Preparative and Nuclear Magnetic Resonance studies of Diazadiphosphetidines. Part VI.[1] 2,4-Dialkyl-2,2,4,4-tetrafluoro-1,3-dimethyl-1,3,2,-4-diazadiphosphetidines

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Proton-decoupled ^{19}F and ^{31}P n.m.r. spectra of a series of dialkyltetrafluorodiazadiphosphetidines, $(RF_2PNMe)_2$ (I; R = Me, Et, Pr^i, or Bu^t), have been recorded and analysed for temperatures high enough for *gauche* $\rightleftharpoons$ *trans* exchange to be rapid on the n.m.r. timescale, and at low temperatures when the exchange is slow. Some ^{1}H n.m.r. data are also given, including the results of a complete analysis of the spectrum of (I; R = Me) on an $[A(X)_2M_3]_2$ basis. Many signs of coupling constants have been obtained either from the spectral analysis or from double-resonance experiments. The coupling constants and chemical shifts are compared and discussed. There is a very large isomer effect on $^2J_{PP}$, especially for the Bu^t compound. Isomer populations have been obtained by several methods. The preparations of the Pr^i and Bu^t compounds, not previously reported, are described in detail.

THE planar four-membered ring structure, $\overline{\text{P–N–P–N}}$, for diazadiphosphetidines has been confirmed for $(F_3PNMe)_2$ in the gas phase by electron diffraction[2] and for $(Cl_3PNMe)_2$ and $(PhF_2PNMe)_2$ in the solid state by *X*-ray diffraction.[3-5] Numerous other data have also supported this structure (*cf.* refs. 6—10). The ^{19}F n.m.r. spectra of the compounds $(F_3PNMe)_2$ [1a] and $(RF_2PNMe)_2$ [1b] (R = Me, Et, NEt$_2$, and Ph) have been analysed and discussed previously. Recently n.m.r. studies were carried out on some unsymmetrical diazadiphosphetidines,[1c] on a range of methyl- and methoxy-diazadiphosphetidines,[1d] and on some chloromethyl compounds.[1e] We report here the results of n.m.r. investigations of some dialkyltetrafluorodiazadiphosphetidines, $(RF_2PNMe)_2$ (I). A full analysis of the ^{1}H spectrum of (I; R = Me) is presented, and additional low-temperature ^{19}F data for (I; R = Et) are given. We also report the preparation

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[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.

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

[3] H. Hess and D. Forst, *Z. anorg. Chem.*, 1966, **342**, 240.

[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] I. Haiduc, 'The Chemistry of Inorganic Ring Systems,' Interscience, London, 1970, vol. 2.

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

[8] R. E. Dunmur and R. Schmutzler, *Fortschr. Chem. Forsch.*, in preparation.

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

[10] M. P. Yagupsky, *Inorg. Chem.*, 1967, **6**, 1770.

Table 1

Fluorine-19 and ^{31}P n.m.r. parameters[a] for diazadiphosphetidines, $(RF_2PNMe)_2$ (I)

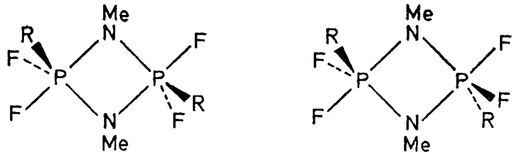
R	Isomer	θ_c/°C	δ_F [b]	δ_P [c]	$^2J_{PP}$ [d]	$^1J_{PF}$ [e]	$^3J_{PF}$ [f]	N_{FF} [d]	L_{FF}
			p.p.m.		Hz				
Me [g]	average	+85	−57.76	−50.4	72.2	−891.5	+5.2	16.3	3.7
	gauche	−60	−51.81	−51.2	54.4	−908.2	−6.1	7.2	3.6
	trans	−60	−55.90	−47.4	92.2	−868.0	+18.7	24.8	6.0
Et [h]	average [e,g]	+85	−65.68	−45.4	67.4	−908.7	+8.7	19.7	4.3 ± 1.5
	gauche	−60	−63.38	−47.9	45 ± 1	−916.0	−6.5	8 ± 1	3 ± 2
	trans	−55	−66.09	−42.9	85 ± 1	−895.1	−15.1 ± 1	25 ± 1	4 ± 2
Pr^i [h]	average	+180	−75.10	*i*	66 ± 2	−929 ± 2	+13 ± 2	*i*	*i*
	gauche	−50	−74.73	−47.7	39.5	−929.0	−7.9	8.2	2 ± 1
	trans	−50	−78.15	−43.8	82.7	−909.8	+17.6	26.5	3.5 ± 1
Bu^t [h,j]	average	+180	−66.7	*i*	80 ± 2	−925 [k]	*i*	*i*	*i*
	gauche	−40	−65.32	−38.8	22.6	−943.1	−8.9	5.7 [l]	5.7
	trans	−40	−67.15	−39.5	93.5	−925.6	+23.0	32.5	19.8

[a] From direct measurement [see ref. 1(*b*)] except for the individual isomers of (I; R = Bu^t); in the latter case iteration from ^{19}F transitions was carried out using the computer program LACX.[19] [b] With respect to $CFCl_3$, positive when the reference is to low frequency; accurate to ± 0.01 p.p.m. [c] With respect to 85% H_3PO_4 (external), positive when the reference is to low frequency; accurate to ±0.2 p.p.m. [d] Sign assumed to be constant; it was determined for the *trans*-isomer (I; R = Bu^t). [e] Sign assumed to be negative.[30] [f] The sign is given relative to J_{PF} by the spectral analysis. [g] Data from refs. 1(*b*) and/or 1(*e*) except for the δ_P(av.) value for Et which is newly reported. [h] Errors in coupling constants are in general ± 0.5 Hz, except where otherwise stated. [i] Not obtained. [j] $^2J_{FF} = -36 \pm 5$ Hz. For the *trans*-isomer. [k] N_{PF} Value. [l] One of the values of $^4J_{FF}$ is <1.5 Hz. The other is 5.7 Hz.

of two new compounds, (I; R = Pr^i and Bu^t), and present their n.m.r. data.

