate that ${}^2J_{PP}$ is positive for this compound if ${}^1J_{PF}$ is taken to be negative.[34] It is reasonable to suppose that the values of ${}^2J_{PP}$ for all the other compounds are also positive [it is conceivable that ${}^2J_{PP}$ for (Id) may be negative, but we assume this is not the case]. The positive sign found for ${}^2J_{PP}$ is in accord with results for a wide variety of compounds,[41] though this is the first determination reported for a diazadiphosphetidine.

(F,F) *Coupling Constants.*—Values of ${}^2J_{FF}$ have only been obtained for two compounds in the present series,

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[38] A. C. Blizzard and D. P. Santry, *J. Chem. Phys.*, 1971, **55**, 950.

[39] K. Hirao, H. Nakasutji, and H. Kato, *J. Amer. Chem. Soc.*, 1973, **95**, 31.

[40] H. A. Bent, *Chem. Rev.*, 1961, **61**, 275.

[41] E. G. Finer and R. K. Harris, *Progr. N.M.R. Spectroscopy*, 1971, **6**, 61.

since in the remaining cases the spectra are not sensitive to this parameter (either because of magnetic equivalence, or because of chemical equivalence with ' special ' values of the n.m.r. parameters,[2] or because PFMe$_2$ groups are involved). However, at low temperatures for (Ic) and (IIc), when the axial ⟷ equatorial exchange is slow on the n.m.r. time scale, $^2J_{FF}$ is accessible and is found to be $-50·9 \pm 0·3$ and -55 ± 2 Hz for the two compounds respectively. The signs come from the computer fitting and are relative to the sign of $^4J_{FF}$. These relative signs have been confirmed by work[42] on [Bu^{t}F$_2$PNMe]$_2$, which has also shown that $^4J_{FF}$ has the same sign as $^2J_{PP}$. The heteronuclear triple resonance experiments on (Ic) complete the chain of sign determinations and show that $^2J_{FF}$ is negative and $^4J_{FF}$ is positive in (Ic) and (IIc) provided no sign changes occur between these compounds and [Bu^{t}F$_2$PNMe]$_2$. Negative signs have been reported[43-45] for ^2J(FPF) involving four-, five-, and six-co-ordinated phosphorus. The magnitudes of our results are normal for this axial–equatorial geminal coupling constant.

TABLE 6

Values of $^2J_{PP}$/Hz for the diazadiphosphetidines of types (I) and (II)

Compound [a]	$^2J_{PP}$ (obs)	$^2J_{PP}$ (calc) [b]	Compound	$^2J_{PP}$ (obs)	$^2J_{PP}$ (calc) [b]
(Ia)	124·6	123·2	(IIa)	202·9	201·1
(Ib)	72·2		(IIb)	192·5	
	[54·4 g 92·2 t] [c]				
(Ic)	43·5 [d]	40·8	(IIc)	180·9 [e]	180·3
(Id)	23·0		(IId)	168·8	

[a] The value of $^2J_{PP}$ for the parent compound, $n = n' = 3$, is 210 Hz (ref. 1). [b] See the text and Table 7. [c] See footnote *e* of Table 2. [d] No observable change down to -60 °C. [e] Kept constant at this value during iterative fitting of the low temperature (-100 °C) spectrum.

TABLE 7

Group parameters for $^2J_{PP}$, according to equation (1)

Group	PF$_3$	PF$_2$Me	PFMe$_2$	PF$_2$OMe	PF(OMe)$_2$
a/Hz$^{\frac{1}{2}}$	14·49	8·50	4·80	13·88	12·99

