Crystal and Molecular Structure of the Adduct Phosphorus Pentafluoride–Pyridine

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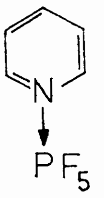
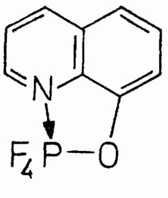
Crystals of $(C_5H_5N),PF_5$ are monoclinic, space group $P2_1/n$, with a = 6·056(2), b = 8·813(2), c = 13·854(2) Å, β = 97·34(2)°, Z = 4. The molecules exhibit an octahedral geometry with the plane of the pyridine ring staggered at 40·8° to one F_3PN plane. The four coplanar fluorine atoms are displaced away from the remaining fluorine, mean F–P–F 91·8(2)°. Rigid-body analysis reveals a pronounced librational motion about the F–P–N axis. Principal bond lengths (corrected for libration) are: P–F 1·607(1) (mean for the coplanar fluorines) and 1·594(3), P–N 1·898(4) Å. The structure was solved by direct methods and refined to R 0·052 for 823 diffractometer measured unique reflections.

THE facility of phosphorus pentafluoride to form stable non-ionic six-co-ordinate complexes with organic donor molecules is well documented.[1-4] Structural studies on species containing six-co-ordinate phosphorus have, however, been limited to numerous determinations of the geometry of the PF_6^- anion and to one recent investigation of the tris-(*o*-phenylenedioxy)phosphate anion.[5] In view of this dearth of information on non-ionic species a series of structural studies of fluorophosphorane and phosphorus pentafluoride complexes with various organic donor molecules has been initiated. The structure of the intermolecular complex $(C_5H_5N),PF_5$ (I) has been determined in order to compare it with the recently reported intramolecular complex (II), $F_4P(oxMe)$ (oxMe = 2-methyl-8-hydroxyquinoline grouping).[6]



(I)



(II)

EXPERIMENTAL

(I) Was prepared [2] by the reaction of PF_5 with pyridine and recrystallised from acetonitrile. A prismatic crystal with dimensions 0·20 × 0·16 × 0·14 mm was sealed into a Lindemann glass capillary tube. Intensity data were collected on a Stoe four-circle diffractometer by use of graphite monochromated Mo-K_α radiation. Measurements were carried out with standard background counts (15 s) and θ—2θ scan of fixed range (60 s) for $2\theta \leqslant 45°$. Three standard reflections were monitored throughout data collection and the measurements were corrected accordingly for crystal deterioration. An error $\sigma(I) = [N_S + (N_{B1} + N_{B2})T_S/(T_{B1} + T_{B2}) + (0{\cdot}03N_S)^2]^{\frac{1}{2}}$ was assigned to each

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net intensity, where $I = N_S - (N_{B1} + N_{B2})T_S/(T_{B1} + T_{B2})$, N_S is gross count, N_{B1} and N_{B2} background counts, and T_S, T_{B1}, and T_{B2} scanning times for these counts.

TABLE 1

Hydrogen atom co-ordinates and isotropic vibrational amplitudes ($Å^2 \times 10^3$) with estimated standard deviations

Atom	x/a	y/b	z/c	$\bar{U}$
H(1)	0·3394(19)	0·0077(12)	0·1483(7)	32(18)
H(2)	0·3803(19)	0·1073(14)	−0·0115(7)	22(15)
H(3)	0·1159(20)	0·2947(12)	−0·0869(7)	29(16)
H(4)	−0·1874(19)	0·3794(12)	0·0009(7)	10(13)
H(5)	−0·2120(17)	0·2755(11)	0·1621(7)	16(15)

With the application of the criterion $I \geqslant 2{\cdot}0\sigma(I)$, 823 of the 1114 unique reflections measured were considered to be observed. Lorentz and polarisation corrections were applied but no absorption corrections ($\mu = 4{\cdot}2$ cm^{-1}) were considered necessary. Accurate unit-cell dimensions were obtained from measurements of 19 high-angle 2θ reflections, by use of Mo-$K_{\alpha 1}$ ($\lambda = 0{\cdot}70926$ Å) radiation.

