Chiral and Environmental Fluorine Non-equivalence in Aminofluorophosphoranes

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Summary Of the new aminofluorophosphoranes, $PhPF_3N(H)CHMePh$ (**1**), $Bu^sPF_3NHPr^i$ (**2**), $PhPF_3NHPr^i$ (**3**), and $Bu^sPF_3NMe_2$ (**4**), compounds (**1**) and (**2**) are diastereomeric owing to the presence of a chiral centre at carbon and a chiral axis along the N–P bond.

SEVERAL fluorophosphoranes of the types $R^1R^2NPF_4$, $RSPF_4$, and $R^1R^2NP(R^3)F_3$ exhibit anisochronous axial fluorine atoms when both N–P or S–P bond rotation and ligand positional interchange are slow on the n.m.r. scale.[1] This anisochrony stems from the fact that the axial fluorine ligands (F_a) reside in different chemical environments. In turn this is due to the preferential coplanar arrangement of the F_a–P–F_a and R^1R^2N- or RS- units within a trigonal bipyramidal phosphorane skeleton. Recently it has been demonstrated[2] that a second type of F_a anisochrony arises in chiral oxyfluorophosphoranes of the type $R^{1*}OP(R^2)F_3$ owing to the fact that the F_a–P–F_a group is prochiral[3] when ligand permutation is slow on the n.m.r. time scale. We now report the syntheses and n.m.r. spectra of some novel aminotrifluorophosphoranes which exhibit both chiral and environmental non-equivalence of the axial fluorine ligands.

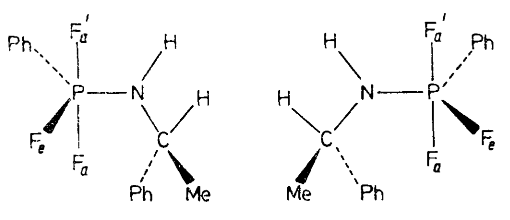
The aminotrifluorophosphoranes (**1**), (**2**), (**3**), and (**4**) were prepared by the liquid-phase reaction between the tetrafluorophosphorane RPF_4, and the appropriate amine or aminosilane $R^1R^2NSiMe_3$.

TABLE. ^{19}F n.m.r. chemical shift[a] and coupling constant[b] data for aminotrifluorophosphoranes

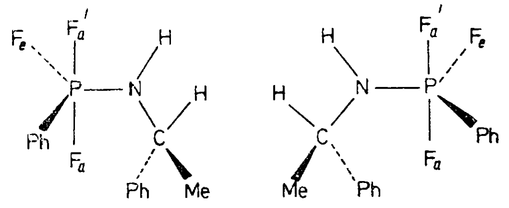
Compound		$\delta(F_a)$	$\delta(F_a')$	$\delta(F_e)$	$J(PF_a)$	$J(PF_a')$	$J(PF_e)$	$J(F_aPF_a')$	$J(F_aPF_e)$ $[=J(F_a'PF_e)]$	$J(F_a'PNH)$	$J(FPCH)$
$PhPF_3N(H)CHMePh$	(**1**)										
(*ca.* 40%)[c]		38·8	48·3	70·9	780	812	980	15	52	23	
(*ca.* 60%)[c]		39·8	47·6	70·0	775	806	972	,,	,,	,,	
$Bu^sPF_3NHPr^i$	(**2**)										
(*ca.* 50%)[c]		46·4	57·1	78·6	784	828	1009	21	52		13
(*ca.* 50%)[c]		47·0	58·0	76·6	792	836	1009	,,	,,		,,
$PhPF_3NHPr^i$	(**3**)	39·0	50	70·7	764	796	980	12	52	27	
$Bu^sPF_3NMe_2$	(**4**)	45·6	46·3	85·0	818	820	994	23	52		13

[a] ^{19}F chemical shifts, δ, in p.p.m. from CCl_3F. [b] Coupling constants, *J*, in Hz. [c] Composition of (+)-(−) mixture.