Our data for $^4J_{FF}$ are reported in Table 8, together with the geometric relationship involved. The latter cannot be ascertained in the case of compounds (Ib) (and its *gauche* and *trans* isomers) and (IIb), though it seems clear from the temperature averaging that for (Ib) the values 9·95, 5·4, (*gauche*) and 15·4 Hz (*trans*) are linked, as are the remaining three. We assume that all values of $^4J_{FF}$ have the same sign (positive, see above), which appears likely, though the values that are small in magnitude may be of either sign. The data certainly show some interesting features which cannot be explained adequately at present. If, for example, the values 15·4 (*trans*) and 1·8 Hz (*gauche*) for (Ib) are assigned to the axial–equatorial arrangement, there is obviously a substantial geometry effect. On the other hand if the alternative assignment is made, then there is a large geometry effect on the axial–axial coupling *or* a wide difference between J_{ee} and $J_{ee'}$. It seems that in view of the averaging the signs of all $^4J_{FF}$ for (Ib) are the same. The values of $^4J_{FF}$ for (Ic), (Id), (IIc), and (IId) show that there is a substantial substituent effect on J_{aa} and that this is in opposite directions for the methyl and methoxy series. In this instance the assignment of the low temperature spectra of (Ic) and (IIc) (on the basis of chemical shifts) results in data for $^4J_{FF}$ which are in agreement with the values found for (Id) and (IId), where the geometry assignment is unambiguous. Further data are required to clarify the influences on $^4J_{FF}$. It is tempting to assume that the ' through-space ' effect is responsible for some of the anomalies, but for reasonable molecular geometries (planar P$_2$N$_2$ ring) the nearest distances between fluorine nuclei are *ca.* 3·3 Å (*gauche* equatorial–equatorial) and *ca.* 4·5 Å (axial–equatorial)

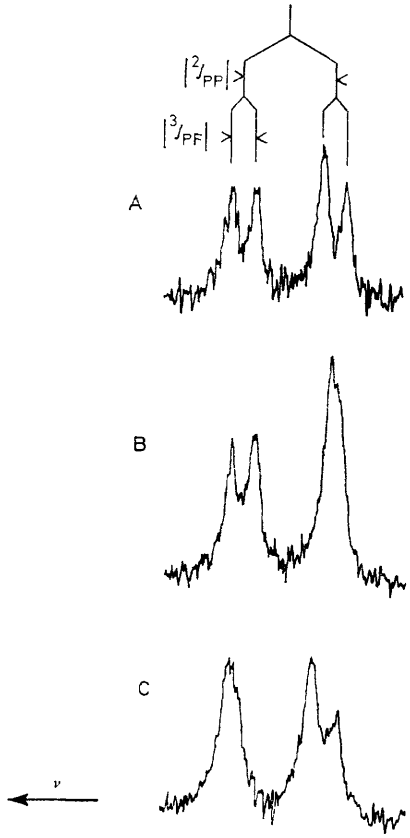

FIGURE 4 40·5 MHz ^{31}P Spectrum (*P*F$_2$Me, central region only) of (Ic) at ambient room temperature: A, normal spectrum; B, with the high frequency half of spectrum due to the lone fluorine irradiated; C, as (B) but irradiating in the low-frequency half of the spectrum for the lone fluorine; all three spectra were recorded under conditions of proton noise decoupling

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[42] R. K. Harris and M. I. M. Wazeer, unpublished work.

[43] R. K. Harris, M. I. M. Wazeer, P. Clare, and D. B. Sowerby, unpublished work.

[44] H. Dreeskamp, C. Schumann, and R. Schmutzler, *Chem. Comm.*, 1970, 671.

[45] W. McFarlane, J. F. Nixon, and J. R. Swain, *Mol. Phys.*, 1970, **19**, 141.

at the closest, compared to a van der Waals radius[46] for fluorine of 1·35 Å.

