Preparation and Nuclear Magnetic Resonance Study of Phosphorus–Fluorine Compounds undergoing Intramolecular Exchange. Part 4.† Rotameric Forms of 1-Piperidyltrifluorophosphoranes

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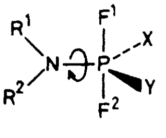
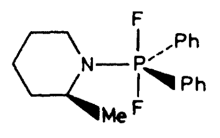
Fluorine-19 and phosphorus-31 n.m.r. spectra are reported at variable temperature under conditions of proton decoupling for four 1-piperidyltrifluorophosphoranes, substituted with a methyl group in the piperidyl ring so as to impart chirality. The axial fluorines are non-equivalent even at ambient probe temperature. As the temperature is lowered the spectrum shows evidence of two isomeric forms in each case, caused by the slowing of internal rotation about the P–N bond. The n.m.r. spectra were analysed to yield chemical shifts and coupling constants. The results are discussed in relation to conformation.

Internal rotation about the P–N bond of aminofluorophosphoranes has been shown [1–3] to occur on a time-scale comparable to that associated with ^{19}F n.m.r. A variety of effects on variable-temperature n.m.r. spectra may be observed depending on the symmetry and substitution pattern of the compounds concerned. In the case of aminofluorophosphoranes of the type (1) (excluding X = Y = F), if it is assumed that (*i*) pseudo-rotation at phosphorus is slow, (*ii*) the nitrogen envionment is effectively planar, and (*iii*) the potential minimum occurs when R^1 and R^2 are in the plane formed by F^1, F^2, P, and N (the axial plane), then there are two possible situations: (*a*) when R^1 = R^2, then F^1 and F^2 are equivalent for n.m.r. purposes under both fast-exchange and slow-exchange conditions of P–N internal rotation; (*b*) when R^1 $\neq$ R^2, then F^1 and F^2 become non-equivalent under conditions of slow P–N internal rotation.



(1)



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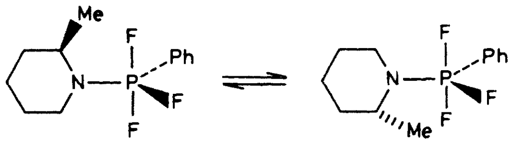
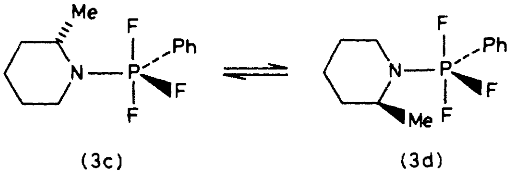


(3a) (3b)



(3c) (3d)

However, these conclusions ignore the nature of R^1 and R^2 and are only valid if these groups have effectively cylindrical symmetry (*e.g.* for CH_3 or CF_3) or adopt suitable conformations (*e.g.* for CH_3CH_2 when the methyl carbon is in the axial plane or is able to reorient rapidly about the C–N bond). If these conditions are not satisfied, then further complications may arise. For instance, Sanchez and Cowley [2] have shown that if R^1 or R^2 is chiral, then for the case X $\neq$ Y diastereoisomerism occurs because there is a chiral axis along the P–N bond, so that under slow-exchange conditions four different axial fluorine environments may be detected by n.m.r. Even in the fast-exchange situation there are two different axial environments regardless of the relative populations of the two rotamers. It is assumed that neither X nor Y is chiral.

A previous paper [3] in this series has presented detailed n.m.r. results for difluoro(2-methyl-1-piperidyl)diphenylphosphorane (2), which is of the type (1) where X = Y = Ph, but 'R$_2$' in this case is effectively chiral. This molecule undergoes mutual exchange as a result of P–N internal rotation, and the proton-decoupled ^{19}F and ^{31}P spectra are of the ABX $\rightleftharpoons$ BAX type, giving a simple A$_2$X spectrum under fast-exchange conditions. The present paper deals with four related (substituted 1-piperidyl)trifluorophosphoranes. The situation for the (2-methyl-1-piperidyl)phenyl compound is shown by (3). Clearly (3a) and (3d) are equivalent, as are (3b) and (3c). However, the interconversions (3a) or (3b) $\rightleftharpoons$ (3c) or (3d) are not feasible, so that for n.m.r. purposes only the forms (3a) and (3b) need be considered. All four axial fluorine environments in these two rotamers are non-equivalent, so the proton-decoupled ^{19}F and ^{31}P n.m.r. spectra are expected to be of the ABCX $\rightleftharpoons$ DEFY type, *i.e.* showing non-mutual exchange and leading to fast-exchange spectra which still exhibit non-equivalent axial fluorines. It may be noted that the situation is not altered if the substituent plane at nitrogen is in the equatorial phosphorane plane, though in this case simple systems of type (1) with R^1 $\neq$ R^2, but where both have effective cylindrical symmetry, would not give non-equivalent axial fluorines for any rate of P–N internal rotation.