RESULTS

The ground-state structure for tetrafluorodiazadiphosphetidines is such that each phosphorus atom has an approximately trigonal-bipyramidal environment with one equatorial and one axial bridging NMe group. Each NMe group



gauche *trans*

(I) R = Me, Et, Pr^i, or Bu^t

is axial to one phosphorus and equatorial to the other. The remaining axial positions are occupied by fluorine so that each phosphorus atom is bonded to one axial and one equatorial fluorine. However, intramolecular exchange between axial and equatorial fluorines is rapid on the n.m.r. timescale.[1] At temperatures below ambient the existence of *gauche* and *trans* isomers may be detected by n.m.r.[1b] The *gauche* $\rightleftharpoons$ *trans* intramolecular exchange becomes rapid on the n.m.r. timescale at room temperature and above.

$$PCl_3 + Pr^iMgCl \longrightarrow Pr^iPCl_2 + MgCl_2 \qquad (1)$$

In general the reactions of fluorophosphoranes with *N*-substituted hexamethyldisilazanes are useful routes to the synthesis of difluorodiazadiphosphetidines.[11-15] The preparation of (I; R = Pr^i) involved steps (1)—(3). The final step and the preparation[16] of Pr^iPF_4 involved the usual methods;[13] the dichlorophosphine, Pr^iPCl_2, was prepared from the reaction of phosphorus trichloride with isopropylmagnesium chloride,[17] which, somewhat unusually, stopped at the monoalkylation stage. The preparation of (I; R = Bu^t) was effected by reaction (4).[18]

N.M.R. Spectral Analysis.—(a) *Proton-decoupled* ^{19}F *and* ^{31}P *spectra*. As has been shown previously[1] for tetrafluorodiazadiphosphetidines of the type discussed here, the intramolecular exchange renders the fluorine atoms chemically equivalent on the n.m.r. timescale, thus reducing the amount of information which can be obtained from the spectra. The high-temperature (100 °C) ^{19}F spectra of the compounds discussed here indicate that in each case only one fluorine environment is present. For (I; R = Me and Et), 85 °C was sufficient to obtain sharp averaged spectra, but for (I; R = Pr^i and Bu^t) it was necessary to go to 180 °C; even then the resolution was not good enough for all the coupling constants to be obtained. The spectral pattern observed when the protons are decoupled is that due to an $[A(X)_2]_2$ spin system[1b] where A and X refer to ^{31}P and ^{19}F respectively. Analysis of the ^{19}F region of these double-resonance spectra was carried out as described previously,[1b] yielding the parameters listed in Table 1, which includes published data[1b] for (I; R = Me). It may be noted that the n.m.r. lines were not in general very sharp, probably because of the presence of the quadrupolar nitrogen atoms (increase in temperature is expected to increase the linewidths from this cause). This usually leads to considerable uncertainty in $L_{FF} = {}^4J_{FF} - {}^4J_{FF'}$ [see ref. 1(*b*)], though $N_{FF} = {}^4J_{FF} + {}^4J_{FF'}$ is generally obtained more accurately.

$$3\,Pr^iPCl_2 + 4\,SbF_3 \longrightarrow 3\,Pr^iPF_4 + 2\,Sb + 2\,SbCl_3 \qquad (2)$$

$$2\,Pr^iPF_4 + 2\,MeN(SiMe_3)_2 \longrightarrow (Pr^iF_2PNMe)_2 + 4\,Me_3SiF \qquad (3)$$

$$(F_3PNMe)_2 + 2\,Bu^tLi \longrightarrow (Bu^tF_2PNMe)_2 + 2\,LiF \qquad (4)$$

At room temperature (for R = Pr^i and Bu^t) and on cooling (for R = Me and Et) to *ca.* −30 °C, the samples showed

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

[12] G. C. Demitras, A. G. MacDiarmid, and R. A. Ken , *Chem. and Ind.*, 1964, 1712; G. C. Demitras and A. G. MacDiarmid, *Inorg. Chem.*, 1967, **6**, 1903.

[13] R. Schmutzler in 'Halogen Chemistry,' ed. V. Gutmann, Academic Press, London, 1967, vol. 2, p. 31.

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

[15] G. C. Demitras, Ph.D. Dissertation, University of Pennsylvania, Philadelphia, 1964.

[16] R. Schmutzler, *Inorg. Chem.*, 1964, **3**, 410.

[17] W. Krüger and H. P. Rieck, Technische Universität Braunschweig, unpublished work.