Low Temperature Results for (Ic) *and* (IIc).—The fact that axial $\rightleftharpoons$ equatorial exchange can be slowed on the n.m.r. time scale at accessible temperatures for the trifluoro-compounds is significant, since this has not proved to be possible[2] for any 2,4-disubstituted tetrafluorodiazadiphosphetidines. However the observations are consistent with our earlier discussion of exchange processes in the latter compounds. For these tetrafluoro-compounds it was assumed that some form of concerted pseudorotation was occurring at the two phosphorus atoms, since *gauche* $\rightleftharpoons$ *trans* exchange (III $\rightleftharpoons$ IV) was much slower than axial $\rightleftharpoons$ equatorial exchange. The limiting factor is the reluctance of the substituents to adopt axial positions, which are occupied preferentially by fluorine atoms. In the cases of (Ic) and (IIc) there are 18 feasible conformations of the type described earlier,[2] assuming that situations with each ring nitrogen axial to one of the phosphorus atoms only are considered. The number of conformations having two, one, and no fluorine atoms axial are four, twelve, and four respectively. The stable forms are expected to be those with two axial fluorine atoms. Interconversions between conformations may occur by conrotatory or disrotatory (see ref. 2) concerted pseudorotations at the phosphorus atoms, or by pseudorotation at one phosphorus atom alone. The easiest pathways for interconversion would be those not involving forms with Me or OMe substituents axial; however, unlike the disubstituted diazadiphosphetidines considered earlier,[2] no such paths exist for (Ic) and (IId). Interchange by the concerted pseudorotation pathway for the trifluoro-compounds can only occur *via* forms with substituents axial, so interchange must occur by pseudorotation at one phosphorus alone. The barrier may therefore be expected to be of the same order of magnitude as that for the *gauche* $\rightleftharpoons$ *trans* process of (Ib) and (IIb). This is borne out for the methyl compounds, though for (IIc) the barrier is apparently significantly larger than for (IIb) since in the latter case attempts to slow the *gauche* $\rightleftharpoons$ *trans* process on the n.m.r. time scale failed (however, this could be due to the effects of varying chemical shift differences). If all the exchange processes in the diazadiphosphetidines involved pseudorotation at one phosphorus alone, then barriers for (Ia) and (Ic) would be expected to be similar. The high barrier for (Ic) relative to (Ia) is therefore good evidence for a *concerted* process for the latter. The barriers for (Ic) and (IIc) have their origins in the rigidity imposed on the PF_2X group by the PFX_2 group. The relative reluctance for the molecules to undergo pseudorotation at a single phosphorus is probably due to the ring strain that would be involved in any intermediate, which would be likely to have one of the nitrogen atoms axial to both phosphorus atoms.

TABLE 8

Values of $^4J_{FF}$/Hz for the diazadiphosphetidines of types (I) and (II)

Compound	$^4J_{FF}$/Hz	Geometry	Compound	$^4J_{FF}$/Hz
(I) or (II), $n = n' = 3$	8·7 ^{b}	$\frac{1}{9}$(aa + 4ae + 2ee + 2ee′)		
(Ia)	7·8 ± 0·3	$\frac{1}{6}$(aa + 3ae + ee + ee′)	(IIa)	8·2 ± 0·3
(Ib)	9·95 ^{c}	$\frac{1}{4}$(aa + 2ae + ee′)	(IIb)	8·5 ± 0·3 ^{e}
	6·3 ^{c}	$\frac{1}{4}$(aa + 2ae + ee)		6·1 ± 0·3 ^{e}
(*gauche*)	5·4 ^{c}	ae		
	1·8 ^{c}	$\frac{1}{2}$(aa + ee)		
(*trans*)	15·4 ^{c}	$\frac{1}{2}$(aa + ee′)		
	9·4 ^{c}	ae		
(Ic)	7·3 ± 0·5	$\frac{1}{2}$(aa + ae)	(IIc)	5·5 ± 0·3
	9·9 ^{d} ± 0·3	aa		*ca.* 0·4 ^{b,d} ± 2
	6·1 ^{d} ± 0·3	ae		9·2 ^{b,d} ± 2
(Id)	14·0 ± 0·3	aa	(IId)	*ca.* 0·0 ± 0·3

[a] a, axial; e, equatorial; with ee and ee′ being the equatorial–equatorial couplings *gauche* and *trans* across the ring respectively. [b] Ref. 1. [c] Ref. 2. [d] Results from low temperature work, with the axial $\rightleftharpoons$ equatorial exchange slowed on the n.m.r. time scale. [e] N_{FF} is more accurate than L_{FF} (ref. 2).

EXPERIMENTAL

The usual precautions, required in handling moisture- and/or air-sensitive materials, were observed. Solvents were dried by standard procedures.

Compound (Ib) was prepared according to the literature.[47,48] The preparation of the remaining compounds is described in the following.