The four compounds chosen here for study are trifluoro (2-methyl-1-piperidyl)phenylphosphorane (3), the corresponding compound with methyl replacing phenyl (4), trifluoro (3-methyl-1-piperidyl)phenylphosphorane (5), and the corresponding compound with methyl replacing phenyl (6). Comparison of the effects of changing the site of substitution in the piperidyl ring and of replacing methyl by phenyl were expected to clarify the steric influences on equilibria for compounds of type (3) and on the degree of non-equivalence induced in the axial fluorines. Some room-temperature ^{19}F data for (3) and (5) have been published previously,[1] but it should be noted that the reported values of δ(F) and *J*(PF) for the equatorial fluorine of (5) appear to be incorrect.

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† Part 3 is R. K. Harris, M. I. M. Wazeer, O. Schlak, and R. Schmutzler, *Phosphorus, Sulphur*, 1981, **11**, 221.

Table 1. Phosphorus-31 and fluorine-19 chemical shift data from ambient-temperature (308 K) spectra

Compound	$\Xi(^{31}P)$/Hz [a]	$\delta(P)$/p.p.m. [b]	$\delta(F_a)$/p.p.m. [c]	$\delta(F'_a)$/p.p.m. [c]	$\delta(F_e)$/p.p.m. [c]
(3)	40 478 568.8	−53.54	−42.57	−44.24	−67.86
(3) [d]	[e]	−53.5 [f]	−42.6	−44.3	−67.8
(4)	40 479 180.0	−38.44	−30.39	−32.63	−68.23
(5)	40 478 466.2	−56.07	−43.27	−43.50	−67.91
(5) [d]	[e]	−55 [f]	−43.4	−43.7	−69.1
(6)	40 479 107.8	−40.23	−31.03	−31.19	−67.88
(7) [d]	[e]	−55.6 [f]	−43.5	−43.5	−68.1

[a] Absolute ^{31}P frequency values (see the text). [b] Phosphorus-31 chemical shifts are quoted with respect to the resonance of 85% H_3PO_4, using the high-frequency–positive convention, and are obtained *via* the value of $\Xi(^{31}P)$. [c] Fluorine-19 chemical shifts are quoted with respect to the $CFCl_3$ resonance, using the high-frequency–positive convention; F_a and F'_a refer to the axial fluorines and F_e to the equatorial fluorine. [d] Ref. 1. [e] Not specified in ref. 1. [f] The sign convention for $\delta(P)$ used in ref. 1 is opposite to that employed here, so the sign of these shifts has been changed.

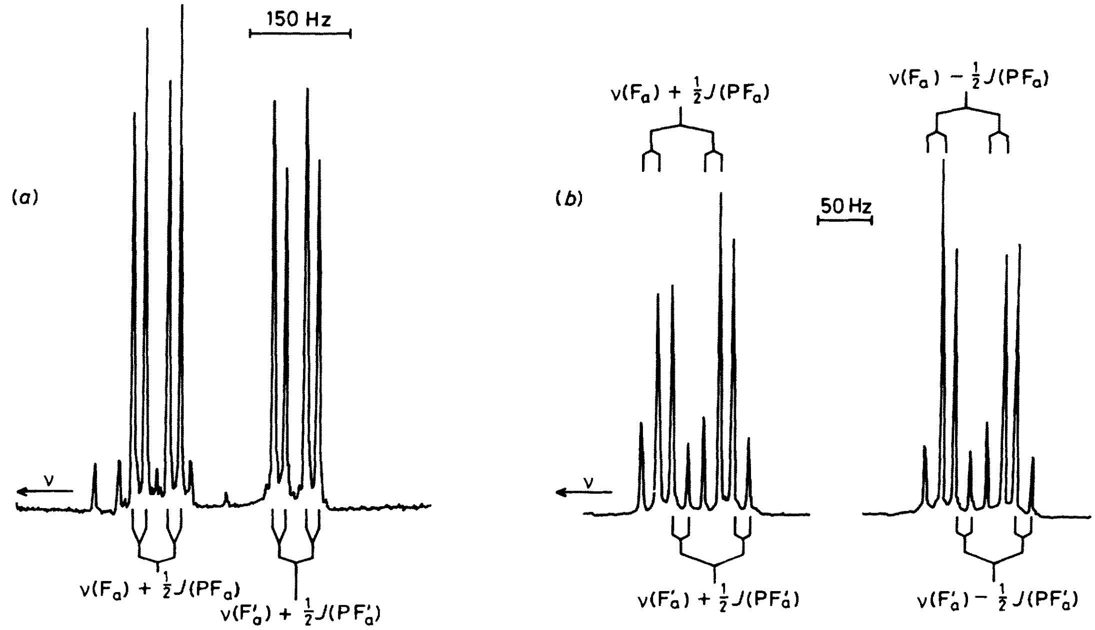

Figure 1. (*a*) The high-frequency half of the ^{19}F n.m.r. spectrum (axial fluorine region) for compound (4) at 308 K. The lines other than the eight most intense are due to the presence of impurities. (*b*) The ^{19}F n.m.r. spectrum (axial fluorine region) for compound (5) at 308 K

