

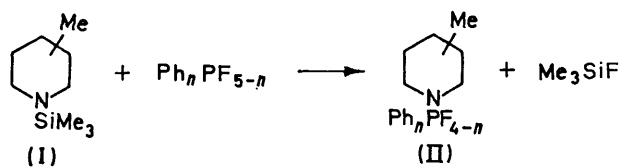
Fluorine-19 Nuclear Magnetic Resonance Studies of Methyl-substituted Piperidylfluorophosphoranes

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Summary ^{19}F n.m.r. data are presented for 2-methyl-, 3-methyl-, and 4-methyl-piperidylfluorophosphoranes in which the magnetic equivalence or non-equivalence of the axial or equatorial fluorine atoms is dependent on the position of the methyl group on the piperidyl ring and position of the ring with reference to the trigonal bipyramidal structure.

METHYLPYPERIDYLTRIMETHYLSILANES (I) have been found to react with fluorophosphoranes, $\text{R}_n\text{PF}_{5-n}$, with the formation of trimethylfluorosilane and the corresponding methylpiperidylfluorophosphorane (II).

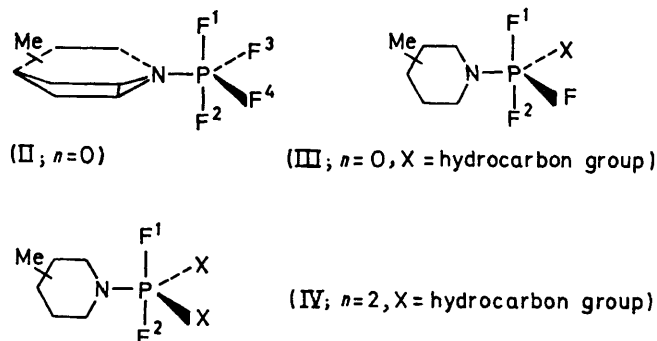


($n=0$; or $n=1$ or 2)

All the compounds were characterised by elemental analysis and n.m.r. spectroscopy. The n.m.r. results obtained were consistent with a trigonal-bipyramidal structure in which the amino and hydrocarbon groups occupy the equatorial positions.¹

At room temperature the ^{19}F n.m.r. spectra of the tetrafluorophosphoranes (IIa, IIb, IIc; $n=0$) show a simple doublet which can be explained by the positional exchange of the fluorine atoms in the axial and equatorial positions of the trigonal bipyramid about phosphorus, thus simplifying the ^{19}F n.m.r. pattern, as in the case of the "parent compound", PF_5 .² As has been observed for diorganoaminotetrafluorophosphoranes, R_2NPF_4 ,^{1,3} on cooling to

below -60°C the rate of positional exchange is slowed down sufficiently, relative to the n.m.r. time scale, to permit observation of distinct axial and equatorial fluorine environments. The low temperature spectra for the 2-methyl- and 3-methyl-piperidyltetrafluorophosphoranes indicate magnetically non-equivalent equatorial fluorine atoms, F^3 and F^4 , and magnetically equivalent axial fluorine atoms, F^1 and F^2 . The low temperature spectrum of 4-methyl-piperidylfluorophosphorane indicates magnetically equivalent fluorine atoms.



The room temperature ^{19}F spectra of 2-, 3-, or 4-methyl-piperidyl difluorophosphoranes also show a simple doublet. On cooling below -60°C this doublet disappears, and in the case of 2- and 3-methylpiperidyl difluorophosphoranes, (IVa and IVb) one observes a,b sub-spectra, suggesting magnetic non-equivalence of the axial fluorine atoms, F^1 and F^2 . For 4-methylpiperidyl difluorophosphorane no substantial spectral change is observed between room temperature and -60°C . This observation is consistent with the axial fluorine atoms, F^1 and F^2 , remaining magnetically equivalent over a wide temperature range.

TABLE I

^{19}F n.m.r. data for methylpiperidyltetrafluorophosphoranes				
Compound	Temperature ($^\circ\text{C}$)	J (Hz)		δ_{F} (p.p.m.) (from internal CCl_3F)
(IIa)	+ 30	J_{PF}	846	δ_{F} (average) +66.9
	-100 (in toluene)	J_{PF^3}	921	δ_{F^3} +72.2
		J_{PF^4}	905	δ_{F^4} +74.2
		J_{PF^1}	781	δ_{F^1} +60.3
		J_{PF^2}	781	δ_{F^2} +60.3
		$J_{\text{F}^3\text{F}^4}$	51	
		$J_{\text{F}^3\text{F}^1}$	74	
$J_{\text{F}^4\text{F}^1}$	67			
(IIb)	+ 30	J_{PF}	849	δ_{F} (average) +67.8
	-100 (in toluene)	J_{PF^3}	940	δ_{F^3} +72.1
		J_{PF^4}	940	δ_{F^4} +74.0
		J_{PF^1}	763	δ_{F^1} +60.2
		J_{PF^2}	763	δ_{F^2} +60.2
		$J_{\text{F}^3\text{F}^4}$	50	
		$J_{\text{F}^3\text{F}^1}$	77	
$J_{\text{F}^4\text{F}^1}$	63			
(IIc)	+30 ^a	J_{PF}	865	δ_{F} (average) +67.6