Preparation of Compound (Ia) [*Reaction of* MeMgI *with* $(F_3PNMe)_2$].—A 500 ml three-necked flask was fitted with a pressure-equalising dropping funnel, a reflux condenser, and a gas inlet for nitrogen. A solution of 44 g (0·188 mol) of $(F_3PNMe)_2$[47,48] in ether (100 ml) was placed in the flask. To this solution 200 ml of MeMgI (46·88 g; 0·282 mol) in ether was added dropwise with stirring at room temperature over 3·5 h. In the course of the mildly exothermic reaction a white precipitate was formed whose colour gradually turned orange after 18 h of stirring. After a 3 h reflux period and a further 3 h of stirring at room temperature the precipitate was filtered with exclusion of moisture; from the filtrate ether was removed by distillation *via* a 30 cm Vigreux column. The higher-boiling product was fractionated (20 cm Vigreux column); 6·8 g (0·0296 mole; 16%) of a yellow-orange liquid were obtained: b.p. 78°, 104 mmHg —68°, 62 mmHg.

The orange colouration could not be removed by either

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[46] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Interscience, 1966, p. 115.

[47] R. Schmutzler, *Chem. Comm.*, 1965, 19.

[48] R. Schmutzler, *J.C.S. Dalton*, 1973, 2687.

treatment with activated carbon, or by three redistillations (observed b.p. 76°, 90 mmHg; 70°, 78 mmHg; 75°, 86 mmHg).

From the n.m.r. spectra the product was identified as (Ia) (Found: C, 16·8; H, 4·1; N, 12·0. $C_3H_9F_5N_2P_2$ requires C, 15·7; H, 3·9; N, 12·2%).

Preparation of (Ic) [*Reaction of* MeLi *with* $(MeF_2PNMe)_2$].—Using an experimental set-up similar to that described in the preceding experiment (250 ml flask), 50·7 g of a 3% solution of methyl-lithium in ether (1·52 g MeLi; 0·069 mol) was added over 1·5 h to a solution of 7·8 g $(MeF_2PNMe)_2$[48] (0·0345 mol) in ether (100 ml); the mixture was stirred and cooled with a dry ice–acetone bath. A white precipitate was formed. Stirring was continued for 18 h at room temperature after the addition had been completed. The reaction mixture was then filtered through a sintered-glass funnel, solvent was stripped off *in vacuo*, and the higher-boiling product was distilled through a micro-still whose receiver was cooled with liquid nitrogen. Over the range 50°, 1·6 mmHg—39°, 0·5 mmHg, 2·3 g [30% as (Ic)] of a liquid distilled over which solidified partly upon condensation. The pure product was obtained through a further distillation; b.p. 42°, 0·8 mmHg, m.p. 32—34°. N.m.r. established the identity of this product as (Ic) (Found: C, 27·1; H, 6·65; N, 12·5. $C_5H_{15}F_3N_2P_2$ requires C, 27·0; H, 6·8; N, 12·6%).

Preparation of (Id) (*Reaction of* $MeNLi_2$ *with* Me_2PF_3).—Methylamine (4·3 g; 0·1385 mol) was condensed into a 250 ml flask. After the addition of ether (40 ml), the mixture was cooled with dry ice–acetone, and 17·75 g of n-butyl-lithium (0·277 mol) as 118 g of a 15% solution in n-hexane was added dropwise with magnetic stirring over 2 h. The mixture was stirred at room temperature for 6 h and was refluxed for 3 h. After cooling to room temperature, 16·35 g (0·1385 mol) of Me_2PF_3[49] in ether (40 ml) was added with stirring and cooling with a dry ice–acetone bath over 1·5 h. The reaction mixture was stirred for a further 24 h. The solids were filtered and the filtrate was distilled through a 20 cm Vigreux column. In the range 70°, 5·8—5·0 mmHg a liquid product distilled which solidified partially upon condensation, and was recovered from the distillation apparatus by sublimation. The yield was 6·0 g [0·0275 mol; 40% as (Id)]. During a further distillation, a b.p. 63°, 5·5 mmHg—64°, 5·0 mmHg was observed. A pure product (by n.m.r.) was finally obtained as a white solid upon repeated sublimation at 40°, 0·5 mmHg; m.p. 112—116° (Found: C, 33·1; H, 8·35; N, 12·7. $C_6H_{18}F_2N_2P_2$ requires C, 33·0; H, 8·3; N, 12·8%).

Besides this compound, a liquid product of b.p. 46°, 0·05 mmHg was obtained whose identity was not established.