Results

Analysis of the Spectra.—At ambient probe temperature (308 K) all four compounds gave proton-decoupled n.m.r. spectra consistent with ABMX spin systems, as expected in the fast-exchange limit. The ^{19}F shift difference between the equatorial fluorine, M, and the axial fluorines, A and B, is sufficiently large in each case that second-order effects from axial–equatorial coupling are negligible, though they can be observed in some cases. The spectra for the two 2-methyl compounds are similar in appearance, as are the spectra for the two 3-methyl compounds, but the latter pair exhibit substantially smaller values of $|\delta(A) - \delta(B)|$. Illustrative spectra are shown in Figure 1. In principle each fluorine spectrum contains four ab subspectra and second-order features can appear in the M and X regions. The data resulting from spectral analysis at 308 K are given in Tables 1 and 2. There are small discrepancies between the results for J(PF) coupling constants obtained from ^{19}F and ^{31}P spectra (which were analysed separately), possibly due to small differences in temperature. The preferred values, which are listed in Table 2, are those from ^{19}F spectra, which contain better digitization than the ^{31}P spectra. The apparent equality of J(PF) for the two axial fluorines of compound (5) [and similarly for (6)] probably arises from the available digitization (*ca.* 0.4 Hz). It may be that the difference in the two values of the axial–equatorial (F,F) coupling constant for (5) [and similarly for (6)] is also not real for the same reason. Literature data [1] for compounds (3) and (5), and for the corresponding 4-methyl-1-piperidyl system (7), are also given in Tables 1 and 2.

As the temperature was lowered, all four compounds showed 'freezing out' of two isomers. This process was complete at 200 K for both 2-methyl-1-piperidyl compounds, (3) and (4), but significantly lower temperatures were required to achieve a similar result with the 3-methyl systems, (5) and (6). In each case the spectra of the rotameric forms can be analysed separately. Some initial difficulties were encountered for one of the rotamers of compound (3) because the shift difference between the axial fluorines is very small. The situation is worse for one of the rotamers of (6), where we were unable to distinguish between the two axial fluorines in terms of ^{19}F shift, ^1J(PF), or axial–equatorial J(FF) coupling. Our results for this species are therefore subject to some uncertainty because of the possibility of a degree of deceptive simplicity, and digitization problems also arise. It is also

Table 2. Coupling constants, J(PF) and J(FF) (Hz), obtained from ambient-temperature (308 K) spectra [a]

Compound	$^1J(\text{PF}_a)$	$^1J(\text{PF}'_a)$	$^1J(\text{PF}_e)$	$^2J(\text{F}_a\text{F}_e)$	$^2J(\text{F}'_a\text{F}_e)$	$^2J(\text{F}_a\text{F}'_a)$
(3)	−826.2	−812.6	−963.5	56.6	54.0	13.9
(3) [b]	−828	−814	−965	55	55	14
(4)	−815.2	−802.1	−966.6	54.8	51.4	18.2
(5)	−821.4	−821.4	−963.3	56.2	55.1	14.3
(5) [b]	−823	−820	−1 066 [c]	55	55	14
(6)	−809.9	−809.4	−966.8	54.5	53.6	18.4
(7) [b]	−820	−820	−965	56	56	0 [c]

[a] Measured from the ^{19}F region (see text). The signs are listed by analogy with other literature compounds. [b] Ref. 1. [c] This result would appear to be incorrect (see text).

Table 3. Phosphorus-31 and fluorine-19 chemical shift data from low-temperature spectra

Compound	Isomer	Temp./K	$\Xi(^{31}\text{P})$/Hz [a]	δ(P)/p.p.m. [a]	$\delta(\text{F}_a)$/p.p.m. [a]	$\delta(\text{F}'_a)$/p.p.m. [a]	$\delta(\text{F}_e)$/p.p.m. [a]
(3)	α	200	40 478 575.3	−53.37	−43.03	−43.09	−66.82
(3)	β	200	40 478 536.4	−54.33	−42.32	−46.28	−66.41
(4)	α	200	40 479 165.0 [b]	−38.81	−31.52	−32.28	−67.14
(4)	β	200	40 479 167.7 [b]	−38.75	−29.06	−34.97	−66.60
(5) [c]	α	163	40 478 465.8 [d]	−56.08	−44.44	−43.92	−67.95
(5) [c]	β	163	40 478 428.0 [d]	−57.01	−44.28	−45.06	−66.24
(6) [c]	α	188	40 479 077.4	−40.98	−32.50 [e]	−32.50 [e]	−67.17
(6) [c]	β	188	40 479 088.9	−40.69	−31.77 [e]	−32.14 [e]	−65.43

[a] See footnotes *a*, *b*, and *c* of Table 1. [b] $\Xi(^{31}\text{P})$ determined at 188 K. [c] All δ(F) values for compound (5) and axial δ(F) values for compound (4) are not as accurate with respect to $CFCl_3$ as the others listed since the samples used contained no $CFCl_3$. The relative shifts, however, are accurate. [d] $\Xi(^{31}\text{P})$ determined at 175 K. [e] δ(F) determined at 168 K.