[18] O. Schlak, Ph.D. Thesis, Braunschweig, 1974.

separate ^{19}F spectra for the two different isomeric forms of each diazadiphosphetidine. The isomer giving the high-frequency ^{19}F resonance is thought to be the *gauche* form.[1b] The spectrum of each isomer is of the same type as the averaged spectrum observed at high temperature. Exchange between axial and equatorial fluorine atoms for a given isomer was still rapid on the n.m.r. timescale at the low temperature used (down to *ca.* −60 °C). The data reported for the separate isomers in Table 1 are therefore average chemical shifts and coupling constants for axial and equatorial fluorine-atom environments. The variable-temperature experiments showed that the barrier to *trans* $\rightleftharpoons$ *gauche* exchange increases in the order R = Me < Et < Pr^i < Bu^t. In fact, for R = Pr^i and Bu^t it was not possible to obtain good average spectra, even at the highest temperatures accessible to the n.m.r. probe. The average values reported here for R = Pr^i and Bu^t were therefore obtained from slightly exchange-broadened spectra and hence carry fairly large errors.

The parameters obtained by the procedure mentioned above were checked by simulating the spectra using the program LACX.[19] All the compounds showed good agreement except for (I; R = Bu^t). For the *trans*-isomer (I; R = Bu^t) there was a discrepancy in the centre lines of χ = 1 bands; the splittings of these centre lines in the inner and outer bands were unequal (Figure 1). This asymmetry gives the relative signs [20] of $^2J_{FF}$ and N_{FF}, which were found to be opposite. This relative sign determination was possible due to the large value of L_{FF} for *trans*- (I; R = Bu^t). It was also possible to obtain the magnitude of $^2J_{FF}$ by an iterative calculation using LACX. An interesting ^{19}F spectrum was observed for *gauche*-(I; R = Bu^t), where the $\chi = 1$ band showed a 1 : 1 : 1 triplet (Figure 1). This arises because $N_{FF} \approx L_{FF}$. The magnitude of $^2J_{PP}$ was small for this case.

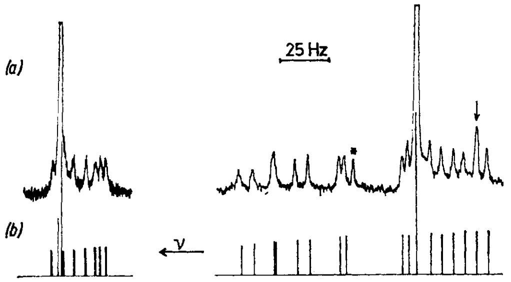

FIGURE 1 94 MHz ^{19}F–{^{1}H} Spectra of $(Bu^tF_2PNMe)_2$ (high-frequency half) at *ca.* −40 °C: (*a*), observed; (*b*), calculated using the program LACX. The spectra on the left-hand side are due to the *gauche* isomer, those on the right to the *trans*. The peak marked with an asterisk is due to an impurity. There is also an impurity contribution to the peak marked with an arrow. In both (*a*) and (*b*) the most intense lines have been truncated

The ^{31}P–{^{1}H} spectra of compounds (I) were in general only used to obtain values of δ_P. Spectra simulated on the basis of the parameters obtained from the ^{19}F–{^{1}H} spectra agreed with those observed. However, the ^{31}P spectrum of *trans*-(I; R = Bu^t) is sensitive [21] to the relative sign of $^2J_{PP}$ and N_{FF}. Two calculations, one with the same sign for J_{PP} and N_{FF}, and the other with opposite signs, were made using LACX. The observed ^{31}P spectrum of the *trans*-compound (I; R = Bu^t) was in good agreement with that calculated with the same sign for J_{PP} and N_{FF} (Figure 2). A negative sign for $^2J_{FPF}$ has been obtained [22–24] for many phosphorus compounds, and on the basis of our results the signs of $^4J_{FF}$ and $^2J_{PP}$ are positive for *trans*- (I; R = Bu^t). A positive sign has also been established for $^2J_{PP}$ in a methyl-substituted diazadiphosphetidine by a triple-resonance experiment.[1d] In principle the ^{31}P spectra of all the compounds reported here are sensitive to the relative signs of J_{PP} and N_{FF}, but in practice only *trans*- (I; R = Bu^t) proved useful in this respect.

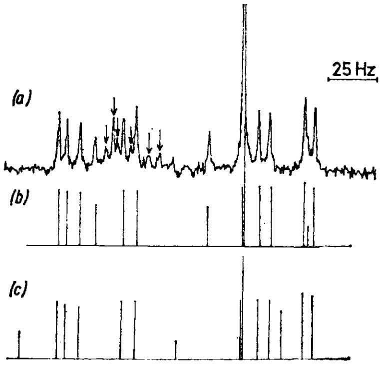

FIGURE 2 40.5 MHz ^{31}P–{^{1}H} spectrum of *trans*-$(Bu^tF_2PNMe)_2$ (high-frequency third) at *ca.* −40 °C: (*a*), observed; (*b*), calculated with $^2J_{PP}$ and N_{FF} the same sign; (*c*) calculated with $^2J_{PP}$ and N_{FF} of opposite sign. The peaks marked with vertical arrows are due to the *gauche* isomer. The most intense line has been truncated

