Crystal Structure of 2-Methyl-5-(tetrafluorophosphoranyl)pyrrole [1]

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Crystals of the title compound are orthorhombic, space group *Pbca*, with a = 16·352(3), b = 11·875(4), c = 7·781(2) Å, Z = 8. The molecules exhibit a trigonal-bipyramidal geometry, in which the pyrrole ring lies in the axial plane, and are linked in chains by F · · · H–N hydrogen bonds. Principal bond lengths (corrected for libration) and bond angles are: P–F(ax) 1·612(8) and 1·633(8), P–F(eq) 1·549(9) and 1·562(7), P–C 1·740(11) Å; F(ax)–P–F(ax) 175·9(5), F(eq)–P–F(eq) 108·1(5)°. The structure was solved by direct methods and was refined to R 0·092 for 576 visually estimated unique reflections.

INTEREST continues to be focused on stereochemistry and bonding in five-co-ordinate phosphorus species.[2,3] A recent molecular orbital description [3] of the bonding of those species with trigonal-bipyramidal geometry has rationalised the preference for apical substitution by more electronegative groups. The prediction has also been made that an equatorial substituent with a single π system will prefer to have its acceptor orbital perpendicular to the equatorial plane or its donor orbital in that plane. Electron diffraction studies [4-6] on the members of the series Me_nPF_{5-n} $0 \leqslant n \leqslant 3$ have demonstrated the existence of a steady increase in the P–F(eq) and P–F(ax) bond lengths with increasing methyl substitution in these trigonal-bipyramidal molecules, in agreement with the predictions of the VSEPR model of Gillespie and Nyholm.[7] Structural data on compounds containing acyclic five-co-ordinate phosphorus in the solid phase, however, are limited to Ph_5P,[8] owing, in the main, to the high volatility and instability of these species. 2-Methyl-5-(tetrafluorophosphoranyl)-pyrrole (I) was found to have the anomalously high m.p. of 44—45 °C, and in view of this, the potential donor properties of the pyrrole π-electron system, and the lack of data on solid acyclic fluorophosphoranes, an X-ray diffraction study has been carried out.

EXPERIMENTAL

(I) Was prepared by the reaction of PF_5 with (2-methylpyrryl)trimethylsilane [9] and recrystallised from ether. Suitable crystals, which were of poor quality and extremely air sensitive, could be obtained upon sublimation. They were sealed in Lindemann glass capillary tubes under nitrogen. Marked decomposition was observed in the X-ray beam. Intensities were estimated visually from equi-inclination Weissenberg photographs (layers $hk0$—6 and $h0$—$2l$ inclusive) taken with Ni-filtered Cu-K_α radiation. The crystals were both of elongated prismatic habit with dimensions 0·16 × 0·34 × 0·90 mm and 0·20 × 0·80 × 0·32 mm respectively. Lorentz, polarisation, and absorption corrections were applied and the data placed on a self-consistent scale by the linear least-squares method of Rae and Blake.[10] Accurate unit-cell dimensions were obtained

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from measurements of 16 $hk0$ and 17 $h0l$ reflections on zero-layer Weissenberg photographs calibrated with tungsten (a = 3·1653 Å), by a least-squares routine which corrected for potential systematic eccentricity errors.

Crystal Data.—$C_5H_6NPF_4$, $M = 159{\cdot}0$, Orthorhombic, $a = 16{\cdot}352(3)$, $b = 11{\cdot}875(4)$, $c = 7{\cdot}781(2)$ Å, $U = 1511{\cdot}0(6)$ Å^3, $Z = 8$, $D_c = 1{\cdot}40$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å, μ(Cu-K_α) = 28·7 cm^{-1}. Centrosymmetric space group $Pbca$ (No. 61) from systematic absences: $0kl$ with k odd, $h0l$ with l odd, and $hk0$ with h odd.