Table 4. Coupling constants, J(PF) and J(FF) (Hz), obtained from low-temperature spectra

Compound	Isomer	$^1J(\text{PF}_a)$	$^1J(\text{PF}'_a)$	$^1J(\text{PF}_e)$	$^2J(\text{F}_a\text{F}_e)$	$^2J(\text{F}'_a\text{F}_e)$	$^2J(\text{F}_a\text{F}'_a)$
(3) [a]	α	−824.0	−810.0	−965.3	56.6	56.6	13.8
	β	−825.6	−805.2	−956.2	56.9	53.7	13.9
(4) [a]	α	−815.1	−801.5	−969.2	56.2	52.9	17.8
	β	−815.1	−793.8	−957.0	56.2	50.7	17.8
(5) [b]	α	−812.5	−812.5	−954.9	52.8	55.7	13.9
	β	−818.8	−822.4	−968.9	63.0	59.4	13.2
(6) [c]	α	−802.3	−802.3	−954.5	52.9	52.9	—
	β	−812.6	−811.5	−973.6	59.0	58.1	18.5

Measured at 200 K. [b] Measured at 163 K. [c] Measured at 168 K.

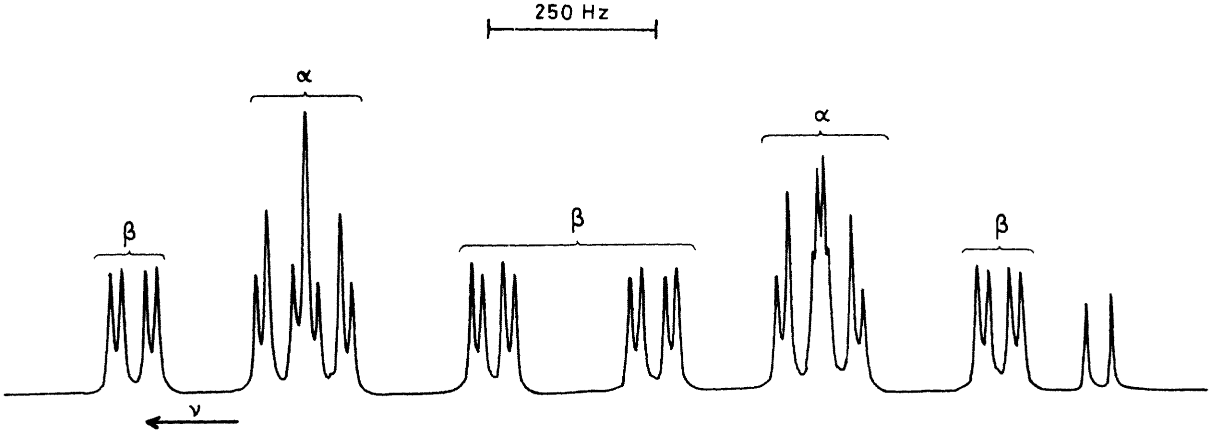

Figure 2. The axial region of the fluorine spectrum for compound (4) at 200 K, showing $\delta(\text{F}_a) - \delta(\text{F}'_a)$ is smaller for isomer α than for isomer β

possible that the apparent equivalence of the axial fluorines in this case may be a result of the very low temperature required to arrest the exchange process. The n.m.r. data for all the low-temperature spectra, obtained by spectral analysis (including computer-fitting where necessary), are given in Tables 3 and 4, and some representative spectra are shown in Figures 2—4. Data [except for $\Xi(^{31}\text{P})$] are derived from the fluorine spectra. The apparent equality of certain parameters

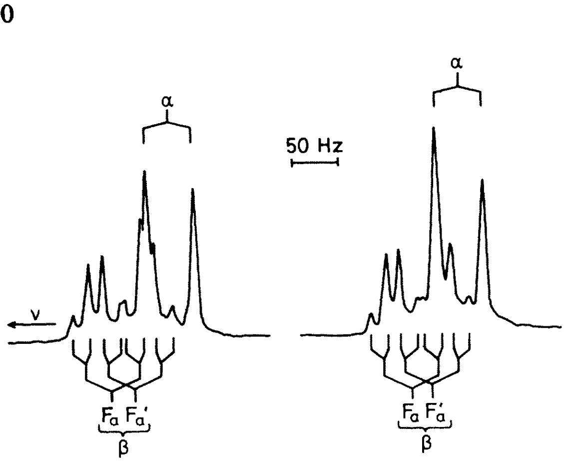

Figure 3. The axial region of the fluorine spectrum of compound (6) at 168 K showing the subspectra due to the two isomeric forms, α and β