TABLE 2

Atom co-ordinates and anisotropic vibrational amplitudes ($Å^2 \times 10^3$),* 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	0·0258(3)	0·0538(2)	0·2877(1)	45(1)	47(1)	39(1)	3(1)	7(1)	−4(1)
F(1)	−0·0035(6)	−0·0133(4)	0·3913(2)	83(3)	78(3)	48(2)	20(2)	18(2)	−6(2)
F(2)	0·0037(6)	0·2232(4)	0·3252(2)	95(3)	58(2)	50(2)	−7(2)	28(2)	−1(2)
F(3)	0·2880(6)	0·0634(4)	0·3148(2)	48(2)	98(3)	53(2)	16(2)	1(2)	−1(2)
F(4)	0·0492(7)	−0·1108(4)	0·2432(2)	105(3)	42(2)	64(2)	6(2)	16(2)	1(2)
F(5)	−0·2349(6)	0·0490(5)	0·2545(3)	42(2)	95(3)	73(2)	19(2)	10(2)	−10(2)
N	0·0587(7)	0·1347(5)	0·1644(3)	37(3)	38(3)	37(2)	0(2)	4(2)	2(2)
C(1)	0·2260(10)	0·0884(7)	0·1161(4)	53(4)	59(4)	50(4)	2(3)	17(3)	9(3)
C(2)	0·2490(11)	0·1445(8)	0·0261(4)	59(4)	80(5)	53(4)	10(4)	22(3)	15(4)
C(3)	0·1001(11)	0·2500(7)	−0·0164(4)	70(5)	62(4)	41(3)	6(3)	9(3)	−9(4)
C(4)	−0·0707(11)	0·2977(7)	0·0330(4)	59(4)	54(4)	47(4)	8(3)	−1(3)	12(3)
C(5)	−0·0845(10)	0·2392(6)	0·1238(4)	48(4)	44(3)	44(3)	−4(3)	6(3)	6(3)

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

TABLE 3

Molecular geometry

(*a*) Interatomic distances (Å), and, in square brackets, librationally corrected values

P–F(1)	1·582(3)	[1·594]
P–F(2)	1·592(4)	[1·609]
P–F(3)	1·586(4)	[1·606]
P–F(4)	1·589(4)	[1·606]
P–F(5)	1·588(4)	[1·607]
P–N	1·885(4)	[1·898]
N–C(1)	1·347(7)	[1·362]
N–C(5)	1·339(7)	[1·353]
C(1)–C(2)	1·364(8)	[1·374]
C(2)–C(3)	1·374(8)	[1·389]
C(3)–C(4)	1·377(8)	[1·392]
C(4)–C(5)	1·371(7)	[1·381]

(*b*) Angles (°)

F(1)–P–F(2)	91·8(2)	N–P–F(2)	87·9(2)
F(1)–P–F(3)	91·7(2)	N–P–F(3)	88·6(2)
F(1)–P–F(4)	92·1(2)	N–P–F(4)	88·2(2)
F(1)–P–F(5)	91·7(2)	N–P–F(5)	87·9(2)
P–N–C(1)	120·6(4)	P–N–C(5)	120·2(4)
C(1)–N–C(5)	119·2(5)	N–C(1)–C(2)	121·0(6)
C(1)–C(2)–C(3)	119·9(6)	C(2)–C(3)–C(4)	119·2(5)
C(3)–C(4)–C(5)	118·6(6)	C(4)–C(5)–N	122·1(5)

Crystal Data.—$C_5H_5F_5NP$, $M = 205{\cdot}0$, Monoclinic, $a = 6{\cdot}056(2)$, $b = 8{\cdot}813(2)$, $c = 13{\cdot}854(2)$ Å, $\beta = 97{\cdot}34(2)°$, $U = 733{\cdot}4(3)$ Å^3, $Z = 4$, $D_c = 1{\cdot}86$. Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å, μ(Mo-K_α) = 4·2 cm^{-1}. Centrosymmetric space group $P2_1/n$ (C_{2h}^5) from systematic absences: $0k0$ with k odd, and $h0l$ with $h + l$ odd; this is related to the standard space group $P2_1/c$ (No. 14) by the transformation matrix (0,0,1), (0,1,0), (1,0,1).

Structure Solution and Refinement.—All non-hydrogen atoms 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,[7] R_G $\{= (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$, where $\Delta = |F_o| - |F_c|$, and the weights are those obtained from the counting statistics$\}$, converged to 0·083 with a corresponding unweighted R index of 0·070. A difference-Fourier synthesis revealed the positions of the pyridine ring hydrogen atoms, which were then defined, for inclusion in the least-squares refinement, by $x_H = 1{\cdot}776x_C - x_O$, *etc.*, where x_C and x_O are fractional co-ordinates of the carbon atom to which the ring is bonded, and of the centroid of the ring, respectively.[8] In the final cycles of this refinement, a total of 114 parameters were varied simultaneously,