Compounds (**1**) and (**2**) are particularly interesting because they exhibit four different F_a resonances in the ^{19}F n.m.r. spectra at room temperature (Figure and Table). This observation is attributed to the combined effects of inhibited N-P bond rotation and chirality of the C(H)MePh or Bu^s group within a nonfluxional trigonal bipyramidal skeleton. This conclusion is supported by the following observations. Firstly, compound (**3**), an achiral analogue of (**1**), exhibits only two F_a resonances (Table). In (**3**) the anisochrony must derive from the fact that F_a and F_a' reside in different chemical environments.[1f]



(1a)



(1b)

Secondly, two types of F_a resonance are also apparent in the ^{19}F n.m.r. spectrum of (**4**). However, in this case the F_a anisochrony is a consequence of the prochiral relationship of the F_a-P-F_a group to the chiral Bu^s unit. Environmental F_a anisochrony is not observed in (**4**) because of the high (effectively C_{2v}) skeletal symmetry of the Me_2N group and the absence of N-H ··· F_a intramolecular hydrogen bonding.[1b,4] Finally, heating (**1**) from 30 to 90 °C (Figure) effects considerable simplification of the F_a and F_e resonances. These changes are attributed to an increase in the N-P rotation rate relative to the n.m.r. time scale and the consequent loss of environmental F_a anisochrony.

Another interesting facet of compounds (**1**) and (**2**) is the fact that the ground-state structures are diastereomeric owing to the presence of a chiral centre at carbon and a chiral axis along the N-P bond. For (**1**) the composition of the diastereomeric (+)-(−) mixture is *ca.* 40:60 whilst for (**2**) the composition is *ca.* 50:50. In the case of (**1**) this results in the observation of two different F_e resonances and two P-F_e coupling constants at 30 °C.

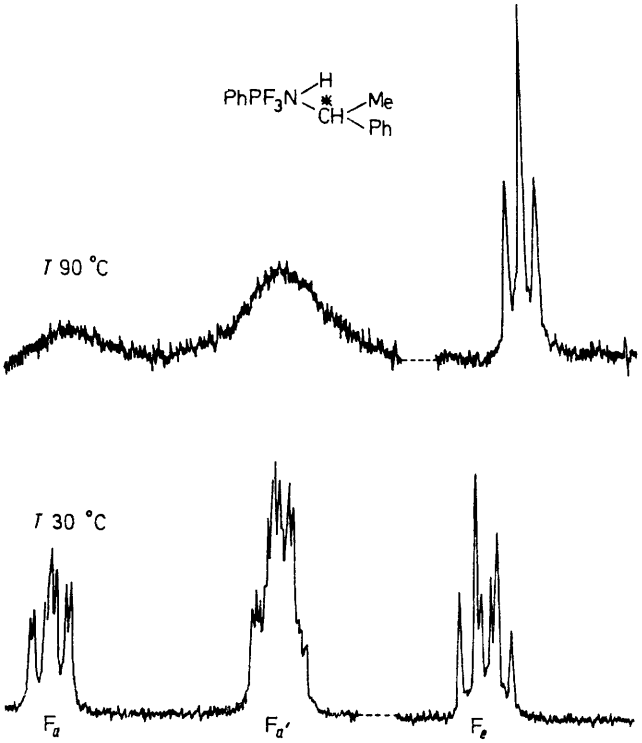


FIGURE. The 94·1 MHz ^{19}F n.m.r. spectra of $PhPF_3N(H)CHMePh$, (**1**), at room temperature and 90 °C. The resonances marked F_a and F_e are the downfield components of the P-F_a and P-F_e doublets. The resonance marked F_a' is a superposition of the upfield component of the F_a resonance and the downfield component of the F_a' resonance.

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[3] The term 'prochiral' was first proposed by K. R. Hanson (*J. Amer. Chem. Soc.*, 1966, **88**, 2731) for tetrahedral arrays of the specific type R_2CXY. In the present manuscript we use the term 'prochiral' with specific reference to trigonal bipyramidal structures of the type R_2MXYZ where the R groups occupy axial sites. For a review of prochirality see W. B. Jennings, *Chem. Rev.*, 1975, **75**, 307.

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