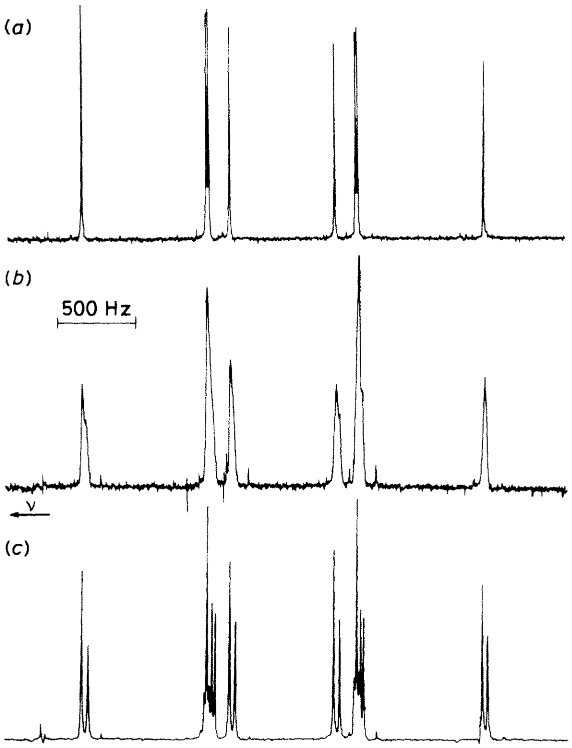

Figure 4. The temperature-dependent ^{31}P spectrum of compound (3) at (a) 307, (b) 223, and (c) 201 K

for the two rotamers of compound (4) may be a result of inadequate resolution and digitization. The equality of the two axial–equatorial J(FF) coupling constants for the α rotamer of compound (3) may be a consequence of the near-equivalence of the axial fluorines.

There are frequently, of course, ambiguities associated with the relative assignments of chemical shifts in the ab subspectra of an ABMX spin system. In the present cases some of the difficulty is removed since the likelihood of ^1J(PF) or ^2J(F_aF_e) varying in sign is remote. The remaining ambiguities were decided by choosing the solution which minimised the difference in the two values of ^2J(F_aF_e).

Discussion

The results described in the preceding section fully corroborate the expectations outlined in the introduction. The effects of decreasing the temperature on n.m.r. spectra of the four compounds studied are consistent with slowing internal rotation about the P–N bond. Such hindered rotation, which has also been observed in benzylmethylamino-[3] and (alkylthio)-fluorophosphoranes,[4,5] has been attributed mainly to d_π–p_π bonding between the P and N (or S). The observed non-equivalences in the axial fluorine environments are consistent with the more stable rotamers having the piperidyl ring oriented essentially in the axial plane. Such a conformation has been suggested [6] to be favoured by single π-system donors in the equatorial position of a trigonal bipyramid in order to maximise the π bonding from the donor (in this case N) to P.

A second effect on the barrier to rotation about the P–N bond which has been postulated [3] (*viz.* steric crowding in the transition state with respect to the ground state) appears to be particularly relevant in relation to compounds (3)—(6). Compounds (5) and (6) required markedly lower temperatures in order to stop the rotation process on the n.m.r. time-scale than were required for compounds (3) and (5), which implies a higher barrier to rotation for the latter pair, although the different effective chemical shift differences being averaged have to be taken into account. To investigate this suggestion further, estimates of such barriers at the coalescence temperatures were obtained using the expression for $\Delta G_c^\ddagger$ given [7] in equation (i), where $a = 1.914 \times 10^{-2}$ ($\Delta G_c^\ddagger$ in kJ mol^{-1}),

$$\Delta G_c^\ddagger = aT_c[9.972 + \log(T_c/\delta\nu)] \qquad \text{(i)}$$

and δν is the chemical shift difference in Hz between the two sites being averaged. It is assumed that the transmission coefficient is unity in each case. Such a calculation can only give rise to *estimations* of the barriers for the present cases (although, as will be shown, reasonably precise estimates), since the concept of a coalescence temperature is necessarily ill defined in such complex coupled spectra, and all complications arising from coupling have been ignored in this approximation.

For compound (3) $T_c \approx$ 245—265 K, and $\Delta G_c^\ddagger$ was found to be *ca.* 50 kJ mol^{-1} (*ca.* 12 kcal mol^{-1}), with a difference of *ca.* 16 K between the coalescence temperatures for the two pairs of fluorines being averaged. Similar calculations were carried out for the remaining compounds and gave $\Delta G_c^\ddagger$ values of *ca.* 46 kJ mol^{-1} (*ca.* 11 kcal mol^{-1}) for compound (4) ($T_c \approx$ 235—245 K), and *ca.* 42 kJ mol^{-1} (*ca.* 10 kcal mol^{-1}) for both compounds (5) and (6) ($T_c \approx$ 195—220 and 205—215 K respectively). It was shown that an error of 10 K in the determination of the coalescence temperature leads to an error of only *ca.* 2.1 kJ mol^{-1} (*ca.* 0.5 kcal mol^{-1}) in the values of $\Delta G_c^\ddagger$ ultimately obtained. As T_c is thought to be known to better than 10 K in each case, it would appear that the barriers to rotation are indeed higher in compounds (3) and (4) than in compounds (5) and (6), and, since the two pairs of compounds differ only in that the latter are substituted at the 3-position on the piperidyl ring while the former are substituted at the 2-position, this seems to substantiate the importance of some form of steric interaction, either attractive in the form of an interaction between H and F in the ground state, or repulsive through steric crowding in the equatorial plane in the excited state. The difference in $\Delta G_c^\ddagger$ between compounds (3) and (4) themselves would appear to favour the latter of these suggestions, since in (3) the bulky phenyl group in the equatorial plane would probably cause a greater degree of steric hindrance to rotation than would be expected from the methyl substituent in (4).