TABLE 4

Non-bonded distances (Å) < 3·5 Å

$P \cdots H(3^{II})$	3·47	$P \cdots H(4^{II})$	3·28
$P \cdots H(5^{III})$	3·23	$F(1) \cdots F(1^{I})$	3·02
$F(1) \cdots H(3^{II})$	3·05	$F(1) \cdots H(4^{II})$	2·57
$F(1) \cdots C(4^{III})$	3·35	$F(1) \cdots H(4^{III})$	2·71
$F(1) \cdots C(5^{III})$	3·30	$F(1) \cdots H(5^{III})$	2·58
$F(2) \cdots H(2^{II})$	2·89	$F(2) \cdots H(3^{II})$	2·79
$F(2) \cdots H(4^{II})$	3·01	$F(2) \cdots F(4^{III})$	3·32
$F(2) \cdots H(1^{III})$	2·69	$F(2) \cdots F(5^{III})$	3·41
$F(3) \cdots C(3^{II})$	3·26	$F(3) \cdots H(3^{II})$	2·58
$F(3) \cdots C(4^{II})$	3·27	$F(3) \cdots H(4^{II})$	2·61
$F(3) \cdots F(4^{III})$	3·17	$F(3) \cdots C(4^{III})$	3·46
$F(3) \cdots C(5^{III})$	3·42	$F(4) \cdots C(3^{I})$	3·39
$F(4) \cdots H(3^{I})$	2·79	$F(4) \cdots N^{III}$	3·40
$F(4) \cdots C(1^{III})$	3·46	$F(4) \cdots H(5^{III})$	2·75
$F(5) \cdots H(3^{II})$	2·84	$F(5) \cdots C(5^{III})$	3·46
$F(5) \cdots H(5^{III})$	2·71	$C(1) \cdots H(2^{I})$	3·41
$C(2) \cdots H(2^{II})$	3·18	$C(3) \cdots H(4^{I})$	3·31
$C(4) \cdots H(4^{I})$	3·31	$H(1) \cdot\cdot (H2^{I})$	2·89
$H(2) \cdots H(2^{II})$	2·38	$H(3) \cdots H(4^{I})$	3·12
$H(4) \cdots H(4^{I})$	3·11		

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

I $-x, -y, -z$ II $0{\cdot}5 + x, 0{\cdot}5 - y, 0{\cdot}5 + z$
III $0{\cdot}5 - x, 0{\cdot}5 + y, 0{\cdot}5 - z$

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[7] W. C. Hamilton, 'Statistics in Physical Science,' Ronald Press, New York, 1964.

[8] G. M. Sheldrick, unpublished work.

consisting of 36 positional parameters, 72 anisotropic temperature-factor components, 5 isotropic temperature factors for the pyridine ring hydrogen atoms, and an overall scale factor. Complex neutral-atom scattering factors [9,10] were employed for all atoms. The terminal value of R_G was 0·062, with R' [$= (\Sigma w^{\frac{1}{2}}\Delta/w^{\frac{1}{2}}F_o)$] 0·053, and the corresponding unweighted index, R, 0·052. A final difference-Fourier synthesis displayed no peaks of density $>$0·3 eÅ^{-3}. The results from the final least-squares cycle, summarised in Tables 1 and 2, were used, together with the full covariance matrix, to calculate bond lengths and angles, and their estimated standard deviations (Table 3). Shortest non-bonded distances are summarised in Table 4. Figure 1 depicts the molecule in perspective, together with the numbering system, and Figure 2 the unit-cell contents shown perpendicular to the [100] axis. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20947 (4 pp., 1 microfiche).*

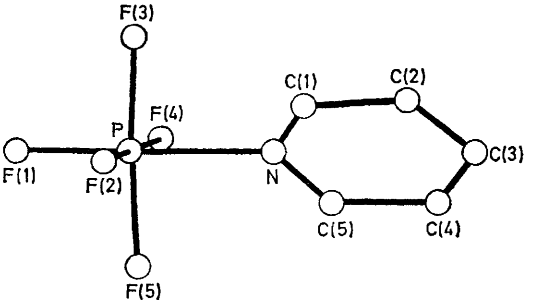

FIGURE 1 The molecule and the atom numbering system used in the analysis

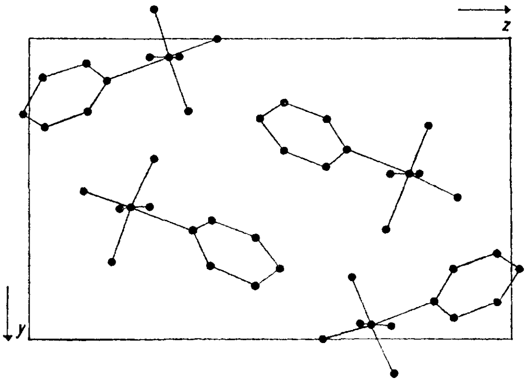

FIGURE 2 Projection of the crystal structure perpendicular to [100]