(b) *Proton spectra.* Some preliminary ^{1}H data for (I; R = Me) have been published.[1e] The ^{1}H n.m.r. spectrum may be classified as that of the M part for an $[A(X)_2M_3]_2$ spin system (excluding the NMe protons). Irradiation with moderate strength in the region of $\nu_F - \frac{1}{2}|N_{PF}|$ produced the spectrum in Figure 3. Since $^1J_{PF}$ is large and negative, irradiation is actually near $\nu_F + \frac{1}{2}N_{PF}$, and such an experiment is affecting all ^{1}H transitions for which the nearest ^{31}P nucleus is β. Spin states with the phosphorus nuclei $\beta\beta$ therefore give a ^{19}F-decoupled proton spectrum, resulting in the very intense line at the low-frequency side of Figure 3(*a*) which must be at $\nu_H + \frac{1}{2}N_{PH}$. The position of the peak shows that N_{PH} is negative (with respect to N_{PF} also negative). The spin states with the ^{31}P nuclei $\beta\alpha$ (or $\alpha\beta$) give rise, approximately, to a ^{1}H sub-spectrum for an $m_3x_2n_3$ system with $\delta_m = \delta_n$. On a first-order basis the ^{1}H sub-spectrum is expected to consist of a 1 : 2 : 1 triplet of spacing $|^3J_{FH}|$ centred at $\nu_H + \frac{1}{2}L_{PH}$ and a 1 : 2 : 1 triplet of spacing $|^5J_{FH}|$ centred at $\nu_H + \frac{1}{2}L_{PH}$. Since $|^5J_{FH}|$ is very small the latter triplet is obscured by the single ^{1}H line from the $\beta\beta$ ^{31}P spin states mentioned above. The triplet of spacing $^3J_{FH}$ cannot be clearly distinguished in Figure 3(*a*), partly because of incomplete decoupling for this sub-spectrum and because the above discussion is oversimplified. However, the remaining ^{31}P spin state, $\alpha\alpha$, is unaffected by the decoupling, giving a $[m_3(x)_2]_2$ sub-spectrum, centred at $\nu_H - \frac{1}{2}N_{PH}$, which can be clearly seen in Figure 3(*a*) and which

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[19] C. W. Haigh, *Ann. Rep. N.M.R. Spectroscopy*, 1971, **4**, 311.

[20] M. I. M. Wazeer, Ph.D. Thesis, University of East Anglia, 1974.

[21] R. M. Lynden-Bell, *Mol. Phys.*, 1963, **6**, 601.

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

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

[24] R. K. Harris, M. I. M. Wazeer, P. Clare, and D. B. Sowerby, *J.C.S. Dalton*, 1975, 625.

TABLE 2

^{1}H N.m.r. parameters[a] for diazadiphosphetidines $(RF_2PNMe)_2$ (I)

R	NMe group			R group					
	δ(Me)	$\lvert ^3J_{PH}\rvert$	$\lvert ^4J_{FH}\rvert$	δ(Me)	δ(CH/CH$_2$)	$^2J_{PH}$[b]	$^3J_{FH}$[c]	$\lvert ^3J_{PH}\rvert$	$^4J_{FH}$
Me[d]	2.50	12.5 ± 0.1	0.8 ± 0.1	1.57		−17.60 ± 0.3	(+)6.93 ± 0.3		
Et[e]	2.46	11.9 ± 0.1	0.75 ± 0.1	1.12	1.86	(−) 16.7	[f]	25.3	±0.8
Pr^i	2.45 ± 0.03	11.4	<1	1.235 ± 0.003	2.16	[f]	[f]	15.8[g]	<1.2[g]
Bu^t[h]	2.60	10.95 ± 0.03	0.65 ± 0.03	1.284 ± 0.003				18.85 ± 0.05	+0.8[g,i]

[a] Chemical shifts are in p.p.m. relative to $SiMe_4$, ±0.01, except where otherwise stated; they are positive when the sample resonates to high frequency of the reference. Coupling constants are in Hz, ±0.2 Hz except where otherwise stated. [b] Sign determined, relative to $^1J_{PF}$, as described in the text for R = Me. [c] Sign determined[1e] for $(Cl_2HCF_2PNMe)_2$ relative to that of $^1J_{PF}$. [d] $^4J_{PH} = +0.15$ Hz, $^5J_{FH} = +0.42$ Hz (signs determined, relative to $^2J_{PH}$ and $^3J_{FH}$ respectively, by spectral analysis). [e] Ref. 1(*b*). [f] Not obtained. [g] *N* values. [h] $^5J_{PH} = +0.85 \pm 0.05$ Hz (sign determined, relative to that of $^3J_{PH}$, by spectral analysis). [i] Sign determined relative to $^1J_{PF}$ as described in the text.

can be computer-simulated as in 3(*b*) using data obtained from the $^{19}F-\{^1H\}$ spectra, and estimated (F,H) coupling constants. In fact the irradiation experiment enables N_{FH} and N_{PH} to be readily recognised. Explicit lines in the single-resonance ^1H spectrum can then be used to obtain accurate values for these parameters. It should be noted that complete $^1H-\{^{19}F\}$ or $^1H-\{^{31}P\}$ decoupling requires much more power than the experiment described here because $|^1J_{PF}|$ is very large. After the above procedure, explicit lines additional to those separated by N_{FH} and N_{PH} can be assigned in the coupled spectrum, on the basis of the spin system $[A(X)_2M]_2$, described earlier[1e] for a diazadiphosphetidine, and with the aid of the coupling-constant data already acquired; the remaining parameters were estimated in this fashion. The complete spectrum was then simulated with the computer program[25] NUMAR, which uses both magnetic and chemical-equivalence factorization. The correct choice between a number of possible assignments of explicit lines was made by such computation. The observed and final computed spectra, which are in good agreement, are shown in Figure 4, and the appropriate ^1H parameters are in Table 2. The spectra analysed were those obtained at ambient probe temperature. No improvement in resolution was seen at 85 °C.