The barriers to P–N internal rotation, reported here, are of

Table 5. Coupling constant and chemical shift changes arising from the conformational effect in compounds (3) and (4)

Compound	Parameter	Difference [a]	Assignment (i) [b]		Assignment (ii) [b]	
			Value	Average	Value	Average
(3)	$\Delta|^1J(\mathrm{PF})|$/Hz	$F_a(\alpha)-F_a(\beta)$	-1.6	-3.2	-15.6	-17.2
		$F'_a(\beta)-F'_a(\alpha)$	-4.8		-18.8	
		$F_a(\alpha)-F'_a(\alpha)$	14.0		-20.4	
		$F'_a(\beta)-F_a(\beta)$	-20.4		-14.0	
	$\Delta|\delta(\mathrm{F})|$/p.p.m.	$F_a(\alpha)-F_a(\beta)$	0.71	1.95	0.77	2.01
		$F'_a(\beta)-F'_a(\alpha)$	3.19		3.25	
		$F_a(\alpha)-F'_a(\alpha)$	-0.06		3.96	
		$F'_a(\beta)-F_a(\beta)$	3.96		0.06	
(4)	$\Delta|^1J(\mathrm{PF})|$/Hz	$F_a(\alpha)-F_a(\beta)$	0.0	-3.9	-13.6	-17.5
		$F'_a(\beta)-F'_a(\alpha)$	-7.7		-21.3	
		$F_a(\alpha)-F'_a(\alpha)$	13.6		-21.3	
		$F'_a(\beta)-F_a(\beta)$	-21.3		-13.6	
	$\Delta|\delta(\mathrm{F})|$/p.p.m.	$F_a(\alpha)-F_a(\beta)$	2.46	2.58	3.22	3.34
		$F'_a(\beta)-F'_a(\alpha)$	2.69		3.45	
		$F_a(\alpha)-F'_a(\alpha)$	-0.76		5.91	
		$F'_a(\beta)-F_a(\beta)$	5.91		0.76	

[a] From the low-temperature data of Tables 3 and 4. [b] See text for the designation of the assignments.

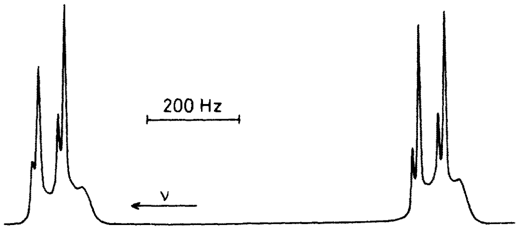

Figure 5. The axial region of the fluorine spectrum for compound (5) at 223 K, showing coalescence for one of the axial fluorines (F_a) but not for the other (F'_a) [*cf.* Figure 1(*b*)]

the same order as those reported previously[3,8] for related compounds.

The data listed in Table 1 show substantial differences in the chemical shifts of the axial and equatorial fluorines, in common with other reported fluorophosphoranes, and also a consistent variation in the chemical shifts of the axial fluorines with a change in the equatorial substituent from phenyl to methyl.

The axial–equatorial chemical shift difference can be rationalised by reference to the greater degree of π bonding to the central P atom expected for substituents in the axial positions than for those in equatorial positions, due to orbital symmetry considerations, as proposed by Kimball.[9] However, this suggestion is one which has led to considerable discussion in the literature (see, for example, refs. 6 and 9—12) and there does not appear to be any consensus on the matter. It is also apparent from Table 1 that the chemical shift of the equatorial fluorine remains relatively unchanged throughout the series of compounds studied, whereas the axial fluorine chemical shifts are strongly influenced by the nature (alkyl or aryl) of the equatorial substituent. Such a situation can be rationalised by invoking a greater degree of π bonding to phosphorus expected from the phenyl substituent than from the methyl group only if it is assumed that the phenyl π bonding would be competing for the same phosphorus orbitals as are involved in π bonding to the axial fluorines. However, the nature of the orbitals involved in π bonding is also subject to controversy.[13]