TABLE 1

Hydrogen-atom co-ordinates, and isotropic vibrational amplitude (Å^2 × 10^3) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U
H(1)	−0·0770	0·1662	0·2091	83(29)
H(3)	−0·2261	0·3824	0·0572	83(29)
H(4)	−0·0975	0·5166	0·1373	83(29)

Structure Solution and Refinement.—All non-hydrogen atoms in the structure were located directly by a least-squares application of Sayre's equation and their positions refined by full-matrix least-squares. On the introduction of anisotropic temperature factors for the phosphorus, fluorine, nitrogen and carbon atoms the generalised index [11] $R_G = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$ $(\Delta = |F_o| - |F_c|)$ converged to 0·127 with a corresponding unweighted R index of 0·096. The positions of the three pyrrole ring hydrogen atoms were then located by difference-Fourier syntheses, and included as fixed parameters in the least-squares refinement. In the final cycles of this refinement, a total of 101 parameters were varied simultaneously, consisting of 33 positional parameters, 66 anisotropic temperature-factor components, an overall isotropic temperature factor for the pyrrole ring hydrogen atoms, and an overall scale factor. No extinction correction was deemed to be required. Complex neutral-atom scattering factors [12,13] were employed for all atoms. The weighting scheme adopted was $w = (5{\cdot}83 + |F_o| + 0{\cdot}095\ F_o^2)^{-1}$, which has been converted to an absolute scale of F_o.

The terminal value of R_G was 0·121 for a total of 576 unique observed reflections, with the weighted index R' $[= (\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}F_o)]$ 0·097 and the corresponding unweighted index, R, 0·092. A final difference-Fourier synthesis failed to reveal the positions of the 3 methyl hydrogen atoms. Otherwise there were no unexpected features. The results from the final least-squares cycle are summarised in Tables 1 and 2; these results, together with the full covariance matrix, were used to calculate the bond lengths and angles, and their estimated standard deviations, presented in Table 3. The shortest non-bonded distances are summarised in Table 4. Figure 1 shows the molecule in perspective, together with the numbering system used, and Figure 2 the unit-cell contents shown perpendicular to the a axis. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20779 (5 pp., 1 microfiche).*

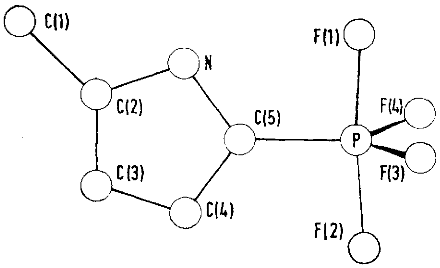

FIGURE 1 The molecule

TABLE 2

Atom co-ordinates and anisotropic vibrational amplitudes * (Å^2 × 10^3), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	0·0498(2)	0·3655(3)	0·2956(4)	59(2)	63(2)	46(2)	−8(2)	3(2)	−9(2)
F(1)	0·0580(4)	0·2350(6)	0·3389(10)	65(4)	81(5)	91(6)	10(4)	−21(4)	6(4)
F(2)	0·0471(5)	0·4992(6)	0·2598(12)	87(5)	69(5)	117(6)	−2(4)	−4(5)	−22(4)
F(3)	0·0744(5)	0·3897(7)	0·4818(10)	97(6)	124(7)	64(5)	−20(5)	−13(5)	−20(5)
F(4)	0·1288(4)	0·3582(8)	0·1862(9)	54(4)	126(7)	79(6)	−19(5)	19(4)	−5(4)
N	−0·0872(5)	0·2477(9)	0·2108(12)	55(6)	66(6)	42(6)	−2(5)	1(5)	6(5)
C(1)	−0·2179(10)	0·1555(15)	0·1143(21)	70(9)	111(13)	110(13)	−28(10)	−12(9)	−24(9)
C(2)	−0·1642(7)	0·2603(12)	0·1432(15)	52(7)	75(9)	52(8)	−8(6)	−5(6)	5(7)
C(3)	−0·1735(8)	0·3711(11)	0·1079(17)	60(9)	76(10)	70(9)	0(7)	−22(7)	10(7)
C(4)	−0·1041(9)	0·4270(13)	0·1573(17)	83(11)	70(9)	54(9)	4(7)	3(7)	0(8)
C(5)	−0·0488(7)	0·3486(9)	0·2201(14)	55(7)	46(6)	50(8)	−3(5)	−13(6)	−3(6)

* In the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}kha^*b^*)]$.