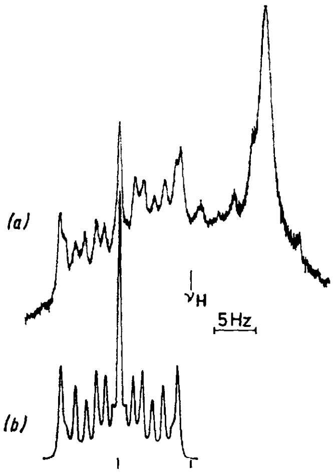

FIGURE 3 100 MHz $^1H-\{^{19}F\}$ spectra of $(MeF_2PNMe)_2$ (PMe region) at ambient probe temperature (see text): (*a*) observed spectrum with irradiation near $\nu_F - \frac{1}{2}|N_{PF}|$; (*b*) computer-simulated $[m_3(x)_2]_2$ sub-spectrum

The proton spectrum of (I; R = Et) was approximately analysed previously.[1b] No new data were obtained in the present study. The proton spectrum of (I; R = Pr^i) was broad because the spin system involved is complex. For the C-methyl groups only the *N* values were obtained. The NMe region was first order and the coupling constants were measured directly. The parameters obtained are in Table 2.

The proton spectrum of (I; R = Bu^t), (Figure 5) had resolved χ lines in the middle. The relevant spin system for this case is $[A(M)_2X_9]_2$. The magnitude of N_{PH} can be obtained readily from the separation of the two most intense lines. These two lines, together with the χ lines, form an $[ax_9]_2$ sub-spectrum. The magnitude of L_{PH} can be calculated[24] from the separation of the χ = 1 (inner) lines and $^2J_{PP}$ (80 Hz). The value of L_{PH} thus obtained is 18.0 Hz. Using this L_{PH} value and J_{PP}, the splittings $S_i(2)$ and $S_i(3)$ (separation of the 2nd and 3rd χ inner lines) were calculated[26] and were in good agreement with the observed values (see below):

	Calc.	Obs.
$S_i(2)$/Hz	5.72	5.75
$S_i(3)$/Hz	8.8	9.0

In the spin system $[A[M]_2X_9]_2$ there are two pairs of intense lines with separation $2N_{MX}$(*i.e.* $^2N_{PH}$). In the observed spectrum there were eight such intense lines and it is difficult to assign the N_{PH} pairs. Tickling the ^{31}P resonances was attempted, but the effect was on both sets of lines and assignment was not feasible. The possible N_{PH} values from the two sets of lines are 0.8 and 1.5 Hz. The N_{PH} value observed[1b] for the CH_3 protons of the ethyl group for (I; R = Et) is 0.8 Hz. On this basis 0.8 Hz was tentatively taken as

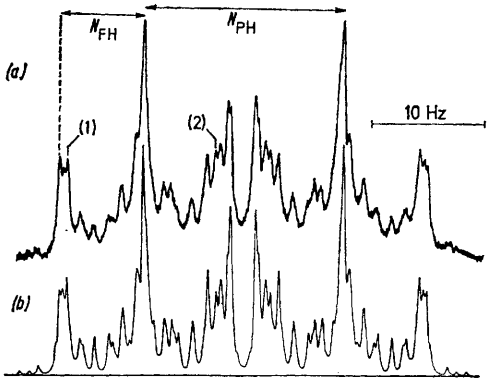

FIGURE 4 100 MHz ^1H spectrum of $(MeF_2PNMe)_2$ (PMe region): (*a*), observed; (*b*), computed; (1) and (2) are at $\nu_H + \frac{1}{2}|L_{PH}| + |L_{FH}|$ and $\nu_H + \frac{1}{2}|L_{PH}| - |L_{FH}|$ respectively

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[25] A. R. Quirt and J. S. Martin, *J. Mag. Res.*, 1971, **5**, 318.

[26] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

N_{FH} for (I; R = Bu^t). The ^{1}H-{^{31}P} tickling experiments showed that N_{FH} and N_{PH} are opposite in sign, *i.e.* $^4J_{FH}$ is positive.

DISCUSSION

Fluorine-19 and ^{31}P parameters for the compounds studied here are given in Table 1. The ^{19}F chemical shifts show some interesting features. The shielding increases from Me to Et to Pr^i but decreases again for Bu^t. It is a remarkably large effect for a change of substituent three bonds away from fluorine (Figure 6). A similar trend of ^{19}F shifts was also found [1e] for the diazadiphosphetidines $(RF_2PNMe)_2$ (R = Me, CH$_2$Cl, CHCl$_2$, and CCl$_3$); the maximum shielding was for the compound with R = CHCl$_2$. An increase in ^{19}F shielding was also observed [27,28] in alkyldifluorophosphoranes, in the order Me < Et < Bu^t. This has been rationalised in terms of the close proximity of methyl hydrogen atoms in the Et and Bu^t groups to the fluorine atom.