In Tables 3 and 4 the rotamer having the lower frequency resonance in the equatorial region has been labelled α, and the other β. There is, of course, no unambiguous way of assigning these to structures of the types (3a) and (3b). There are also ambiguities in linking a given axial fluorine in isomer α with its counterpart in isomer β (or in the averaged room-temperature situation) because both δ(F) and ^1J(PF) vary with temperature irrespective of isomer considerations. However, from the calculations carried out to determine $\Delta G_c^‡$ for the rotation process in compound (5), it would appear that the assignment of Tables 3 and 4 is correct, since this is consistent with the observed difference in the coalescence temperatures for the two averaging processes of *ca.* 15—20 K, whereas the opposite assignment (for, *e.g.*, the α isomer) gives values for $\Delta G_c^‡$ differing by up to *ca.* 4.2 kJ mol^{-1} (*ca.* 1 kcal mol^{-1}) using similar ΔT_c values. Figure 5 shows clearly that at 223 K the signals due to one of the axial fluorines are already averaged whereas those of the other fluorine are near coalescence, implying a substantial difference in the chemical shifts being averaged for the latter but not the former. For compound (6) there is no ambiguity in linking fluorine signals for the two isomers since, within experimental error, the chemical shifts for the two axial fluorines in the α isomer are equal, as are the values of ^1J(PF).

On the other hand, the assignment problem is substantial for compounds (3) and (4). Attempts will be made (see below) to correlate the axial fluorines between different isomers in the light of the origins of their non-equivalence. One of the possible correlations is that the high value of $|^1J(\mathrm{PF}_a)|$ is for the same fluorine in each rotamer in a given compound. Tables 3 and 4 are in fact drawn up with this assumption, which is referred to as assignment (i). For both isomers of both (3) and (4) the axial fluorine with the larger $|J(\mathrm{PF})|$ also has the smaller $|\delta(\mathrm{F})|$ value and is distinguished as F_a, the other axial fluorine being designated F'_a (this criterion has already governed the choice of F_a for the room-temperature data given in Tables 1 and 2). Assignment possibility (ii) may be obtained by interchanging the data for F_a and F'_a in each α isomer.

Conceptually, the cause of the non-equivalence can be separated into two parts, *viz.* (*a*) that caused by the orientation of the piperidyl substituent with respect to the observed fluorine, and (*b*) that caused by the presence of three different groups in the equatorial plane, one of which is chiral. These will be referred to as the conformational and chirality effects respectively.

There are several ways of obtaining data regarding the conformational effect, based on comparing results for the

Table 6. Coupling constant and chemical shift changes arising from the chirality effect in compounds (3) and (4)

Compound	Parameter [a]	Assignment (i) [b]	Assignment (ii) [b]	Room temperature
(3)	$\vert{}^{1}J(\mathrm{PF})(\mathrm{av.})\vert$/Hz	824.8, 807.6	817.8, 814.6	826.2, 812.6
	$\Delta\vert{}^{1}J(\mathrm{PF})(\mathrm{av.})\vert$/Hz [c]	17.2	3.2	13.6
	$\vert\delta(\mathrm{F})(\mathrm{av.})\vert$/p.p.m.	42.68, 44.69	44.66, 42.71	42.57, 44.24
	$\Delta\vert\delta(\mathrm{F})(\mathrm{av.})\vert$/p.p.m. [c]	−2.01	−1.95	−1.67
(4)	$\vert{}^{1}J(\mathrm{PF})(\mathrm{av.})\vert$/Hz	815.1, 797.7	808.3, 804.5	815.2, 802.1
	$\Delta\vert{}^{1}J(\mathrm{PF})(\mathrm{av.})\vert$/Hz [c]	17.5	3.9	13.1
	$\vert\delta(\mathrm{F})(\mathrm{av.})\vert$/Hz	30.29, 33.63	30.67, 33.25	30.39, 32.63
	$\Delta\vert\delta(\mathrm{F})(\mathrm{av.})\vert$/Hz [c]	−3.34	−2.58	−2.24

[a] These are averages for a given axial fluorine over the two rotamers. [b] See text for the designation of the assignments. [c] Differences between the axial fluorines.

different axial fluorines in the same rotamer or for the same axial fluorine in different rotamers of the same compound. Such data are given in Table 5. Chirality causes the four values for a given parameter to differ, and the results are also markedly dependent on the assignment chosen. The chemical shift and coupling constant data are clearly not fully compatible, showing the complexity of the phenomenon. For example, for compound (4) under assignment (i), $F_a(\alpha)$ and $F_a(\beta)$ do not differ measurably in J(PF), but there is a substantial difference in δ(F). The data for the two compounds (3) and (4) are, however, closely comparable. It may be noted that the net effect of interchanging the isomeric designations α and β is merely to change the sign of all the numbers in Table 5.

The chirality effect may in principle be broken down further into intrinsic and population effects, but for the compounds studied here the differences in population are small, and therefore the intrinsic effect is the more important. At room temperature, differences between axial fluorines may be attributed solely to the intrinsic chirality effect, though it should be borne in mind that both conformation and chirality are essential parts of the total phenomenon. Table 6 gives data on ^1J(PF) and δ(F) for the two axial fluorines in each of the compounds (3) and (4), using appropriate averaging, for both low-temperature and room-temperature situations.