Preparation of (IIa) *and* (IIb) [*Reaction of* $(F_3PNMe)_2$ *with* LiOMe].—To a mixture of methanol (6·2 g; 0·1935 mol) and ether (50 ml) in a 500 ml flask was added dropwise, with stirring and cooling with dry ice–acetone, 12·4 g (0·1935 mol) of Bu^nLi (as 82·7 g of a 15% solution of Bu^nLi in n-hexane) over a 1·5 h period. Stirring was continued for a further 3 h at room temperature. The reaction mixture was transferred to a dropping funnel and was added dropwise with stirring over 2·5 h to a solution of 30 g (0·1285 mol) of $(F_3PNMe)_2$[31,32] in 150 ml of ether; the reaction was controlled by cooling with a dry ice–acetone mixture. Formation of a precipitate commenced immediately. Stirring at room temperature was continued for 12 h after the addition had been completed; solvent was then removed *via* a 30 cm Vigreux column; the less volatile products thus remaining were subsequently pumped off (up to 60°, 0·05 mmHg) *via* a smaller still (receiver cooled with liquid nitrogen). This product was then fractionated through a 20 cm Vigreux column. In the range 73°, 82 mmHg—50°, 26 mmHg, 10·4 g [33% as (IIa)] of a liquid, identified as (IIa) from the n.m.r. spectrum, were obtained. The product was obtained pure by a further distillation over a 30 cm Vigreux column; b.p. 67°, 67 mmHg (Found: C, 14·8; H, 3·65; F, 38·6. $C_3H_9F_5N_2OP_2$ requires C, 14·6; H, 3·7; F, 38·85%).

A further liquid product distilled over the range 79°, 26 mmHg—74°, 18 mmHg; part of it crystallised in the still and was recovered by sublimation. The yield was 11·0 g [33% as (IIb); identified by n.m.r.]. Repeated sublimation at 60°, 6 mmHg furnished the pure product; m.p. 64—65° (Found: C, 18·45; H, 4·6; F, 29·3. $C_4H_{12}F_4N_2O_2P_2$ requires C, 18·6; H, 4·7; F, 29·4%).

Preparation of (IIc) *and* (IId) [*Reaction of* $(F_3PNMe)_2$ *with* LiOMe].—As described in the preceding experiment, a solution of LiOMe was prepared at −40° from 13·9 g of methanol (0·434 mol; 20% excess) in 100 ml of ether and 23·3 g (0·364 mol) of Bu^nLi (as 155 g solution in n-hexane). After 3 h stirring at room temperature and 1 h at reflux, this mixture was added to a solution of 24·3 g (0·104 mol) of $(F_3PNMe)_2$[31,32] in ether (200 ml) at −40°. After 24 h at room temperature, the solid product was filtered off; from the filtrate, after removal of solvent, a liquid was obtained upon distillation (b.p. 56°, 1·5 mmHg—50°, 1·0 mmHg) which partially solidified in the still and was recovered by sublimation. Redistillation (b.p. 55°, 1·0 mmHg) furnished 12·3 g (0·0456 mol; 44%) of (IIc) (identified from its n.m.r.) which was sublimed at 40°, 0·5 mmHg; m.p. 40—42° (Found: C, 22·4; H, 5·7; F, 20·9. $C_5H_{15}F_3N_2O_3P_2$ requires C, 22·2; H, 5·6; F, 21·1%).

A finely divided white solid was left as a residue in this distillation. It was first sublimed repeatedly at 60°, 0·05 mmHg, then recrystallised from dichloromethane; yield 3·7 g, 13%, identified as (IId) from its n.m.r., m.p. 133—134° (Found: C, 25·35; H, 6·5; F, 13·1. $C_6H_{18}F_2N_2O_4P_2$ requires C, 25·5; H, 6·4; F, 13·5%).

N.M.R. Experiments.—The solutions used for the n.m.r. studies were made up in a 1 : 1 CD_2Cl_2 and CH_2Cl_2 mixture, and a few drops of $CFCl_3$ were added to provide field-frequency locking for ^{19}F resonance. The sample tubes were 5 mm outside diameter; samples were degassed using the freeze–pump–thaw technique with a vacuum line and then sealed.