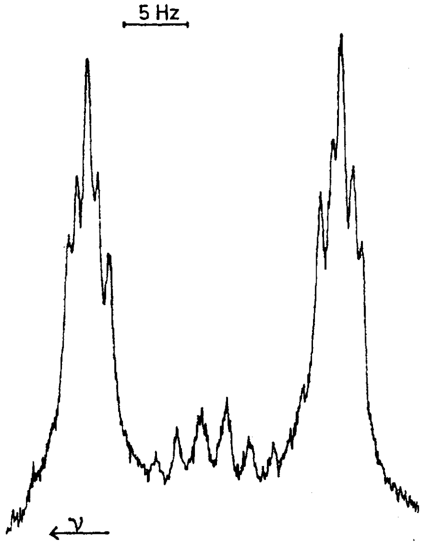

FIGURE 5 100 MHz ^{1}H spectrum of $(Bu^tF_2PNMe)_2$ (Bu^t region)

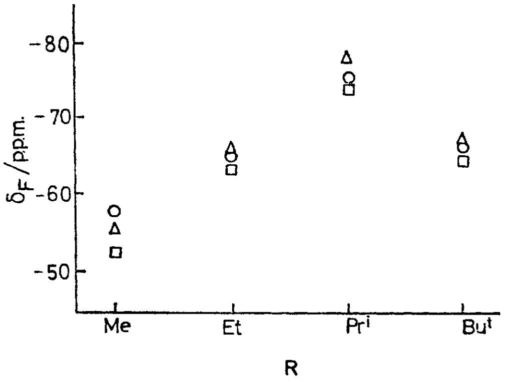

FIGURE 6 Variation of δ_F for $(RF_2PNMe)_2$ with the nature of R: (□), *gauche* isomer; (△), *trans* isomer; (○), weighted average

The *gauche*-isomer ^{19}F resonances are at higher frequency than those of the *trans* isomer. This is presumably due to the differences in electric and magnetic fields produced by different substituents. The differences between the two isomers are long range (*i.e.* the local grouping PF$_2$R is the same for the two isomers). The average chemical shift lies between the separate results for the two isomers except for R = Me. The exception may be due to different temperatures involved; fairly large shift variations have been observed [18] with change of temperature. The ^{31}P chemical shifts for the *trans* isomers are at higher frequency than those of the *gauche*, except for R = Bu^t. This phenomenon was also observed [1e] in the series $(CH_{3-x}Cl_xF_2PNMe)_2$ (x = 1—3) where the reversal of the shift was observed for the bulkiest group, CCl$_3$.

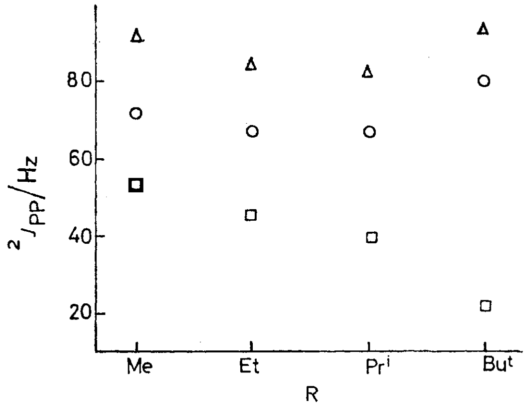

FIGURE 7 Variation of $^2J_{PP}$ for $(RF_2PNMe)_2$ with the nature of R. For key see Figure 6

The value of $^1J_{PF}$ in each case is $\frac{1}{2}[^1J_{PF(eq)} + {}^1J_{PF(ax)}]$, as there is fast exchange of fluorines between axial and equatorial sites. There is a smooth increase in $^1J_{PF}$ for *gauche* and *trans* isomers in the order Me < Et < Pr^i < Bu^t. There is no such smooth trend [29] in $^1J_{PF}$ for R$_3$PF$_2$ (R = Me, Et, and Pr^i). The values of $^1J_{PF}$ for *gauche* isomers are consistently larger than those for the corresponding *trans* isomers, but the difference is appreciably greater for (I; R = Me) than for the other compounds. The values of $^3J_{PF}$ also show a consistent trend with increasing bulk of the substituent, but this is largely due to the changes in isomer population; $^3J_{PF}$ (*gauche*) values are negative and decrease with increasing bulk of the substituent, whereas the values of $^3J_{PF}$(*trans*) are positive and are at a minimum for R = Et.

The J_{PP} values show some interesting trends. Thus,

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[27] G. S. Reddy and R. Schmutzler, *Z. Naturforsch.*, 1970, **B25**, 1199.

[28] M. Fild and R. Schmutzler, *J. Chem. Soc.* (*A*), 1970, 2359.

[29] J. Grosse and R. Schmutzler, *Phosphorus*, 1974, **4**, 49.

whereas J_{PP}(*trans*) varies little (and in fact is at a minimum for R = Pr^i), the value of J_{PP}(*gauche*) decreases in the order Me > Et > Pr^i > Bu^t (Figure 7). The values of J_{PP} for (I; R = Bu^t) are such that the *trans* isomer gives the largest J_{PP} and the *gauche* isomer shows the smallest J_{PP} in the series. This influence of configuration on a coupling not directly involving the substituents is remarkable. Since it is strongly influenced by the bulk of the substituents, the effect presumably indicates the importance of ring planarity for the J_{PP} values. As for J_{PP}, the data for N_{FF} show that extremes of values for the two isomers are obtained for (I; R = Bu^t); for *gauche*-(I; R = Bu^t), $N_{FF} \approx L_{FF}$, implying that one $^4J_{FF}$ is very small.