The considerable anisotropy of thermal motion exhibited by the atoms in this structure suggested that it would be instructive to investigate how appropriate the rigid-body hypothesis is in describing the librational motion in a molecule of trigonal-bipyramidal geometry. Accordingly, an analysis was performed by the method of Schomaker and Trueblood,[14] with both unit weights and weights given by the reciprocals of the variances of the parameters from the least-squares refinement of the structure. The values of the generalised index, $R_G = [\Sigma w(U_c - U_o)^2/\Sigma wU_o^2]^{1/2}$, were 0·112 (unit weights) and 0·119 (weighted) with root-mean-square discrepancies of 0·0074 and 0·0077 Å^2 respectively. The agreement between the observed and calculated temperature factors is satisfactory when the large estimated standard deviations of the former are taken into account.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full-size copies.)

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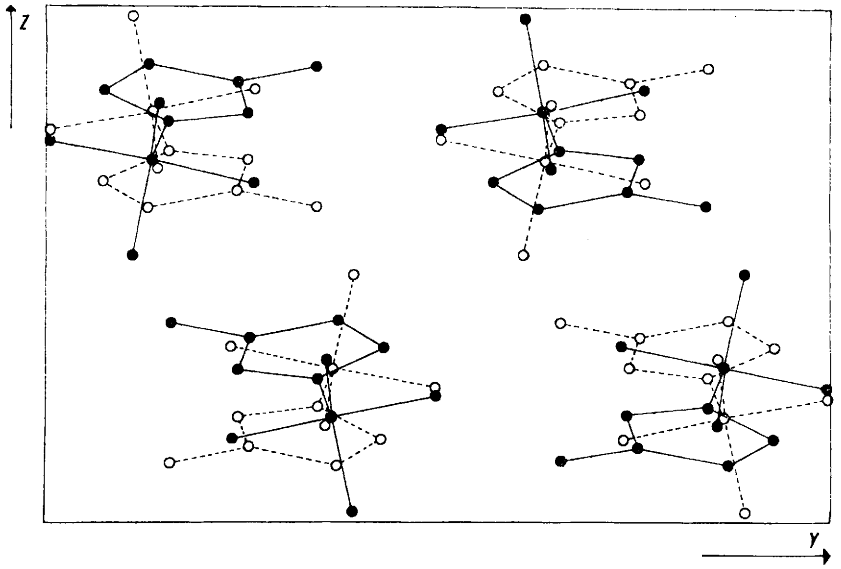

FIGURE 2 Projection of the crystal structure perpendicular to *a*. The molecules depicted in full lines lie above those in dotted lines

TABLE 3

Interatomic distances (Å), with librationally corrected values in square brackets, and bond angles (deg.)

(*a*) Distances

P–F(1)	1·592(8) [1·612]
P–F(2)	1·612(8) [1·633]
P–F(3)	1·531(9) [1·549]
P–F(4)	1·550(7) [1·562]
P–C(5)	1·728(11) [1·740]
N–C(2)	1·373(13) [1·383]
N–C(5)	1·354(13) [1·370]
C(1)–C(2)	1·540(19) [1·556]
C(2)–C(3)	1·354(17) [1·370]
C(3)–C(4)	1·370(19) [1·381]
C(4)–C(5)	1·386(17) [1·401]
N–H(1)	0·98
C(3)–H(3)	0·96
C(4)–H(4)	1·08