^{19}F Spectra were obtained using a Varian HA 100 spectrometer in the frequency sweep HA mode at 94·155 MHz. The $^{19}F\{^1H\}$ double resonance experiments were carried out using the double-tuned transmitter circuit illustrated in Figure 5 and a Schlumberger FSX 3005 frequency synthesiser as the 100 MHz source. Noise decoupling was achieved using a Hewlett-Packard noise generator (HP 3722A). Spectra were calibrated with a frequency counter to minimise effects of chart nonlinearity, and average measurements of each line were taken from three spectra.

^{31}P Spectra were obtained at 40·5 MHz using a Varian XL-100 n.m.r. spectrometer in the continuous wave, frequency-sweep, mode. The ^2D resonance of CD_2Cl_2 was used to provide the field frequency lock. Proton noise decoupling was used in recording all ^{31}P spectra. Most spectra were obtained with multiscan averaging by interfacing a Varian 620/i computer to the spectrometer.

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The ^{31}P resonance frequencies were measured directly using an El Dorado–Varian MHz frequency counter, as was the frequency of the lock signal. The ^{31}P frequencies were then scaled to be appropriate for a field at which the ^{1}H resonance of tetramethylsilane occurs at exactly 100 MHz.

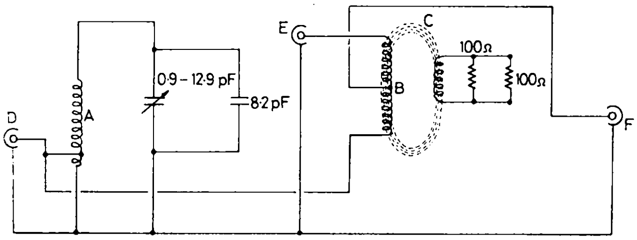

FIGURE 5 Circuit for double-tuning the HA 100 transmitter coil for $^{19}F\{^{1}H\}$ heteronuclear double resonance. Components are as follows: A, coil of 1 in length, with $8\frac{3}{4}$ turns of 18 SWG wire at $\frac{1}{4}$ in inside diameter, tapped at $\frac{3}{4}$ of a turn; B, coil with 3 × $3\frac{1}{2}$ turns of 22 SWG wire, trifiler wound; C, ferrite ring core (ITT CRO 71-6 A/C), 6 mm outside diameter, and 3 mm inside diameter, 1·5 mm in height, material SA 503; D, UHF plug for the observing frequency from the transmitter; E, BNC socket for the decoupling power; F, UHF socket to the probe

The ^{31}P chemical shifts (Table 3) were then obtained by subtracting the frequency for 85% H_3PO_4, which we have measured directly as 40 480 720 Hz (the published [50] value, obtained indirectly, is 40 480 740 Hz) and converting to a p.p.m. scale.

The variable temperatures were obtained using the Varian V 4341/V 6057 variable temperature accessory. The probe temperatures were calibrated using the relative chemical shifts of the methanol –OH or glycol –OH proton in the appropriate temperature region; they are considered to be accurate to ±2 °C. Results given in the Tables are for ambient probe temperature (*ca.* 35 °C) except where otherwise stated.

The heteronuclear triple resonance experiment, observing ^{31}P and irradiating ^{1}H and ^{19}F at the same time, was carried out on the Varian XL-100 spectrometer. In place of the normal ^{1}H decoupling matching network, the $^{19}F\{^{1}H\}$ Varian matching network was used to double tune the decoupler coil for 100 and 94 MHz. The 100 MHz noise-decoupling power was obtained from the XL-100 ' Gyrocode ' and the 94 MHz signal for partially decoupling ^{19}F nuclei was derived from a Schlumberger frequency synthesiser (Type FSX 3000) with a R.F. Communications Inc. type HB 805 signal amplifier.

The ^{19}F chemical shifts given in Table 2 are estimated to be accurate to ±0·01 p.p.m.; the ^{31}P chemical shifts (Table 3) are expected to be correct to ±0·2 p.p.m. The greater error for the ^{31}P measurements arises from drifts in the master oscillator used in the referencing procedure. The likely errors in the coupling constants are ±0·5 Hz, except (i) for the low temperature results for (IIc), which are less accurate, and (ii) as denoted for $^{4}J_{FF}$ in Table 8.

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