It was shown [1e] that high-temperature populations for compounds of type (I) can be determined to a fair accuracy from the average n.m.r. parameters and the corresponding data for the individual isomers, assuming that the parameters are temperature invariant. The values of $^2J_{PP}$ and $^3J_{PF}$ are particularly suitable for this purpose. Such calculations were made for the compounds studied here (Table 3). A reasonable agreement was found for all cases, though for R = Pr^i there was a considerable spread of values (which may be attributed to the large errors in the average parameters for this compound). As is the case with the series $[(Cl_xH_{3-x}C)F_2PNMe]_2$, the population of the *trans* isomer increases with the bulk of the substituents. This is somewhat unexpected since models do not show appreciable steric crowding for either isomer. However, the assignment of the isomers is not completely unambiguous.

TABLE 3

Isomer populations [a] for the compounds (I)

Parameter	R = Me	Et	Pr^i	Bu^t
$^2J_{PP}$ [b]	0.47	0.56	0.61	0.92
$^3J_{PF}$ [b]	0.46	0.56	0.82	*c*
Integration [d]	0.52	0.62	0.75	0.82

[a] Fractional population of the *trans* isomer. [b] High-temperature values. [c] Not obtained. [d] Low-temperature values.

The ^1H n.m.r. parameters (Table 2) are mostly unremarkable. It is somewhat surprising, however, that $^4J_{PH}$ for (I; R = Me) is positive, since for $(Cl_2HCF_2\text{-}PNMe)_2$ it was found [1e] to be −0.22 Hz. However, the signs of $^5J_{FH}$ for the latter compound and for (I; R = Me) are both positive, though they are small in magnitude. The value of $^3J_{PH}$ for the NMe protons varies significantly and smoothly in the series R = Me to Bu^t, whereas it remains [1e] effectively constant for the $[(Cl_xH_{3-x}C)F_2PNMe]_2$ compounds.

It may be noted that the spectral analyses, plus the double-resonance experiments, result in the determination of many of the signs of the coupling constants for the compounds (I) (Tables 1 and 2). These are mostly given with respect to $^1J_{PF}$ (negative [30]) though some assume a positive sign for $^3J_{PH}$. In all cases where the magnitudes are large enough to make the signs meaningful, the latter are in agreement with previous determinations for related compounds.

EXPERIMENTAL

N.M.R. Spectra.—Three n.m.r. spectrometers were used in the present work. Initial single-resonance spectra were obtained using a Varian HA 60A spectrometer at 60 MHz for ^1H, 56.4 MHz for ^{19}F, and 24.3 MHz for ^{31}P resonance. The more detailed ^1H and ^{19}F work and all $^{19}F\text{-}\{^1H\}$ and $^1H\text{-}\{^{31}P\}$ heteronuclear double-resonance experiments were made with a Varian HA 100 spectrometer (99.896 MHz for ^1H and 94.155 MHz for ^{19}F) in the frequency-sweep mode. The $^{19}F\text{-}\{^1H\}$ experiments were carried out using a double-tuned transmitter circuit discussed elsewhere,[1d] and $^1H\text{-}^{31}\{P\}$ experiments were made using a double-tuned probe,[31] in conjunction with a Schlumberger FSX 3005 frequency synthesiser. The $^{31}P\text{-}\{^1H\}$ spectra were obtained at 40·50 MHz using a Varian XL 100 spectrometer in the CW mode; the ^2H signal of the CD_2Cl_2 solvent was used for field–frequency locking purposes.

The ^{31}P chemical shifts were calculated by measuring the ^{31}P resonance frequencies using a radiofrequency counter, converting into the equivalent frequency for a magnetic field such that the protons in $SiMe_4$ resonate at exactly 100 MHz, subtracting the corresponding scaled ^{31}P frequency for 85% H_3PO_4 (40 480 720 Hz),[1d] and converting into p.p.m. The ^{19}F shifts were obtained directly with respect to internal $CFCl_3$, and the ^1H shifts directly with respect to internal $SiMe_4$, separate samples being used for the ^{19}F and ^1H spectra (in each case with CH_2Cl_2/CD_2Cl_2 as solvent). All chemical shifts are reported on the appropriate δ scale, such that positive values occur when the sample resonates to high frequency of the reference. The high-temperature ^{19}F spectra of (I; R = Pr^i and Bu^t) were obtained using 1,2,4-trichlorobenzene as solvent, with $(CFCl_2)_2$ added for field–frequency locking.

N.m.r. tubes were of 5 mm outside diameter throughout; samples for the HA 100 and XL 100 work were degassed, using the freeze–pump–thaw technique with a vacuum line, and then sealed. Samples for the HA 60A instrument were not degassed. In all cases temperatures were measured using the spectrometer manufacturer's recommended procedure. They are only considered to be accurate to ±4 °C. Computer fitting of spectra was carried out using the program [19] LACX with an I.C.L. 1905E computer at the University of East Anglia, and the program [25] NUMAR with the I.B.M. 360 computer at Cambridge University.

