Preparation and Structure of 2-Methyl-5-tetrafluorophosphoranylpyrrole

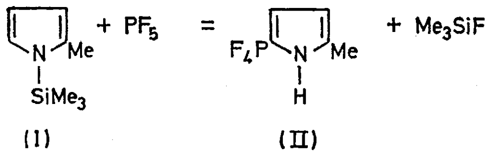
By Michael J. C. Hewson, Reinhard Schmutzler, and William S. Sheldrick*

(*Lehrstuhl B für Anorganische Chemie, Technische Universität,* 33, *Braunschweig, Pockelsstrasse* 4, *West Germany*)

Summary The preparation of 2-methyl-5-tetrafluorophosphoranyl pyrrole has been carried out, and the compound investigated structurally by means of n.m.r. and i.r. spectroscopy and *X*-ray diffraction.

Although the structures of molecules containing penta-co-ordinated phosphorus are a topic of considerable current interest,[1] there have been few diffraction studies of such compounds. We report the first *X*-ray diffraction study of an acyclic fluorophosphorane.

Compound (I) was allowed to react with phosphorus pentafluoride, with the formation of trimethylfluorosilane and 2-methyl-5-tetrafluorophosphoranylpyrrole (II),[2] a white crystalline solid of m.p. 44—45 °C and b.p. 76 °C at 25 mm in 62% yield. I.r. data indicated the presence of a P–C bond instead of the expected P–N bond, the strong absorption at 3450 cm^{-1} being attributed to an N–H stretch. The ^{19}F n.m.r. spectrum of (II) (toluene solution) at room temperature consists of a doublet centred at δ $+60{\cdot}7$, relative to internal CCl_3F, J(PF) 892 Hz. However, the low temperature ^{19}F n.m.r. spectrum (-50°C) shows the presence of three distinct fluorine atom environments, the resonances being centered at $\delta + 50{\cdot}4$ (F^1), $+46{\cdot}6$ (F^2), and $+73{\cdot}2$ (F^3 and F^4). The following coupling constants are observed: $J(PF^1)$ 856, J (PF^2) 838, $J(PF^3)$ 967, $J(PF^4)$ 967, $J(F^1F^2)$ 17, $J(F^1F^3)$ 76, and $J(F^2F^3)$ 66 Hz. All the n.m.r. results obtained were consistent with a trigonal-bipyramidal structure in which the pyrrole ring occupies an equatorial position.[3] It may, therefore, be concluded that the pyrrole ring takes up a position in the axial plane of the trigonal bipyramid, thus accounting for the magnetic nonequivalence of the axial fluorine atoms, F^1 and F^2.



(I) (II)

Crystals of (II) are orthorhombic *Pbca;* $a = 16{\cdot}352(3)$, $b = 11{\cdot}875(4)$, $c = 7{\cdot}781(2)$ Å, $Z = 8$. Intensity measurements were estimated visually from equi-inclination Weissenberg photographs taken with Ni-filtered Cu-K_α radiation. The structure was solved directly by a least-squares application of Sayre's equation and refined by full-matrix least-squares. With the introduction of anisotropic temperature factors for all refined atoms the R factor converged to 0·096 for 576 unique reflections. The hydrogen atom positions were not successfully refined.

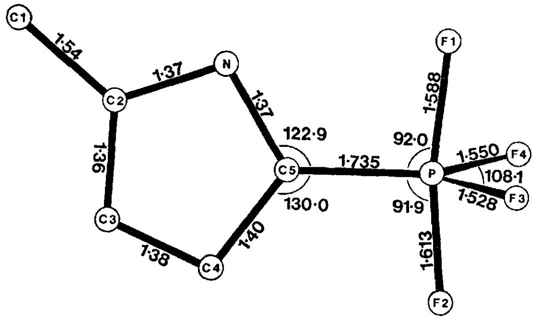


FIGURE. *The molecule* (II) *showing bond lengths and angles. The e.s.d.s. are* P–F 0·008, P–C 0·012, N–C 0·01, C–C 0·02 Å, *angles at* P 0·5°, *angles at* C(5) 0·9°.

The crystal structure (see Figure) confirms the n.m.r. interpretation. Co-ordination round the phosphorus is trigonal-bipyramidal and the maximum deviation from a weighted least-squares plane through the P, F(1), and F(2) atoms and pyrrole ring is 0·036 Å at C(4). The mean P–F(axial) and P–F(equatorial) bond lengths are similar to those observed in $MePF_4$.[4] The P–C bond length is shorter than that previously observed in acyclic compounds containing penta-co-ordinate phosphorus.[1] In particular, a comparison with the values of 1·780 and 1·798 Å observed in $MePF_4$ and Me_2PF_3 respectively,[4] suggests the existence of some degree of interaction between the π-orbital system of the pyrrole ring and the framework σ- or $3d$-orbitals of phosphorus. This is confirmed by the observed narrowing of the equatorial F–P–F angle to 108·1° A similar, though not so pronounced, narrowing has been observed on the replacement of fluorine by a less electronegative substituent in $MePF_4$ and HPF_4.[5] It may therefore be inferred, in accordance with the simple electron pair repulsion model of Gillespie, that the electron density in the P–C bond is greater at phosphorus in (II) than in the tetrafluorophosphoranes mentioned above. The position of the pyrrole donor π-orbitals in the equatorial plane is in agreement with a recent prediction concerning equatorial substituents in a trigonal-bipyramidal system.[6] The molecules are linked by hydrogen bonds into linear chains, as demonstrated by the F(2) · · · H–N distance of 3·01 Å, and the relatively high melting point of (II).

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