^a Due to viscosity problems no adequate low temperature spectrum could be obtained.

TABLE 2

¹⁹F n.m.r. data for methylpiperidyl-di- and tri-fluorophosphoranes

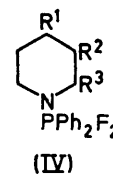
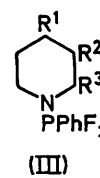
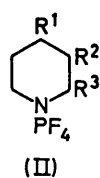
Compound	Temperature (°C)	J (Hz)	δ_F (p.p.m.) (from internal CCl ₃ F)		
(IIIa)	+30	J_{PF^1}	828	δ_{F^1}	+42.6
		J_{PF^2}	814	δ_{F^2}	+44.3
		J_{PF^3}	965	δ_{F^3}	+67.8
		$J_{F^1F^2}$	14		
		$J_{F^1F^3}$	55		
		$J_{F^2F^3}$	55		
(IIIb)	+30	J_{PF^1}	823	δ_{F^1}	+43.4
		J_{PF^2}	820	δ_{F^2}	+43.7
		J_{PF^3}	1066	δ_{F^3}	+69.1
		$J_{F^1F^2}$	14		
		$J_{F^1F^3}$	55		
		$J_{F^2F^3}$	55		
(IIIc)	+30	J_{PF^1}	820	δ_{F^1}	+43.5
		J_{PF^2}	820	δ_{F^2}	+43.5
		J_{PF^3}	965	δ_{F^3}	+68.1
		$J_{F^1F^2}$	0		
		$J_{F^1F^3}$	56		
		$J_{F^2F^3}$	56		
(IVa)	-70 (in toluene)	J_{PF^1}	689	δ_{F^1}	+34.6
		J_{PF^2}	689	δ_{F^2}	+36.8
	+30 (in toluene)	$J_{F^1F^2}$	14		
		J_{FF}	712	δ_F	+37.9
(IVc)	+30 (in toluene)	J_{FF}	715	δ_F	+38.1
	-70 (in toluene)	no change in spectral form			

F¹ and F² are axial fluorine atoms, F³ represents equatorial fluorine.

For both the di- and tetra-fluorophosphoranes (IVa, IIa, IIb) the observation of magnetically non-equivalent axial and equatorial atoms, respectively, in the case of the 2- or 3-methyl substituted derivatives, can be explained by a slowing down of the phosphorus-nitrogen single bond rotation to within the time scale of the n.m.r. measurement, thus placing the axial or equatorial fluorine atoms in distinctively different environments. For 2- and 3-methylpiperidyltrifluorophosphorane (IIIa and IIIb) the room temperature spectra show three different fluorine environments while in the spectrum of 4-methylpiperidyltrifluorophosphorane (IIIc), even upon cooling to -90 °C, only two fluorine environments are apparent. These observations can also be explained by the rate of positional exchange of fluorine atoms and the rate of P-N bond rotation being within the time scale of the n.m.r. measurements.

We therefore suggest for the methylpiperidylfluorophosphoranes the structures shown. It is suggested that the piperidyl ring will take the position of least stereochemical hindrance, this being in the equatorial plane for (II; $n = 0$) and axial plane for (III; $n = 1$ and IV; $n = 2$).

No such effect has been noted for the 4-methylpiperidylfluorophosphoranes. In all cases the axial or equatorial fluorine atoms remain magnetically equivalent.



	R ¹	R ²	R ³
a;	H	H	Me
b;	H	Me	H
c;	Me	H	H

A similar phenomenon has also been observed in the case of the alkylthio- and arylthio-substituted fluorophosphoranes, R_n(RS)PF_{4-n},⁴ the primary aminofluorophosphoranes, R¹HNPFR₂,⁵ and the secondary aminofluorophosphoranes, BzMeNR_nPF_{4-n}.⁶

Tables 1 and 2 list ¹⁹F n.m.r. data.

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