Preparations.—The n.m.r. data in this section are for HA 60A measurements. Mass spectra were recorded using an A.E.I. MS9 or a Hitachi RMU-6L spectrometer at 70 eV.*

2,2,4,4-*Tetrafluoro*-2,4-*di-isopropyl*-1,3-*dimethyl*-1,3,2,4-*diazadiphosphetidine*, (I; R = Pr^i). Dichloroisopropylphosphine, as obtained in the Grignard reaction, was first fractionated using a spinning-band column to give a liquid, b.p. 28° (13 mmHg). The ^1H n.m.r. spectrum (interpreted on a first-order basis; solution in benzene at 28 °C) gave: $\delta_H(CH)$ 2.13 ($|^2J_{PH}|$ 10.0, $|^3J_{HH}|$ 6.5) and $\delta_H(CH_3)$ 1.28 p.p.m. ($|^3J_{PH}|$ 15.5, $|^3J_{HH}|$ 6.5 Hz); integration, CH : $(CH_3)_2$ 1 : 5.6 (calc. 1 : 6). The ^{31}P n.m.r. spectrum (neat, 23 °C) gave δ_P 195.4 p.p.m.

The dichlorophosphine (26.3 g, 0.18 mol) and antimony trifluoride (47.6 g; 0.27 mol ≡ 10% excess) were combined gradually during 1.5 h. After 2 h reflux, tetrafluoroiso-

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* 1 eV ≈ 1.60 × 10^{-19} J, 1 mmHg ≈ 13.6 × 9.8 Pa.

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

[31] J. R. Woplin, Ph.D. Thesis, University of East Anglia, 1970.

propylphosphorane was recovered by fractionation through a 20 cm Vigreux column; 21.9 g (80%) of product, boiling range 42—52 °C, was obtained. A b.p. of 48—49 °C was obtained for a product distilled twice over sodium fluoride (Found: C, 24.0; H, 4.7. Calc. for $C_3H_7F_4P$: C, 24.85; H, 5.0%), *m/e* 131 $[M]^+-F$ [strongest fragment; no parent ion seen (calc. for M^+: *m/e* 150) in line with observations [32] on other RPF_4]; ^1H n.m.r. (in CH_2Cl_2 at 28 °C) $\delta_H(CH)$ 2.44 ($|^2J_{PH}|$ 20.0, $|^3J_{HH}|$ 6.9, $|^3J_{FH}|$ 6.1) and $\delta_H(CH_3)$ 1.36 ($|^3J_{PH}|$ 26.1, $|^3J_{HH}|$ 6.9, $|^4J_{FH}|$ 1.1 Hz), integration CH : $(CH_3)_2$ = 1 : 6 (calc. 1 : 6); ^{19}F n.m.r. (neat at 24 °C) δ_F −56.0 p.p.m. ($|^1J_{PF}|$ 989.2 $|^3J_{FH}|$ 6.1, $|^4J_{FH}|$ 1.1 Hz); ^{31}P n.m.r. (in CH_2Cl_2 at 26 °C) δ_P −30.5 p.p.m. ($|^1J_{PF}|$ 990.3, $|J_{PH}|$ (av) 24 Hz).

The preparation of (I; R = Pr^i) was then conducted in a heavy-walled glass tube. A small quantity (*ca.* 1 g) of caesium fluoride was placed in the tube and was carefully dried by heating *in vacuo*. With exclusion of moisture, tetrafluoroisopropylphosphorane (11.2 g, 0.075 mol) and heptamethyldisilazane (13.1 g, 0.075 mol) were placed in the tube at dry-ice temperature. The tube was then cooled with liquid nitrogen, sealed *in vacuo*, and heated to 100 °C for 4 h. Fractionation of the reaction product at 65 (2)—59 °C (1 mmHg)[13] furnished the product (10.7 g, 51%) as a colourless liquid which solidified subsequently. On redistillation a b.p. of 64 °C (2 mmHg) was obtained; after two sublimations at 40 °C (0.1 mmHg) the m.p. was 42—43 °C (Found: C, 34.05; H, 7.2; N, 9.8. Calc. for $C_8H_{20}F_4N_2P_2$: C, 34.05; H, 7.1; N, 9.9%), *m/e* 282 (calc. 282.20).

2,2,4,4-*Tetrafluoro*-1,3-*dimethyl*-2,4-*di-t-butyl*-1,3,2,4-*diazadiphosphetidine*, (I; R = Bu^t). This compound was prepared as in reaction (2) according to a procedure adopted from unpublished work of Schlak.[18] The reaction was conducted in a three-necked flask, fitted with a reflux condenser (topped by a drying tube), a pressure-equalizing dropping funnel, and a thermometer. To a solution of $(F_3PNMe)_2$ (8.8g, 0.038 mol) in dry hexane (40 cm^3) was added 32.1 g of a 15% solution of t-butyl-lithium in hexane [corresponding to 4.82 g (0.075 mol) of Bu^tLi] with cooling (dry ice–acetone) and magnetic stirring over 2 h. The reaction mixture was allowed to warm up to room temperature (2 h) and was stirred for a further 12 h at room temperature. A solid precipitate that had formed was removed by filtration; fractionation of the residue remaining after removal of solvent furnished the product as a colourless liquid, b.p. 67 °C (0.5 mmHg) (7.8 g, 67%), which eventually solidified. After sublimation at 40 °C (0.1 mmHg) a m.p. of 51—56 °C was observed (Found: C, 38.6; H, 7.7; N, 9.3. Calc. for $C_{10}H_{24}F_4N_4P_2$: C, 38.7; H, 7.8; N, 9.0%), *m/e* 310 (calc. 310.26). CAUTION. The reaction often commences only after an induction period, and may proceed very violently; careful temperature control is, therefore, imperative.

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[5/429 *Received*, *3rd March*, 1975]

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[32] T. A. Blazer, I. K. Gregor, and R. Schmutzler, *Z. Naturforsch.*, 1969, **B24**, 1081.