Synthesis and Sterochemistry of Aminotetrafluorophosphorane

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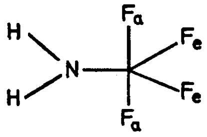
Summary Aminotetrafluorophosphorane, H_2NPF_4, has been prepared by the vapour phase reaction of PF_4Cl with NH_3 and n.m.r. studies of this compound suggest the presence of intramolecular hydrogen bonding.

There is considerable interest concerning the stereochemistry of aminotetrafluorophosphoranes mainly in regard to the mechanism of ligand permutation,[1,2] but also because of the possibility of intramolecular hydrogen bonding in alkylaminotetrafluorophosphoranes.[3] Here we report the quantitative preparation of the parent compound, aminotetrafluorophosphorane, H_2NPF_4 (**1**) by the vapour phase reaction of PF_4Cl[4] with NH_3, followed by fractional distillation *in vacuo* and collection of the product at −90 °C. The formula of (**1**) is established primarily by the mass spectrum which displays fragments assignable to $HNPF_4^+$, PF_4^+, and $H_2NPF_3^+$. The i.r. spectrum of (**1**) (vapour) also exhibits the anticipated features: ν_{N-H} 3465 and 3575 cm^{-1}, ν_{P-F} (axial) 967, 977, 1030, 1039, and 1058 cm^{-1}, and ν_{P-F} (equatorial) 840 (sh) 850 and 858 cm^{-1}. The ^{19}F n.m.r. spectrum of (**1**) ($HCCl_2F$ solution) consists of two resonances of equal intensity centred at $-24{\cdot}3$ p.p.m. (F_a)



and −1·33 p.p.m. (F_e) relative to internal $HCCl_2F$. This is consistent with the amino-group occupying an equatorial site of a trigonal bipyramid.

The complex ^{19}F and ^{1}H spectra of $H_2{}^{15}NPF_4$ are ascribed to the fact that the axial fluorines and amino protons constitute an AA′XX′ spin system. Only approximate values are available for the coupling constants $J(F_aPF_e)$ *ca.* 71 Hz, $J(F_aPNH)$ *ca.* 42 Hz, and $J(F_ePNH)$ *ca.* 1·6 Hz pending the completion of the appropriate iterative calculations. However, the couplings $J(PF_e)$ 936, $J(PF_a)$ 760, $J(^{25}NH)$ 90·3, $J(^{15}NPF_a)$ 23·8, and $J(PNH)$ 17·7 Hz can be recognised on a first-order basis.

From the phenomenological equation of Binsch *et al.*[5] a scalar $^{15}N-^{1}H$ coupling constant of 90·3 Hz corresponds to a nitrogen 2*s* character of 32·8% thus suggesting that the nitrogen atom in (**1**) is trigonal planar. Furthermore, the observation that the axial fluorines and amino protons are equivalent with respect to chemical shift but non-equivalent with respect to spin coupling implies that these nuclei are symmetrically disposed with respect to each other. Presumably the ground state geometry of (**1**) involves a coplanar arrangement of the amino hydrogens and axial fluorine atoms since this would permit maximum F...H–N intramolecular hydrogen bonding. This suggestion is also in accord with the high barrier to intramolecular ligand exchange in (**1**). Although broadened, separate F_a and F_e resonances are still discernible at 30°, thus $\Delta G^{\ddagger}$ is in excess of 15 kcal mol^{-1}. Such an increase over *e.g.* Me_2NPF_4 [where $\Delta G^{\ddagger}$ *ca.* 9·0 kcal mol^{-1} (ref. 1)] is presumably a consequence of intramolecular hydrogen bonding.

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