Although the data of Tables 5 and 6 are not easy fully to rationalise, one consistency is that, irrespective of the problem of assignment, the changes in ^1J(PF) and δ(F) are always of the opposite sign for a given fluorine. Tables 5 and 6 enable discussion to be made of the assignment in two ways. For the conformational effect (Table 5) comparison may be made with the results for compound (2), which has no chirality. This exhibits [3] δ(F) = −36.67 and −34.24 p.p.m., with ^1J(PF) = −677.3 and −685.5 Hz respectively. Thus, if it is assumed that for this case F_a has the *lower* value of $|^1J(\mathrm{PF})|$ then $\Delta|^1J(\mathrm{PF})| = -8.2$ Hz and $\Delta|\delta(\mathrm{F})| = 2.43$ p.p.m. Table 5 then shows that the results for ^1J(PF) favour assignment (i) whereas those for δ(F) are in somewhat closer agreement with assignment (ii). Of course, good agreement is not anticipated because of the direct influence of the additional phenyl substituent of (2) on the n.m.r. parameters. The second consideration of assignment is supplied by the results of Table 6, comparing low-temperature averages with room-temperature values. It is best to take account of the differences between fluorines rather than individual data. Such comparisons yield the same conclusion as the conformation results: values of ^1J(PF) favour assignment (i) whereas δ(F) data favour assignment (ii). Intrinsic temperature dependences of J(PF) and δ(F) are presumably responsible for the discrepancies in comparisons using the data of Table 6.

Overall, no definitive conclusion on assignment is possible. However, we favour assignment (i) on the grounds that δ(F) is expected to be more sensitive to extraneous factors (such as intrinsic temperature or substituent dependence) than ^1J(PF). This is borne out by the variation with temperature of ^1J(PF) and δ(F) for the *equatorial* fluorines of (3) and (4) (see Tables 1—4): the former is clearly 'better behaved' than the latter. If assignment (i) is indeed correct, then the conformational effect is very markedly dependent on the way in which comparisons are made (see Table 5). In other words, chirality has an apparently bigger effect than conformation. Such a conclusion can be reached directly by comparing room-temperature differences between axial fluorines for compounds (3) and (4) with those found at low temperature for compound (2). This in turn implies that geometric distortions are likely to be different in rotamers (3a) and (3b), for instance. Chirality effects are frequently assigned to unsymmetrical relationships of the affected nuclei to phenyl rings. However, for compound (3), provided normal geometries are maintained, the axial fluorine nuclei are equivalently related to the phenyl group, regardless of rotational effects about the P–C(phenyl) bond. Moreover, the results for (4) are similar to those of (3). Consequently, geometrical differences between the rotamers would seem to be indicated.

It is not possible to relate unambiguously F_a and F'_a to situations near or distant from the methyl of the piperidyl ring. In principle the ^{19}F-{^{1}H} nuclear Overhauser effect might be used to distinguish, but we were unable to detect intensity differences between F_a and F'_a at low temperature.

Experimental

Compounds (3)—(6) were prepared by Dr. M. J. C. Hewson from the reaction of (methyl-1-piperidyl)methylsilanes with fluorophosphoranes of the type PF_4R (where R = alkyl or aryl) to give fluorotrimethylsilane and the corresponding (methyl-1-piperidyl)fluorophosphorane, as described for the case of benzylmethylamino-compounds in ref. 3. The preparation of compounds (3) and (5) is discussed in ref. 1, whereas compounds (4) and (6) have not previously been reported.

The usual precautions in handling moisture-sensitive phosphorus compounds were observed. N.m.r. samples were prepared under an atmosphere of dry nitrogen gas, then degassed and sealed in 5-mm outside diameter (o.d.) tubes by the usual method. The samples contained no ^{31}P reference compound. The ^{31}P absolute resonance frequencies were calculated using the method of Harris and Kimber.[14] The resonance frequency of 85% H_3PO_4 was determined in a similar manner to be 40 480 737 Hz in the standard magnetic field [14] and so can be used as a reference. All samples contained *ca.* 20% each of CD_2Cl_2 and $CFCl_3$ (providing a deuterium lock and an internal fluorine reference respectively) except those used in the low-temperature limit for compounds

(5) and (6), for which a mixture of CD_2Cl_2, $CHCl_3$, and CCl_4 (5 : 5 : 1) was used. Ethanol present in the $CHCl_3$ as a stabilising agent was removed by a standard procedure. The low-temperature samples contained only *ca.* 10% of solute in order to minimise solubility problems.

The n.m.r. data were obtained by the Fourier-transform method using a JEOL FX100 spectrometer operating at 93.7 MHz for the ^{19}F spectra, and a Varian XL-100 spectrometer operating at 40.5 MHz for the ^{31}P spectra. Temperature control was effected using a JEOL NM 5471 VT controller in the former case, and a Varian V4343 variable-temperature accessory in the latter. Temperatures were monitored by means of a thermocouple placed in a 5-mm o.d. n.m.r. tube containing the solvent used in the particular experiment.

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