(*b*) Angles

F(1)–P–F(2)	176·0(5)	F(3)–P–F(4)	108·1(5)
F(1)–P–F(3)	87·7(5)	F(1)–P–F(4)	89·5(5)
F(2)–P–F(3)	89·2(5)	F(2)–P–F(4)	89·0(5)
F(1)–P–C(5)	92·1(5)	F(2)–P–C(5)	91·7(5)
F(3)–P–C(5)	126·1(5)	F(4)–P–C(5)	125·8(5)
C(1)–C(2)–N	119·4(12)	C(1)–C(2)–C(3)	133·8(13)
C(2)–C(3)–C(4)	108·7(12)	C(3)–C(4)–C(5)	108·3(13)
C(4)–C(5)–N	105·9(11)	C(2)–N–C(5)	110·4(10
C(4)–C(5)–P	130·5(10)	N–C(5)–P	123·5(8)
N–C(2)–C(3)	106·7(11)		

TABLE 4

Non-bonded distances (Å) <3·5 Å

$F(2) \cdots F(3^{I})$	3·12	$F(1) \cdots F(3^{III})$	3·16
$F(2) \cdots H(4^{I})$	3·20	$F(3) \cdots F(4^{III})$	3·46
$F(4) \cdots H(4^{I})$	2·97	$C(5) \cdots H(3^{I})$	3·48
$F(2) \cdots C(4^{I})$	3·49	$F(1) \cdots F(4^{III})$	3·14
$F(3) \cdots H(4^{I})$	3·19	$F(3) \cdots H(1^{III})$	3·11
$F(1) \cdots F(2^{II})$	3·37	$F(4) \cdots C(5^{IV})$	3·43
$F(2) \cdots C(5^{II})$	3·49	$C(5) \cdots H(3^{V})$	3·40
$F(2) \cdots H(1^{II})$	2·06	$F(4) \cdots H(3^{VI})$	3·11
$F(2) \cdots N^{II}$	3·03	$C(5) \cdots H(4^{V})$	3·45
$F(1) \cdots H(4^{II})$	2·68		

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at *x, y, z*:

I $-x, -y, -z$	IV $\frac{1}{2}+x, \frac{1}{2}-y, -z$
II $-x, \frac{1}{2}+y, \frac{1}{2}-z$	V $\frac{1}{2}-x, \frac{1}{2}+y, z$
III $x, \frac{1}{2}-y, \frac{1}{2}+z$	VI $\frac{1}{2}+x, y\ \frac{1}{2}-z$

The results of the Schomaker and Trueblood analysis with unit weights are displayed in Table 5, where the tensors are defined as in ref. 14, and have been used to apply the librational corrections (0·010—0·021 Å) to the bond lengths given in Table 3. Although the translational motion is relatively isotropic, the librational motion is particularly pronounced about an axis centred 0·46 Å from the phosphorus atom and approximately perpendicular (86·7°) to the axial plane of the trigonal bipyramid.

TABLE 5

Rigid-body librational analysis

Centre of mass (crystal co-ordinates): − 0·0129, 0·3409, 0·2491

Tensors with respect to original orthogonal axes and origin at the centre of mass, with estimated standard deviations in parentheses

$T/\text{Å} \times 10^{-4}$	559(25)	11(31)	21(26)
		560(31)	−36(24)
			352(38)
$L/\text{rad}^2 \times 10^{-4}$	187(19)	33(8)	34(10)
		62(9)	19(7)
			68(7)
$S/\text{Å.rad} \times 10^{-4}$	17(12)	−1(16)	16(12)
	13(10)	−3(9)	−40(7)
	−30(9)	38(9)	−14(12)

Origin (crystal co-ordinates) which gives symmetric *S*: 0·0350, 0·3487, 0·2532

Principal root-mean-square amplitudes and direction cosines

T/Å *			
0·229	0·8117	−0·4095	−0·4165
0·223	0·5467	0·7837	0·2949
0·176	0·2056	−0·4671	0·8500
L/rad			
0·143	0·9323	0·2480	0·2635
0·068	−0·0407	0·7955	−0·6046
0·081	−0·3595	0·5530	0·7517

* Reduced to keep *U* invariant.

