The Crystal and Molecular Structure of Fluorodiphenyl-*N*-methylphosphine Imide, Ph$_2$FPNMe

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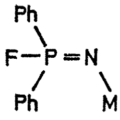
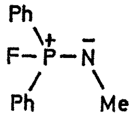
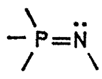
Summary The Ph$_2$FPNMe molecule is monomeric in the crystal with a phosphorus–nitrogen bond length which indicates appreciable multiple bonding.

THE electronic structure of fluorodiphenyl-*N*-methylphosphine imide[1] can be represented as a resonance hybrid of structures (I) and (II). The P:N bond is isoelectronic with the P:C(methylene) bond in the phosphorus ylides. The compound contains the structural unit (III) which is the repeating unit on which the cyclic phosphonitrilic compounds are based.[2] Whereas this compound is monomeric in solution, a related compound, (PhF$_2$PNMe)$_2$, is a dimer with a four-membered 1,3,2,4-diazadiphosphetidine ring.[1,3] An accurate knowledge of the molecular structure of Ph$_2$FPNMe is thus of importance in adding to the understanding of the bonding and reactions of a number of classes of phosphorus compounds.


(I)


(II)


(III)

We have determined the crystal structure of Ph$_2$FPNMe. Suitable crystals were obtained from a sample which was kindly supplied by Dr. R. Schmutzler. They are monoclinic, space group $P2_1$, with a = 8·527, b = 6·682, c = 11·346 Å and β = 106° 40′. There are two molecules of formula $C_{13}H_{13}FNP$ in the unit cell. The intensities of the diffracted X-rays were measured on a Hilger and Watts linear diffractometer. The structure was determined by three-dimensional Patterson and Fourier techniques and refined by least-squares with individual anisotropic temperature factors for all atoms except hydrogen. The positions of the hydrogen atoms were determined from an electron density difference synthesis. The present value of R is 4·0% for 1450 independent reflections.

In contrast to (PhF$_2$PNMe)$_2$,[3] Ph$_2$FPNMe is monomeric in the crystal. The bond angles at the phosphorus and nitrogen atoms are: F–P–N = 118·7°, F–P–C(1) = 110·9°, F–P–C(7) = 110·6°, N–P–C(1) = 104·2°, N–P–C(7) = 104·5°, C(1)–P–C(7) = 107·1°, P–N–C(13) = 119·1°, the e.s.d.s being less than 0·2°. The bond lengths, except those of the C–H bonds are shown in the Figure.

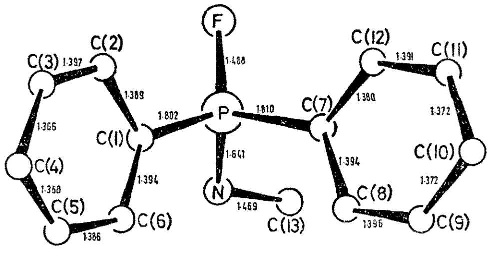


FIGURE. *Perspective drawing of the* Ph$_2$FPNMe *molecule showing the bond lengths. The e.s.d.s are* P–F, 0·002; P=N, 0·002; P–C, 0·003; N–C, 0·004; C–C(av.), 0·005 Å.

The bonding between ring atoms in cyclic phosphonitrilic compounds has been described as being due to P–N σ-bonds, π-bonding by electrons in orbitals perpendicular to the plane of the ring and π'-bonding involving the use of nitrogen lone-pair orbitals.[2] Similar possibilities seem to exist in Ph$_2$FPNMe. The bond angles in Ph$_2$FPNMe are consistent with approximate sp^3 hybridization on the phosphorus and sp^2 hybridization on the nitrogen as is found in the phosphonitrilic compounds. However, the phosphorus–nitrogen bond length of 1·641(2) Å in Ph$_2$FPNMe is longer than any of the phosphorus–nitrogen bond lengths which have so far been observed in phosphonitrilic compounds.[4] It is similar to the value of 1·64 Å which is obtained for a P:N double bond from covalent radii[5] and to the value of 1·661 Å which has been observed for the P:C(methylene) bond length in Ph$_3$P:CH$_2$.[6] In phosphonitrilic compounds the size of the P–N–P ring angle has been used to estimate the amount of π'-bonding.[2] If this criterion is applied to Ph$_2$FPNMe then the P–N–C(13) angle of 119·1° indicates that the amount of π'-bonding is not large.

The P–F distance of 1·488(2) Å is shorter than the average value of 1·52 Å which was found in (PNF$_2$)$_3$[7] and (PNF$_2$)$_4$[8] and the values of 1·57 and 1·62 Å which were found in (PhF$_2$PNMe)$_2$.[3] The N–C(13) bond length is 1·469(4) Å compared with 1·475 Å which is given as a standard value for a C(sp^3)–N(sp^2) bond.[9]

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