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 octahedral geometry. Accordingly, an analysis was performed by the method of Schomaker and Trueblood,[11] with both unit weights and weights given by the reciprocals of the variances of the parameters from the least-squares refinement of the structure. Satisfactory agreement was obtained between observed and calculated temperature factors, with values of 0·066 (unit weights) and 0·073 (weighted) for the generalised index, $R_G = [\Sigma w(U_c - U_o)^2/\Sigma wU_o^2]^{\frac{1}{2}}$, and root-mean-square discrepancies of 0·0034 and 0·0035 Å^2 respectively. The results of the Schomaker and Trueblood analysis with unit weights are displayed in Table 5, where the tensors are defined as in ref. 11, and have been used to apply the librational corrections to the bond lengths listed in Table 3. Although the translational motion is relatively isotropic, the librational motion is particularly pronounced about an axis centred close to the phosphorus atom (position in orthogonal co-ordinates: −0·0413, 0·0538, 0·2877) and approximately perpendicular to the F_4P plane (85·3°). This is to be expected, as rotation of the molecule about the FPN axis will involve the minimal volume displacement. As a consequence of the anisotropic nature of this librational motion, the correction in the P–F(1) bond length (0·012 Å) is smaller than for the other P–F bonds (0·017—0·019 Å).

TABLE 5

Rigid-body librational analysis

Centre of mass (orthogonal co-ordinates *): − 0·0207, 0·0991, 0·2183. Tensors with respect to orthogonal axes and origin at the centre of mass with estimated standard deviations in parentheses

T/Å × 10^{-4}	357(15)	−20(11)	8(11)
		383(15)	−12(13)
			415(11)
L/rad^2 × 10^{-4}	42(3)	12(3)	−21(3)
		68(4)	−61(4)
			188(7)
S/Å rad × 10^{-4}	3(4)	−35(3)	−22(4)
	19(4)	−4(4)	18(4)
	26(5)	7(5)	1(4)

Origin (orthogonal co-ordinates) which gives symmetric S: −0·0152, 0·0895, 0·2802

Principal root-mean-square amplitudes and direction cosines

T/Å †			
0·183	0·7970	−0·5824	−0·1601
0·178	0·5684	0·8128	−0·1275
0·203	0·2044	0·0106	0·9788
L/rad			
0·061	0·8801	−0·4703	−0·0659
0·066	0·4545	0·7940	0·4037
0·147	−0·1375	−0·3852	0·9125

* Referred to *a*, *b*, *c* sin β. † Reduced to keep U invariant.

DISCUSSION

The molecules of (I) possess octahedral geometry with the plane of the pyridine ring ($0·5369x + 0·7323y + 0·3510z = 1·852$) staggered at an angle of 40·8° to the F(1),F(3),F(5),P,N plane ($-0·1352x + 0·9250y + 0·3708z = 1·8861$) and 49·2° to the F(1),F(2),F(4),P,N plane ($0·9733x + 0·0394y + 0·1332z = 0·6937$). In the calculations of these weighted least-squares planes, the atoms were assigned weights equal to their atomic numbers. Deviations (Å) from the plane of the pyridine ring are: N −0·007, C(1) 0·001, C(2) 0·003, C(3) −0·001, C(4) −0·006, C(5) 0·010. No deviation $>$0·003 Å is

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are sent as full-size copies).

[9] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[10] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

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observed for the other two planes. An explanation for the observed rotation of the pyridine ring away from the most sterically favourable position at 45° to both F_3PN planes (C_{2v} symmetry) may be sought in terms of the many short F · · · H intermolecular interactions (Table 4).

The N→P co-ordinate bond length of **1·898(4)** Å is shorter than that [1·911(4) Å, uncorrected for libration] in (II).[6] A stronger co-ordinate bond is to be expected in (I), since PF_5 is a stronger Lewis acid than the F_4PO grouping in the intramolecular complex, but an exact bond-length comparison is hindered by the geometrical constraints present in the latter compound. The N–P(σ) bond length is 1·769 Å.[12]

The P–F(1) bond length [1·594(3) Å] opposite the N→P co-ordinate bond is significantly shorter than the mean value of 1·607(1) Å obtained for the coplanar fluorine atoms. A similar effect was observed for (II) and may be explained in terms of the electron density at phosphorus in the opposite bond of the octahedron, being higher when that bond is to a donor nitrogen atom than when it is to a highly electronegative fluorine atom. The values of the P–F bond lengths are close to that of 1·58 Å observed in the octahedral PF_6^- anion.[13] The coplanar fluorine atoms are distorted away from F(1), mean F–P–F 91·8(2)°, presumably reflecting the smaller degree of repulsion associated with the long N→P bond in comparison with the 0·30 Å shorter P–F(1) bond. The bond lengths and angles in the pyridine ring are not exceptional.

Calculations were performed on the Braunschweig ICL 1906S computer, using programs written by Dr. G. M. Sheldrick and myself. I thank Dipl-Chem. K.-P. John for the preparation of crystals, Doz. Dr. U. Thewalt for the use of his diffractometer, Professor R. Schmutzler for his interest, and the Alexander von Humboldt-Stiftung for the award of a Research Fellowship.

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