DISCUSSION

The molecules of (I) possess trigonal-bipyramidal geometry with the pyrrole ring positioned in the axial plane and are linked into linear chains by N–H $\cdots$ F hydrogen bonds. This result is consistent with the interpretation of the low-temperature ^{19}F n.m.r. spectrum at

—50°C which showed the presence of three distinct fluorine-atom environments.[1] The weighted least-squares plane through the P, F(1), F(2), and pyrrole ring atoms has the equation $-0{\cdot}3619x + 0{\cdot}1527y + 0{\cdot}9205z = 2{\cdot}4912$. In this calculation the atoms were assigned weights equal to their atomic numbers. Deviations (Å) from this plane are: P —0·009, F(1) 0·015, F(2) —0·007, N —0·010, C(2) —0·011, C(3) —0·007, C(4) 0·003, C(5) 0·009, with the methyl carbon C(1) —0·087.

The equatorial P–C bond length [1·728(11) Å] is considerably shorter than that previously observed in acyclic compounds containing five-co-ordinate phosphorus.[15] A value of 1·75(2) Å has, however, been reported for an equatorial P–C(aryl bond length in a four-membered cyclic oxyphosphorane.[16] A comparison with the values of 1·780 and 1·798 Å observed in $MePF_4$ and Me_2PF_3 respectively,[5] suggests the existence of some degree of interaction between the π-orbital system of the pyrrole ring and the framework σ- or 3*d*-orbitals of phosphorus. This conclusion is reinforced by the observed narrowing of the equatorial F–P–F angle to 108·1(5)°. A similar, though less pronounced, narrowing to 115·6 and 112° has been observed on the replacement of fluorine by a less electronegative substituent in $MePF_4$ and HPF_4.[17] It may therefore be inferred, in accordance with the VSEPR model, that the electron-density in the P–C bond is greater at phosphorus in (I) than in the tetrafluorophosphoranes mentioned in the foregoing. As predicted by this model the mean librationally corrected P–F(ax) and P–F(eq) bond lengths of 1·622(11) and 1·555(7) Å are greater than the equivalent values of 1·612(4) and 1·543(4) Å observed in $MePF_4$. However, these differences are not significant and in addition the role of the F(2) atom in hydrogen bonding, the effects of other short intermolecular contacts to this and the other fluorine atoms, and the reliability of the rigid-body hypothesis must be taken into account. The position of the pyrrole donor π-orbitals in the equatorial plane of the trigonal bipyramid is in accordance with the predictions of the MO model.[3]

Pyrrole is normally regarded as being weakly aromatic with some degree of delocalisation of the nitrogen lone-pair electrons around the ring. This view is confirmed by the differing C_α–C_α and C_β–C_β bond lengths of 1·387(5) and 1·420(5) Å in free pyrrole.[18] A comparison of the bond lengths and angles in the pyrrole ring system of (I) with those in the free molecule reveals the shortening of the C_β–C_β bond length to 1·370(19) Å (1·381 librationally corrected). Otherwise there are no significant differences. This increase in aromatic character may be attributed to the α-substitution of an electron-donating methyl group and to the existence of an extended π-system due to interaction with phosphorus.

The weak polymerisation of the molecules through linear N–H(1) · · · F(2) hydrogen bonds of length 3·03(1) Å accounts for the anomalously high m.p.

Calculations were carried out on the Braunschweig ICL 1907 computer using programs written by the author and Dr. G. M. Sheldrick. I thank Dr. M. J. C. Hewson for crystals and for stimulating discussions, Professor U. Wannagat for experimental facilities, and the Alexander von Humboldt-Stiftung for the award of a research fellowship.

[3/714 *Received, 5th April,* 1973]

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